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THE REMOVAL OF RADIOACTIVE COMPOUNDS FROM FLUOROZIRCONIC ACID SOLUTIONS

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by

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Abstract

Three purification methods have been employed for the removal of radioactivity from fluoro zirconic acid solutions, being selective precipitation, solvent extraction and ion-exchange. The selective precipitation method emerged as being the best with solvent extraction being the least effective. The precipitation method using CaO as precipitant has associated with it an advantage of being cost effective and a disadvantage of the generation of radioactive waste. The ion-exchange method has an advantage of good performance and a disadvantage of the resin not being satisfactorily regenerable and thereby rendering the method not cost effective on plant scale.

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CHAPTER 1
INTRODUCTION AND PURPOSE OF STUDY

1.1. INTRODUCTION

Radioactivity has become a serious environmental issue both for the public and industry. This is due to the very dangerous and sometimes fatal effects resulting from exposure to radioactivity. The seriousness of this has led to most governments even legislating on radioactivity levels in products emitting even natural radioactivity. There has been increased pressure on the buyers and suppliers of zirconium and zirconium products to lower the radioactivity thereof and especially countries like Japan, USA and European Union have moved to tighten regulations in this regard. Japan, for instance, has tightened regulations governing the disposal of waste from zirconia pigment production plants[1].

In anticipation of the regulations also being tightened in our region, and also to satisfy international standards when exporting materials, projects are underway to try to reduce the radioactivity content in most of these products. Zirconia which the AEC intends producing is also receiving attention. This study concerns itself about the purification processes, in a bid to reduce radioactivity, of intermediate zirconium solutions which are precursors to the production of zirconia.

1.2. AIM OF THE STUDY

At the AEC a method has been established for the preparation of zirconia (ZrO_2) from zircon ($ZrSiO_4$), which is the major source of zirconium[2,3]. This process can shortly be described as follows: It starts off by the dissociation of zircon, which is itself a very inert material. Dissociation into ZrO_2 and SiO_2 by means of arc plasma process makes it very reactive towards dissolution in HF. This dissociation is carried out in a plasma at a very high temperature, and thus the formed $ZrO_2.SiO_2$ is referred to as plasma dissociated zircon (PDZ). The dissolution of PDZ in aqueous HF produces a H_2ZrF_6+H_2SiF_6 solution according to the following equation:

$$ZrO_2.SiO_2 + 12HF \rightarrow H_2ZrF_6 + H_2SiF_6 + 4H_2O \qquad (1)$$

During this process most of the impurities are also dissolved. The H_2ZrF_6+H_2SiF_6 species are separated by means of distillation producing a zirconium fluoride salt. The zirconium fluoride crystals can be steam pyrolysed to produce zirconia according to the following reaction:

$$H_2ZrF_6 + 2H_2O \rightarrow ZrO_2 + 6HF \qquad (2)$$

This final product, by virtue of having been prepared from zircon which contains radioactive elements such as uranium and thorium, will also contain these radioactive elements. This study is aimed at reducing the content of these elements to very low limits. Focus is put on the H_2ZrF_6+H_2SiF_6 solution and several methods of solution purification are employed in an attempt to remove mainly uranium and thorium. These purification methods include ion-exchange, solvent extraction and precipitation.

Since the medium in which we are working is HF, there are lots of limitations in experimental procedures. e.g., apparatus such as glass could not be used. Extreme safety measures have to be taken when doing the experiments.

1.3. CONTENTS OF THE STUDY

The report consists of seven chapters. Chapter one, already discussed above, gives an outline of the purpose of study. The second chapter gives the theoretical background of the purification methods employed in this study. Chapter three looks into the issue of radioactivity in mineral sands and how it has been handled in other countries. Chapter four gives the background of the analytical methods used in this study. The fifth chapter looks into the experimental methods and results. Chapter six is the discussion of results and the final chapter is a summary.

CHAPTER 2

THEORETICAL ASPECTS OF ION EXCHANGE AND SOLVENT EXTRACTION

2.1. ION-EXCHANGE

2.1.1. INTRODUCTION

Ion-exchange is by far one of the most successful purification methods to date. It has been extensively used in, among others, dealing with wastes, recovery of highly desired metals such as uranium, and very important processes such as water purification. It also has received a lot of application in analytical chemistry.

2.1.2. GENERAL THEORETICAL DISCUSSION ON ION-EXCHANGE

An ion-exchanger is basically an electrolyte solution containing cations, anions and water, differing, however, in that one or the other ion is bound to an insoluble micro porous matrix. In water-filled pores the remaining ion, of opposite charge to the fixed ion, is present in sufficient numbers to render the whole exchanger electrically neutral. These, the counter ions, are free to move through the matrix by diffusion or under electrical field and may be replaced by other counter ions (same charge) from solution, in the process of ion exchange.

Thus, an ion-exchange process is in one sense not a chemical reaction but simply a rearrangement of existing species in solution and exchanger, such as to achieve maximum chemical stability. No chemical bonds are broken or formed and there are no new chemical products.

2.1.3. ION-EXCHANGE RESINS

Ion-exchange resin are high molecular weight polyacids or polybases which are virtually insoluble in most aqueous and non-aqueous media. The ion-exchange resin can either be a cation exchange resin or an anion exchange resin.

2.1.3.1. CATION EXCHANGE RESIN

It is a high molecular weight, cross-linked polymer containing sulphonic, carboxylic, phenolic, etc., groups as an integral part of resin and an equivalent amount of cations. The cations can be exchanged for cations in solution in the following way:

$(Res.A^-)B^+ + C^+(Solution) \rightleftharpoons (Res.A^-)C^+ + B^+(Solution)$

(Where "Res" is the resin polymer)

2.1.3.2. ANION EXCHANGE RESIN

It is a polymer containing amine (or quartenary ammonium) groups as integral parts of the polymer lattice and an equivalent amount of anions such as chloride, hydroxyl, or sulphate ions. Strongly basic anion exchange resins are fully ionized in both the hydroxide and the salt forms. Some of their typical reactions may be represented as in the following example:

$(Quat^+)Cl^- + Br^-\ (solution) \rightleftharpoons (Quat^+)Br^- + Cl^-\ (solution)$

(Where Quat can be a quartenary ammonium group).

2.1.3.3. CHELATING ION-EXCHANGE RESIN

The current study concerns itself about a specialised type of resins, being the chelating ion exchange resin.

They are ion-exchangers in which various chelating groups (e.g., dimethylglyoxime and iminodiacetic acid) have been incorporated and are attached to the resin matrix. Their important feature is the greater selectivity which they offer compared with the conventional type of ion exchangers[4]. The affinity of a particular metal ion for a certain chelating resin depends mainly on the nature of the chelating group, and the selective behaviour of the resin is largely based on the different stabilities of the metal complexes formed on the resin under various pH conditions. The exchange process in a chelating resin is generally slower than in the ordinary type of exchangers, the rate apparently being controlled by a particle diffusion mechanism.

2.1.4. ION EXCHANGE CAPACITY

The total ion exchange capacity of a resin is dependant upon the total number of ion-active groups per unit weight of material, and the greater the number of ions, the greater will be the capacity. The capacity of the given ion-exchange resin can be measured in terms of K_D values, which are the relationship between the amount of solute in the resin and the amount of solute in the solution.

2.1.5. LITERATURE STUDY ON THE REMOVAL OF U AND Th BY ION-EXCHANGE

Chelating ion exchange resin have received a lot of applications given their advantages over the ordinary ion exchange resins, as discussed above. The diphosphonic ion exchange (diphonix) resin, for example, which is a polyfunctional resin containing sulphonic and gem-diphosphonic acid groups chemically bonded in a styrene-divinylbenzene polymeric network, has shown a lot of success in the up take of different metals in different media. Its application, just like the application of other chelating ion exchange resins, has been in conditions under which the conventional ion-exchange resins are ineffective. In metal contaminated aqueous waste solution, as an example, mineral acids are contained in high concentrations. This is particularly true with wastes containing actinide ions. Under such acidic conditions conventional ion exchange resins are ineffective and lack sufficient selectivity for transition metals and actinides over alkali and alkaline-earth cations which are generally present in large excesses in the waste solutions. To overcome the selectivity problem, a number of chelating ion-exchangers, carrying functional groups capable of forming chelate complexes with selected ions, have been prepared and in some cases commercialised[5,6]

The diphonix resin has indicated a remarkably high retention of hexavalent uranium and tetravalent actinides in the whole acidity range even up to 10M HNO_3[7]. The up take of uranium and thorium by this resin further showed at least some inverse hydrogen ion dependency, as expected for a cation-exchange resin.

Studies by Argonne National Laboratory on TUCS (Thermally Unstable Complexants)[8] showed that one of the TUCS families, based on substituted methane diphosphonic acids, are powerful complexing agents in acid solutions[9]. Their ability to complex trivalent lanthanides and Th(IV) in acid solutions has been investigated[10,11] and is mainly attributed to the high acidity of the diphosphonic acid group. Vinylidene-1,1-diphosphonic acid, VDPA, for example, has been reported to have a $pK_{a,1} = 1.4$ and a $pK_{a,2} = 2.8$[10]. The relatively strong acidity of the diphosphonic acid group and its tendency to form protonated metal complexes makes possible the formation of metal complexes under conditions too acidic for appreciable complexation by carboxylic and monophosphonic acids to occur[11].

The chelating bifunctional phosphinic acid resins were also found to be very good in the extraction of uranium. This was confirmed by the extraction of uranium as UO_2^{2+}.

2.2. SOLVENT EXTRACTION

2.2.1. INTRODUCTION

Solvent extraction has also received wide application in recovery of precious metals and purification processes. As an example, large amounts of uranium have been recovered from sea water by the solvent extraction method[12]. It is a process in which a solute of interest transfers from one solvent into a second solvent that is essentially immiscible with the first. The extent of transfer can be varied from negligible to essentially total extraction through control of experimental conditions. Solvent extraction can be applied in any of the three methods, these being batch extraction, continuous extraction and counter-current extraction.

In practice in the solvent extraction process, metal ions in aqueous medium are brought into contact with an organic solvent, which is sparingly soluble in water. The enhanced stability of the undissociated species in the organic phase results in a transfer of the compound from the aqueous to the non-aqueous phase. Transfer in the reverse direction from the organic back to the aqueous phase correspondingly requires a shift of chemical equilibrium in the reverse direction and this process is known as 'stripping'[12].

Solvent extraction thus enjoys a favoured position among separation techniques because of its ease, simplicity, speed and wide scope. It is a method applicable to both trace-level impurities and major constituents. Furthermore, inorganic constituents are often separated in a form suitable for direct analysis by different types of analytical techniques.

2.2.2. SYNERGISM IN SOLVENT EXTRACTION

Synergism in solvent extraction refers to the enhanced extraction which results from the combination of two extractants as compared to their individual extraction ability. This term first occurred in the literature of solvent extraction in connection with observations made by US workers who noted that the extraction of uranium(VI) from aqueous solution by one of a dialkylphosphoric acid in an organic solvent was considerably enhanced by the addition of formally neutral organo-phosphorus compound R_3PO, where R is an alkyl or alkoxy group[13]. This phenomenon was also studied by Blake and his coworkers[14] who at first thought that uranium is the only metal which extracts synergistically. However, it was only after two years that they reported another synergism[15] in the extraction of Pu(IV) and Pu(VI). From that point onwards synergism was a phenomenon subject to intensive study and many workers in solvent extraction have reported a series of mixtures of extractants displaying this behaviour.

2.2.3. GENERAL THEORETICAL DISCUSSION ON SOLVENT EXTRACTION

Extraction of both uranium and thorium from different media has previously received a lot of attention. A lot of solvent extraction processes has been done to deal with wastes, to recover these metals and in purification systems. Chelating extractants have also been employed and they too have shown a lot of success, especially with regard to the extraction of uranium and thorium.

The degree of success of extraction of a metal by a given extractant depends, in some cases, on the acidity of the solution (its pH). As an example the extraction of U(VI) at a concentration of $5x10^{-3}M$ from acetate media by 10%(v/v) LIX 84 (2-hydroxy-5-nonylacetophenone oxime in kerosene)[16] in benzene was found to be pH dependant. The extraction was found to attain maximum at pH 2.6, with the maximum extraction being 70%, and no extraction was observed at pH beyond 3.3. The extraction of U(VI) at a concentration of $5x10^{-3}M$ from the nitrate media by 10%LIX 622 (dodecylsalicylaldoxime in a mixture of tridecyl alcohol and kerosene) in benzene was also studied over the equilibrium pH range of 3.0 to 6.0 (the pH varied by the addition of pyridine)[17]. The extraction was found to increase with increasing pH and becomes quantitative at pH 5.9. The effect of variation of percentage of LIX 622 and TBP in their mixture on the extraction of U(VI) has also been studied. It was observed that the extraction increases with increasing percentage of LIX 622 in its mixture with 10%(v/v) TBP and 0.03ml pyridine (percentage LIX 622 varied from 1-25) in the pH range of 4.0 to 4.5. Similarly, the influence of the variation of percentage of TBP in its mixture with 10%(v/v) LIX 622 and 0.03ml pyridine in benzene on the extraction of this metal ion shows that the extraction is an optimum at 2%(v/v)TBP and decreases thereafter. Hence, TBP can be used as a synergist up to 2%(v/v) after which it acts as an antagonist.

Organophosphorus acids, used as commercial extractants, have found wide application in solvent extraction. Initial studies were limited to dialkylphosphoric acids particularly di-(2-ethylhexyl)-phosphoric acid (D2EHPA)[18,19]. Further investigations led to the development of phosphinic acid extractants such as 2-ethylhexyl-phosphonic acid mono-2-ethylhexyl ester (PC-88A) and bis(2,4,4-trimethylpentyl)phosphinic acid (Cyanex 272). Cyanex 302 and Cyanex 301, the respective monothio and dithio analogs of Cyanex 272, have also been added to this category. Sulphur substitution proves beneficial to the extraction of metals at lower pH. These are all cation exchangers and extraction is carried out in weakly acidic media.

Investigating the ability of these extractants in extracting uranium[20] it was found that extraction of U(VI) by 1%(v/v) PC-88A, 1%(v/v) Cyanex 272, gives a gradual decrease in the percentage of extraction with increase in the acid concentration. The acid range under consideration was 0.1M to 1.0M HCl and below this range uranium predominantly exists as UO_2^{2+} ion. The extraction is quantitative for PC-88A (~97.4%) and Cyanex 272 (~98.0%) at ~ 0.1M acid concentration and decreases slowly down to ~45.9%(PC-88A) and ~52.4%(Cyanex 272) at ~1M HCl solution. For Cyanex 301, extraction is poor (33.3%) even at very low acid concentration (~0.1M). In case of Cyanex 302, extraction is poor (~47.4%) at 0.1M and decreases very rapidly with increase in acid concentration. The extraction was found to be independent of Cl^- ions. A comparative account of the efficiencies of these extractants in extraction of U(VI) was found to follow the order: Cyanex 272>PC-88A>Cyanex 302>Cyanex 301. With these extractants it further was observed that percentage of extraction is greater with mixtures of any two extractants as compared to that of individual ones. Strong synergism is observed when extraction occurs with the mixtures of PC-88A and Cyanex 272, PC-88A and Cyanex 302, and PC-88A and Cyanex 301. This is attributed to the replacement of one extractant by the other in the extracted complex due to greater stability and formation of chelate complexes. The extent of synergism was found to gradually decrease with increase in acidity. Synergistic effects are quite low for the mixtures of any other pairs of extractants.

The other interesting groups of extractants which have been used in the extraction of uranium and thorium are the carboxylic acid amides. Their ability to extract these metals was investigated in the nitrate media[21]. In this extraction it was found that increasing the steric bulk of the alkyl groups in the amides causes a marked decrease in the extraction of Th with a much smaller effect on the extraction of uranium, thus considerably enhancing the separation between these metals.

There are only a few satisfactory extractants for the isolation of U(VI) from high pH solution and in the presence of large salt concentrations[22]. Extraction of actinides from alkaline solutions has not received much attention either. It has been reported that actinides, including trans plutonium elements, have been extracted and concentrated from alkaline and carbonate in the presence of various complexing agents[23]. Some commercially available chelating extractants such as LIX 26 (an alkyl derivative of 8-hydroxyquinoline)[24] and LIX 54 (a phenyl alkyl β-diketone)[25,26], have been used as extractants in the solvent extraction of U(VI) and Th(IV) from acidic pH solutions and in the presence of large salt concentrations.

This study also focuses on the solvent extraction of uranium and thorium from H_2ZrF_6+H_2SiF_6 solution. The uniqueness of this study is the fact that this extraction takes place in a fluoride medium. This medium has been shown to have a lot of negative impact in the application of some purification methods and solvent extraction is no exception.

2.3. PROPERTIES OF ZIRCONIA

As mentioned in the introduction, zirconia is one of the products in line for production at the AEC. Zirconia (ZrO_2) is the most important and stable oxide of zirconium. It has as its main source zircon. Zirconia further has an impressive combination of intrinsic properties including high hardness, strength, high melting point, and biocompatibility[27]. Pure zirconia is a white powder with a melting point of 2710±35°C and exists in three well-defined crystalline forms: monoclinic, tetragonal, and cubic. Cubic zirconia is widely used as a diamond substitute[28] for both industrial and decorative applications. Chemical purity is essential for either purpose. Calcia-, and Yttria- stabilised zirconia play important roles as materials of great scientific and technological importance. They are associated with great strength, toughness, and reliability. They compete with metals and alloys in some applications[29] where high temperature performance, erosion resistance are required.

High purity zirconia can be produced by hydrothermal treatment[30], spray pyrolysis of zirconium containing solutions[31], crystallisation of zirconium oxychloride[32], and precipitation of zirconium as its basic sulphate[33] and hydrate sulphate[34,35].

A solvent extraction technique has been applied extensively for the purification of zirconium from most of its impurities, including hafnium[36]. Because ion exchange purification is the most powerful technique for purification, both cation and anion-exchange resins[37,38] have been utilised for the purification of zirconium solution, mainly for analytical purposes, by using one type of acid at a time. Murty *et al*[27] reported the success of the usage of a mixture of two acids HCl-H_2SO_4 with the anion-exchange resin. This method was also found to have several advantages over the usage of only one acid at a time.

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CHAPTER 3

THE ISSUE OF RADIOACTIVITY IN MINERAL SANDS

3. LITERATURE STUDY ON ZIRCON AND ITS PRODUCTS

3.1. INTRODUCTION

Due to the very dangerous and sometimes fatal effects resulting from exposure to radioactivity, it has become a thorny issue both for the public and industry. There are several sources of radioactivity but of more concern in this study is the radioactivity from minerals.

Mineral sands deposits are produced from weathering of granite and sandstone and usually consist of unconsolidated clayey sands. Radioactive contamination of mineral sands arises mainly through the presence of monazite which contains 5% to 7% thorium and 0.1% to 0.3% uranium. Monazite contamination occurs as free grains and as inclusions in ilmenite, rutile and zircon[1]. There are two other potential sources of radioactivity in the major mineral sands products [2,3]:

(1) alteration processes that result in adsorption of radioactive elements from ground water on external and fracture surfaces; and

(2) incorporation of thorium and uranium into the crystal lattice of the minerals at the time of formation in their original host rocks.

Disposal of radioactive solid wastes from mineral sands processing and subsequent refinement may pose potential risks to the public, the environment and to future land use. Because of the industry's proximity to population centres and the wide spread community phobia about radioactivity, public concern has been regularly expressed through the media and community action groups in relation to the radiological impact of mineral sands operations. Several governments, including South Africa, have responded by legislating on radioactivity levels.

There was previously some laxity regarding radioactivity. In Australia, as an example, environmental problems were given low priority and pollution control measures were rudimentary and unacceptable by today's standards at the first uranium mining operations[1]. The poorly designed tailings dams and oxidation of sulphides in waste heaps led to destruction of vegetation and heavy metal pollution in nearby rivers.

Exposure of human beings to radioactive compounds, such as the use of zircon having the typical low level of radioactivity associated with commercially available zircons, can also be shown to pose potential health risks. Inhalation of fine zircon dusts results in retention of particles within the lungs of those exposed to dust laden air. This is especially true in zircon milling operation. Partial resolution of radionuclides from these particles in body fluids can result in distribution of alpha radiation to areas within the body where radiological damage can occur.

