Chapter 2

Experimental Methods and Techniques
2.1 Introduction

Mechanistic description of sorption process requires delineation of the chemical reactions occurring at the solid liquid interface. Various approaches to investigate the sorption mechanism span from determination of metal ion partitioning in different chemical conditions such as, varying ionic strength of the sorption medium, through semi-empirical (Langmuir and Freundlich isotherms) approaches, to modelling of sorption processes assuming probable surface chemical reactions, to application of molecular level spectroscopic techniques. While the partition coefficient infers some important information such as formation of outer/inner sphere complex formation (Hayes and Leckie, 1987), fitting of sorption data into isotherm equations cannot by itself provide information about the reaction involved (Sposito, 1984; Scheidegger and Sparks, 1996). Surface complexation model (SCM) has been most successful in revealing the sorption mechanism; though various variants of the SCMs have been found to fit the sorption data equally well (Westall and Hohl, 1980) making prediction of surface speciation model dependent. Molecular level spectroscopic techniques help in identifying the surface speciation and thus in fixing the exact mechanism operating at the interface. McBride pioneered the application of spectroscopic techniques in studying surface speciation of Cu(II) on iron oxide surface by electron paramagnetic resonance spectroscopy. These spectroscopic techniques are however fraught with the lower sensitivity in view of dilute samples of environmental origin. Solubility of actinides and fission products in natural ground water systems is very low (trace to ultra-trace level). Complete understanding of the sorption reactions thus invariably requires synergism of all the methods and the same methodology has been followed in the thesis. The present chapter gives a brief account of the methods and techniques used. Further details can be
found elsewhere (Dzombak and Morel, 1990; Stumm, 1996; Bunker, 2010) and are available in several reviews (Denecke, 2006; Edelstein, et al., 2006; Geipel, 2006; Simoni, 2007).

2.2 Batch Sorption Method

Batch sorption method is used to study the equilibrium distribution of radionuclides between the mineral surface and the aqueous phase under well defined experimental conditions of temperature, pH, ionic strength and solid/liquid ratio. Partitioning is expressed by the distribution coefficient, $K_d$, defined as:

$$K_d \ (ml/g) = \frac{C_s}{C_L}$$

Where, $C_s$ is the concentration of the metal ion per g of the solid and $C_L$ is the concentration of the metal ion present per ml of the aqueous phase. As the radionuclides may have multiple speciation in the same pH condition, $K_d$ basically represents the combined distribution of the all the species.

Considerable sorption data, especially for single mineral sorbents such as oxides, have been collected describing pH influence on sorption process. The pH sorption edge thus obtained represents percentage sorption of radionuclide on solid surface against pH. Percentage sorption is calculated by the formula given below.

$\% \ sorption = \left( \frac{C_i - C_f}{C_i} \right) \times 100$ (2.2)
Where, $C_i$ is the concentration of the metal ion added to the sorption system and $C_f$ is the concentration left over in the aqueous phase after the attainment of equilibrium.

### 2.2.1 Experimental details

Distribution experiments were carried out in 50 ml polypropylene tubes (Oak ridge Centrifuge tubes). The design of the experiments was as follows: Nanometer sized powder samples of mineral solids (oxides and clays) previously characterized for surface characteristics (surface area, mineral phase, surface charge, etc.) were suspended in aqueous phase containing simple electrolyte (NaCl, NaClO$_4$) in fixed solid to liquid ratio for 24 to 48 hours equilibration before metal ion addition. After the addition of the acidic solution of metal ion, pH of the suspension was adjusted over 2-10 by dropwise addition of dilute mineral acid (HClO$_4$) or base (NaOH) under constant stirring of the suspensions. The suspensions were left, in a shaker, for attainment of sorption equilibrium over a time period which was fixed based on the kinetic experiments. After the equilibration period, pH of the equilibrium was checked and suspensions were centrifuged at 16 000 rpm for 45 minutes to separate the two phases present in the suspension. 1 ml of the supernatant was aliquotted and assayed for the determination of metal ion concentration left in the supernatant after equilibration. In sorption systems, where the effect of humic acid presence was investigated, suspensions were first equilibrated with humic acid before metal ion addition. Both the humic acid and metal ion equilibration were carried out at the same pH.

### 2.2.2 Methods of assaying

As the fission products and actinides used are radioactive, radiometric methods ($\gamma$-Counting in NaI(Tl) detector and Liquid Scintillation Counting (LSE) for $\alpha$-decaying isotope) (Friedlander et al., 1990) were used for assaying the metal ion left in the supernatant while UV-Visible
spectrophotometry ($\lambda=254$ nm) was used for assaying humic acid concentration (Stevenson, 1994). $^{137}$Cs, $^{95,96}$Tc, $^{241}$Am have suitable $\gamma$- energies 661, 204, 582, 778, 850, and 59.9 keV, respectively for assay by gamma counting, while $^{238}$Pu was assayed by alpha counting in liquid scintillation counter.

