SYNOPSIS

The use of nuclear energy for production of electricity leads to generation of a substantial amount of high level radioactive waste. The spent fuel from nuclear reactor contains radioactive actinides and fission products. Thus, it is a renewable resource that can be reprocessed into new nuclear fuel and valuable isotopes. Plutonium and other actinide elements present in the spent fuel dominate in radio-toxicity. It takes millions of years for reducing radio-toxicity. Most of the fission products have half life of less than 10 years [1]. Hence in order to recover useful actinides from the spent fuel, to reduce generation of substantial amount of high level radioactive waste, and to reduce the hazard due to radiotoxicity, the spent fuel needs to be reprocessed. PUREX (Plutonium – Uranium Reduction Extraction) is one of the most widely used and well established methods of separation of fission products and minor actinides from spent nuclear fuel. It is basically liquid-liquid extraction, which involves separating components of a solution by exploiting an unequal distribution of the components between two immiscible liquid phases. One phase will be aqueous solution containing the components to be separated and the other phase will be an organic solvent having a high affinity for some specific component in solution. In PUREX process, the aqueous phase is nitric acid solution and the organic phase is 30% tri-butyl phosphate in n-paraffin hydrocarbon or n-dodecane as diluents [2].

There are many challenges associated with the management of nuclear waste. One of the major challenges encountered during aqueous reprocessing, and waste disposal in geological repositories, is the hydrolysis and polymerization leading to colloid formation of actinides. Actinides are hard Lewis acids, and exhibit a strong tendency towards hydrolysis and subsequent polymerization or ‘eigen-colloid’ formation
mainly due to the electrostatic interaction energy between the actinide ion and the OH⁻ ligand [3]. Among the actinide elements, Pu has high ionic potential and hence shows inordinate tendency to undergo hydrolysis and forms polynuclear species/colloids of larger aggregates with 10 to 10¹⁰ units whose molecular weight varies from 4000 Da to 10¹⁰ Da [4]. This can be clearly understood from the general order of hydrolysis chemistry of tetravalent actinides, Pu⁴⁺ > Np⁴⁺ > U⁴⁺ > Pa⁴⁺ > Th⁴⁺ [5].

During aqueous reprocessing, the hydrolysis reactions occur due to accidental dilution of fuel or leaking cooling coils or steam lines and sometimes by overheating of solutions by evaporation operations leading to the formation of polymers and colloids [6]. These polymeric colloidal species are different from those of their mononuclear precursors. They are resistant to extraction by ion exchange, leads to emulsification and interfacial crud formation during solvent extraction [7]. It exhibits a marked resistance toward depolymerization which increases with ageing at extended period of times at room temperature and at high temperatures. They also undergo surface complexation and pose greatest risk to the environment by enhancing the colloid mediated radionuclide transport because it was believed that colloids may enhance the migration of radioactive elements in aquifer systems [8]. With respect to repository failure, and release of plutonium to the ground water, it is important to understand the hydrolytic behaviour of plutonium due to its high radiotoxicity, long half-life and very complex aqueous chemistry. It also requires knowledge of the possible plutonium compounds and their state of aggregation as a prerequisite to predict plutonium transport in the ground water, for safety assessment of nuclear repositories and to avoid its formation during process operations. But there are many
complications associated with the study of aqueous chemistry of Pu. Some of the problems associated with it are,

i. **Disproportionation reaction:** Equilibrium of two or more oxidation state may occur in solution due to same redox potentials.

ii. **Reproportionation reaction:** Two plutonium ions of different oxidation state may get simultaneously oxidised and reduced to form two ions of the same oxidation state.

iii. **Pu isotopes are radioactive:** One milligram of Pu emits about $10^6$ alpha particles per second, and the radioactive decay is constantly adding energy to the Pu solution. This leads to radiolytic decomposition of water producing redox reagents such as short lived radicals ·H, ·OH, and ·O. These radicals recombine to form H$_2$, O$_2$ and H$_2$O$_2$. Thus radiolysis tends to reduce Pu(VI) and Pu(V) to Pu(IV) and Pu(III) states.

