Chapter 1

Introduction
1.1 Environmental relevance

Discovery of artificial radioactivity by Irene Curie and Frederick Joliot in 1934 opened a new chapter in the peaceful uses of radioisotopes in diverse fields, such as, health, agriculture, industry, etc. Major step forward in this direction, however, took place with the discovery of nuclear fission in 1939 by Hahn and Strassmann. It opened up a frontier for utilization of the vast natural resources of uranium for electricity generation as an alternative to fossil fuels.

Associated with its usage, one major concern before environmentalists, policy makers, and common people regarding radioactivity has been its unregulated presence in geosphere. Exploitation of radioactivity during war time and its numerous subsequent applications has introduced large amount of radioactivity into environment. Apart from chemical toxicity, radionuclides cause radiation hazard by emanating ionizing radiations, $\alpha$, $\beta$, $\gamma$, and neutrons. Radionuclides’ application has, therefore, been put under strict regulations worldwide. With everyday increasing demand on nuclear applications, chances of appearance of radioactivity in the environment cannot be discounted. A safe and scientific approach to deal with this issue lies in developing robust understanding about the environmental geochemistry of radioactive contaminants. This will help not only in assessing the risk posed by future applications but also in remediating the present contaminations.

1.2 Sources of radionuclides in geosphere

Radioisotopes are present in the geosphere both naturally as well as from artificial production routes (Leiser, 1995; Siegel and Bryan, 2009; Runde and Neu, 2010).
1.2.1 Natural radioactivity

Natural radioactivity is present in the form of uranium-thorium decay series wherein $^{238}\text{U}$ $(4n+2)$, $^{235}\text{U}$ $(4n+3)$, and $^{232}\text{Th}$ $(4n)$ decay through intermediate daughter products to $^{206}\text{Pb}$, $^{207}\text{Pb}$ and $^{208}\text{Pb}$ respectively. On mining and milling, large amount of these activities are brought to the earth surface. Residue (mill tailings) of the milling process are dumped on the low lying areas (mill tailing ponds) which creates a potential source of long lived radioisotopes of Th, U, Ra, and Po in the geosphere. Other naturally occurring radioisotopes such as $^{14}\text{C}$, and $^3\text{H}$ are being continuously formed in environment due to cosmic ray bombardment; their concentration is, however, not a matter of concern owing to the low level of radioactivity.

1.2.2 Nuclear weapon tests

A large number of atmospheric tests were conducted by the US, the USSR, UK, France and China, between 1946 and 1962. After the atmospheric test ban treaty in 1963, underground nuclear tests have been conducted by them along with countries like India, Pakistan, and North Korea. Only France and China continued atmospheric testing till 1974 and 1980, respectively (Runde and Neu, 2010). All these nuclear tests have resulted in the contamination of the geosphere with actinides and long lived fission products.

1.2.3 Accidental releases from nuclear facilities

There have been a few disastrous accidents in the history of nuclear industry. Radioactivity was released from (i) the fire accident at the reactors in Windscale in UK in 1957, (ii) loss of coolant accident at the Three Mile Island nuclear reactors in US in 1979, (iii) explosions at the Chernobyl reactor in USSR in 1986, and recently (iv) release of gaseous fission products from the spent fuel storage bay at Fukusima in 2011 due to the post Tsunamic events. These accidental
releases have resulted in the contamination of the large geographical area and atmosphere with long lived fission products and in some cases actinides as well. In addition there have been releases of actinides and fission products from the spent fuel reprocessing plants, viz., (i) leakage from the Hanford high level radioactive liquid waste storage tanks near the Columbia river, (ii) routine and accidental discharges from the Mayak plutonium production complex in USSR, to list a few.

1.2.4 Nuclear Applications

$^{238}$Pu has been used as a power source in satellites. Some of the satellites have reentered the earth’s atmosphere upon the completion of their life cycle in space or as a result of the incomplete mission. $^{238}$Pu thus spread in the upper atmosphere and might have ended up partly in the geosphere (Kim, 1986).

$^{99}$Tc$^{m}$ is widely used in nuclear medicine for diagnostic applications. The daughter product of this isomer is $^{99}$Tc$^{6}$ which has a long half life and hence remains in the geosphere for millions of years after the use.