3.2. ORIGIN OF RADIOACTIVITY IN ZIRCON SAND

Three potential sources of radioactivity in zircon sand has been discussed in paragraph 3.1. One of these sources is the incorporation of thorium and uranium into the crystal lattice of the minerals at the time of formation in their original host rocks. This arises from the fact that zircon generally forms a minor phase early during the magma crystallization process and is often enclosed within other more abundant minerals. Enclosure by other minerals can result in the formation of concentric bands representing variations in composition of minor elements, including thorium and uranium, within the individual grains. Tetravalent Th and U are capable of direct replacement for Zr^{4+} in zircon[3]. Concentrations as high as 6 weight percent U + Th have been reported although more commonly they are in the 20-4000 ppm range[4].

Thus, all commercially available zircons contain radioactivity in the form of U-238 and Th-232 radionuclides in the zircon lattice, and their respective radioactive progeny elements[5]. The significance of the progeny elements formed by radioactive decay of the parent nuclides is that for each radioactive decomposition of a parent there will ultimately follow a chain of decompositions until stable elements, subject to no further decomposition, are formed. In the case of Th-232 effectively nine further decompositions follow the initial decomposition while thirteen further decompositions follow the initial decomposition of U-238. These decompositions are schematically represented in annexure A. This therefore means that it is not completely correct to specify only the U and Th concentrations as a measure of their radioactivity, but that all the decomposition products must be analysed for. However, due to the very complicated radioanalytical procedures and the associated high costs that this entails, this is very seldom done. Commercially available zircons are of sufficient age from formation in original host rocks to allow establishment of "secular equilibrium", at which all radioactive progeny elements express the same rate of decomposition as the parent nuclides. Under such circumstances the rate of radionuclide decomposition, i.e. the radioactivity of zircon, is the sum of the rate of decompositions of each parent multiplied by the number of effective decompositions in the decomposition chain of the parent. Thus, the decay chain acts as a multiplier for the radioactivity of the parent. It is therefore more correctly to specify the radioactivity in zircon sand by the number of decompositions per second (Becquerel), i.e. total $\alpha+\beta$. This phenomenon is extensively used in the determination of the age of rocks and geological events[5].

3.3. METHODS USED FOR THE REMOVAL OF RADIOACTIVITY FROM ZIRCON AND ZIRCONIUM COMPOUNDS

There has been some attempts to remove radioactives from zircon and these have met with very limited success. All prior attempts have involved the direct use of mineral and organic acids in aqueous solution for leaching of radionuclides. Hollit *et al* reported that leaching with acetic, hydrochloric and nitric acid was found to be effective in reducing immediate beta radioactivity by up to 36%[5]. However, it is not clear to what extent such reduction was sustained over time, as removal of only short lived beta emitting progeny elements would result in fast re-establishment of original levels, as such progeny are regenerated by decay of the parent elements.

In other prior work some removal of uranium and thorium has been achieved when treating zircon for removal of surface coatings containing iron and organic matter in order to achieve prime grades[5]. Hence, it is known that treatment with sulphuric acid (e.g. at 150 °C) has resulted in 28% removal of uranium and 47% removal of thorium. The effect on the residual level of radioactivity is unknown, however, as progeny deportment has not been assessed. Since the main contribution to radioactivity comes from progeny elements of uranium rather than thorium, significantly higher removal of the entire uranium progeny chain than observed would be required for effective reduction in the level of radioactivity.

Hollitt *et al*[5] presented an invention which provides a process for reducing the content of radioactive components in a zircon concentrate. This process comprises of the following steps:

(i) heating the zircon concentrate (at temperatures in the range from 800°C to 1800°C) in the presence of an additive and under conditions that are capable of causing the zircon concentrate to at least partially decompose;
(ii) cooling the product of step (i)
(iii) subjecting the product of step (ii) to a chemical treatment (leaching with a mineral or organic acid with the leaching performed at temperatures in the range from 20 to 150°C) for removing at least a portion of the radioactive components present in the product of step (ii) but without necessarily significant removal of silica or zirconia; and
(iv) recovering zirconia and silica from the product of step (iii).

The above steps may optionally be followed by one or more of the following steps:

(v) washing the product of step (iv);
(vi) drying and calcining the product of step (v) for removal of retained moisture and production of a dry powdered product having a significant reduction in the level of radioactivity;
(vii) regeneration of acid and/or stabilisation of separated radionuclides in a solid waste form.

It has already been stated that one of the possible sources of radioactivity in zircon sands is the alteration processes due to weathering, leading to accumulation of radionuclides on external and fracture surfaces. The major alteration process in zircon is the transformation to the metamict state (metamict minerals are minerals in which the crystalline structure has been disrupted by alpha particles produced by radioactive nuclei within the minerals[7]) which is accompanied by a decrease in density. The altered surface has a tendency to hydrate and take up contaminants, especially iron. The changes in physical properties associated with these processes are potentially exploitable to segregate the more radioactive zircons from the bulk concentrate[3]. Chemical processing is also likely to be successful in selective removal of radionuclides from zones of alteration. Leaching tests at ANSTO[3] have demonstrated selective leaching of U and Th from a zircon concentrate using a number of leachants. About 30% of the zircon grains in the concentrate contained metamict zones. The best result was dissolution of approximately 80% of the Th and 60% of the U. Approximately 14% of the zirconium was leached in the process. There appears to be an inevitable trade off between loss of radionuclides and zirconium.

The third source of radioactivity - that incorporated in the crystal structure- is the most difficult to remove and generally requires destruction of the matrix.

Wimmera Industrial Minerals[6] have developed a process to remove radioactive and other contaminants from zircon by roasting with a suitable additive (e.g. CaO or MgO) at a temperature within the range 800-1500°C. The radionuclides are then dissolved by leaching in acid.

3.4. LEGISLATIVE ASPECTS AND PERMISSIBLE EXPOSURE

There has been increased pressure in recent years from buyers to lower the radioactivity levels in concentrates and regulations have been tightened in some countries. Japan in particular, has tightened regulations governing the disposal of waste from pigment production plants and the US and the European Community are also looking at tighter regulations[3]. The Japanese regulations affect pigment manufacturers by limiting the radioactivity in waste sent to landfills. Depending on the process being used for pigment manufacture, the regulations are equivalent to a total U+Th in ilmenite of about 50ppm. Japanese pigment manufacturers are being encouraged to only import rutile, synthetic rutile and ilmenite that can satisfy the new regulations.

Until recently there has been less attention paid to the radioactivity levels in zircon, mainly because only a small portion of zircon concentrates are processed in a manner that produces wastes enriched in radionuclides. At this stage it appears likely that the acceptable limits for U+Th in zircon could be reduced from 500ppm to 250ppm[3].

In Australia, the regulatory instrument is the Mines Regulation Act 1946 and its associated regulations. The current regulations (effective 20 January 1989) adopt a Commonwealth of Australia Radioactive Waste Management (Mining and Milling) Code [CA 1982][2]. This code provides for prior development and approval (and subsequent updating) of a waste management programme for each mining operation to which the code applies. *Radioactive waste* is defined to include radioactive material which requires management such that the exposure to radiation of employees and members of the public shall be as low as reasonably achievable and below the relevant prescribed limits (namely, 1mSv/y for the public and 5mSv/y for employees, as also per International Council for Radiological Protection (ICRP) recommendation[5]). The application clause of the code (clause 14) states that the Code applies to the management of radioactive waste arising from all operations involving the mining and milling of *specified material.* Specified material is defined as the material which contains more than 0.02%U or 0.05%Th dry weight, or other radioactive material designated by the State Mining Engineer (the appropriate authority under the code).

Previously, the zircon producers never had a significant concern regarding the implications of the regulations governing the trace concentrations of naturally radioactive elements in zircon. This has been because the zircon industry's main focus has been on the U.S. Nuclear Regulatory Commission's (NRC's) licensing threshold for source material under which materials are exempt from NRC classification as licensable "source material" provided that the uranium and thorium content does not exceed 0.05 percent by weight, a value that a typical zircon sand will not exceed.

Now because the environmental regulation is predicated increasingly on "exposure," "dose," and "risk", the regulatory landscape for zircon is changing.

Quite recently, control over radioactive substances has been the subject of increased attention by federal authorities in the United States. In May 1994, the U.S. Environmental Protection Agency

(EPA) published draft regulation for cleanup of radioactive contamination that would establish an exposure-based standard and require cleanup to very low levels (15 millirem per year above background)[19]. This was followed by the NRC proposed decommissioning standards that would apply an identical 15mrem per year cleanup standard to all NRC-licensed facilities. Another unsuccessful legislative effort was initiated by Congress to revise the Comprehensive Environmental Response, Compensation and Liability Act (CERCLA or Superfund) that governs hazardous site cleanup. According to this zircon would have been classified as a chemical carcinogen, implying that it would be affected by the carcinogen cleanup standard intended to achieve a one-in-a-million cancer risk level. Finally in the end of 1994, EPA proposed revised federal guidelines for protection of general public against ionizing radiation that, while nominally adopting the internationally accepted public protection standard (100mrem per year above background), also recommended limiting public exposures from specific sources of radiation to only a fraction of that standard.

These regulations underline the increasingly stringent control over radioactive substances. This trend in regulation of radioactive substances in U.S. is shifting towards targeting materials at lower radioactivity levels and seeking to lower permissible exposures. Whatever reasons advanced for such stricter controlling rules, the reality of the situation is that low numerical standards proposed once established by law are likely to be applied to any location containing low specific activity materials, even disposal sites for zircon-containing materials.

The essence of the problem is that the U.S. government agencies have not established an adequate technical basis for applying stringent cleanup or exposure standards to very low level natural radioactive materials. Very stringent regulatory standards are the result of extremely conservative radiation exposure pathway models, unrealistic exposure scenarios (e.g. continuous exposure, influence of multiple radiation sites, no landfill cover), and outdated assumptions regarding the relationship of radiation and adverse health effects.

Given the current Congressional emphasis on risk-assessment and economic (cost-benefit) justification of new regulations, the opportunity exists to achieve legislative solutions to naturally occuring radioactive materials (NORM) disposal and cleanup problems without imposing undue burdens on the regulated community. Regulators in many States are aware that significant adverse economic consequences for industry will follow over-regulating beneficial materials that do not pose a significant health risk. Absent accurate data on the actual radiation exposure risks presented by zircon materials, however, will lead to regulatory decisions likely being based on "worst case" assumptions.

Because of the uncertain status of radiation regulation in the U.S. and the potential for adverse impacts on the zircon industry, members of the zircon community have joined together in a collective effort to address regulatory issues at federal and state levels.

3.5. REFERENCES FOR CHAPTER 3

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* These were presented at the "International Conference on Radiation Protection and Radioactive Waste Management in the Mining and Minerals Processing Industries" held in Johannesburg (South Africa) in February 1995.

CHAPTER 4

ANALYTICAL TECHNIQUES

4.1. INTRODUCTION

In the course of this study three analytical techniques have been employed. These are the XRF (X-ray Fluorescence) and NAA (neutron activation analysis). An $\alpha\beta$ counter for radioactivity measurements has also been used in some cases for the determination the radioactivity level. The XRF analyses were done at the Pelindaba Analytical Labs, NAA analyses were done at Radioanalysis and radioactivity measurements were done at Plant Support Technology, all of the AEC.

4.2. THE XRF METHOD

4.2.1. THE XRF INSTRUMENT

The XRF instrument used is a Phillips 1440 which uses the rhodium tube. The scanning for each element takes 30 minutes.

4.2.2. THE ANALYSIS OF LIQUID SAMPLES

The analysis of the H_2ZrF_6+H_2SiF_6 solution has been done using the XRF technique. In this case the analysis is done directly, that is, the solution is put in a sample holder and analysed. Though this is a simple process as it does not involve sample preparation, it has, associated with it, some problems. This stems from the fact that the solution in to be analysed is in the fluoride medium. This presents some complications to the instrument as it has a very sensitive window which cannot tolerate the medium (HF vapour) for too long. Given that the sample has to stay in the instrument for a relatively long time, ten minutes, the analysis becomes problematic in the sense that there is a high risk of the window being damaged. To overcome this problem the analysis was done on solid samples as outlined in paragraph 4.2.3. Thus, in the experiments done analyses were originally done on liquid sample until the above problem was experienced. Thereafter the analyses done were on solid samples.

4.2.3. THE ANALYSIS OF SOLID SAMPLES.

To obtain solid samples, the H_2ZrF_6+H_2SiF_6 solution is evaporated to dryness and thereafter kept in an oven for at least 2 hours at 200°C to obtain a stable product.

For the analysis using the XRF technique, 0.6g of the sample is mixed with 5.4g of lithium tetraborate and the two fused for four hours in a platinum crucible at 1100°C to obtain a clear glass bead. A small amount of potassium iodide is then added, and this melt is then cast into a glass bead. The purpose of potassium iodide is to loosen the glass bead. The analysis is then done on the glass bead.

This analysis is very complex. This is because the uranium and thorium peaks are very small compared to the zirconium peaks. The higher the zirconium content the less pronounced are the uranium and thorium peaks, to an extent that it sometimes becomes difficult to separate these peaks from the background. Because the zirconium content of the sample has the same effect on the uranium and thorium peaks a rhodium Compton peak is used as an internal standard in correcting the uranium and thorium peaks. This is achieved by using samples of different zirconium content and monitoring the effect on the Rh-Compton peak. This is then taken as the effect on the uranium and thorium peaks as they will have the same effect.

Despite the difficulties experienced with the XRF technique, it still remains the best technique to do the analysis in this study. The inductive coupled plasma (ICP) technique, for example, does not provide a good technique at all, because for sensitive uranium lines there is always interference from either zirconium or hafnium.

Since the preparation, as outlined, entails dilution, the detection limit for uranium is 30ppm and for thorium is 20ppm.

4.3. THE NAA TECHNIQUE

This method is also regarded as good for the analysis of uranium and thorium. The samples were analysed in solid form, i.e. liquid samples were evaporated to dryness under an infrared light. Sub-samples are taken from the homogenized materials, weighed and sealed in specially designed irradiation vials for irradiation in a neutron flux in the SAFARI nuclear reactor. After irradiation, and cooling (i.e. allowing the radiation in the sample to come down to acceptable levels), samples were counted with gamma-spectrometer system.

In the case of uranium and thorium determination where the analysis is done with NAA, a solid sample of 200mg is used, while in the case of a liquid sample 500μl is evaporated down.

4.4. METHOD OF αβ COUNTING

An αβ counter was used in the determination of radioactivity levels in samples. The sample preparation for counting entails grinding the sample to fineness. This finely ground powder is thinly spread on a filter paper. The sample must be spread thin enough to allow the alpha particles to travel through to the detector. Thereafter the sample on a filter paper is placed on a planchette and placed in a sample holder in the instrument.

The counting is done for 30 minutes. The results are given from the instrument in alpha and beta counts and using the programme especially made for this the alpha and beta activities in Bq/g are calculated.

CHAPTER 5

SELECTIVE PRECIPITATION METHOD

5.1. INTRODUCTION

Selective precipitation has been one of the best purification methods employed to date in the removal of radioactive impurities in H_2ZrF_6+H_2SiF_6 solution. The precipitation process is in one part carried out by stirring a given amount of precipitant in the mother liquor for a given period of time after which the solution is filtered out. In the other part a precipitant forms part of the reagents. It is mixed with PDZ and the mixture reacted with HF in the same way that the H_2ZrF_6+H_2SiF_6 solution (mother liquor) is prepared.

Various types of calcium based compounds have been used as precipitants. Some of these gave some measurable success whereas others gave poor results or it will not be cost effective to use them. The usage of Ca-based compounds stems from the fact that the "white fraction", which forms as a precipitate in the preparation of H_2ZrF_6+H_2SiF_6 solution, contains calcium. Previous results have suggested an inverse relationship between the uranium and thorium content of the solution and the calcium content of the "white fraction". It was observed that the higher the calcium content of the "white fraction" is, the lower was the uranium and thorium content of the solution.

5.2. GENERAL EXPERIMENTAL METHOD

As indicated in chapter one, the mother liquor (H_2ZrF_6+H_2SiF_6 solution) is prepared by reacting PDZ with HF. This is done by stirring PDZ in HF for 24 hours.

As already mentioned above there are two ways of carrying out the selective precipitation processes. In the first case a given amount of precipitant is stirred in the mother liquor for a specified period of time with the intention that the impurities will be precipitated from the solution and settle with the precipitant at the bottom. At the end of the experiment the solution is separated from the precipitant by gravity filtration using filter paper.

The other method of selective precipitation is carried out by mixing the precipitant with the PDZ and reacting the mixture with HF. In this case the precipitant will also react with HF to form, mostly, CaF_2. At the end the precipitant will settle at the bottom with the "white fraction" (which is normally the resultant of preparation of the mother liquor) and the solids filtered out using filter paper.

The analysis for uranium, thorium, and zirconium content have been done on the liquid form of the mother liquor and on the mother liquor evaporated to dryness. The latter form was prefered after realising that the results of the liquid form are not as reliable as the results in the solid form. Preparation of the sample in the solid form involves heating the mother liquor to dryness followed by heating at 200°C for at least two hours to get a more stable compound. The analysis of the above mentioned elements is done at the AEC's analytical department using the XRF technique.

5.3. PRECIPITATION WITH CaF_2

Table 5.1: Concentrations of U and Th in liquid samples (mg/l) and in the precipitants (mg/kg) and the concentration of Zr in both the liquid samples and the precipitants

Duration	mass (g) of precipitant	[U](mg/kg) in precipitate	[U](mg/l) in solution	%U removed	[Th](mg/kg) in precipitate	%Zr in precipitate
	blank	-	53	0.0	-	-
16h	0.5	392	44	17.0	372	8.4
	2.5	419	33	37.7	311	9.0
	5.0	263	23	56.6	187	8.9
	7.5	136	18	66.0	93	9.0
1h	0.5	195	47	11.3	219	8.7
	2.5	306	34	35.8	254	7.4
	5.0	216	18	66.0	153	9.4
	7.5	153	19	64.1	98	9.7

NB: The concentration of thorium in solution was in all cases less than 3mg/l and the percentage Zr in solution was in all cases 17.2.

Though the uranium removal is not as good as in the case of $CaH_4O_8P_2.H_2O$ (see section 5.7 later) it seems not to be dependent on the duration of the stirring process. The results also show an increase in the percentage removal as the amount of CaF_2 used increases.

5.4. PRECIPITATION WITH CALCIUM GLUCONATE

Table 5.2: ***The concentrations (mg/l) of U and Th and the concentration of Zr in liquid samples when calcium gluconate is not used (blank) and when it is used as a precipitant***

Duration	**Calcium gluconate**			
60 minutes	mass of precipitant (g)	[U] (mg/l)	[Th] (mg/l)	%Zr
	blank	46	30	10.6
	2.0	40	29	9.5
	5.0	31	24	8.3
	10.0	25	19	6.3
3 h	2.0	42	28	9.5
	5.0	36	26	8.3
16 h	2.0	43	35	8.3
	5.0	39	25	8.3

The results demonstrate, in general, the ineffectiveness of this compound in precipitating uranium and thorium from H_2ZrF_6+H_2SiF_6 solution. It is clear that calcium gluconate could only remove a maximum of 46% uranium when 10.0g of this compound was stirred for 60 minutes. This removal is accompanied by a 41% change in the Zr content of the solution. This high percentage change of Zr and the low percentage uranium removal renders this compound ineffective.

Despite the generally low percentage removals, these percentages seem to be enhanced at shorter contact times

5.5. PRECIPITATION WITH CALCIUM TARTRATE

Table 5.3: ***The concentrations (mg/l) of U and Th and the concentration of Zr in liquid samples when calcium tartrate is not used (blank) and when it is used as a precipitant***

Duration	**Calcium tartrate**			
	mass of precipitant (g)	[U] (mg/l)	[Th] (mg/l)	Zr (%)
	blank	44	29	10.6
1h	2.0	38	25	9.5
	5.0	13	18	8.3
3h	2.0	32	23	9.5
	5.0	34	30	6.3
16h	2.0	37	30	8.3
	5.0	37	35	6.1

The above results demonstrate, in general, the ineffectiveness of these compounds in precipitating uranium and thorium from H_2ZrF_6+H_2SiF_6 solution. It is worth noting, however, that calcium tartrate is capable of removing up to 70% of uranium from the solution when 5.0g of this compound was stirred for 60 minutes. This removal is unfortunately accompanied by about 22% change in the Zr content of the solution, a result which might suggest the formation of some other insoluble Zr compounds.