All the reactions take place simultaneously and it becomes very difficult to study one particular reaction without the interference of the other. Hence as a common practice in radiochemistry, preliminary experiments were performed with stable or less radioactive analogs prior to the investigation of the element of interest mainly to validate new experimental methods, to minimize radioactive dose and to save rare material. In the case of tetravalent plutonium, two most frequently used homologues are the stable element zirconium and the very long lived actinide isotope $^{232}$Th. Both elements form exclusively tetravalent ions in solution and offer the possibility to study complexation processes and perform solubility experiments without interference of the complex redox chemistry which is typical for plutonium. Another element
which can be considered is uranium. It is the heaviest naturally occurring element and is mainly used as fuel in nuclear reactors by increasing the relative concentration of $^{235}$U (only fissile isotope of uranium). U(IV) also shows high tendency for hydrolysis, polymerization and colloid formation. Finally, in order to avoid polymers during process operation, to understand the role of colloids in waste disposal and for precise geochemical modeling to know the relative stability of the compounds, it is necessary to understand the source and mechanism of formation of colloids.

Colloids can be characterized by different techniques. Since aquatic colloids are delicately balanced systems and are very sensitive to handling, characterization of these colloids requires a non-invasive technique which can serve the purpose without disturbing the whole system. Hence light scattering technique (based on interaction of system with visible light) is considered as a better option as it is one of the most standard size characterization techniques which allow in-situ measurements without sample preparation. It is very sensitive, non invasive and non destructive colloid characterization technique which allows detection of colloids whose size ranges from 2 nm – 2 μm. Also during process operation, the molecular weight of polymers plays significant role. In addition to characterizing the size variation of colloids, the molecular weight of the polymers can also be determined using static light scattering technique [9].

The main objective of the thesis is to investigate the hydrolytic behaviour of Zr(IV), U(IV), U(VI) and Th(IV) by light scattering technique and to correlate their behaviour with Pu(IV). In the present work, preliminary studies were performed on metal ions such as Sr$^{2+}$, Al$^{3+}$ and Bi$^{3+}$. Light scattering studies were carried out for polymeric solutions of Zr(IV), U(IV), U(VI) and Th(IV) and the results were
correlated to the data of Pu(IV) reported in literature. Spectroscopic techniques were used to detect the initial formation of colloids, and molecular weight of the colloidal polymers was determined using static light scattering technique. The thesis consists of seven chapters and the summary of each chapter is as follows:

**Chapter 1**

This chapter gives a detailed introduction on the importance of nuclear energy and the development of nuclear power program in India. Spent nuclear fuel reprocessing and its needs are also discussed in this chapter. PUREX process is the well established aqueous reprocessing method which is used widely in the nuclear industry. The general procedure involved in the process is given in detail. The major challenges faced during aqueous reprocessing due to hydrolysis of tetravalent metal ions are discussed. In addition to that, the basic introduction to metal ion hydrolysis and the difficulties in studying the behavior of a metal ion in aqueous systems are elaborated. Plutonium is considered as one of the key component of spent fuel and it has a very complicated aqueous chemistry. Important literature data available on hydrolysis of Pu(IV) are briefed. A summary of the reported data available on the mechanism of formation of colloids, studies performed to probe its structure, size and morphology, solubility of colloids and different methods to remove or avoid its formation are briefly described. Reasons for choosing zirconium, thorium and uranium as surrogate to study Pu hydrolytic behaviour is also discussed. As tetravalent metal ions are highly prone to the formation of colloids and polymer in aqueous systems, a general introduction on colloids, the parameters necessary for the stability of colloidal system and the various techniques used for characterizing the colloids are also discussed. The occurrences, chemical properties of Zr, U and Th which are taken as analogues for the
present study are elaborated. A short note on motivation, objective of the present study and overview of the thesis concludes this chapter.

**Chapter 2**

Chapter 2 provides a detailed description on the chemicals and the experimental techniques used for the present work. The hydrolysis reaction is monitored using spectroscopic techniques such as Ultraviolet-visible and Attenuated Total Reflectance – Fourier Transform Infrared spectroscopy (ATR- FTIR). Formation of colloids or polymeric species can be identified by the change in spectrum. Theory and its experimental details are included in this chapter. Light scattering technique is used for the present study to characterize colloids formed in the system. Mean size of the colloids were determined by using this technique. Theory of light scattering (dynamic and static) and the details of the experimental set up used are also discussed. Since colloids were synthesized at various pH conditions, details of pH measurements are also discussed in detail. Debye plot is generated to determine the second virial coefficient and weight average molecular weight of the polymers. In order to generate the plot, parameter such as differential refractive index and the density has to be given as input. A brief account on the working principle of refractometer and its experimental details are also included in this chapter. X-ray diffraction is used to investigate the precipitates that are formed at different pH conditions.