1.2.5 Nuclear waste

The reprocessing of spent nuclear fuel to recover plutonium and uranium results in various waste streams, such as low level waste (LLW) (< 1 mCi/L), intermediate level waste (ILW) (1 mCi/L to 1 Ci/L), and high level waste (HLW) (> 1 Ci/L) depending upon the level of radioactivity. ILW is concentrated in cementous solid matrices and stored in shallow trenches, while the HLW is vitrified in a suitable glass matrix and after an interim storage period, is planned to dispose of in deep underground repositories (Schwyn et al., 2012).
Current and potential future inventories of radioactivity in environment may thus be grouped in three main classes:

- Legacy sources such as contaminated geographical areas, etc.
- Nuclear applications and accidents.
- Nuclear energy: With expanding nuclear energy program in country like India, increasing inventory of nuclear HLW increases the relevance of understanding of geochemical behaviour of long lived radionuclides in environment.

1.3 Actinides and long lived fission products

Actinide isotopes, such as, $^{235}\text{U}$, $^{239}\text{Pu}$, $^{233}\text{U}$, etc. undergo neutron induced fission in nuclear reactors, thermonuclear explosions, etc. A host of fission products spanning the atomic number 35 to 63 with varying yield are produced. Most of the fission products have shorter half-lives and hence do not remain relevant over a longer period of time. Fertile isotopes of actinides can undergo neutron capture reaction to produce a large number of actinide isotopes, most of them having long half lives, viz.,

$$^{232}\text{Th} (n,\gamma) \xrightarrow{\beta^{-}} ^{233}\text{Pa} \xrightarrow{\beta^{-}} ^{233}\text{U} (1.593 \times 10^5 \text{ y})$$

$$^{238}\text{U} (n,\gamma) \xrightarrow{\beta^{-}} ^{239}\text{Np} \xrightarrow{\beta^{-}} ^{239}\text{Pu} (2.411 \times 10^4 \text{ y})$$

$$^{239}\text{Pu} (n,\gamma) \xrightarrow{\beta^{-}} ^{240}\text{Pu} (n,\gamma) \xrightarrow{\beta^{-}} ^{241}\text{Pu} (n,\gamma) \xrightarrow{\beta^{-}} ^{242}\text{Pu} (n,\gamma) \xrightarrow{\beta^{-}} ^{243}\text{Am} (7370 \text{ y})$$

$$^{241}\text{Pu} \xrightarrow{\beta^{-}} ^{241}\text{Am} (432.2 \text{ y})$$

$$^{241}\text{Am} (n,\gamma) \xrightarrow{\beta^{-}} ^{242}\text{Am} \xrightarrow{\beta^{-}} ^{242}\text{Cm} (162.94 \text{ d})$$

$$^{243}\text{Am} (n,\gamma) \xrightarrow{\beta^{-}} ^{244}\text{Am} \xrightarrow{\beta^{-}} ^{244}\text{Cm} (18.1 \text{ y})$$

Table 1.1 and 1.2 give the nuclear data of the long lived actinides and fission products typically present in nuclear HLW.
Table 1.1: List of long-lived fission products present in HLW