Despite the generally low percentage removals, these percentages seem to be enhanced at shorter contact times

5.6. PRECIPITATION WITH AMMONIUM CARBONATE [$(NH_4)_2CO_3$]

Table 5.4: The percentage U and Th removed from the H_2ZrF_6+H_2SiF_6 *solution and the concentration of Zr in solution after precipitation with* $(NH_4)_2CO_3$

Duration	mass(g) of precipitant used	%U removed	%Th removed	%Zr
60 min.	5.0	86.0	63.0	45.0
	10.0	91.0	66.7	65.0
	15.0	92.0	70.4	56.1
	20.0	71.0	59.2	38.2
3 h	5.0	71.0	40.7	42.2
	10.0	87.0	63.0	64.2
	15.0	88.0	63.0	53.2
	20.0	95.0	63.0	39.3
5 h	5.0	86.0	59.2	50.3
16 h	5.0	78.0	48.1	58.4
18h	1.0	38.5	51.8	6.9

The results indicate good uranium and thorium removal. They seem to indicate that for shorter periods of time small amounts of the compound give higher percentage removals than larger amounts, with the situation reversed for longer periods of time. Though the results are satisfactory with regard to the removal of U and Th, the serious problem is the subsequent percentage change in the Zr content of the solution (which is also high). This result might probably be due to the formation of a $(NH_4)_3ZrF_7.xH_2O$ type compounds in the precipitate.

The preceeding discussions clearly demonstrate the outstanding ability of $(NH_4)_2CO_3$, as compared to other compounds used, in precipitating uranium from H_2ZrF_6+H_2SiF_6 solution. It, however, has the disadvantage of effecting the change in the percentage Zr content of the solution. CaF_2 and $CaH_4O_8P_2.H_2O$ (see section 5.7) on the other hand offer the advantage of not effecting any percentage change of the Zr content of the solution even though their success in removing uranium and thorium from the solution is less compared to that of $(NH_4)_2CO_3$. Contact time seems to have an influence on the percentage removal, which seems to be enhanced at shorter contact times than longer contact times.

5.7. PRECIPITATION WITH $CaH_4O_8P_2.H_2O$

Different amounts of this compound were used and Table 5.5 below gives the results with regard to the removal of uranium and thorium in the solution. The precipitates were also analysed and their results are also presented in Table 5.5.

Table 5.5: Concentrations of U and Th in liquid samples (mg/l) and in the precipitants (mg/kg) and the concentration of Zr in both the liquid samples and the precipitants

Duration	mass (g) of precipitant	[U](mg/kg) in precipitate	[U](mg/l) in solution	%U removed	[Th](mg/kg) in precipitate	%Zr in precipitate
	blank	-	51	0.0	-	-
16h	0.5	785	42	17.6	646	43.6
	2.5	111	38	25.5	102	24.2
	5.0	63	35	31.4	65	22.4
1h	0.5	1285	41	19.6	902	41.5
	2.5	204	24	52.9	130	24.4
	5.0	93	16	68.3	69	22.3
	7.5	49	14	72.5	42	19.7

NB: The %Zr in solution was in all cases 17.2 and the concentration of Th in solution was in all cases less than 3mg/l.

The results indicate the removal of an appreciable amount of uranium in shorter time intervals (as compared to the longer time intervals) with the percentage of uranium removed increasing with the increase in the amount of $CaH_4O_8P_2.H_2O$ used.

5.7.1. REMARK ON OBSERVATIONS

As it has been mentioned in the above discussions, calcium *bis*(dihydrogenphosphate) monohydrate, $CaH_4O_8P_2.H_2O$ provides the most plausible way of removing uranium from H_2ZrF_6+H_2SiF_6 solution by precipitation methods. It was further observed that this compound gives better percentage removal when stirred for 60 minutes as compared to longer periods of time. Given this, further investigations were launched in a bid to optimise our results. Factors investigated were the amount of the compound used, the reaction temperature, the surface area of the particles of the compound and the contact time.

5.7.2. THE EFFECT OF CONTACT TIMES AND MASS WHEN $CaH_4O_8P_2.H_2O$ IS USED AS A PRECIPITANT.

Contact times between 10 and 60 minutes were evaluated. Different amounts of $CaH_4O_8P_2.H_2O$ were each stirred in 50ml of H_2ZrF_6+H_2SiF_6 solution for diffferent durations. The results obtained are given in Table 5.6.

Table 5.6 ***Percentage U removed from H_2ZrF_6+H_2SiF_6 solution when $CaH_4O_8P_2.H_2O$ is used as a precipitant***

Contact time	mass (g)	%U removed
10 minutes	2.5	33.0
	5.0	25.0
	7.5	36.0
20 minutes	2.5	36.0
	5.0	54.0
	7.5	67.0
30 minutes	2.5	29.0
	5.0	60.0
	7.5	71.0
45 minutes	2.5	40.0
	5.0	69.0
	7.5	65.0
60 minutes	2.5	48.0
	5.0	58.0
	7.5	71.0

The results clearly indicate an increase in the percentage removal as the contact time increases from 10 to 60 minutes. Furthermore, larger amounts of precipitant enhance percentage removal of uranium. It can then be concluded that up to so far 60 minutes is the optimum time and 7.5g the optimum mass when $CaH_4O_8P_2.H_2O$ is used.

5.7.3. THE EFFECT OF TEMPERATURE WHEN $CaH_4O_8P_2.H_2O$ IS USED

Different amounts of $CaH_4O_8P_2.H_2O$ were each stirred in 50ml H_2ZrF_6+H_2SiF_6 solution at different temperatures for evaluating the effect of temperature on the capacity of this compound in precipitating U and Th from the solution. The contact time in each of the experiments was 60 minutes. The results obtained are given in Table 5.7:

Table 5.7: ***The effect of temperature on the removal of U from H_2ZrF_6+H_2SiF_6 solution when $CaH_4O_8P_2.H_2O$ is used as a precipitant***

mass of precipitant(g)	Temperature (°C)	%U removal
5.0	22	58.0
5.0	50	26.0
5.0	5	40.0
7.5	22	71.0
7.5	50	38.0
7.5	5	41.0

Temperatures different from 22°C (room temperature) seem not to enhance uranium removal. Using the suggestion that the precipitation process might be reversible as the basis of our argument, it can be argued that higher temperatures speed up the process with 60 minutes being enough for the reverse process to go to a significant extent. Thus, although the equilibrium is quickly attained it lies more to the left. On the other hand lower temperatures will slow down the process leading to slow attainment of equilibrium. These results are also given graphically in Figure 1.

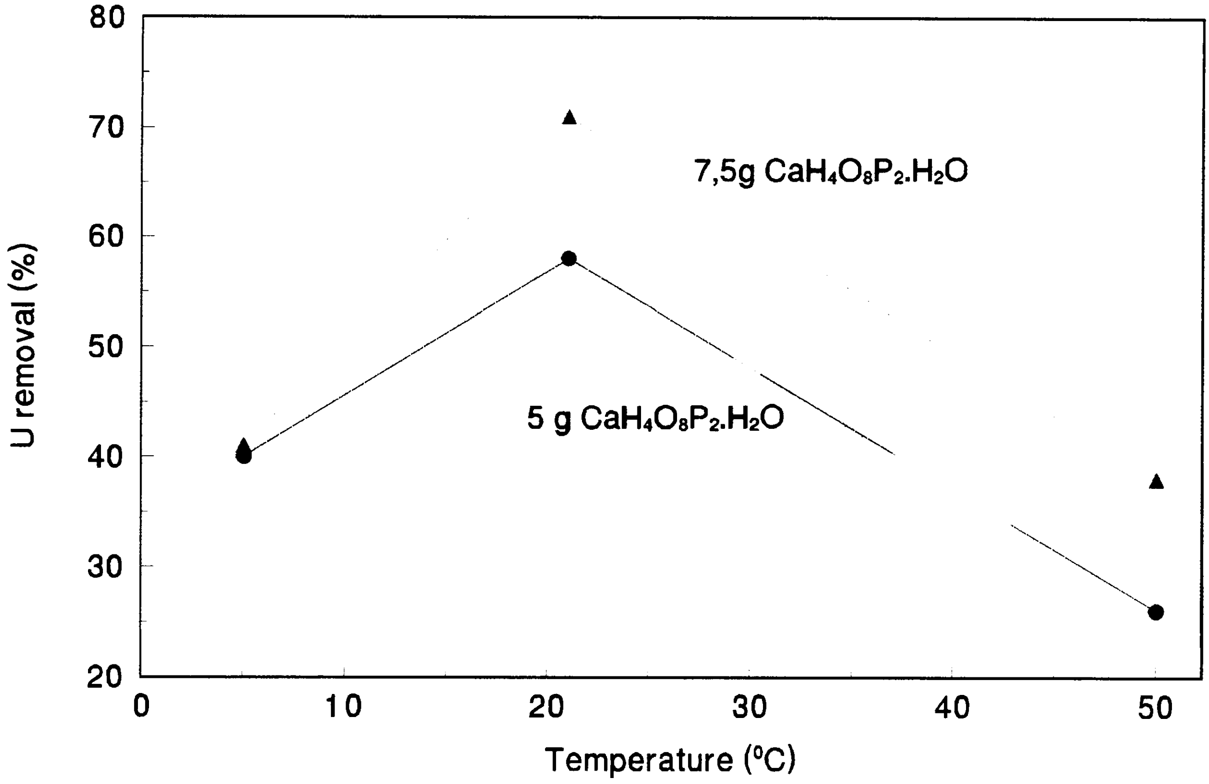


Figure 1: The effect of temperature on the removal of U when $CaH_4O_8P_2.H_2O$ is used.

5.7.4. THE EFFECT OF PHYSICAL FORM OF $CaH_4O_8P_2.H_2O$

Different amounts of $CaH_4O_8P_2.H_2O$ were finely ground and each stirred in 50 ml of H_2ZrF_6+H_2SiF_6 solution. The results obtained are given in Table 5.8.

Table 5.8: Effect of physical form of $CaH_4O_8P_2.H_2O$ particles on uranium removal.

Amount(g)	%U removed	%Zr in solution
7.5*	57	9
7.5	51	9
5.0	42	10
7.5#	53	9

*The compound was initially heated at about 110°C to make grinding easier.

#In this case the sample was unground.

The results do not indicate any major difference in the ground and unground precipitant.

5.7.5 REPEATED PRECIPITATION FROM THE SAME SOLUTION

In investigating the number of times a solution can be treated to attain the maximum possible uranium removal, several batches of $H_2ZrF_6+H_2SiF_6$ solutions were each treated more than once with a new amount of the precipitant used each time. The results obtained are given in Table 5.9.

Table 5.9: Concentrations (in mg/l) of U and Th in solutions and %Zr after treatment

solution	[U](mg/l)	%U removed	[Th](mg/l)	%Zr	%Zr removed
blank	47	-	<3	16.2	-
P	7	85.1	20	9.5	41
Q	9	80.8	27	9.7	40
R	<3	>93.6	17	5.3	67
S	21	55.3	14	12.6	22
T	18	61.7	17	9.8	40

P = 2 x 5g $CaH_4O_8P_2.H_2O$ in 50ml of solution

S = 1 x 7.5g $CaH_4O_8P_2.H_2O$ in 100ml solution

Q = 3 x 7.5g $CaH_4O_8P_2.H_2O$ in 100ml of solution

T = 1 x 10.5g $CaH_4O_8P_2.H_2O$ in 100ml solution

R = 2 x 10.0g $CaH_4O_8P_2.H_2O$ in 100ml of solution followed by 5.0g of $CaH_4O8P_2.H_2O$.

The results indicate good uranium removal. The setback is the suggestion that zirconium is also being removed. This is not in line with the previous experiments which suggested no zirconium removal when $CaH_4O_8P_2.H_2O$ is used.

Further investigation of the number of times a solution can be treated to attain the maximum possible uranium removal, were done. In this case also several batches of $H_2ZrF_6+H_2SiF_6$ solutions were each treated more than once with a new amount of the precipitant used each time. The final solutions were evaporated to dryness and analysed in solid form. The results with regard to the removal of uranium and thorium are given in Table 5.10.

Table 5.10: The concentrations of U and Th (in mg/kg) in the H_2ZrF_6 powder and the respective %U and %Th removal

Sample	**[U] (mg/kg)**	**%U removed**	**[Th] (mg/kg)**	**%Th removed**	**%Zr**	**∆ %Zr**
blank	372	-	212	-	54	-
A	52	86	<20	>90.6	24.9	53.9
B	49	86.8	<20	>90.6	32.3	40.2
C	27	92.7	<20	>90.6	20.6	61.8
D	54	85.5	<20	>90.6	22.3	58.7
E	107	71.2	<20	>90.6	39.0	27.8

A = 2 x 10.0g $CaH_4O_8P_2.H_2O$ in 100ml solution
B = 2 x 7.5g $CaH_4O_8P_2.H_2O$ in 100ml solution
C = 10.0g $CaH_4O_8P_2.H_2O$ in 100ml solution follwed by 5.0g and finally 3.0g.
D = 7.5g $CaH_4O_8P_2.H_2O$ in 100ml solution followed by 5.0g and finally 3.0g.
E = 5.0g $CaH_4O_8P_2.H_2O$ in 50ml solution followed by 2.0g.

The results indicate very good uranium and thorium removal. The reduction in the percentage of zirconium in our compound is discouraging as it might suggest the formation of a different compound (which might be through the coordination with the calcium compound used) the nature of which is unknown. The same trend has been observed with results of similar experiments done previously. As there is some consistency in the results of these experiments we have to investigate what type of a compound is being formed here. This will help in deducing the success or otherwise of this method.

5.7.6 REUSING THE PRECIPITANT

Several previously used precipitants ($CaH_4O_8P_2.H_2O$) were each, after drying, ground and reused. This was done to investigate the possibility of reusing the precipitant. The success of this will be a big incentive as it will go a long way in reducing costs. The results with regard to the removal of uranium and thorium from the solution are given in Table 5.11.

Table 5.11: The amounts of U and Th in precipitants before and after reusing

	Before reusing		**After reusing**		**% accumulated**	
Sample	**U(mg/kg)**	**Th(mg/kg)**	**U(mg/kg)**	**Th(mg/kg)**	**U**	**Th**
A	103	68	234	132	127	98
B	167	160	200	174	20	9
C	145	114	219	126	51	11
D	146	116	184	132	26	14

The results indicate some success in reusing the precipitant since each time more uranium has been accumulated than when it was used for the first time.

A measure of successs has been achieved up to now with regard to the removal of uranium and thorium from H_2ZrF_6+H_2SiF_6 solution using the selective precipitation method. In this method use has been made of $CaH_4O_8P_2.H_2O$. Of interest now is the reusability of this compound as a precipitant. To achieve this, attempts have been made to remove uranium and thorium from the already used precipitant so as to "regenerate" this precipitant. We have up to so far had some success with the decontamination solution (Na_2CO_3+H_2O_2+NH_3) and we have previously noted that an increase in the amount of this solution enhances the removal (see paragraphs 5.7.7 and 5.7.8). Reported here is the effect of the increased concentration of this solution. We have furthermore investigated the reusability of this precipitant after treating with the decontamination solution

5.7.7. REGENERATION OF THE PRECIPITANT USING DECONTAMINATION SOLUTION

Several previously used precipitants were each stirred in a different volume of the decontamination solution (5% Na_2CO_3 + 1% H_2O_2 + 1% NH_3) for 60 minutes and the results with regard to the removal of uranium and thorium are given in Table 5.12. Decontamination solution solubilises the uranium. It is expected that this will make it easy to rid the precipitant of uranium and thorium. In the decontamination solution, the peroxide oxidizes uranium to a soluble oxidation state whereas ammonia and the carbonate ion form soluble complexes with uranium.

Table 5.12: Concentrations (mg/kg) of U and Th in the precipitants before and after treating with decontamination solution.

volume of solution (ml)	Before treatment		After treatment		% removed	
	U(mg/kg)	Th(mg/kg)	U(mg/kg)	Th(mg/kg)	U	Th
100	170	149	157	136	8	9
150	200	119	119	135	41	-
200	150	107	31	136	80	-

The results indicate an increase in the removal of uranium from the precipitant when the volume of the decontamination solution is increased. It is encouraging to realise an 80% uranium removal from the precipitant when 200 ml is used.

In further attempts to regenerate the precipitant, the concentration of the decontamination solution was increased and its effects investigated. The aim is to have the regeneration of the precipitant enhanced. The concentration of this solution has now been increased to $7\%Na_2CO_3+2\%H_2O_2+2\%NH_3$. As in the previous case the previously used precipitants were each stirred in different amounts of this solution for 60 minutes and the results are given in Table 5.13.

Table 5.13: Concentrations (mg/kg) of U and Th in the precipitants before and after treating with 7%$NaCO_3$+2%H_2O_2+2%NH_3 solution

	Before treatment		After treatment		% removed	
volume (ml) **of soln**	**[U] (mg/kg)**	**[Th] (mg/kg)**	**[U] (mg/kg)**	**[Th] (mg/kg)**	**U**	**Th**
50	200	119	119	135	40.5	-
100	223	148	203	198	9.0	-
100	235	149	123	152	47.7	-
100	161	85	112	156	30.4	-
100	145	89	134	215	7.6	-
100	200	174	125	249	37.5	-
150	202	86	88	101	56.4	-
150	302	105	33	156	89.1	-
200	234	132	33	308	85.9	-
200	219	126	57	291	74.0	-
200	184	132	113	176	38.6	-

In the case of the usage of the decontamination solution with lower concentration the dependence of the amount of uranium removed on the amount of solution used was evident. With the increase in the concentration of the decontamination solution, it can also be seen that on average the increase in the amount of the solution leads to the increase in the amount of uranium removed though this trend is not too evident. Furthermore the increased concentration of the decontamination solution does not seem to bring much difference with regard to the amount of uranium removed. A slight increase is, however, observed.

The results further indicate an increase in the concentration of Th after the precipitant has been treated with decontamination solution. This might be as a result of the possible dissolution of the precipitant by the decontamination solution while not affecting Th in the precipitant, as the amount of Th will remain the same in a lesser matrix after treatment with the decontamination solution. If this is true then the situation as regards uranium removal is even better than it appears since the matrix being less would also lead to an apparent increase in uranium concentration. Even so the uranium concentration decreased which shows the effectiveness of the decontamination solution.

5.7.8. INVESTIGATION OF THE REUSABILITY OF THE PRECIPITANTS AFTER TREATING WITH THE DECONTAMINATION SOLUTION

The precipitants, after being subjected to treatment with decontamination solution, were reused in the precipitation process. In each case, each precipitant was stirred in a given amount of the mother liquor for 60 minutes and the results obtained with regard to the removal of uranium and thorium are given in Table 5.14.

Each precipitant was, as its first usage, stirred in 50ml of H_2ZrF_6+H_2SiF_6 solution for 60 minutes. It was then air dried at room temperature and thereafter stirred in a given amount of a given concentration of the decontamination solution. It was again dried and after grinding stirred in H_2ZrF_6+H_2SiF_6 solution for 60 minutes. Table 5.14 thus gives the amount of uranium accumulated during the first usage, the amount removed after being treated with the decontamination solution and the percentage of uranium removed from the mother liquor (which was evaporated to dryness prior to analysing) after the final use.

Table 5.14: The concentrations (mg/kg) of U in precipitants before and after treating with decontamination solution.

[U] after first precipitation	Treatment	[U] after treatment	% U removed from precipitant	%U removed from mother liq.
249	50ml 7%$NaCO_3$+2%H_2O_2+2%NH_3	203	18.5	64.0
223	100ml 7%$NaCO_3$+2%H_2O_2+2%NH_3	203	9.0	47.0
235	100ml 7%$NaCO_3$+2%H_2O_2+2%NH_3	123	47.7	73.0
161	100ml 7%$NaCO_3$+2%H_2O_2+2%NH_3	112	30.4	72.0
145	100ml 7%$NaCO_3$+2%H_2O_2+2%NH_3	134	7.6	80.3
202	150ml 7%$NaCO_3$+2%H_2O_2+2%NH_3	33	83.7	86.0
202	150ml 7%$NaCO_3$+2%H_2O_2+2%NH_3	88	56.4	55.0

The results with regard to the removal of uranium from the precipitants after being treated with the decontamination solution are not impressive as they show low percentage removals. This, however, seems not to have any impact on the success of the reusability of these precipitants. On the other hand there is some great success with regard to the reusability of precipitants with up to 86% of uranium being removed from the mother liquor. Given these high percentage removals of uranium from the mother liquor after the sometimes unsuccessful removal of uranium from the precipitants one might reach the conclusion that treatment of these precipitants with the decontamination solution enhances uranium removal from the mother liquor regardless of how successful the decontamination solution is in removing uranium from the precipitants.