**Chapter 3**

Chapter 3 covers the light scattering studies related to hydrolysis reactions of multivalent metal ions such as Sr$^{2+}$, Al$^{3+}$ and Bi$^{3+}$ in aqueous nitric acid solutions. Different concentrations of the metal ions were prepared in aqueous nitric acid solutions. For Sr$^{2+}$ and Al$^{3+}$ only initial hydrolysis was investigated. The change in
refractive index of the solution with change in concentration of solute was measured using refractometer. The differential refractive index was obtained from its slope and used for generating Debye plot. The weight average molecular weight of the hydrated \(\text{Sr}^{2+}\) and \(\text{Al}^{3+}\) was determined from the intercept of the plot. In case of \(\text{Bi}^{3+}\), polymerization and colloid formation at different pH conditions is also investigated. The variation in size at different pH conditions was monitored. The weight average molecular weight and the second virial coefficient which measures solute-solvent interaction parameter were determined and the results are discussed.

**Chapter 4**

Chapter 4 discusses the results obtained from the hydrolysis of tetravalent zirconium. A spectrophotometric method was developed in order to determine the micro-level concentration of Zr(IV) in aqueous solution. Zr(IV) colloids were synthesized in nitric acid medium at high acidity. Size of the colloids was determined using dynamic light scattering technique. pH was varied and the change in the size of the colloids were also reported. The polymers were aged at different time intervals. Size and molecular weight of freshly prepared and aged polymers were determined and the results were discussed in detail in this chapter.

**Chapter 5**

Chapter 5 mainly deals with the hydrolysis reactions leading to polymerization and colloid formation of tetravalent and hexavalent uranium. U(VI) hydrolysis was monitored by UV-visible and FTIR spectroscopy. The colloids formed at different acidities were studied using dynamic light scattering. The solid phase formed at near neutral condition was dried and analysed by x-ray diffraction. Size variation at different pH conditions was investigated and the molecular weight of the colloid was
determined. The results obtained from these studies were discussed in first part of the chapter. The second part of the chapter constitutes the results obtained from the studies performed on U(IV) which was generated using electrolytic reduction of U(VI). The method adopted for U(IV) generation was given in detail. Stability of U(IV) at the condition of investigation was ensured by monitoring the UV-visible spectrum. U(IV) colloids were synthesized by varying the acidities. The course of the reaction was monitored by UV-visible and ATR-FTIR spectroscopy. Size of the colloids formed at varying conditions was measured. The second virial coefficient and weight average molecular weight of freshly prepared as well as colloids aged for different time intervals were determined and the results were discussed in detail in this chapter.

Chapter 6

Chapter 6 describes the results obtained from the hydrolysis and polymerization reactions of tetravalent thorium. Th(IV) polymers were prepared by varying pH of the solution. Sizes of the colloids formed at different pH are measured. The molecular weight of the freshly formed polymer as well as polymers aged at different time intervals are determined using Debye plot. Second virial coefficient was also determined and the results are discussed in detail.

Chapter 7

This chapter constitutes the summary of the results discussed in the thesis. Use of light scattering technique as one of the method for immediate detection of polymers formed during process operation is clearly demonstrated. The investigations on aqueous species forming in solutions of tetravalent ions which are compiled in the present work are sub divided into four categories, i.e., the experiments performed on
Al\textsuperscript{3+}, Sr\textsuperscript{2+} and Bi\textsuperscript{3+} and those performed on Zr\textsuperscript{4+}, U\textsuperscript{4+, 6+} and Th\textsuperscript{4+}. The highlights of the results obtained are as follows:

- Light scattering technique was used to determine the diameter of the hydrated ion of Sr(II) and Al(III) ions in aqueous nitric acid medium. At high acidity with OH/Al ratio of 0, the number of solvating molecules was observed to be 5 and for strontium, 9 water molecules were in the primary hydration sphere possibly existing in the form of Sr(H\textsubscript{2}O)\textsubscript{9}\textsuperscript{2+}.

- Particle size of hydrolyzed Bi\textsuperscript{3+} increases as the concentration of Bi increases. The weight average molecular weight of hydrolyzed species shows that Bi\textsuperscript{3+} undergoes hydrolysis and forms hydrous polymers with 5-6 units.