<table>
<thead>
<tr>
<th>Radionuclide</th>
<th>Half-life</th>
<th>Yield (%) in $^{235}$U(n$<em>{th}$,f) and $^{239}$Pu(n$</em>{f}$,f)*</th>
<th>Radiation type</th>
<th>Energy</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{90}$Sr - $^{90}$Y</td>
<td>28.5 y</td>
<td>5.772 (2.088)</td>
<td>Pure β</td>
<td>0.5, 2.3 MeV</td>
</tr>
<tr>
<td>$^{93}$Zr</td>
<td>$1.5 \times 10^6$ y</td>
<td>6.375 (3.734)</td>
<td>Pure β</td>
<td>0.06 MeV</td>
</tr>
<tr>
<td>$^{99}$Tc</td>
<td>$2.1 \times 10^5$ y</td>
<td>6.074 (5.608)</td>
<td>Pure β</td>
<td>0.3 MeV</td>
</tr>
<tr>
<td>$^{106}$Ru - $^{106}$Rh</td>
<td>368 d</td>
<td>0.4019 (4.5219)</td>
<td>γ</td>
<td>512 keV</td>
</tr>
<tr>
<td>$^{107}$Pd</td>
<td>$6.5 \times 10^6$ y</td>
<td>0.1914 (3.5776)</td>
<td>Pure β</td>
<td>0.03 MeV</td>
</tr>
<tr>
<td>$^{125}$Sb</td>
<td>2.77 y</td>
<td>0.0253 (0.1964)</td>
<td>γ</td>
<td>426, 601 keV</td>
</tr>
<tr>
<td>$^{129}$I</td>
<td>$1.57 \times 10^7$ y</td>
<td>0.8533 (0.922)</td>
<td>β, γ</td>
<td>0.2 MeV, 40 keV</td>
</tr>
<tr>
<td>$^{134}$Cs</td>
<td>2.06 y</td>
<td>4e-06 (1e-03)</td>
<td>β, γ</td>
<td>0.7 MeV, 605 keV</td>
</tr>
<tr>
<td>$^{135}$Cs</td>
<td>$2 \times 10^6$ y</td>
<td>6.726 (7.449)</td>
<td>Pure β</td>
<td>0.02 MeV</td>
</tr>
<tr>
<td>$^{137}$Cs</td>
<td>30.17 y</td>
<td>6.2295(6.6255)</td>
<td>β</td>
<td>0.5, 1.2 MeV</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>γ</td>
<td>662 KeV</td>
</tr>
<tr>
<td>$^{144}$Ce - $^{144}$Pr</td>
<td>284 d</td>
<td>5.4492 (3.6089)</td>
<td>β</td>
<td>0.3, 3.0 MeV</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>γ</td>
<td>133,697 keV</td>
</tr>
<tr>
<td>$^{147}$Pm</td>
<td>2.62 y</td>
<td>2.2551 (2.0263)</td>
<td>Pure β</td>
<td>0.2 MeV</td>
</tr>
<tr>
<td>$^{151}$Sm</td>
<td>93 y</td>
<td>0.435 (0.8202)</td>
<td>Pure β</td>
<td>0.1 MeV</td>
</tr>
<tr>
<td>$^{152}$Eu</td>
<td>13.33 y</td>
<td>$5.28e-07$ (2.05e-05)</td>
<td>γ</td>
<td>121.8 KeV, etc.</td>
</tr>
<tr>
<td>$^{154}$Eu</td>
<td>8.8 y</td>
<td>0.00017 (0.00449)</td>
<td>γ</td>
<td>123 KeV, etc.</td>
</tr>
<tr>
<td>$^{155}$Eu</td>
<td>4.96 y</td>
<td>0.03328 (0.2579)</td>
<td>β</td>
<td>0.1, 0.2 MeV</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>γ</td>
<td>87, 105 keV</td>
</tr>
</tbody>
</table>

*in bracket
Table 1.2 List of transuranium isotopes present in HLW

<table>
<thead>
<tr>
<th>Radionuclide</th>
<th>Half life (y)</th>
<th>Radiation type</th>
<th>Radiation energy (MeV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{237}$Np</td>
<td>$2.14 \times 10^6$</td>
<td>$\alpha$</td>
<td>4.788</td>
</tr>
<tr>
<td>$^{239}$Pu</td>
<td>$2.411 \times 10^4$</td>
<td>$\alpha$</td>
<td>5.155</td>
</tr>
<tr>
<td>$^{238}$Pu</td>
<td>87.74</td>
<td>$\alpha$</td>
<td>5.499</td>
</tr>
<tr>
<td>$^{240}$Pu</td>
<td>6550</td>
<td>$\alpha$</td>
<td>5.168</td>
</tr>
<tr>
<td>$^{241}$Pu</td>
<td>14.4</td>
<td>$\beta$</td>
<td>0.02</td>
</tr>
<tr>
<td>$^{241}$Am</td>
<td>432.6</td>
<td>$\alpha$</td>
<td>5.486</td>
</tr>
<tr>
<td>$^{243}$Am</td>
<td>7370</td>
<td>$\alpha$</td>
<td>5.275</td>
</tr>
<tr>
<td>$^{244}$Cm</td>
<td>18.11</td>
<td>$\alpha$</td>
<td>5.805</td>
</tr>
<tr>
<td>$^{245}$Cm</td>
<td>8500</td>
<td>$\alpha$</td>
<td>5.362</td>
</tr>
</tbody>
</table>