There have been some interesting results when some of the precipitants are being reused. Some precipitants after being stirred in the mother liquor were dried, ground and stirred again in the mother liquor without having been treated with the decontamination solution. The results showed low uranium and thorium removal when used for the second time. These precipitants were then treated with decontamination solution and after drying stirred in the mother liquor. The results with regard to uranium and thorium removal are given in Table 5.15.

Table 5.15: ***The % U and Th removals from precipitants and the concentrations (in mg/kg) of U and Th after the final stirring in the mother liquor (which was evaporated to dryness)***

Treatment	**%U removed from precipitant**	**%Th removed from precipitant**	**[U](mg/kg) in H_2ZrF_6**	**[Th](mg/kg) in H_2ZrF_6**
-	-	-	365	198
200ml 7%$NaCO_3$+2%H_2O_2+2%NH_3	85.9	0.0	454	45
100ml 7%$NaCO_3$+2%H_2O_2+2%NH_3	37.5	0.0	456	88
200ml 7%$NaCO_3$+2%H_2O_2+2%NH_3	74.0	0.0	408	91
200ml 7%$NaCO_3$+2%H_2O_2+2%NH_3	38.6	0.0	717	305

The results as given in Table 5.15 above suggest the uptake of uranium from the precipitant into the H_2ZrF_6+H_2SiF_6 solution during stirring. This is evidenced by the increase in the amount of

H_2ZrF_6+H_2SiF_6 after the precipitant has been stirred in. These results are observed despite the encouraging uranium removal from the precipitants by the decontamination solution.

Reusing precipitants without prior treatment with decontamination solution seems to diminish chances of reusing them even after treatment. It is not clear at this stage how this happens but comparison of results in Table 5.14 (where the precipitants were treated with decontamination solution before reusing) and Table 5.15 above clearly indicates this behaviour. In searching for explanation for this, more experiments should be done.

5.8. PRECIPITATION WITH CaO

5.8.1. INTRODUCTION

After realising the success of some Ca-compounds in “trapping” uranium out of the H_2ZrF_6+H_2SiF_6 solution it was thought of using them differently. It was thought that adding the compound as part of the reagents in the preparation of this solution (according to equation 2) would make the process more effective as this would save a lot of time. In this precipitation process, the precipitant is mixed with PDZ and the mixture reacted with HF in the same way as the mother liquor is prepared.

The H_2ZrF_6+H_2SiF_6 solution was prepared by mixing the starting material, $ZrO_2.SiO_2$ (PDZ), with a stoichiometrically equivalent amount of CaO and the process carried out by stirring this mixture in HF solution. The solution was also prepared without the addition of CaO for comparison purposes. Based on the reactions when CaO is used and when it is not used the volume of HF used will be different.

$$ZrO_2.SiO_2 + 14HF + CaO \text{-------->} H_2ZrF_6 + H_2SiF_6 + CaF_2 + 5H_2O\text{..........(2)}$$

The results of the experiments with regard to the removal of uranium and thorium are given in Table 5.16.

Table 5.16: ***The concentrations (in mg/kg) of U and Th in $H_2ZrF+H_2SiF_6$ solution (which was evaporated to dryness) and the percentage Zr with and without CaO added as a reagent.***

reaction type	**%Zr**	**[U](mg/kg)**	**% U removed**	**[Th](mg/kg)**	**% Th removed**
No CaO added	52.8	396	-	197	-
CaO added	52.9	40	**90**	7	**97**
CaO added	52.5	56	**86**	34	**83**

The results show very good uranium and thorium removals without a significant change in the Zr content.

5.8.2. VARIATION OF CaO MASS

The success of calcium oxide (CaO) in "trapping" uranium out of the $H_2ZrF_6+H_2SiF_6$ solution when used as a reagent in the preparation of this compound has been shown above. A uranium removal of up to 90% and thorium removal of up to 97% were reported. Taking both the cost and the problem of dealing with radioactive wastes into account it is desirable to use as small an amount of CaO as possible with the high radioactivity removal. Reported here is the effect of a decreased amount of CaO in the removal of these radioactive compounds.

Different amounts of CaO were mixed with $Zr0_2.SiO_2$ (PDZ) and the mixture used in the preparation of $H_2ZrF_6+H_2SiF_6$ solution. Different types of calcium based compounds were also used. The following is a brief outline of how the experiments were done:

Experiment A: 113.25g of 88.3% PDZ (0.546mol) stirred overnight in 283ml of 40% HF. i.e. no calcium compound added.

Experiment B: 113.25g of 88.3% PDZ (0.546mol) mixed with 30.62g CaO (0.546mol) and the mixture stirred in 330ml of 40%HF overnight.

Experiment C: 113.25g of 88.3% PDZ (0.546mol) mixed with 20.0g CaO (0.357mol) and the mixture stirred in 330ml of 40% HF overnight.

Experiment D: 113.25g of 88.3% PDZ (0.546mol) mixed with 10.0g CaO (0.178mol) and the mixture stirred in 330ml of 40% HF overnight.

Experiment E: 113.25g of 88.3% PDZ (0.546mol) mixed with 42.63g CaF_2 (0.546mol) and the mixture stirred in 283ml of 40% HF overnight.

Experiment F: 113.25g of 88.3% PDZ (0.546mol) mixed with 30.0g $CaH_4O_8P_2.H_2O$ and the mixture stirred in 330ml of 40% HF overnight.

After filtering the liquids recovered were evaporated to dryness before analysing.

The results of these experiments with regard to the removal of uranium, thorium and other trace elements are given in Table 5.17.

Table 5.17: The concentrations of U, Th, and some other trace elements (in mg/kg) and %Zr after the precipitation experiments

Exp	%Zr	[Ti]mg/kg	[Fe]mg/kg	[Ca]mg/kg	[P]mg/kg	[U]mg/kg	**%U removed**	[Th]mg/kg	**%Th removed**
A	54.7	334	736	36	334	360	-	198	-
B	54.3	565	585	69	575	29	**91.9**	*	#
C	53.4	721	695	44	767	94	**73.9**	17	**91.4**
D	55.3	426	472	64	424	90	**75.0**	46	**76.8**
E	53.7	421	413	91	439	150	**58.3**	56	**71.7**
F	50.8	308	687	3	67493	142	**61.1**	44	**77.8**

*=value below the detection limit. # = the value is greater than the maximum detectable value

Using CaO as part of the reagents undoubtedly gives very good uranium and thorium removal with up to 92% uranium and 100% thorium removed when PDZ and CaO are in the mole ratio of 1:1. A decrease in the amount of CaO used gives a slightly lower but still good uranium and thorium removal. It is also encouraging to note that the amount of calcium used does not appreciably increase the calcium content of the mother liquor. These results may suggest the formation of insoluble compounds between calcium and uranium and calcium and thorium which get trapped in the precipitate when the solution is filtered out.

Calcium fluoride on the other hand gives high percentage thorium removal (71.7%) and slightly lower percentage uranium removal (58.3%). $CaH_4O_8P_2.H_2O$ whilst giving good uranium removal (61.1%) and good thorium removal (77.8%), has a problem of heavily increasing the amount of phosphorus in the solution. This will limit its usage in this method of precipitation.

5.8.3. REPEATABILITY OF RESULTS OF EXPERIMENTS WITH CaO

The success of calcium oxide (CaO) in precipitating uranium and thorium from H_2ZrF_6+H_2SiF_6 solution has been reported above (paragraph 5.8.2). It further was reported (paragraph 5.8.1) that the amount of CaO used does have an effect on the removal of both uranium and thorium. A decrease in the amount of CaO used was found to result in a decrease in the amount of uranium and thorium removed. Reported here are the results of similar experiments done to check the consistency of this trend. Radioactivity measurements on the precipitants obtained after filtering were also done to reconcile these values with the amounts of U and Th removed from the solution.

In these experiments different amounts of CaO were mixed with $ZrO_2.SiO_2$ (PDZ) and the mixture used in the preparation of H_2ZrF_6+H_2SiF_6 solution. The following is an outline of how experiments were done:

Experiment A: 113.25g of 88.3% PDZ (0.546mol) stirred overnight in 283ml of 40% HF. i.e. no calcium compound added.

Experiment B: 113.25g of 88.3% PDZ (0.546mol) mixed with 20.0g CaO (0.357mol) and the mixture stirred in 330ml of 40% HF overnight.

Experiment C: 113.25g of 88.3% PDZ (0.546mol) mixed with 10.0g CaO (0.178mol) and the mixture stirred in 330ml of 40% HF overnight.

Experiment D: 113.25g of 88.3% PDZ (0.546mol) mixed with 5.0g CaO (0.089mol) and the mixture stirred in 330ml of 40% HF overnight.

After filtering the liquid samples were evaporated to dryness before analysing. The precipitates were dried and counted for radioactivity measurement using the αβ Counter.

The results of the experiments are given in Table 5.18. The results of the radioactivity measurements are given in Table 5.19.

Table 5.18: The concentrations (mg/kg) of uranium and thorium and their percentage removal from the evaporated solutions after being subjected to treatment with CaO and the percentage yield of the product*.

Exp	**mass after evaporation (g)**	**% yield**	**[U] (mg/kg)**	**%U removed**	**[Th] (mg/kg)**	**%Th removed**
A	60.23	**76.0**	364	-	197	-
B	31.19	**39.4**	76	79.0	26	86.8
C	60.59	**76.5**	145	60.2	64	67.5
D	74.35	**93.9**	107	70.6	50	74.6

* This percentage yield is calculated on the assumption that the final product (after the evaporation of H_2ZrF_6+H_2SiF_6 solution) is $ZrOF_2$.

The results indicate a drop in the percentage of uranium removed from 79.0% when 20.0g CaO was used to 70.6% when 5.0g CaO was used. There is also a drop in the amount of thorium removed from 86.8% when 20.0g CaO was used to 74.6% when 5.0g CaO was used. This serves to confirm the trend observed in the previous experiments. The results when 20.0g CaO is used, however, seem not to follow the trend with regard to the removal of both uranium and thorium. A similar behaviour was observed in the previous results, the reason for which is not understood at present. It is, however, important to note that the decreases in the percentage removals of U and Th with the decrease in the amount of CaO used is not enormous, resulting in still a generally good removal.

Whilst the percentage removal of uranium and thorium looks encouraging at this stage the percentage yield is a little disappointing. Thus, future experiments will be geared towards achieving, amongst others, better percentage yield.

Table 5.19: Activity (Bq/g) measurements of precipitates obtained in the preparation of H_2ZrF_6+H_2SiF_6 solution when CaO is used as a precipitant.

Exp	mass of precipitate (g)	α-activity (Bq/g)	β-activity (Bq/g)	Total Activity (Bq/g)
A	41.55	24.79	13.59	38.38
B	100.77	12.74	11.62	24.36
C	64.20	6.99	3.98	10.97
D	44.02	37.02	26.08	63.10

The results surprisingly show a drop in the activity when CaO is used. By virtue of having removed uranium and thorium from the solution it is expected that the precipitates will have higher activity than when CaO is not used. These results bring the reliability of the αβ-Counter instrument into question. More counting of these precipitates will, however, be done to verify these results.

For the repeatability of the CaO experiments, five experiments were carried out under identical conditions, with the procedure the same as outlined in the above experiments. In each of the experiments, 100g of PDZ was mixed with 5.0g CaO and the mixture reacted with 390ml of 40% HF for 18 hours. In the case of the blank, 100g PDZ was reacted with 290ml of 40% HF. The results of the experiments with regard to uranium and thorium removal and radioactivity removal are given in Table 5.20.

Table 5.20: The concentrations (mg/kg) of uranium, thorium and zirconium and the radioactivity (Bq/g) in the H_2ZrF_6 crystals when CaO was used as a precipitant in the preparation of H_2ZrF_6+H_2SiF_6 solution.

	CONCENTRATIONS					RADIOACTIVITY			
Exp	%Zr	[U] (mg/kg)	%U removed	[Th] (mg/kg)	%Th removed	α-activity (Bq/g)	β-activity (Bq/g)	Total activity (Bq/g)	% activity removed
blank	54.3	239	-	109	-	14.6	13.1	27.7	-
1	54.3	58	76	24	78	2.1	0.8	2.9	89.5
2	54.7	55	77	21	81	2.2	0.4	2.6	90.6
3	55.3	58	76	*17	>84	1.6	0.6	2.2	92.1
4	54.9	63	74	28	74	1.3	0.5	1.8	93.5
5	54.3	41	83	21	81	1.0	0.6	1.6	94.2

Of importance to note with these results is their consistency. This is a clear indication that the methods works, especially on a small scale. The percentage uranium and thorium removed together with the percentage radioactivity removed are at encouraging level. Their consistency is also an indication of their reliability. The results are the confirmation of the success of the method and now focus should be put on the scaling up of this method.

5.9. PRECIPITATION WITH BARIUM CHLORIDE

5.9.1. INTRODUCTION

Though the actual mechanism behind the success of CaO in the precipitation of uranium and thorium from H_2ZrF_6+H_2SiF_6 solution is not clear, it is strongly suspected that it has to do with the formation of CaF_2. This then led to the suggestion that the formation of a precipitant in and during the preparation of H_2ZrF_6+H_2SiF_6 solution might result in the coprecipitation of uranium and thorium. Thus the suggestion means that the success of CaO in the removal of uranium and thorium is not characteristic of it only, but might also be observed with other compounds.

Having that in mind, it was thought wise to use $BaCl_2$ as a possible precipitant of uranium and thorium from H_2ZrF_6+H_2SiF_6 solution. Barium chloride will in its reaction with H_2SO_4 form an insoluble $BaSO_4$. Thus in an attempt to form this precipitate there should be sulphate ions in the solution. This led to the spiking of the solution with H_2SO_4 as explained in the following paragraph.

5.9.2. EXPERIMENTAL

Several experiments were carried out with a view of determining the effect (if any) of $BaCl_2$ as a precipitant of uranium and thorium from H_2ZrF_6+H_2SiF_6 solution. To this effect an experiment was done in which 118.0g of 84.7% PDZ was mixed with 10.0g $BaCl_2$ and this mixture reacted with a 295ml solution of 1.7%(v/v) H_2SO_4 in 40%(m/m) HF for 24 hours. The solution was filtered and evaporated to dryness prior to analysing. The analysis was done by the XRF technique.

A control experiment was done by reacting 118.0g of 84.7% PDZ with 290ml of 40%(m/m)HF for 24 hours.

The results are given in Table 5.21.

Table 5.21: The concentrations (mg/kg) of uranium and thorium in samples not treated (control) and samples treated with $BaCl_2$

Experiment	**[U] (mg/kg)**	**%U removed**	**[Th] (mg/kg)**	**%Th removed**
control experiment	224	-	95	-
$BaCl_2$ used	143	36.2	1*	98.9

* = results below the detection limit

The results show very little amount of uranium removed. On the other hand almost maximum thorium has been removed. The selectivity of thorium over uranium is inexplicable.

Though not satisfactory as regards the amount of uranium being removed, $BaCl_2$ show some potential of removing uranium and thorium from the solution. The usage of both CaO and $BaCl_2$ simultaneously was investigated to establish if they might have a synergistic effect. The following experiments were carried out:

Experiment A:	A control experiment done by reacting 118.0g of 84.7%PDZ with 290ml of 40%(m/m) HF for 24 hours.
Experiment B:	A mixture of 5.0g CaO, 10.0g $BaCl_2$ and 118.0g of 84.7%PDZ was reacted for 24 hours with 390ml of 40%(m/m) HF spiked with 5ml of concentrated H_2SO_4.
Experiment C:	A mixture of 20.0g $BaCl_2$ and 118.0g of 84.7% PDZ was reacted for 24 hours with 290ml of 40%(m/m) HF spiked with 10ml of concentrated H_2SO_4. The purpose of this experiment was to determine the effect of increased amount of $BaCl_2$.

After filtering the solutions were evaporated to dryness prior to analysing. The analysis was done by the XRF method.

The results of the experiments are given in Table 5.22

Table 5.22: The concentrations (mg/kg) of uranium and thorium and the radioactivity measurements (Bq/g) and their percentage removal relative to the control experiment

Reaction	**[U] (mg/kg)**	**%U removed**	**[Th] (mg/kg)**	**%Th removed**	**α-activity (Bq/g)**	**β-activity (Bq/g)**	**Total activity (Bq/g)**	**%activity removed**
A	267	-	143	-	41.4	15.4	56.8	-
B	*15	>94.4	*13	>90.9	4.7	0.6	5.3	90.7
C	*14	>94.8	*11	>92.3	4.6	0.4	5.0	91.2

* = results below the detection limit

These are very good results in as far as the removal of uranium and thorium is concerned and in as far as the removal of total radioactivity is concerned. Of importance to note is that a mixture of CaO and $BaCl_2$ gives better results than either of these compounds used alone. This is a confirmation of the synergistic effect of the two compounds. Furthermore the results indicate that an increase in the amount of $BaCl_2$ used enhances especially the removal of uranium.

It is also encouraging to see the very high percentage of radioactivity removed. This underlines the success of the method.

5.10. CONCLUSIVE DISCUSSION

Calcium oxide has undoubtedly demonstrated its success in precipitating radioactive elements from H_2ZrF_6+H_2SiF_6 solution as compared to other precipitants tried. It is up to now the best precipitant to use. The amounts of uranium and thorium removed from the solution when CaO is used as a precipitant were found to depend on the the amount of CaO used. The larger the amount of CaO used the more will uranium and thorium be precipitated from the solution. However, the balance has to be found between the amount of waste generated and the amount of radioactivity that can be removed. The amount of waste generated has to be kept at minimum and manageable levels and to achieve that, the amount of CaO used has also to be at minimum levels. It therefore was thought that the best amount of CaO that should be used is 5% of the amount of PDZ used for the reaction. This will allow the generation of manageable amounts of waste whilst at the same time leading to the removal of substantial amounts of uranium and thorium.

It is further recommended that when CaO is used, it be homogeneously mixed with PDZ to allow the reactions between these reagents and HF to occur simultaneously.

On the other hand barium chloride ($BaCl_2$) showed some success, especially with larger amounts thereof. For optimum results it can be used together with CaO as the experiments performed underlined the existence of synergism between them.

CHAPTER 6

SOLVENT EXTRACTION METHOD

6.1. INTRODUCTION

Solvent extraction is a method that has been extensively applied in the recovery of metals, and the recovery of uranium is a process that benefitted a lot. The process of solvent extraction also received wide application in the purification processes.

Solvent extraction has also been employed in this study in a bid to remove radioactive elements from the H_2ZrF_6+H_2SiF_6 solution. The medium in which this solution is (the fluoride medium) makes the process unique and more challenging. It has, however proved not easy to work in this medium, as will be demonstrated by the results of the experiments given in this chapter.

In this work, the solvent extraction process was carried out by manually shaking the organic phase (extractant) and the aqueous phase (the mother liquor) together for 20 minutes. Thereafter they were allowed to separate overnight.

6.2. EXTRACTION WITH NON CHELATING EXTRACTANTS

The following are a list of non chelating extractants employed. In each case (unless stated otherwise) 100ml of H_2ZrF_6+H_2SiF_6 solution was extracted with 100ml of the extractant.

(I) Extractant A - undiluted TBP(tributyl phosphate)
(ii) Extractant B - 20%(v/v) TBP in CCl_4
(iii) Extractant C - 50%(v/v) TBP/Benzene. In this case 23.44g of $Al(NO_3)_3.9H_2O$ was dissolved in 100ml of H_2ZrF_6+H_2SiF_6 solution prior to extraction to add the nitrate medium.
(iv) Extractant D - 20%(v/v) TBP in benzene
(v) Extractant E - 50%(v/v) TBP/1-Propanol
(vi) Extractant F - 50%(v/v) TBP/n-butanol

(vii) Extractant G- 25%(v/v) n-butanol and 25%(v/v) TBP in benzene used to extract 50ml of the solution.