2.2.3 Preparation of radiotracer at environmental concentration level

Early actinides and some of the fission products, such as, technetium exhibit multiple valencies and strong hydrolyzing tendency in their higher oxidation states. Solubility of radionuclides in neutral pH conditions is thus very low. To study the sorption of actinides and fission products at environmental concentration level, radioisotopes of lower half life/higher specific activity can be used. In the present thesis to study technetium speciation at picomolar concentration, $^{95}$Tcm ($t_{1/2} = 60$ days) was produced by nuclear reaction $^{96}$Mo(p, 2n)$^{95}$Tcm. $^{95}$Tcm is

![Figure 2.1 Gamma spectrum of $^{96,95}$Tc tracers](image)

**Figure 2.1 Gamma spectrum of $^{96,95}$Tc tracers**
a $\gamma$ (204, 582 keV) emitting isotope and does not require much of sample preparation as in liquid scintillation counting. Figure 2.1 shows the gamma spectrum of the $^{95,96}$Tc tracer produced by proton induced reaction on natural molybdenum target and followed by radiochemical separation. Schematic of Tc separation from bulk Mo is given in figure 2.2.

**Figure 2.2 Separation scheme of Tc from irradiated Mo target**

2.2.4 Error analysis of the sorption data

Owing to higher hydrolyzing tendency of actinides, during sorption they can sorb on the inner wall of the polypropylene container. Neglecting wall sorption in the estimation of the sorption data may result in large errors, especially if the wall sorption is significant. With the
container (polypropylene tubes) used in the present study, sorption on wall was very small (< 5%). Wall sorption was, nevertheless, quantified by leaching the sorbed metal ions with 1.0 M HNO₃. For this purpose, after the equilibrium sorption, the suspensions were removed from the tubes. The tubes were given gentle wash with distilled water, and then the leaching was carried out (overnight) with the same volume of the 1.0 M HNO₃ acid solution as that used in the sorption experiments. The activity leached into the solution was assayed for the radioactivity in a manner similar to the sorption experiment. The wall sorption was calculated as the ratio of activity per ml leached into the leachate to the initial activity per ml before sorption equilibrium.

Experimental uncertainties on the sorption data were determined by calculating the standard deviation of the sorption data obtained with duplicate sorption samples. When this method was not followed, error on the radioactive counting was propagated to calculate the error on sorption data. Program used to calculate the error on sorption data is listed in appendix 1.

2.3 Modelling approaches

Modelling approaches adopted to delineate the sorption mechanisms in the present thesis involve (1) Linear additive modelling (LAM), and (2) Surface complexation modelling (SCM). Linear additive models simulate the ternary system of radionuclides-humic substances (HS)-mineral surfaces in terms of binary interactions, radionuclides-HS, radionuclides-mineral surfaces, and HS-mineral surfaces assuming independence of one binary interaction of the other. On the other hand, SCM considers all possible chemical interactions of the sorption system in thermodynamic terms. Though LAM considers the gross behaviour of the systems and in this way neglects the true intricacies of the ternary system, comparison of the sorption behaviour
with that produced by LAM helps in characterizing the interactions in the ternary system due to the interactions among binary systems. These informations once incorporated into the SCM promise to make the prediction of sorption behaviour more robust.

### 2.3.1 Formulation for sorption behaviour in ternary system by LAM

Following Davies-Colley et al. (1984), distribution coefficient for a multiple sorbent mixture \( K_{d,tot} \) is assumed to equal the sorptive contributions of the individual phases:

\[
K_{d,tot} = \sum K_{d,n} \chi_n \tag{2.3}
\]

where, \( K_{d,n} \) is the distribution coefficient for the nth phase and \( \chi_n \) is its mass or surface area fraction. Implicit in equation (2.3) are the following assumptions: (1) the sorbing phases exhibit linear isotherms over the concentration range of interest, and (2) the sorptive contributions of different phases are additive.

Zachara et al. (1994) modified equation (2.3) by incorporating the effect of desorption of HS and aqueous complexation using the following relationship:

\[
K_{d,tot} = \sum K_{d,n} \chi_n / [1 + C_{HS} K_{d,HS}] \tag{2.4}
\]

where, \( C_{HS} \) is the aqueous concentration of HS (g/l) and \( K_{d,HS} \) is the sorption coefficient of metal ions for dissolved HS.