The radioactivity of the radionuclides decays exponentially with time and hence once formed they contribute differently to the total radioactive burden depending upon their half lives. Variation of the radioactivity of different actinides and long-lived fission products present in the HLW produced by an Indian PHWR is plotted as a function of time in figure 1.1. Bulk of radioactivity initially is due to short-lived fission products $^{137}$Cs and $^{90}$Sr. After 1000 yrs the radioactive hazard is due to transuranics $^{241}$Am, $^{243}$Am, $^{239,240}$Pu, and $^{237}$Np and during the longest time periods a mixture of the isotopes $^{99}$Tc, $^{237}$Np, $^{210}$Pb, and $^{226}$Ra dominates the small amount of radioactivity that remains (Figure 1.1).
Once released into the environment, the radionuclides may migrate to the far field areas. Water acts as the dominant transport medium (Stumm and Morgan, 1995; Siegel and Bryan, 2009). Fate of the radionuclides in geosphere is thus decided by the hydro-geochemistry of radionuclides and transport phenomena. Flux of radionuclide available for transport is generally determined in terms of partitioning coefficient ($K_d$) of a radionuclide between aqueous phase and the radionuclide’ sorbing phase and transport is modelled on its basis. As the chemical condition over the flow path cannot be considered same, it is required that all the pertinent chemical
reactions of radionuclides in environmental aquatic medium should be identified and understood in framework of robust thermodynamic model.

1.5 Hydrogeochemistry of actinides and long lived fission products

Geochemistry of fission products in aquatic system is relatively simple compared to actinides. Though the present section details about actinides, chemical reactions applicable to both the class of metal ions are similar.

**Solubility and Speciation in groundwater**

Solubility of metal ions is primarily decided by their oxidation state. Early actinides (Th - Pu) exhibit multiple oxidation states (+3 to +6 in aquatic medium) owing to the small difference in the energy of 6d and 5f orbitals. +3 becomes the dominant oxidation state of actinides beyond americium (Am) as 5f orbital gets stabilized with increasing atomic number. (Eh, pH) condition of the aquatic body affects the stability of the oxidation state. Complexing ligands present in the aquatic body could also change the oxidative state of redox sensitive elements. Pu exhibits multiple valencies some of which coexist in natural water.

Dominant inorganic complexing ligands of aqueous systems are hydroxide, carbonate, and chloride. Solubility limiting solid phase of actinides are thus oxides, hydroxides or carbonates. The general pattern of solubility of actinides in different oxidation states is: +4 < +6 < +5 < +3. In absence of large scale precipitation reaction, higher valent actinides may hydrolyze, form colloidal sized (hydr)oxide polymer and remain suspended in the aqueous medium. Such particulate species are termed “intrinsic colloids” of actinides. Secondary solid phase formation of actinides with silicate ions has also been observed (Wronkiewicz and Buck, 1999).
In dilute natural aqueous system, speciation of metal ions is dominantly decided by the
complexation with inorganic and organic ligands. Actinides are hard acids and interact strongly
with hard donor ligands. For a given oxidation state, the relative stability of actinide complexes
with hard base ligands can be divided into three groups in the order: $\text{CO}_3^{2-}$, $\text{OH}^-$, $\text{HPO}_4^{2-}$,
$\text{SO}_4^{2-}$, $\text{Cl}^-$, $\text{NO}_3^-$. However, speciation gets severely changed in presence of large molecular
weight humic substances (HS) and metal ion complexation with HS becomes the speciation
governing chemical reaction in the neutral pH range (Choppin, 1988).