- The investigations on Zr(IV) showed unambiguously that colloids are formed at very low pH. The molecular weight of the colloid shows that around ~10 zirconium atoms are present in the freshly prepared Zr(IV) polymer and it increases to ~30 in the case of aged polymer. Hydrolysis of Zr(IV) followed a similar behaviour to Pu(IV).

- The onset of colloid formation starts at pH = 3.46 in 2.5 mM U(IV) solutions. It is now proposed that in case of U(IV), colloids are formed in different domains of pH and U(IV) concentrations and that these colloids may differ in their structure. In the more acidic range, the size of the colloids formed is very small and thus considered to be crystalline in nature. However, at higher pH amorphous colloids form spontaneously from the over saturated solution. The colloids of U(IV) formed in low pH domain are oxo bridged and those formed at high pH are hydroxo bridged species. Ageing of colloids for 3 days lead to increase of molecular weight from ~1,800 to 13,000 Da. About 40-50 atoms of U are considered to be present in the aged
polymer. Positive value of second virial coefficient shows that solute-solvent interaction is high leading to stable suspension.

- Light scattering measurements were performed on colloidal U(VI) solutions formed at pH range of 7-8. The average particle diameter was determined as 32-36 nm. Well defined colloidal species are formed with no considerable change in particle size with increasing U(VI) concentration. The weight average molecular weight of colloidal species was predicted as ~763 Da by Debye plot. The behaviour of U(VI) is contradictory to U(IV) and Zr(IV). Even at neutral pH conditions there was no indication of polymerization and only oligomers with 2 – 3 uranyl units are considered to be present.

- Th(IV) forms colloids in solutions of pH = 1-3 with [Th(IV)]\text{tot} = 0.2 to 10 mM and 0.05 to 0.4 M. Colloids are formed at two different pH domains and Th(IV) concentration. Th(IV) forms polymers of high molecular weight similar to that of Pu(IV).

- In contrast to the continuous transformation from mononuclear to polynuclear species the onset of colloid formation for Zr(IV), U(IV) and Th(IV) seems to behave differently. But similarity is the formation of polymers of considerable size up to billions of atomic mass unit. The light scattering measurements for Zr(IV), U(IV) and Th(IV) gives direct evidence that their hydrolysis behaviour is similar to Pu(IV) and hence it will help in future investigations on its chemical behaviour and for basic insights in polymer and colloid chemistry of tetravalent Pu. Light scattering technique provides faster and non-invasive measurement which is considered to be more advantageous compared to other methods for immediate detection of colloids.
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# Abbreviations

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<tr>
<td>MWe</td>
<td>Mega Watt electric</td>
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<tr>
<td>MOX</td>
<td>Mixed Oxide</td>
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<tr>
<td>FBRs</td>
<td>Fast Breeder Reactors</td>
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<tr>
<td>PUREX</td>
<td>Plutonium Uranium Reductive Extraction</td>
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<td>TBP</td>
<td>Tributyl Phosphate</td>
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<td>An</td>
<td>Actinide</td>
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<td>SANS</td>
<td>Small Angle Neutron Scattering</td>
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<td>SAXS</td>
<td>Small Angle X-ray Scattering</td>
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<tr>
<td>XAFS</td>
<td>X-ray Absorption Fine Structure</td>
</tr>
<tr>
<td>EXAFS</td>
<td>Extended X-ray Absorption Fine Structure</td>
</tr>
<tr>
<td>LIBD</td>
<td>Laser Induced Breakdown Detection</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission electron microscope</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray Diffraction</td>
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<tr>
<td>K$_{sp}$</td>
<td>Solubility product</td>
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<tr>
<td>ATR</td>
<td>Attenuated Total Reflection</td>
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<tr>
<td>TOC</td>
<td>Total Organic Carbon</td>
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<tr>
<td>DLS</td>
<td>Dynamic Light Scattering</td>
</tr>
<tr>
<td>FFT</td>
<td>Fast Fourier Transform</td>
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<tr>
<td>PCS</td>
<td>Photon Correlation Spectroscopy</td>
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<td>SLS</td>
<td>Static Light Scattering</td>
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<td>LED</td>
<td>Light Emitting Diode</td>
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<td>A$_2$</td>
<td>Second virial coefficient</td>
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<td>M$_w$</td>
<td>Weight average molecular weight</td>
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<td>Acronym</td>
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<td>NDIS</td>
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<td>AXD</td>
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<td>$\gamma$</td>
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