(viii) Extractant H - 50%(v/v) ethyl acetate in benzene used to extract 50ml of the solution

(ix) Extractant I - 25% TBP + 25% ethyl acetate in benzene used to extract 50ml of the solution.

(x) Extractant J - 50%(v/v) ethyl acetate in TBP used to extract 50ml of the solution.

The results with regard to the removal of uranium and thorium are given in Table 6.1.

Table 6.1: The concentrations (mg/l) of uranium, thorium and zirconium in the organic and aqueous phases before (blank) and after extraction.

Extraction	**Blank**			**organic phase**			**Aqueous phase**		
	[U] (mg/l)	**[Th] (mg/l)**	**%Zr**	**[U] (mg/l)**	**[Th] (mg/l)**	**[Zr]**	**[U] (mg/l)**	**[Th] (mg/l)**	**%Zr**
A	75	29	*	<3	<3	*	58	40	*
B	75	29	*	<3	<3	*	83	32	*
C	75	29	*	<3	<3	*	68	31	*
D	75	29	*	<3	<3	*	89	35	*
E	87	27	16.2	<3	<3	5.0%	72	32	14.7
F	87	27	16.2	<3	<3	0.4%	68	27	15.2
G	79	26	17.8	<3	<3	413ppm	86	28	17.3
H	79	26	17.8	<3	<3	7ppm	78	24	18.7
I	79	26	17.8	<3	<3	9ppm	87	26	18.6
J	79	26	17.8	<3	<3	266ppm	84	32	18

* = not analysed for

The results do not indicate any success in the extraction of uranium and thorium. This might suggest that both uranium and thorium are in the form of non extractible compounds in the solution. The failure of these non chelating extractants prompted the usage of chelating extractants in a view of investigating their effect.

6.3. EXTRACTION WITH CHELATING EXTRACTANTS

The following is a list of chelating extractants used in the extraction of uranium and thorium from the H_2ZrF_6+H_2SiF_6 solution. In each case 100ml of the extractant was used to extract 100ml of the solution.

(i) Extractant 1: 3% Tri-*n*-octylphosphine oxide (TOPO) in benzene
(ii) Extractant 2: 0.1M TOPO in cyclohexane
(iii) Extractant 3: 4.4% TOPO in toluene
(iv) Extractant 4: 0.045M 2-thenoyltrifluoroacetone (HTTA) and 36% TBP in cyclohexane
(v) Extractant 5: 10% acetylacetone (HAA)+0.1M Butyl phosphate in benzene
(vi) Extractant 6: 10% HAA + 3% TOPO in benzene
(vii) Extractant 7: 0.005M HTTA in benzene
(viii) Extractant 8: 5%HAA+5%TBP in benzene
(ix) Extractant 9: 20% HAA in benzene
(x) Extractant 10: 1x10^{-3}M EDTA in 10% HAA + 10%TBP in benzene

The results with regard to the removal of uranium and thorium are given in Table 6.2

Table 6.2: The concentrations(mg/l) of uranium, thorium and zirconium in organic and aqueous phases before (blank) and after extraction.

Extraction	**Blank**			**Organic phase**			**Aqueous phase**		
	[U] (mg/l)	**[Th] (mg/l)**	**[Zr]**	**[U] (mg/l)**	**[Th] (mg/l)**	**[Zr]**	**[U] (mg/l)**	**[Th] (mg/l)**	**[Zr]**
1	77	25	*	<3	<3	*	79	22	*
2	77	25	*	<3	<3	*	67	24	*
3	77	25	*	<3	<3	*	75	23	*
4	74	23	*	<3	<3	*	79	23	*
5	73	24	17%	<3	<3	45ppm	74	24	17%
6	73	24	17%	<3	<3	201ppm	80	24	17%
7	73	24	17%	<3	<3	6ppm	80	24	17%
8	73	24	17%	<3	<3	24ppm	73	26	17%
9	73	24	17%	<3	<3	10ppm	86	25	17%
10	73	24	17%	<3	<3	1ppm	82	22	17%

* = not analysed for

These results do not show any success in the removal of U from H_2ZrF_6+H_2SiF_6 solution. This is despite the employment of chelating extractants which have proved successful in the extraction of uranium from among others the perchlorate and nitrate media[1,2,3] and several other media. Furthermore U(VI) has been appreciably extracted at pH 2-7 by HAA in benzene or chloroform[4,5,6] with TBP acting as a synergist[7]. The U(VI)-HTTA-TBP and U(VI)-HTTA-TBPO mixtures have given synergic enhancement factors of the order of 10^3 and 10^4 respectively[8,9,10]. On the other hand tri-*n*-octylphosphine oxide (TOPO) has been used for the extraction and determination of, among others, uranium. Broadly speaking, TOPO yields more definite solvates than TBP and binds acids more strongly than TBP[11]. Using this, U(VI) was readily extracted from acid nitrate or chloride solutions and to a lesser extent from acid sulphate and perchlorate media[12]. U(VI) has also been successfully separated from Th, Zr and lanthanides by extraction with 3% TOPO in benzene[13]. However, it has been reported[12] that quantitative extraction of U(VI) from acidic solutions with TOPO is difficult to achieve because oxidation of U(IV) to U(VI) occurs to varying extent during equilibration. The oxidation is rapid and almost quantitative in HNO_3 media, nearly complete in H_2SO_4 and relatively slow in HCl systems. Given these and many other successes chelating extractants have had in the extraction of uranium, it would seem at this stage that the medium being used (the fluoride medium), is the reason for the unsuccessful extraction.

6.4. FURTHER INVESTIGATION OF OTHER CHELATING EXTRACTANTS

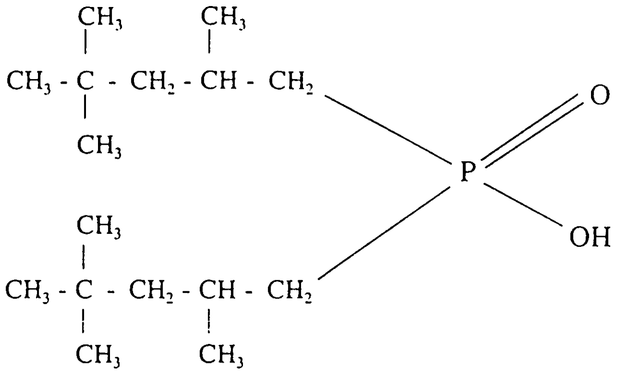
6.4.1. BACKGROUND

Three other chelating extractants have demonstrated huge successes in the extraction of metals. Their successes prompted their investigation in this study. These extractants are Cyanex 272 (*bis*(2,4,4-trimethylpentyl)phosphinic acid), LIX 84 (2-hydroxy-5-nonylacetophenone oxime in kerosene) and PC-88A (2-ethylhexylphosphonic acid mono-2-ethylhexyl ester).

6.4.1.1. CYANEX 272 EXTRACTANT

This extraction has proven to be the reagent of choice for the separation of cobalt from nickel from both sulphate and chloride medium. It is now being used to produce a major portion of the world's cobalt[14].

The active component of Cyanex 272 extractant is *bis*(2,4,4-trimethylpentyl)phosphinic acid.

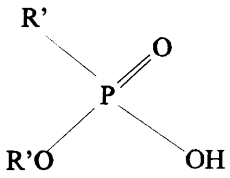


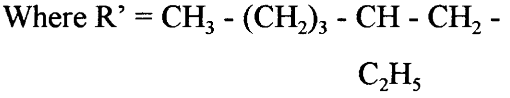
Since the active component of Cyanex 272 extractant is a phosphinic acid, metals are extracted through a cation exchange mechanism. The extractant is totally miscible with common aromatic and aliphatic diluents and is extremely stable to both heat and hydrolysis.

6.4.1.2. LIX 84(2-HYDROXY-5-NONYLACETOPHENONE OXIME IN KEROSENE)

This commercially oxime-based chelating reagent has been used as an extractant for U(VI) and Mo(VI), but very little extraction was observed in the case of Th(IV)[15]. Quantitative extraction has been observed for U(VI) by a mixture of 10%(v/v) LIX 84 and 0.1M dibenzoylmethane at pH 4.2 and by a mixture of 10%LIX 84 and 0.05M HTTA in the pH range 5.5-7.3 from chloride media.

6.4.1.3. PC-88A(2-ETHYLHEXYLPHOSPHONIC ACID MONO-2-ETHYLHEXYL ESTER)





Where R' = $CH_3 - (CH_2)_3 - \underset{C_2H_5}{CH} - CH_2 -$

This phosphonic acid extractant has been shown to quantitatively extract uranium from 0.1M HCl solution (~97.4%) with the percentage decreasing slowly up to ~45.9% at ~1M HCl solution[16].

6.4.2. EXPERIMENTAL

Each of the following extractants were prepared and in each case 50ml of the extractant used to extract 50ml of $H_2ZrF_6+H_2SiF_6$ solution.

(i) Extractant 1: 1%(v/v) Cyanex 272 in benzene
(ii) Extractant 2: 5%(v/v) Cyanex 272 in benzene
(iii) Extractant 3: 10%(v/v) Cyanex 272 in benzene
(iv) Extractant 4: 1%(v/v) PC-88A in benzene
(v) Extractant 5: 5%(v/v) PC-88A in benzene
(vi) Extractant 6: 10%(v/v) PC-88A in benzene
(vii) Extractant 7: 1%(v/v) Cyanex 272 + 1%(v/v) PC-88A in benzene
(viii) Extractant 8: 5%(v/v) Cyanex 272 + 5%(v/v) PC-88A in benzene
(ix) Extractant 9: 10%(v/v) Cyanex 272 +10%(v/v) PC-88A in benzene
(x) Extractant 10: 5% LIX 84 in benzene
(xi) Extractant 11: 10% LIX in benzene
(xii) Extractant 12: 5% LIX 84, 0.05M HTTA in benzene
(xiii) Extractant 13: 10% LIX 84, 0.05M HTTA in benzene
(xiv) Extractant 14: 5% LIX 84, 0.15M HTTA in benzene.

The results of the experiments are given in Table 6.3.

Table 6.3: ***The concentration (mg/l) of uranium, thorium and zirconium in organic and aqueous phases before (blank) and after extraction.***

Exraction	**Blank**			**Organic**			**Aqueous phase**		
	[U] (mg/l)	**[Th] (mg/l)**	**[Zr]**	**[U] (mg/l)**	**[Th] (mg/l)**	**[Zr]**	**[U] (mg/l)**	**[Th] (mg/l)**	**[Zr]**
1	42	<3	16.4%	<3	<3	94ppm	43	<3	16.4%
2	42	<3	16.4%	<3	3	0.9g/l	43	<3	16.4%
3	42	<3	16.4%	<3	6	1.5g/l	41	<3	16.4%
4	42	<3	16.4%	<3	<3	84ppm	47	6	16.4%
5	42	24	10.4%	<3	<3	770ppm	41	21	10.4%
6	42	24	10.4%	<3	7	2.8g/l	42	22	10.4%
7	42	24	10.4%	<3	<3	1.6g/l	43	23	10.4%
8	42	24	10.4%	<3	8	3.6g/l	41	28	10.4%
9	42	24	10.4%	5	9	6.7g/l	39	32	10.4%
10	42	24	10.4%	<3	8	1.4g/l	44	32	10.4%
11	42	24	10.4%	<3	12	1.5g/l	45	29	10.4%
12	43	24	10.1%	<3	<3	18ppm	43	21	10.1%
13	43	24	10.1%	<3	4	36ppm	42	25	10.1%
14	43	24	10.1%	<3	14	12ppm	43	25	10.1%

None of these extractants shows any success in the extraction of uranium from H_2ZrF_6+H_2SiF_6 solution. This demonstrates the complex matrix of this system which makes it difficult to successfully extract uranium. This is because these extractants have demonstrated their ability to extract uranium from other medium.

Given the success of these extractants in other media, it was thought it wise to spike the H_2ZrF_6+H_2SiF_6 solution with some acid to obtain a slightly different medium. Because, for example, Cyanex 272 has proved to be good in the sulphate medium, the solution was spiked with some sulphuric acid prior to extraction. This brought some success, as will be indicated below.

In this case a solution of 40% 5M H_2SO_4 in H_2ZrF_6+H_2SiF_6 was prepared and in each case 50ml of this solution was extracted twice with 50ml of the extractant. The following is a list of extractants used:

(i) Extractant A: 20% Cyanex 272 in benzene
(ii) Extractant B: 10% Cyanex 272 in benzene
(iii) Extractant C: 10%Cyanex 272 + 10%PC-88A in benzene
(iii) Extractant D: 30% Cyanex 272 in benzene
(iv) Extractant E: 15%Cyanex272+15%PC-88A in benzene

After extraction the aqueous phases were evaporated to dryness prior to analysing and the results with regard to uranium and thorium are given in Table 6.4.

Table 6.4: The concentration (mg/kg) of uranium and thorium in the solution (which was evaporated to dryness) before (blank) and after extraction.

Extractant	**%Zr**	**[U] (mg/kg)**	**%U removed**	**[Th] (mg/kg)**	**%Th removed**
blank	32.0	316	-	146	-
A	35.2	87	72.5	105	28.1
B	28.8	137	56.6	128	12.2
C	33.3	45	85.8	115	21.2
D	35.6	16	94.8	*	*
E	35.1	35	88.9	*	*

*= analytical problems were encountered with Th analysis in these samples.

The results show an encouraging success of Cyanex 272 in extracting uranium from the solution. There seems to be a direct proportionality between the amount of uranium removed and the concentration of Cyanex 272 in the extractant. This is evidenced by the extraction of 56.6% when 10%(v/v) Cyanex 272 is used and an increase to 72.5% uranium extracted when the Cyanex concentration is increased to 20%(v/v) and 94.8% uranium extraction when the concentration of Cyanex 272 is increased further to 30% (v/v). Furthermore, the results show an increase in the percentage extraction when a mixture of Cyanex 272 and PC-88A is used. This may be a confirmation of the synergism between the two extractants. The high percentage uranium removal is encouraging and paves way for further investigations.

The results do not indicate the substantial removal of thorium from the solution. It is encouraging to see no significant amount of Zr extracted. The change in the percentage of Zr in the mother liquor when H_2SO_4 is added might be as a result of the formation of a zirconium sulphate compound.

The concentrations of the extracted elements in the organic phases are given in Table 6.5.

Table 6.5: ***The concentrations of uranium, thorium (mg/l) and zirconium (g/l)in organic phases used to extract.***

Extractant	Extraction No.	[U] (mg/l)	[Th] (mg/l)	[Zr] (g/l)
A	1	99	8	8.6
	2	67	8	3.8
B	1	82	7	4.2
	2	40	6	3.9
C	1	144	9	6.8
	2	25	5	7.3
D	1	177	17	7.2
	2	51	10	3.4
E	1	140	14	26.8
	2	90	14	11.5

These results confirm the extraction of uranium by Cyanex 272. The second extraction does not extract as much as the first extraction. This is understandable since after the first extraction not as much concentration of uranium as before is left and thus only smaller amounts are available for extraction.

The results seem to further indicate the extraction of appreciable amounts of zirconium. This is disturbing and invites further work. Future work must look into this issue where perhaps masking zirconium might be of help.

6.5. CONCLUSION

Solvent extraction has, in this study, not yielded much success. It is however encouraging to note that adding sulphate to the solution turns things around. This comes as a little surprise since the extractant has proved successful in sulphate media.

As can be seen from the results presented in the tables above, spiking the mother liquor with sulphuric acid leads to a drop in the percentage of the zirconium content of the product. Future work can be geared towards investigating the effects of such an observation, given the fact that the solution is to be processed further to form other compounds.

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CHAPTER 7

THE ION EXCHANGE METHOD

7.1. INTRODUCTION

Ion exchange is one of the methods widely used in industry for purification purposes. It has also been employed in this study to remove radioactive elements such as uranium and thorium from the H_2ZrF_6+H_2SiF_6 solution. For the purpose of this project a good resin will be the one that whilst it removes satisfactory amounts of impurities, it is regenerable.

Since the medium in which the experiments are done is HF, it is desired to find a resin that will be able to tolerate it and also performs well. In this search for a suitable type of resin, various types of resins have been tried and, as will be shown later, most of them did not work, despite having a good history of having done well in some other media. This led to the conclusion that their failure in this case is as a result of the HF medium.

7.2. EVALUATION OF DIFFERENT TYPES OF RESIN

Types of resins evaluated include Dowex 50W-X8 (a strongly acidic cation exchanger -SO_3), Purolite S940 (an aminophosphonic chelating resin), SCR-mine (a strongly acidic cation exchanger) and Diphonix (diphosphonic chelating resin). Each of these types of resin was tried with two different contact methods, the batch method and the column method. In both methods the resin was put in contact with H_2ZrF_6+H_2SiF_6 solution and the percentage uranium removal from the solution determined after contact. It was found that in either method Purolite S940 resin yields best results. The comparison of the batch method and column methods revealed that the column method provides better results.

Using the batch method to determine which type of resin will be suitable, 0.5g of each type of resin was shaken in 50ml of a solution for 16 hours. The uranium and thorium concentrations in the solutions were determined before (blank) and after treatment of the solutions with the resin. The results with regard to the removal of uranium and thorium are given in Table 7.1.

Table 7.1: ***Comparison of different types of resins. The concentration (mg/l) of uranium in samples before treatment with the resin (blank) and after treatment with different types of resin and the percentage uranium removal from each solution.***

						% removal		
	solution	**blank**	**Purolite**	**Dowex**	**SCR**	**Purolite**	**Dowex**	**SCR**
[U] (mg/l)	0.2M H_2ZrF_6	140	23	55	54	83.6	60.7	61.4
	0.5M H_2ZrF_6	140	32	117	50	77.1	16.4	64.3
	1.0M H_2ZrF_6	140	39	105	136	72.1	25.0	2.9
	2.0M H_2ZrF_6	140	48	111	114	65.7	20.7	18.6
[Th] (mg/l)	0.2M H_2ZrF_6	37	22	20	20	40.5	46.0	46.0
	0.5M H_2ZrF_6	37	31	34	35	16.2	8.1	5.41
	1.0M H_2ZrF_6	37	33	25	20	10.8	32.4	46.0
	2.0M H_2ZrF_6	37	22	20	12	40.5	46.0	67.6

It looks clear from the results presented here that Purolite is the best in as far as the removal of uranium is concerned. This can also be clearly seen in Figure 7.1 (a). Its removal of thorium is comparable to that of the other types of resin, as can also be clearly seen in Figure 7.1(b). The good performance of Purolite S940 resin is a suggestion that Purolite can form stronger complexes with uranium than any of the other types of resins used.

The above mentioned success of Purolite S940 resin in removing uranium from H_2ZrF_6+H_2SiF_6 solution, using the batch method, seemed to be dependent on the concentration of H_2ZrF_6+H_2SiF_6. This was evidenced by its apparent inability to remove any significant amounts of uranium and thorium from the concentrated solution. Such results were obtained from an experiment in which 1.0g Purolite S940 resin was shaken in 50ml of 12M H_2ZrF_6+H_2SiF_6 solution. To determine the optimum time, the experiments were carried out at different time intervals. The results, obtained using NAA, are given in Table 7.2.

Table 7.2: ***The effect of time in the batch method for the removal of uranium and thorium from H_2ZrF_6+H_2SiF_6 solution. The concentration (mg/l) of uranium and thorium before (blank) and after treatment with the resin in a given time period (minutes) are also given.***

EXPERIMENT 1		
DURATION OF SHAKING (minutes)	**[U] (mg/l)**	**[Th] (mg/l)**
0 (blank)	62.1	17.0
30	55.0	17.0
60	53.1	17.6
240	54.0	16.1
EXPERIMENT 2		
0 (blank)	53.8	14.1
30	49.0	12.1
60	48.0	13.0
120	47.2	12.6
240	46.9	12.1
420	49.4	12.4
16 hours	49.1	12.2

The results clearly indicate that no substantial amounts of uranium and thorium were removed. This is not reflective of what was previously achieved when the H_2ZrF_6+H_2SiF_6 concentration was lower. It can also be seen from Figure 7.2 (the plot of results of experiment 2) that time does not have any influence on the uranium and thorium removal.