**Sorption at the solid-liquid interface**

Sorption onto geologic materials regulates the mobility of radionuclides in environment. It
refers to a host of chemical processes - adsorption, absorption, (co)precipitation, and diffusion
into the solid matrix - happening at the solid-water interface, whereby sorbing metal ion gets
accumulated at the surface (Bruno and Montoya, 2012). Extensive laboratory scale sorption
studies have been carried out to investigate sorption of actinides and fission products on
and Bryan, 2003, Runde and Neu, 2010). The focus of these studies has been on the
determination of distribution coefficient in a purely empirical approach, to the use of adsorption
isotherms, surface complexation models, and spectroscopic techniques (Geipel, 2006; Denecke,
2006; Edelstein et al. 2006, Zaera, 2012) to delineate the sorption mechanism. To this two
compartment (solid-liquid) description of sorption process, observation of colloidal particle
assisted migration of radionuclides has added another dimension (Honeyman, 1999; Kersting et
al., 1999; Novikov et al., 2006; Utsunomiya et al., 2009). Here, radionuclides ride on the surface
of colloidal sized inorganic/organic particles and migrate with the colloidal particles. Inorganic
particles are the weathered products of surrounding solid surfaces while organic particles are mainly HS.

Surface complexation models extend the concept of aquatic complexation to the sorption reaction. It visualizes the solid surface as populated by surface sites formed on the hydration/hydroxylation of dangling terminated bond, such as $≡\text{SiOH}$ on silica surface. Sorption occurs as a result of the interaction of metal ion with the surface sites. Surface interaction includes both electrostatic as well as complexation reaction. Putting sorption process into a complexation description made the model susceptible to chemical conditions and an internally consistent robust sorption model promises to bring the sorption process on predictive level.

1.6 Objective of the thesis

Experimental studies of actinides and fission products have shown their sorption process as dependent on environmental variables such as pH, ionic strength, and temperature, the presence of complexing ligands such as carbonate or organic species, and surface coverage. Attempts of surface complexation models along with spectroscopic and microscopic inputs have been successful to investigate such effects in model systems (Geckeis and Rabung, 2008), but complexities of natural sorption systems are yet to be fully understood (Lützenkirchen, 2012).

Natural sorbents are generally heterogeneous with regard to mineral composition and with the presence of natural organic matter. Changing chemical condition of the aquatic medium can turn sorption mechanism from surface complexation to surface precipitation. Presence of small inorganic as well organic complexants adds complexity by introducing competition between sorbent surface and complexants for metal ions. Understanding of the complexities of the natural
systems in framework of surface complexation models is thus required for more accurate prediction of transport process. The present thesis aims to identify some of the complexities of the natural sorption systems and delineate the sorption mechanism of radionuclides under such complexities.

**Complexities investigated in the present thesis**

Interactions of Radionuclides with mineral surfaces in presence of HS can be depicted schematically as in figure 1.2. HS are polydisperse, polyelectrolyte and undergo fractionation during sorption on mineral surfaces (Davis and Gloor, 1981; Zhou et al., 2001; Hur and Schlautman, 2003). Being polyelectrolyte, humic acid complexation with metal ions increases with pH (Choppin, 1988; Tipping, 1998, Kinniburgh et al., 1999). In view of an array of simultaneously operating interactions in the ternary systems, predictions of radionuclides sorption behaviour in such systems are hard (Fairhurst et al., 1995). Complexity to such systems is further added by the fact that interaction mechanisms between humic substances and minerals

![Figure 1.2 Interactions in ternary sorption system of radionuclides - humic acid - mineral (Bryan et al. 2012).](image-url)
are uncertain, and the mechanism of sorption of humic substance-metal ion complexes is not fully understood (Bryan et al. 2012).

Solid sorbents participate in the sorption reactions differently (Banwart, 1997; Piasecki and Sverjensky, 2008). This is attributed to the difference in their surface characteristics (Tournassat et al., 2004). Depending upon the electro-negativity of the structural atom, solid surface may behave as acidic or basic in the pH range. Dissolution of the solid sorbents also changes with the change of surface central atom. Structural arrangement of the surface atoms has been found guiding the formation of surface species (Cheah et al., 1998). Transition of surface complexation to surface precipitation involves continuum of chemical process where mononuclear surface complex leads to multinuclear complex, to precipitation of metal ions in pure homogenous phase or coprecipitation with dissolved species of solid surface, and finally to formation of a new phase on the surface (figure 1.3) (Banwart, 1997). How the structural characteristics relates with the

\[
\Gamma \quad \text{mol} \cdot \text{m}^{-2}
\]

\[
\Gamma_{\text{T}} \quad \text{Adsorption Maximum}
\]

\[
\{a\} \quad \text{mol} \cdot \text{L}^{-1}
\]

**Figure 1.3** Typical adsorption isotherm obtained in metal ion sorption on solid surfaces (Banwart, 1997).
sorption behaviour needs to be investigated for accurate description of sorption process.