The column method was also investigated for the removal of uranium and thorium. This method was evaluated using Purolite S940 resin, as it has already demonstrated its ability as compared to other types of resin. In this experiment, two columns of 5g (experiment A) and 10g (experiment B) Purolite S940 resin were packed and 200ml of 0.5M H_2ZrF_6+H_2SiF_6 solution run through each column at a volume flow rate of 10ml/min. The results are given in Table 7.3.

Table 7.3: ***The concentrations (mg/l) of uranium and thorium in the mother liquor before (blank) and after running through the column and their percentage removal.***

Experiment	**[U] (mg/l)**	**[Th] (mg/l)**	**%U removed**	**%Th removed**
blank	199	77	-	-
A	126	54	36.7	29.9
B	71	46	64.3	40.3

Uranium removal, though being low with the 5g resin column, looks promising as there is a drastic jump to about 64% when the resin mass is increased to 10g. Furthermore the resin, despite having removed 64% of uranium, may have not reached its capacity. Further experiments done were focused at optimising the results.

7.3. PUROLITE S940 RESIN URANIUM CAPACITY

Having realised some success in the removal of uranium from H_2ZrF_6+H_2SiF_6 with Purolite S940 resin, its capacity had to be determined so as to get an indication of the minimum amount that will be necessary to remove the maximum amount of uranium from the solution.

In determining the resin capacity, a 50g Purolite S940 resin was packed and 2*l* of H_2ZrF_6+H_2SiF_6 solution run through, collecting 20x100ml fractions at a linear flow rate of 0.35cm/min. The results are given in Table 7.4.

Table 7.4: ***The uranium concentration (mg/l) in fractions before (blank) and after running through the column for the determination of the breakthrough curve.***

Fraction No.	**[U] (mg/l)**	**%U removed**
blank	82.0	-
1	0.5	99.4
2	1.5	98.2
3	5.7	93.1
4	11.2	86.3
5	19.6	76.1
6	26.8	67.3
7	34.2	58.3
8	38.6	52.9
9	44.2	46.1
10	49.9	39.2
11	52.8	34.4
12	58.2	32.7
13	61.7	24.8
14	59.2	27.8
15	68.4	16.6
16	70.6	13.9
17	61.5	25.0
18	74.5	9.2
19	72.9	11.1
20	75.2	8.3

The results are also given in Figure 7.3. It is clear from this figure that the breakthrough curve is not sharp. It rises gradually to the maximum point. The calculation of the capacity reveals that the uranium capacity for this resin is 75.28mgU/50g resin at a linear flow rate of 0.35cm/min.

The calculation of the uranium capacity entails determining the uranium content of each fraction and adding that up. Subtracting this amount from the total initial uranium content of the solution will give us the amount of uranium captured by the resin.

7.4. RESULTS OPTIMISATION

In optimising the results with regard to the removal of uranium and thorium from H_2ZrF_6+H_2SiF_6 solution using the column method, several factors were looked into. These include the flow rate, pretreatment of the resin and addition of sulphuric acid to the mother liquor.

7.4.1. THE EFFECT OF FLOW RATE

In investigating the effect of flow rate in the removal of uranium, four columns were packed each with 50g Purolite S940 resin. Through each column 2000ml of H_2ZrF_6+H_2SiF_6 solution was run. In column A 20x100ml fractions were collected at a linear flow rate of 1.32cm/min, in column B 20x100ml fractions were collected at a linear flow rate of 1.30cm/min, in column C 20x100ml fractions were collected at a linear flow rate of 0.70cm/min and in column D 20x100ml fractions were collected at a linear flow rate of 0.35cm/min. The results are given in Table 7.5.

Table 7.5: ***The effect of flow rate in uranium removal. The concentration (mg/l) of uranium and the percentage removal before (blank) and after running through different columns at different flow rates.***

	LINEAR FLOW RATES (cm/min)							
	1.32		**1.30**		**0.70**		**0.35**	
fraction	**[U] (mg/l)**	**%U removed**	**[U] (mg/l)**	**%U removed**	**[U] (mg/l)**	**%U removed**	**[U] (mg/l)**	**%U removed**
blank	82.4	-	84.4	-	85.0	-	82.0	-
1	0.93	98.9	1.86	97.8	0.62	99.3	0.5	99.4
2	10.7	87.0	11.0	87.0	4.84	94.3	1.5	98.2
3	22.8	72.3	21.3	74.8	14.4	83.1	5.7	93.1
4	34.2	58.5	32.5	61.5	25.8	69.6	11.2	86.3
5	45.2	45.2	41.6	50.7	34.3	59.6	19.6	76.1
6	48.3	41.4	48.5	42.5	42.1	50.5	26.8	67.3
7	45.4	44.9	50.8	39.8	47.1	44.6	34.2	58.3
8	58.6	28.9	52.9	37.3	52.0	38.8	38.6	52.9
9	60.8	26.2	60.2	28.7	53.8	36.7	44.2	46.1
10	62.2	24.5	61.2	27.5	57.4	32.5	49.9	39.2
11	63.6	22.8	63.6	24.6	59.3	30.2	52.8	34.4
12	65.8	20.2	67.7	19.8	59.4	30.1	58.2	32.7
13	67.5	18.1	69.1	18.1	63.3	25.5	61.7	24.8
14	67.7	17.8	67.3	20.3	65.0	23.5	59.2	27.8
15	70.4	14.6	69.3	17.9	65.7	22.7	68.4	16.6
16	72.4	12.1	60.4	28.4	69.0	18.8	70.6	13.9
17	72.3	12.3	73.1	13.4	71.7	15.6	61.5	25.0
18	73.2	11.2	69.3	17.9	72.7	14.5	74.5	9.2
19	68.0	17.5	73.2	13.3	77.1	9.3	72.9	11.1
20	75.2	8.7	73.2	13.3	73.0	14.1	75.2	8.3

The results are also given in Figure 7.4 (a). This figure depicts the uranium concentration in each fraction versus the fraction number. It is clear from this graph that the slower volume flow rates provides the least uranium concentration in each fraction as compared to other linear flow rates. The trend is very clear when looking at this graph. Thus, in each case, the slower flow rate provides the best results.

On the other hand, Figure 7.4(b) gives the percentage uranium removed from each fraction versus the fraction number. This figure also demonstrates the trend clearly. The slower flow rates provide better uranium percentage removal for each fraction as compared to faster flow rates.

The calculation of the uranium up take of the resin reveals that for column A (linear flow rate = 1.35cm/min) the up take is 56.27mgU/50g resin, the up take for column B (linear flow rate = 1.30cm/min) is 61.99mgU/50g resin, the up take for column C (linear flow rate = 0.70cm/min) is 69.15mgU/50g resin and the up take for of column D (linear flow rate = 0.35cm/min) is 75.28mgU/50 resin. Thus, the trend in the performance of columns is also very clear in this case, with slow flow rates giving better uranium up take.

The reason for good performance of slower flow rates as compared to faster flow rates may be as a result of the solution not having enough contact time with the resin to result in complete complexation of uranium with the resin when the flow rate is faster. Whereas, on the other hand, the slower flow rates ensure sufficient contact time with the resin to allow uranium complexation.

The fact that slower flow rates give better uranium results was further confirmed when the linear flow rate was lowered even further to 0.32cm/min. In this case 50g Purolite S940 resin column was packed and 2000ml H_2ZrF_6+H_2SiF_6 solution run through. Fractions (4x500ml) were collected at a linear flow rate of 0.32cm/min. The results are given in Table 7.6.

Table 7.6: ***Uranium concentration in fractions before (blank) and after running through the column at a linear flow rate of 0.32cm/min.***

Fraction No.	**[U] (mg/l)**	**%U removed**
blank	75.9	-
1	5.42	92.9
2	29.2	38.5
3	47.0	38.1
4	54.3	28.5

The results clearly demonstrate a further increase in the up take of uranium as the amount of uranium already retained in the resin after running 2000ml of solution through is 83.84mg. This amount exceeds the amount obtained when the flow rate was 0.35cm/min. These results therefore underline the conclusion that the slower flow rate provides better results in as far as the removal of uranium is concerned.

7.4.2. THE EFFECT OF PRETREATMENT OF THE RESIN

The resin pretreatment was investigated with the view of trying to improve the capacity. The pretreatment solution used was ammonium carbonate $(NH_4)_2CO_3$. This stems from the fact that the carbonate is known to form strong complexes with uranium. It therefore was thought that the pretreatment might lead to the carbonate remaining in the resin and eventually increasing the uranium affinity of the resin. In this case a comparison was made between the capacities of the untreated resin and the pretreated resin. Two 50g Purolite S940 resin columns were packed. In one column (Column A) 500ml of 3% $(NH_4)_2CO_3$ was run through the column at a linear flow rate of 0.32cm/min, followed by a water wash step. Thereafter 4.0*l* of H_2ZrF_6+H_2SiF_6 solution was run through the column collecting 8x500ml fractions at a linear flow rate of 0.32cm/min. The other column (Column B) was not pretreated. A volume of 4.0*l* H_2ZrF_6+H_2SiF_6 solution was run through the column collecting 8x500ml fractions at a linear flow rate of 0.32cm/min. The results are given in Table 7.7

Table 7.7: ***The effect of pretreating the resin. The uranium concentration (mg/l) in fractions before (blank) and after running through the columns one of which (A) was pretreated and the other (B) was not.***

	COLUMN A (pretreated)		**COLUMN B (not pretreated)**	
Fraction No	**[U] (mg/l)**	**%U removed**	**[U] (mg/l)**	**%U removed**
blank	44	-	48	-
1	4	90.9	3	93.8
2	6	86.4	9	81.2
3	10	77.3	12	75.0
4	17	61.4	21	56.2
5	16	63.6	30	37.5
6	24	45.4	34	29.2
7	28	36.4	32	33.3
8	31	29.6	52	-

The results do not indicate any major difference in the uranium removal. There is, however, a slight increase in the uranium up take from 97.5mgU/50g resin when the resin is not pretreated to 108mgU/50g resin when the resin is pretreated. This translates to about 11% capacity improvement. Thus, pretreating the resin does not significantly lead to an increase in the resin capacity for uranium.

7.4.3. THE EFFECT OF ADDING H_2SO_4 TO MOTHER LIQUOR

Purolite S940 resin has been found to perform well in a sulphate medium. This then prompted the suggestion that the mother liquor be spiked with some amount of sulphuric acid. The idea is to introduce some sulphate ions so that if they are behind the success of the resin in the sulphate medium they also enhance the performance of the resin in the solution in this study. An experiment was therefore carried out in which 500ml of 5M H_2SO_4 was added to 3500ml of mother liquor (i.e. a 12.5% of 5M H_2SO_4 concentration). This solution was run through a 50g Purolite S940 resin column collecting 16x250ml fractions. The results are given in Table 7.8.

Table 7.8: ***The effect of spiking the mother liquor with H_2SO_4. The concentration of uranium (mg/l) in fractions before (blank) and after running through the column and the percentage uranium removal.***

Fraction no	**[U] (mg/l)**	**%U removed**
blank	49	-
1	5	89.8
2	5	89.8
3	12	75.5
4	15	69.4
5	21	57.1
6	24	51.0
7	26	46.9
8	30	38.8
9	28	42.9
10	32	34.7
11	33	32.6
12	38	22.4
13	41	16.3
14	42	14.3
15	45	8.2
16	42	14.3

The results do not indicate any significant impact on the uranium up take by the resin, which in this case is 86.25mgU/50g resin, and is slightly lower than the previously obtained values. There is instead a slight drop in the percentage uranium removal in fractions collected as compared to the other cases were the mother liquor was not spiked with H_2SO_4. Thus, the results indicate no positive influence of spiking the mother liquor with H_2SO_4.

7.4.4. THE EFFECT OF FREE HF IN THE SOLUTION

In establishing the effect of free HF in the mother liquor in uranium removal, experiments were done in which several H_2ZrF_6+H_2SiF_6 solutions were each spiked with different concentrations of HF. Each of these solutions was shaken with 10g of Purolite S940 resin for 16 hours. Thereafter the solutions were analysed for uranium concentration and the results are given in Table 7.9.

Table 7.9: ***The uranium concentrations in the mother liquor before (initial) and after shaking with the resin (final) at different free HF concentrations.***

Solution	[HF] (M)	$[U]_0$ (mg/l)	$[U]_f$ (mg/l)	%U removed
A	0.1	49.2	1.38	97.2
B	0.5	48.3	1.52	96.8
C	2.0	48.0	2.03	95.8
D	5.0	44.7	4.56	89.8
E	11.9	48.4	13.4	72.3

$[U]_0$ = initial uranium concentration; $[U]_f$ = final uranium concentration.

The results indicate a gradual decrease in the percentage uranium removed as the HF concentration is increased. This is indicates that free HF has an adverse effect on the uranium removal from the solution by Purolite S940 resin.

The results are also presented in Figure 7.5.

7.5. REGENERATION OF THE RESIN

As pointed out earlier, regenerability of the resin for re-use is a very important factor that will render the resin cost effective. In this case, since Purolite S940 has shown to be the most successful in removing uranium and thorium from H_2ZrF_6+H_2SiF_6 solution, its regenerability is essential. To that effect experiments have been done to establish its regenerability.

The first regeneration attempt was through the usage of different (hydrofluoric acid) HF and (1-hydroxyethane-1,1-diphosphonic acid) HEDPA concentrations. In these experiments, a given amount of Purolite S940 resin was stirred in a given volume of the mother liquor of a certain uranium concentration mixed with the eluting agent. The uranium concentration was measured before and after stirring with the resin. This was to determine which (between the resin and the eluting agent) can better complex uranium. If the resultant uranium concentration in the solution is very much less after stirring compared to the initial concentration then it means that the resin has complexed a lot more of the uranium than the eluting agent. This will then mean that the resin is a better complexant of uranium than the eluting agent and therefore this eluting agent cannot remove the complexed uranium from the resin, implying that it will not be a suitable eluting agent. On the other hand if the concentration of uranium in the solution remains high even after stirring then this will be an indication that the eluting agent is a better complexant of uranium than the resin and therefore it can manage to remove the complexed uranium from the resin.

This might not be a definitive way of determining whether the eluting agent will work or not but is just screening, as the eluting agents are not necessarily stronger complexes than the resin, but may work through altering the resin or through establishing equilibria that allow the uranium to move through and out of the column.

The results are given in Table 7.10

Table 7.10: The concentrations (mg/l) before and after treatment with the Purolite S940 resin and in some cases with the potential eluting agent.

Description	[U] (before stirring) (mg/l)	[U] (after stirring) (mg/l)
50ml mother liquor + 50ml 0.1M HF + 10g Purolite	49.2	1.38
50ml mother liquor + 50ml 0.5M HF + 10g Purolite	48.3	1.52
50ml mother liquor + 50ml 2M HF + 10g Purolite	48.0	2.03
50ml mother liquor + 50ml 5M HF + 10g Purolite	44.7	4.56
50ml mother liquor + 50ml 12M HF + 10g Purolite	48.4	13.40
50ml mother liquor + 50ml 0.1M HEDPA + 10g Purolite	47.9	1.88
50ml mother liquor + 50ml 1M HEDPA + 10g Purolite	50.0	2.23
50ml mother liquor + 50ml 2M HEDPA + 10g Purolite	51.2	27.4

It is clear from the results that if the above argument holds then HF does not qualify as an eluting agent. HEDPA shows some potential when its concentration is increased.

In further investigations in regenerating the resin, oxalic acid, EDTA (at different pH values) and H_2SO_4 were each used. The use of the acid stems from the fact that since the resin, in complexing with the metal ion from the solution, released the proton, it may help the resin to regain the proton and lose the complexed ion in turn, thereby regenerating the resin. On the other hand it was thought that EDTA can better complex the metal ions in the resin than the resin itself. If that is the case, its usage would result in it complexing away the ions from the resin leading to the ultimate regeneration of the resin. In these experiments also, the resin was stirred in the solution tested as an eluting agent. The analysis of the resin was done using the NAA technique. The results of these experiments are given in Table 7.11.

Table 7.11: Uranium concentrations in the resin before and after the resin was treated with the eluting agent.

Eluting agent	**Eluent analysis mgU/kg resin**		
	Before elution	**After elution**	**%Elution**
0.5M oxalic acid	1631	1622	0.50
1M oxalic acid	1035	1029	0.55
0.05M EDTA (pH 3.5)	1677	1638	2.3
0.05M EDTA (pH 4.01)	1694	1651	2.5
3% $(NH_4)_2CO_3$	1139	932	18.15
5M H_2SO_4	1576	1571	0.32
2M H_2SO_4	1176	1169	0.60
0.5M H_2SO_4	1183	1180	0.25
0.5M H_3PO_4	1444	1441	0.21
2M H_3PO_4	1485	1481	0.27
5M HCl + 1M NH_4F	1126	1116	0.88
0.1M HCl	1383	1382	0.06
0.1M EDTA	1240	1054	14.99

The results clearly indicate that the solutions do not qualify as eluting agents. Ammonium carbonate $(NH_4)_2CO_3$ showed potential but CO_2 forms during the process which makes it difficult to properly carry out the process.

So far, promising results have been realised only with HEDPA. Efforts need therefore to be applied to optimising the results. Furthermore, ammonium carbonate and EDTA also look promising and it was deemed wise to investigate their effects under certain conditions. This prompted the investigation of the effect of temperature and contact time in the performance of these solutions as eluting agents. In each case 50.0g Purolite S940 resin, which was previously brought to a saturation point by running through 200ml of uranium and thorium containing mother liquor, was treated with a 1000ml of the eluting agent by either stirring or column method. The results are given in Table 7.12.

Table 7.12: The percentage uranium elution as a function of temperature and contact time when EDTA and $(NH_4)_2CO_3$ are used as eluting agents.

Experimental Conditions		**%Elution**	
		0.1M EDTA	**3% $(NH_4)_2CO_3$**
Temperature	50°C	3.89	52.97
Contact time	16h (stirred)		
Temperature	80°C	-	3.71
Contact time	5h (stirred)		
Temperature	50°C	3.95	16.35
Contact time	3h40min column method (0.35cm/min)		

According to these results, at higher temperatures and longer contact times there is a decrease in the elution ability of EDTA. According to the previous results (Table 7.10) 14.99% elution was achieved with 0.1M EDTA at room temperature and a contact time of 62 minutes. These indicate that under these new conditions, the resin forms a stronger complex with uranium than the EDTA - uranium complexes. On the other hand, higher temperatures and longer contact times seem to lead to stronger uranium carbonate complexes than the resin uranium complexes. This is an encouraging observation as it brings hope of ultimately being able to find a suitable eluting agent. It would seem that if the temperature is increased to even higher levels, then the carbonates become less effective as good uranium complexant. This is evidenced by a sharp decrease in the percentage elution when $(NH_4)_2CO_3$ is used at 80°C.

Undoubtedly, ammonium carbonate and HEDPA have emerged as the best eluting agents. Efforts had to be made to optimise their results. Furthermore the extent to which the resin has been regenerated had to be investigated.

Attempts were made to try and optimise the results of HEDPA as an eluting agent. In this case 100g Purolite S940 resin was made saturated by running through 4000ml of H_2ZrF_6+H_2SiF_6 solution. After washing through with water, 1000ml of 0.5M HEDPA was run through the column at a linear flow rate of 0.32cm/min at 21°C. The analysis indicated a 52.75% uranium removal from the resin. This is highly encouraging as previous experiments indicated no uranium removal from the resin with any concentration of HEDPA below 2M. This proves that the column method is the best for effecting better elution with HEDPA than the batch method.

Having realised the success of ammonium carbonate and HEDPA as eluting agents, the "regenerated" resin had to be reused to establish the extent to which it has been regenerated.

7.6. USING THE REGENERATED RESIN

A 50g Purolite S940 resin column (column A) was prepared and 2000ml H_2ZrF_6+H_2SiF_6 solution run through the column with 4x500ml fractions (fractions 1 to 4 in Table 7.13) collected at a linear flow rate of 0.32cm/min. This was followed by a 200ml water wash step. The elution step was done by running 1*l* of 0.02M HEDPA through the column and collecting 2x500ml fractions also at a linear flow rate of 0.32cm/min. After the elution step, 1000ml of H_2ZrF_6+H_2SiF_6 solution was run through the column and 2x500ml fractions (fractions 5 and 6 in Table 7.13) collected at the same rate. The results are given in Table 7.13.