Sorption of actinides and fission products on clay minerals has been studied and modelled using ion exchange and surface complex reactions. These processes get significantly affected by the presence of various cations and anions (Bradbury and Baeyens, 2005; Bachmaf et al., 2008). Sorption process may change by the overlapping sorption characteristics of different mineral phases present in the natural sorbents (Missana et al., 2009; Bradbury and Baeyens, 2011). Different “top-down” and “bottom-up” approaches have been tried in the literature for modelling sorption of radionuclides on natural sediments (Altmann, 2001). In top-down strategy, the natural system is modeled on the basis of bulk system parameters while in the alternate “bottom-up” approach one identifies all the significant components of the system and attempts to systematically understand and model the interactions of each component with the contaminant of interest. The latter approach involves detailed study of both the mineralogy of the solid phase and the chemistry of the aqueous phase and works in agreement with molecular level informations. Such studies in site specific conditions may serve as link between laboratory scale experiment and field level observations and may help in calibrating the sorption models to predict real system transport behaviour.

Focus of the studies in this thesis

- Understanding the sorption mechanism of Cs(I) and Tc(IV) on mineral oxides in presence of humic acid (HA) with an aim to explore the role of humic acid in determining the sorption behaviour of the ternary system of metal ion – HA – oxide surfaces.
• Investigation of Am(III) speciation on alumina-water interface under varying surface coverage. Emphasis is on spectroscopic identification of speciation at higher surface coverage and study the evolution of surface speciation under varying surface coverage.
• Role of oxides surface characteristics in governing Pu speciation on surface as well as solution, and
• Development of surface complexation model for Am sorption on smectite rich natural clay from granitic ground water.

1.7 Outline of the thesis

The thesis is composed of six chapters. This (chapter 1 Introduction) is the first chapter. Chapter 2 describes the experimental methods and techniques employed in the thesis work. The next three chapters details the studies carried out for the thesis work and the last chapter (chapter 6 Summary and Conclusions) summarizes the findings.

In chapter 3, the sorption mechanism of Cs(I) and Tc(VII, IV) on mineral oxides – silica, alumina, hematite – in presence of humic acid have been investigated using batch sorption experiment and surface complexation modelling. The study revealed the non additivity of the ternary system and emphasized the requirement of understanding humic acid sorption on mineral surfaces for modelling such systems. Interaction of metal ion with humic acid governs the sorption of Tc(IV) while presence of humic acid affects the sorptivity of Cs(I) even though Cs(I) interacts weakly with humic acid.

In chapter 4, role of surface reactivity in guiding sorption process was studied by Am(III) and Pu(IV) sorption on silica and alumina surfaces. The objective was to study surface reactivity due to surface charge, dissolution of solid sorbents, and structural difference. Batch sorption,
kinetics experiments and molecule level spectroscopic techniques – Time Resolved Fluorescence Spectroscopy and Extended X-ray Absorption Fine Structure Spectroscopy – were employed to reveal the change in surface speciation with the change of surface reactivity.

In chapter 5, Am(III) sorption on smectite rich natural clay from granitic ground water was studied and modelled using a surface complexation model. Study on model clay mixtures – montmorillonite and Kaolinite - helped in identifying the mineral surface governing sorption in the complex natural sorbent. Role of cations and anions present in groundwater was studied by investigating effect of their presence in individual experiments. Based on the informations obtained from these experiments, a ion exchange and surface complexation based sorption model was developed for Am(III) sorption on natural clay from simple electrolyte medium with varying pH and ionic strength. Finally, the model prediction was checked for Am(III) sorption on natural clay from granitic ground water.