Another column (column B) was prepared the same way as column A and 2000ml H_2ZrF_6+H_2SiF_6 solution run through and 4x500ml fractions (fractions 1 to 4 in Table 7.13) collected at a linear flow rate of 0.32cm/min. This was followed by the 200ml wash step. Thereafter the resin was stirred in 1*l* of 3%$(NH_4)_2CO_3$ at 50°C for 4.5 hours and then filtered out. The resin was used to pack a column again and 1000ml of H_2ZrF_6+H_2SiF_6 solution run through the column collecting 2x500ml fractions (fractions 5 and 6 in Table 7.13) at a linear flow rate of 0.32cm/min. The results are also given in Table 7.13.

Table 7.13: ***The concentrations (mg/l) of uranium and thorium in*** H_2ZrF_6+H_2SiF_6 ***fractions before and after elution.***

BEFORE ELUTION								
	COLUMN A				COLUMN B			
fraction	**[U] (mg/l)**	**[Th] (mg/l)**	**%U removed**	**%Th removed**	**[U] (mg/l)**	**[Th] (mg/l)**	**%U removed**	**%Th removed**
blank	71	28	-	-	71	28	-	-
1	11	11	84.5	60.7	6	9	87.3	67.9
2	22	12	69.0	57.1	25	13	64.7	53.6
3	31	16	56.3	42.9	54	20	23.9	28.6
4	46	17	35.2	39.3	54	19	23.9	32.1
AFTER ELUTION								
fraction	**[U] (mg/l)**	**[Th] (mg/l)**	**%U removed**	**%Th removed**	**[U] (mg/l)**	**[Th] (mg/l)**	**%U removed**	**%Th removed**
5	40	17	43.7	39.3	23	15	67.6	46.4
6	64	20	9.9	28.6	43	21	39.4	25.0

The results do not indicate any significant improvement in the removal of uranium and thorium after an attempt to regenerate the resin with 0.02M HEDPA. This might suggest that the concentration of HEDPA was too small to complex out significant amount of uranium and thorium from the resin. On the other hand there is some little improvement when a regeneration attempt was done with 3%$(NH_4)_2CO_3$.

A regeneration attempt was also carried out using an increased HEDPA concentration. In this case 4000ml H_2ZrF_6+H_2SiF_6 solution was run through a 100g Purolite S940 resin and 8x500ml fractions collected at a linear flow rate of 0.32cm/min. After washing with water, the elution step was carried out by running 1000ml of 0.5M HEDPA through the column and collecting 4x250ml fraction also at a linear flow rate of 0.32cm/min. This was then followed by 4000ml of H_2ZrF_6+H_2SiF_6 solution run through the column with 8x500ml fractions collected at a linear flow rate of 0.32cm/min. The results are given in Table 7.14.

Table 7.14: ***The uranium concentration (mg/l) of the H_2ZrF_6+H_2SiF_6 fractions collected from the Purolite S940 resin column before and after elution.***

	BEFORE ELUTION	
Fraction No.	**[U] (mg/l)**	**%U removed**
blank	48	-
1	4	91.7
2	10	79.2
3	15	68.8
4	24	50.0
5	30	37.5
6	32	33.3
7	34	29.2
8	42	12.5
AFTER ELUTION		
Fraction No.	**[U] (mg/l)**	**%U removed**
blank	44	-
1	17	61.4
2	19	56.8
3	24	45.4
4	32	27.3
5	36	18.2
6	38	13.6
7	40	9.1
8	45	0.0

The results indicate that prior to elution, the capacity of the column was 96mgU/100g resin.

After elution the capacity was reduced to 51mgU/100g resin. Whilst this is not good, it is the best one was able to achieve (about 47% reduction in the original capacity). It is really not good because in the plant situation this might seriously affect the economics of the process. These results demonstrate some success with regard to the regeneration of the resin.

Problems were encountered here with the thorium analysis and the results are therefore not reported.

The eluting agent was also analysed for uranium, thorium and zirconium content and the results are given in Table 7.15.

Table 7.15: The concentrations of uranium, thorium and zirconium in the eluting agent fractions.

Fraction No.	**[Zr]**	**[U] (mg/l)**	**[Th] (mg/l)**
1	3.7g/l	62	88
2	2.5g/l	65	101
3	723ppm	47	80
4	482ppm	29	54

According to the results 0.5M HEDPA managed to remove 50.75mg of uranium from the resin. This, compared to 96mg of uranium in the resin, is not too encouraging. It represents a 47% elution. It looks as though more volumes of the eluting agent will be able to remove more uranium from the resin.

On the other hand, the results also indicate the removal of substantial amounts of zirconium from the resin. This is an indication that the resin did not complex uranium and thorium only, but also and to a large extent zirconium. This implies that there is a competition between zirconium and uranium for sites in the resin, thereby reducing the resin capacity for uranium and thorium.

In investigating the change in the capacity of the resin when 3%$(NH_4)_2CO_3$ is used as an eluting agent, the following experiment was done. A 50g Purolite S940 resin column was packed and 4000ml H_2ZrF_6+H_2SiF_6 solution run through and 8x500ml fractions collected at a linear flow rate of 0.32cm/min. After washing the column the resin was gently stirred in 1*l* of 3%$(NH_4)_2CO_3$ solution at 50^0C for 16 hours. After filtering, the resin was reused to pack the column and a further 4000ml H_2ZrF_6+H_2SiF_6 solution run through the column. Fractions (8x500ml) were collected at a linear flow rate of 0.32cm/min. The results are given in Table 7.16.

Table 7.16: ***Uranium concentrations (mg/l) in the $H_2ZrF_6+H_2SiF_6$ fractions collected before and after the treatment of the resin by $(NH_4)_2CO_3$***

BEFORE ELUTION		
Fraction No.	**[U] (mg/l)**	**%U removed**
blank	48	-
1	11	77.1
2	22	54.2
3	38	20.8
4	38	20.8
5	46	4.2
6	46	4.2
7	50	-
8	49	-
AFTER ELUTION		
Fraction No.	**[U] (mg/l)**	**%U removed**
blank	48	-
1	16	66.7
2	40	16.7
3	50	-
4	56	-
5	61	-
6	58	-
7	56	-
8	52	-

The results indicate that prior to elution the uranium up take by the resin was 44mgU/50g resin. After elution the uranium up take was 20mgU/50g resin. This represents a 54% reduction in the original uranium up take by the resin.

It must be pointed out that the above results indicate a reduction in the uranium up take by the new resin. It is not clear at this stage how this could be the case. However, having established that the resin also complexes zirconium, it might be possible that the more of zirconium has been complexed to the resin than in the previous case, leading to less sites available for uranium complexation.

The elution with $(NH_4)_2CO_3$ seemed not to bear fruits. Its success in this regard is highly limited. This prompted the suggestion that the ammonium carbonate be used in conjunction with an oxidizing agent, as the uranium in the resin might not be in a proper oxidation state to have ammonium carbonate easily eluting it. This then led to the usage of hydrogen peroxide. A solution was prepared in which 3%$(NH_4)_2CO_3$ was mixed with 0.05M H_2O_2 and the mixture used as an eluting agent. The uranium up take by the resin was investigated after this eluting agent was employed.

In this experiment, a 50g Purolite S940 resin column was packed and 4000ml H_2ZrF_6+H_2SiF_6 solution run through, collecting 8x500ml fractions at a linear flow rate of 0.32cm/min. This was followed by a water wash step. Thereafter the resin was stirred gently in a 1000ml solution of 3%$(NH_4)_2CO_3$ + 0.05M H_2O_2 at 50^0C for 16 hours. The resin was used again to pack the column and 3500ml of H_2ZrF_6+H_2SiF_6 solution run through, collecting 7x500ml fractions also at a linear flow rate of 0.32cm/min.

The results are given in Table 7.17

Table 7.17: ***The concentrations (mg/l) of uranium and thorium in fractions before and after elution and also in the eluting solution.***

Fraction No.	**[U]** **(mg/l)**	**%U removed**
blank	48	-
1	3	93.8
2	9	81.2
3	12	75.0
4	21	56.2
5	30	37.5
6	34	29.2
7	32	33.3
8	52	-
Eluting solution	118	
AFTER ELUTION		
Fraction No.	**[U]** **(mg/l)**	**%U removed**
blank	48	-
1	10	79.2
2	28	41.7
3	37	22.9
4	50	-
5	44	8.3
6	47	2.1
7	47	2.1

Prior to elution the results indicate a uranium up take of 97mgU/50g resin. After elution the uranium up take by the resin was calculated to 37.5mgU/50g resin, a 61.5% reduction in the original up take. This makes the solution ineffective as an eluting agent. As compared to other eluting agents tried so far, it has the highest percentage reduction when compared to the original capacity of the resin.

This is inexplicable as the analysis of the eluting agent suggest that all of the uranium trapped by the resin has been successfully eluted. The results showed that 118mg of uranium have been removed from the resin, whereas (according to the results) only 97mg of uranium have been retained by the resin. Thus, according to the results, the capacity of the resin should have not changed so dramatically after elution. The conclusion likely to be reached is that the solution might have altered the resin, a consequence that might be attributed to the presence of peroxide.

7.7 LARGE SCALE EXPERIMENT

Having realised the success of the Purolite S940 resin in the removal of uranium from the solution on a small scale, the next step was to scale up the process to determine if the observed success will also be demonstrated on a larger scale.

The experiment was scaled up to 30*l*. The initial uranium concentration of the solution was 49mg/l. A column of inside diameter of 131mm was packed with 1.65kg of Purolite S940 resin. The solution (30*l*) was run through the column at a linear flow rate of 0.66cm/min. The analysis was done on the first 20*l* collected. The last 10*l* was collected separately and also analysed. Thereafter these solutions were mixed together and also analysed. The analysis was done using the XRF technique and the results are given in Table 7.18

Table 7.18: Uranium concentrations (mg/l) in H_2ZrF_6+H_2SiF_6 solution before and after running through a column in a bigger scale experiment.

	[U](mg/l)
Before running through the column	49
First 20*l* run through the column	9
Last 10*l* run through the column	19
mixture of solutions	10

The Purolite resin has continued to demonstrate its success. The total percentage uranium removal is 79.6. These are very encouraging results as they show the applicability of this method on a large scale.

Figure 7.1(a)

%U removal by different resins

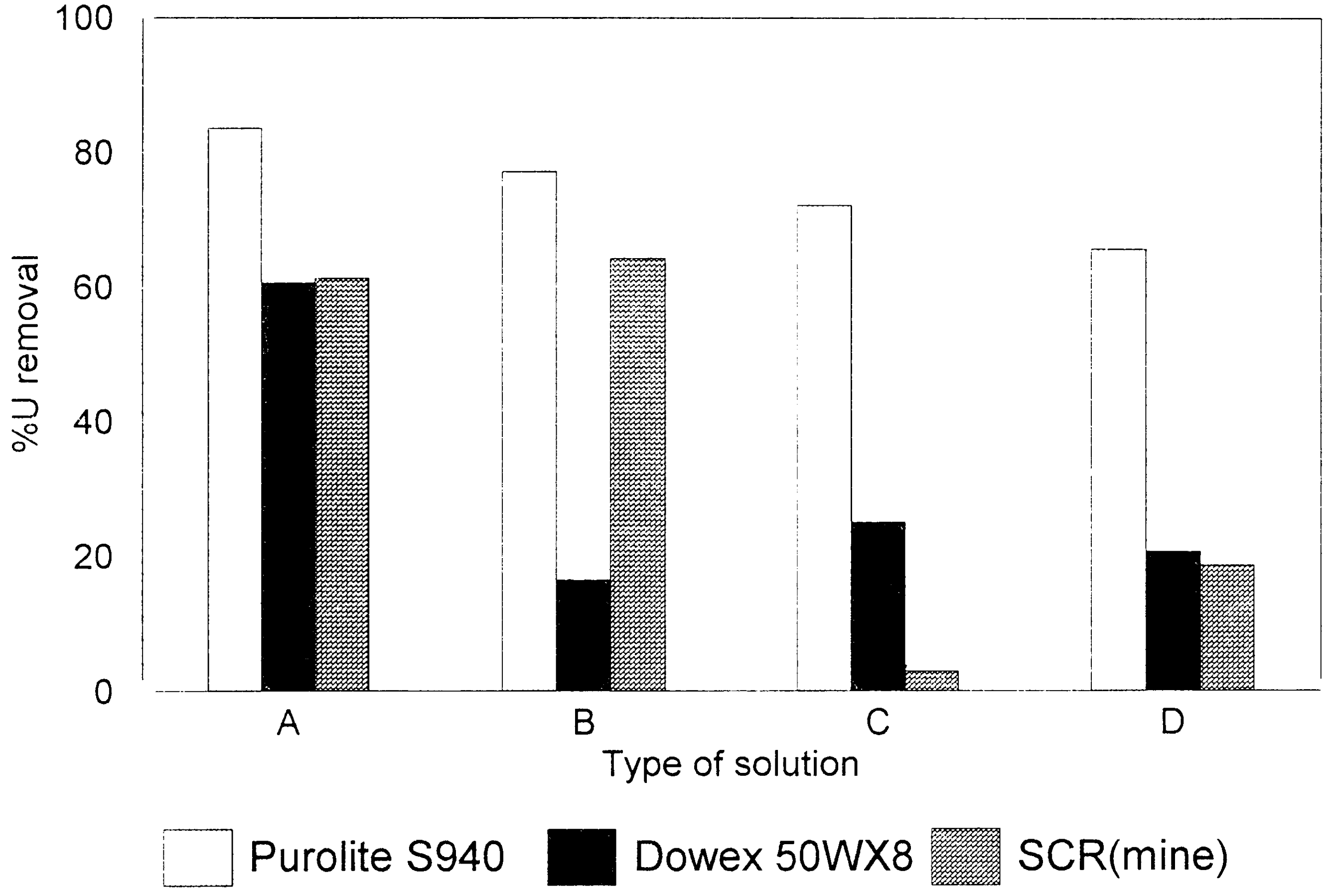


Figure 7.1(b)

%Th removal by different resins

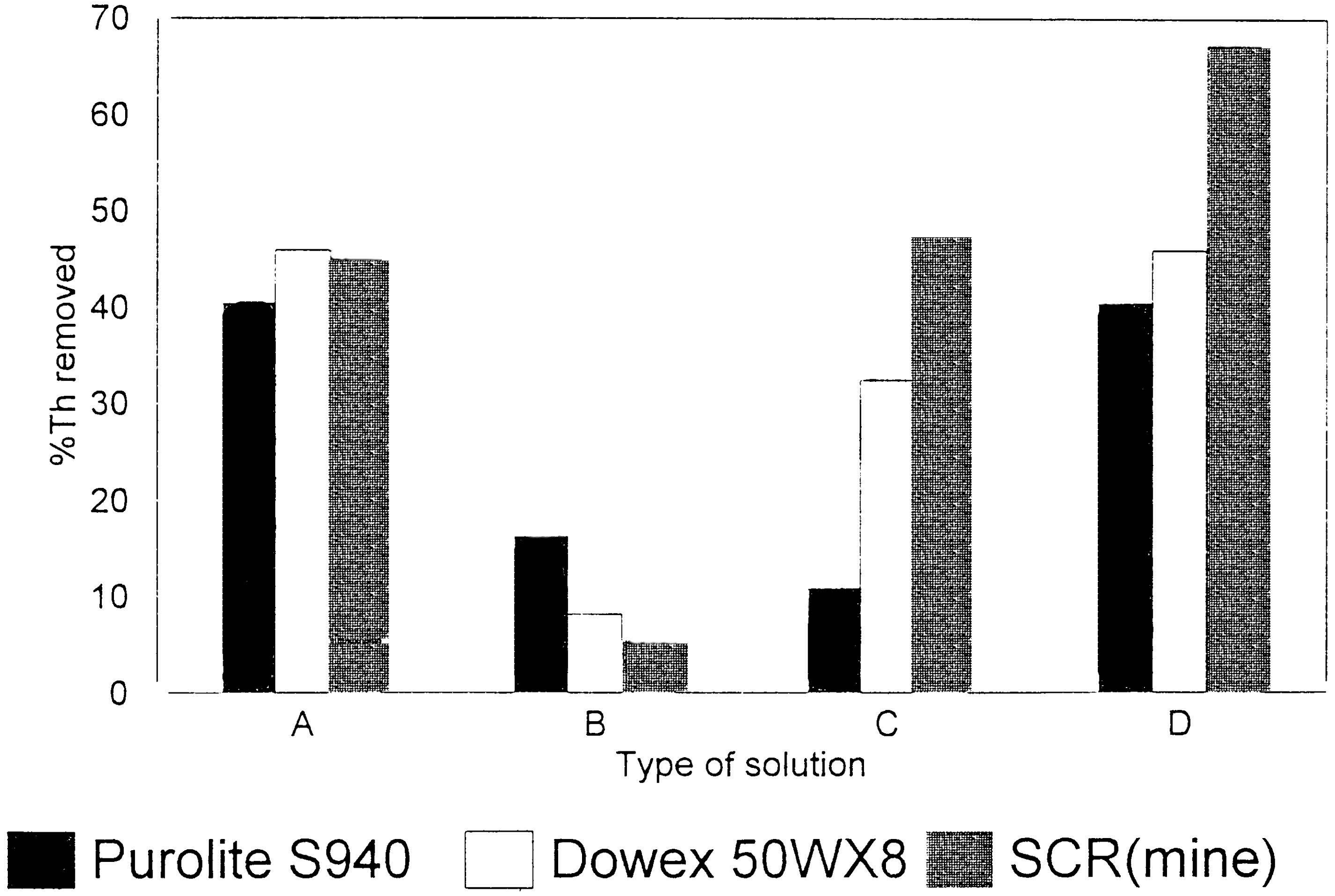


Figure 7.2
Contact time vs U and Th removal

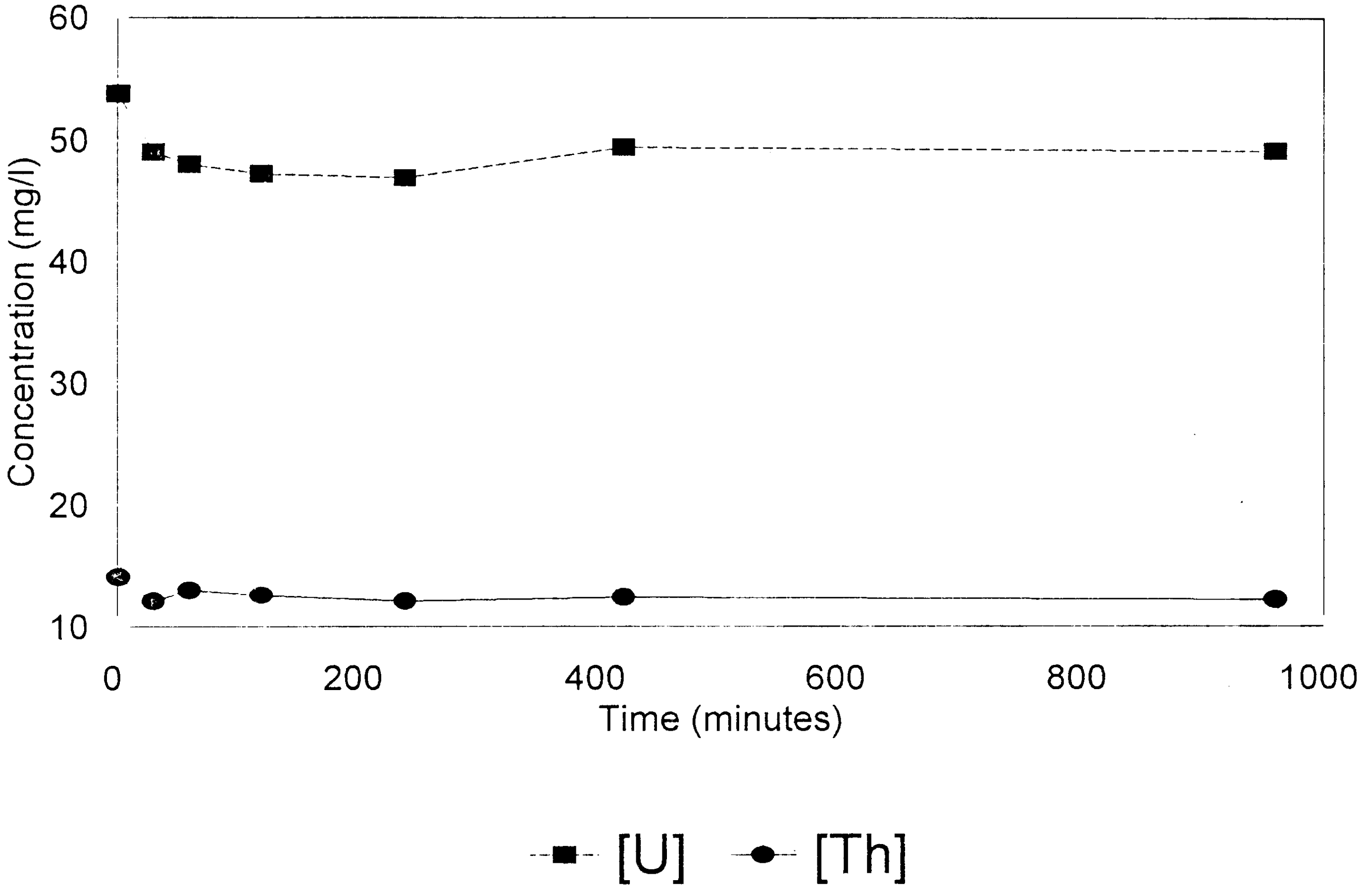


Figure 7.3

Uranium concentration vs fraction no.

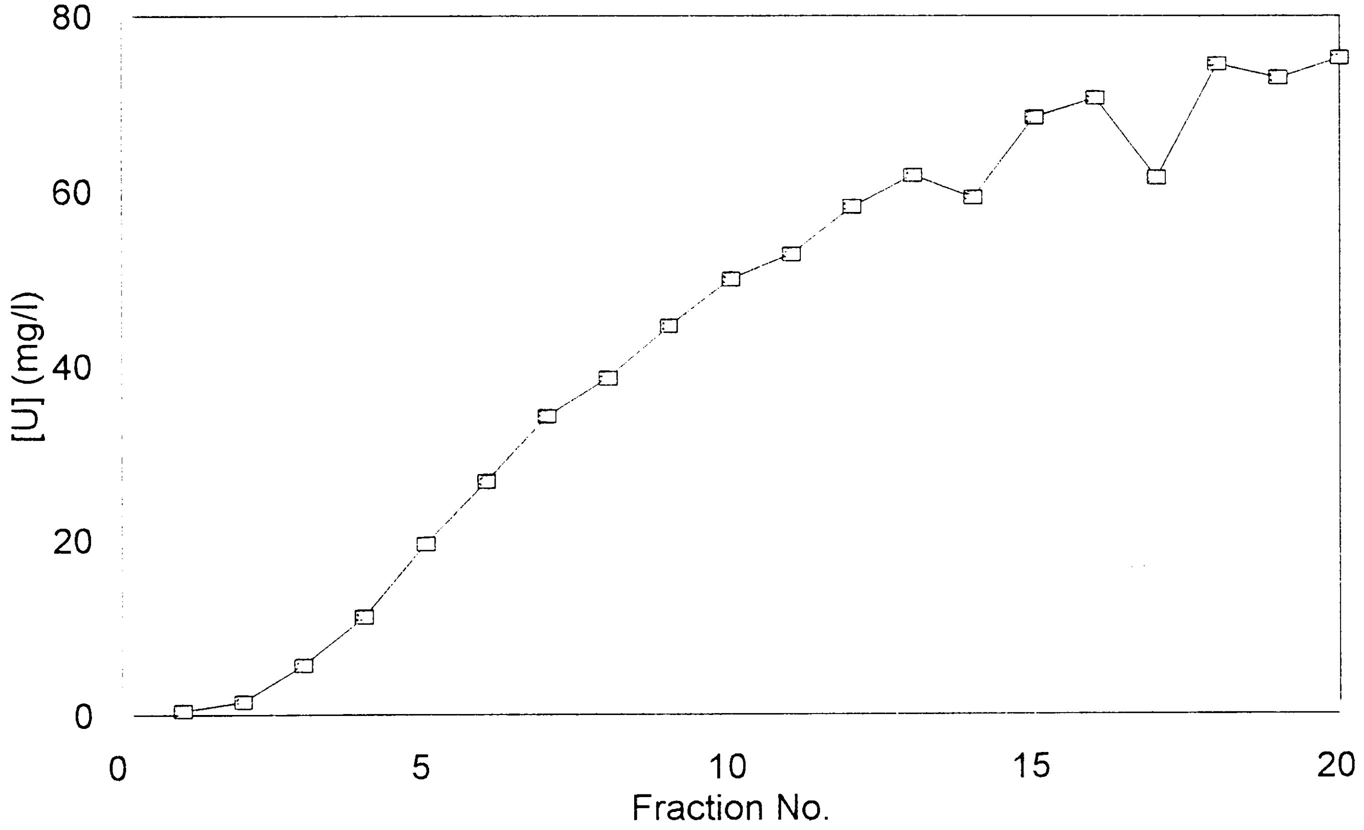


Figure 7.4(a)

Fraction No. vs [U]

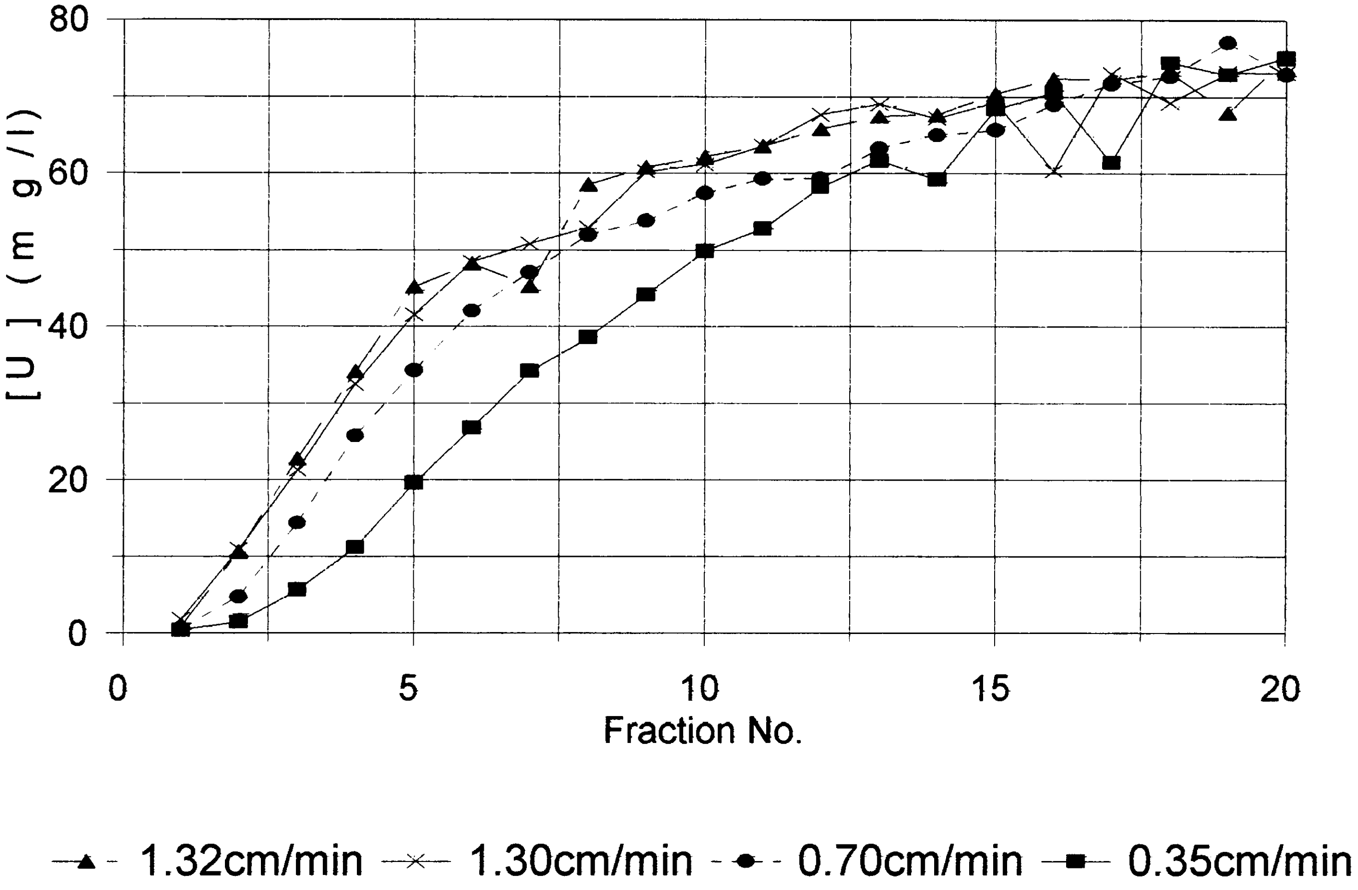


Figure 7.4(b)

Fraction No. vs %U removed

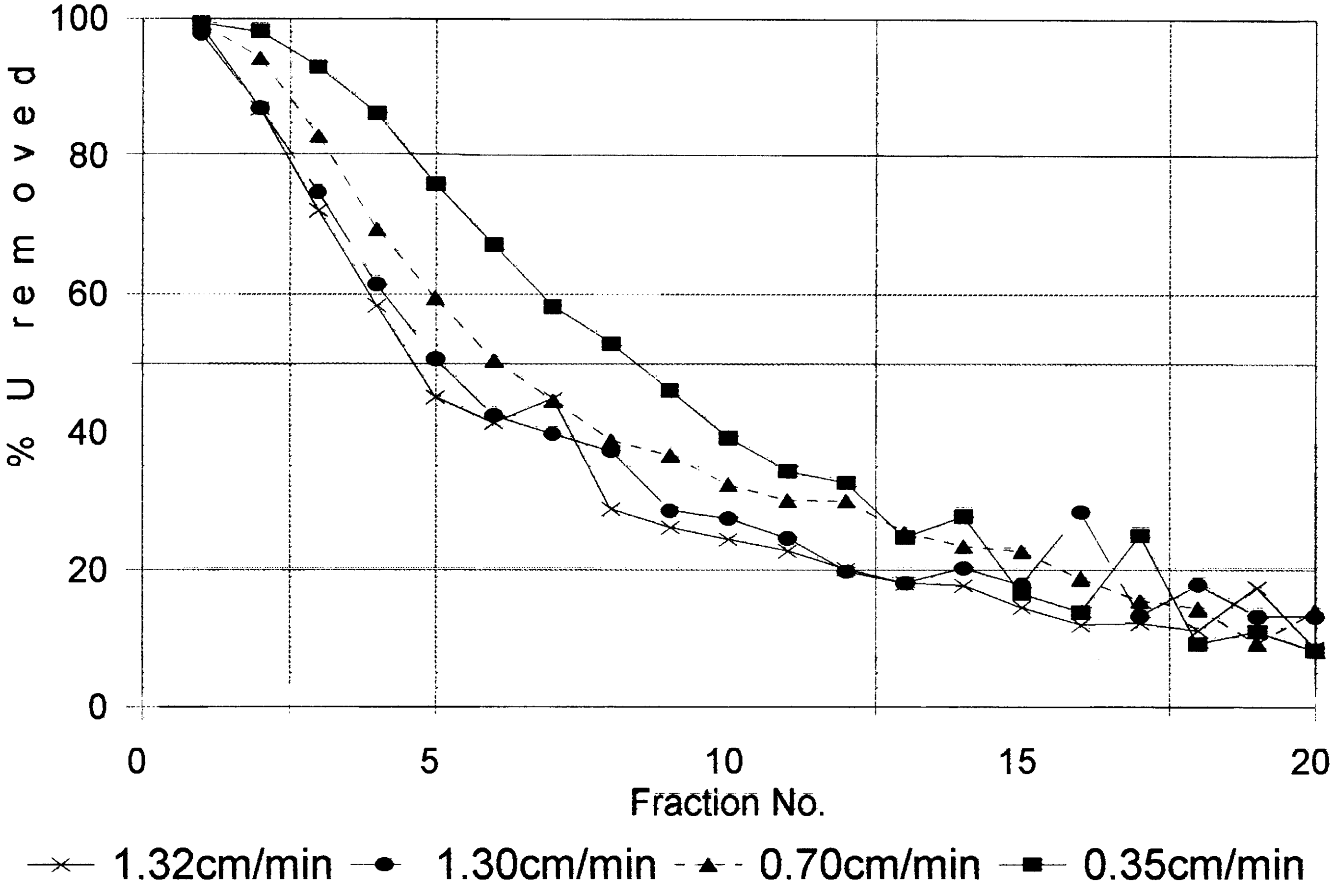
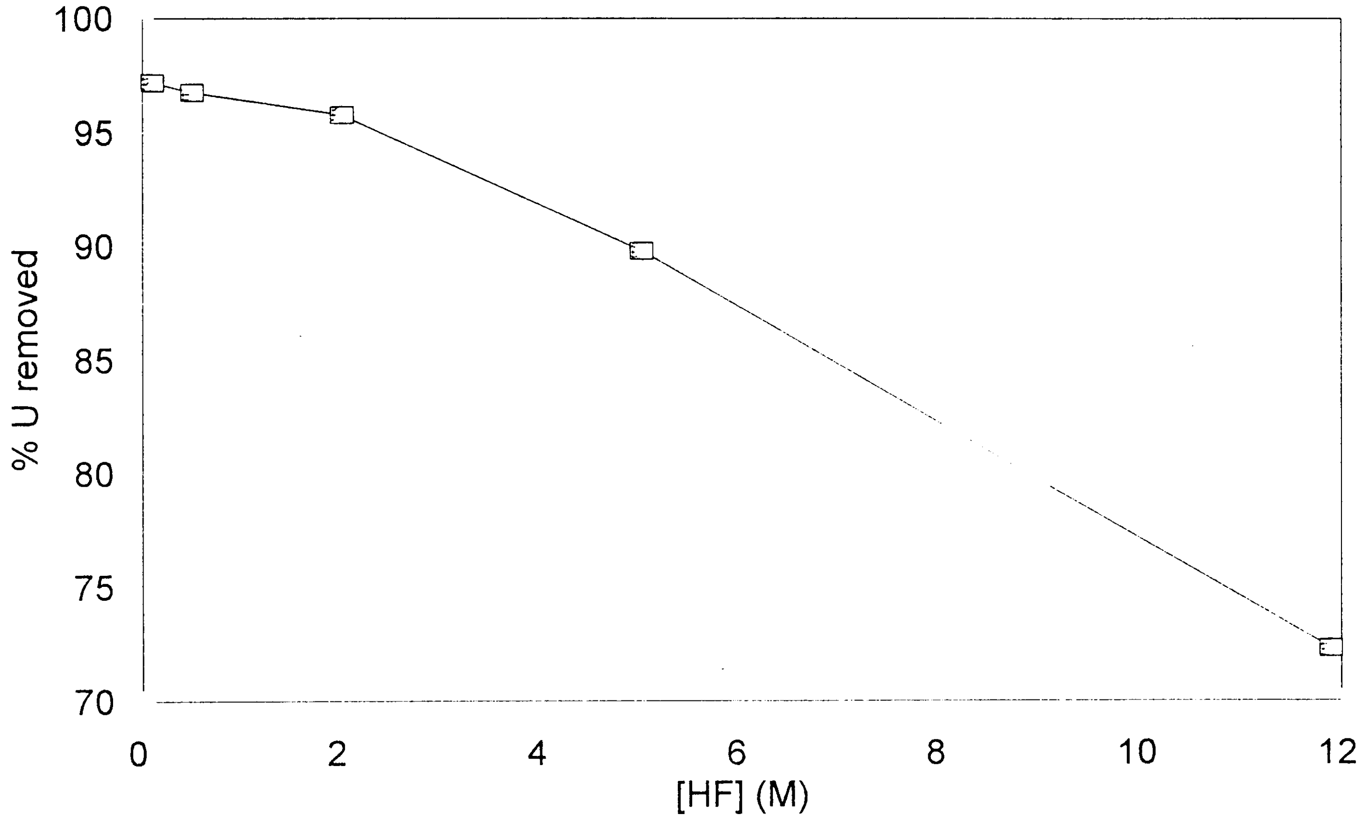


Figure 7.5

%U removal vs [HF]



CHAPTER 8

CONCLUSION

In this study three different purification methods have been investigated for the removal of radioactive substances from fluoro zirconic acid solutions. These are the precipitation, solvent extraction and ion exchange methods. Different observations have been found with each method and discussed below is the summary of these observations for each of the methods.

8.1. SOLVENT EXTRACTION METHOD

Not a great deal of success has been achieved with this method. A number of extractants have been employed without any success. This led to the conclusion that their failure is as a result of the medium in which they have to operate, being the fluoride medium. However, it was found that when the solution is spiked with some H_2SO_4 an extractant like Cyanex 272 does selectively remove some amounts of uranium and thereby reducing the level of radioactivity. Up to 94% uranium has been removed from the product with this method under these conditions. Only up to 28% Th has been removed. There also seemed to be some synergistic effects between Cyanex 272 and PC-88A. Thus, future work should be focused at exploring this combination further.

8.2. ION-EXCHANGE METHOD

In as far as this study is concerned, this is the second best method. Optimum results were obtained with the usage of Purolite S940, a type of a chelating resin. The success of this method was demonstrated by the removal of up to 79% uranium when used on a larger scale. This was an experiment which underlined the success of the method.

The serious setback of the method is its cost implications. This stems from the fact that the type of resin which gives good results is expensive and so far no method has been found to regenerate the resin to a satisfactory degree. This implies that the current method will not be viable on a plant scale.

Added to the financial implications is the other disadvantage being the time the process requires. It was observed that very slow flow rates yield better results, implying that on a plant scale the process might require up to days.

Despite these disadvantages, the method is itself not cumbersome and the resin (Purolite S940) is doing the job in as far as the removal of uranium and thorium from fluoro zirconic acid solution is concerned.

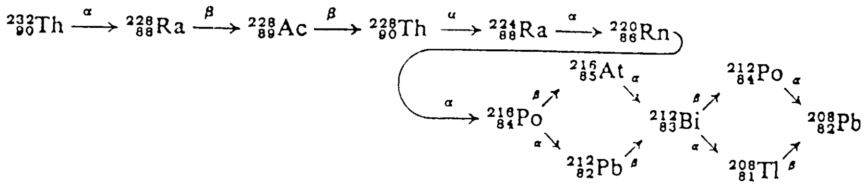
8.3. SELECTIVE PRECIPITATION METHOD

As compared to other purification methods employed, this is certainly the best. Optimum results have been achieved with CaO as a precipitant, with up to 94% radioactivity removed from the product. For better results CaO has to form part of the reagents, that is, CaO should be mixed with PDZ and the reaction carried out simultaneously. The advantage of this method is the ease with which it is carried out and its cost effectiveness, given that CaO is a relatively cheap compound. Furthermore for optimum results, only 5% of CaO to PDZ has to be used. This was found to be the optimum amount of CaO necessary as one has to strike a balance between the amount of radioactivity removed and the amount of waste generated.

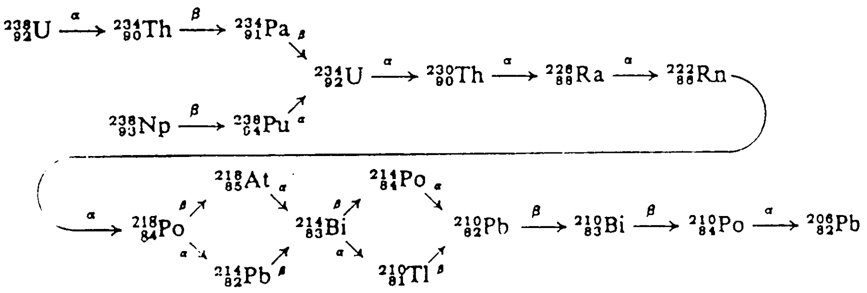
Despite its success and the advantages of this method as given in the above paragraph, it has associated with it some disadvantages. The most worrying is the amount of radioactive waste generated by the process. This presents a serious problem as now a lot of effort has to be geared towards dealing with the waste, a process that might have some negative financial implications. Despite this disadvantage, this method is, in as far as removing radioactivity from fluorozirconic acid solution is concerned, a great success.

ANNEXURE A

1. THE THORIUM SERIES



2. THE URANIUM SERIES



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