In the ternary sorption system, mineral surface and the HS compete for the metal ion and therefore eq. (2.4) can be simplified to:
\[ K_d = \frac{K_d^0 + K_{d,HS} \chi_{HS}}{1 + C_{HS} K_{d,HS}^0} \]  \hspace{1cm} (2.5)

where, \( K_{d,HS} \) is the sorption coefficient of metal ions onto dissolved HS, and \( K_d \) and \( K_d^0 \) are the sorption coefficients of metal ions onto mineral surface in the presence and absence of HS, respectively. While formulating eq. (2.5) following assumptions were made: (1) the affinity of metal ions toward HS molecules is identical for both the mineral-bound and dissolved HS, and (2) the mass of mineral-bound HS is much smaller than the mass of solid sorbent, \( \chi_{HS}/\chi_{SS} \ll 1 \); \( \chi_{HS} \) and \( \chi_{SS} \) are the mass fractions of HS and solid sorbent in the HS coated sorbent.

The strength of the metal binding with HS can be expressed by an apparent stability constant, \( \beta \), defined as,

\[ M^{n+} + HS \rightarrow M-HS \]

\[ \beta = \frac{[M-HS]}{[M^{n+}][HS]} \]  \hspace{1cm} (2.6)

where, \([HS]\) is the concentration of free HS ligands capable of binding with metal ions, and is almost constant and equal to the total concentration of HS ligands in view of the very low concentration of metal ions generally used in the experiment. The molar concentration of HS is operationally defined as the concentration of carboxylic groups of HS (equivalent per liter). \( K_{d,HS} \) is related to \( \beta \) by the equation,

\[ K_{d,HS} = \beta \times [HA] \times \frac{V}{W_{HS}} \]  \hspace{1cm} (2.7)
In eq. (2.7) [HA] is the total (mineral-bound + dissolved) concentration of HS in suspension, and \( W_{HS} \) is the total (mineral-bound + dissolved) mass of HS in the suspension of volume, \( V \). \( \chi_{HS} \) and \( C_{HS} \) can be represented by,

\[
\chi_{HS} = f_{HS} \times \frac{W_{HS}}{W}
\]  
(2.8)

and

\[
C_{HS} = (1-f_{HS}) \times \frac{W_{HS}}{V}
\]  
(2.9)

where \( W \) represents the mass of solid sorbent in the suspension. \( f_{HS} \) is the fraction of HS sorbed on the solid sorbent. Substituting eqs. (2.7-2.9) in eq. (2.5) yields

\[
K_d = \frac{K_d^0 + (V/W)f_{HS} \beta [HS]}{1+(1-f_{HS}) \beta [HS]}
\]  
(2.10)

which should represent the sorption behaviour in the ternary system.

2.3.2 Surface complexation model

Surface complexation model (SCM) follows a thermodynamic approach (Schindler, 1981; Sposito, 1984; Schindler and Stumm, 1987) to model the sorption reaction. It extends the ion-association concept of aquatic complexation to the sorption process. Dzombak and Morel (1990) describe the basic postulates of SCM developed for oxides as:

- Sorption on oxide surfaces takes place at specific coordination sites. Such sites are produced by the dissociative chemisorption of water molecules on dangling oxygen atoms present on the surface, such as \( \equiv \text{SiOH} \) on silica surface. These sites are amphoteric in nature and undergo protonation/deprotonation depending on the pH of the suspension, viz.,
Sorption reactions on oxide surfaces can be described quantitatively via mass law equations. A typical sorption reaction on an oxide surface can be expressed as:

\[
\equiv \text{SiOH}^+ \xleftrightarrow{K_{1}} \text{SiOH} \xleftrightarrow{K_{2}} \text{SiO}^-
\]  \hspace{1cm} (2.11)

where,

\[
\equiv \text{SiOH}^+ + (n-1)^+ + \text{SiOH} + M \xrightarrow{K} \text{SiOM}^{(n-1)+} + H^+
\]  \hspace{1cm} (2.12)

\[
K = \frac{[\equiv \text{SiOM}^{(n-1)+}][H^+]}{[\equiv \text{SiOH}][M^{n+}]}
\]

The activity coefficients of the surface species have been taken as unity.

Surface charge results from the sorption reactions themselves. Protonation/deprotonation and metal ion binding on the surface sites creates the charge on the surface.

The effect of surface charge on sorption can be taken into account by applying a correction factor derived from the electrical double layer (EDL) theory to mass law constants for surface reactions. Depending upon the description of the charge distribution in the EDL, different variants of SCM have been proposed (Hayes et al. 1991). A typical expression for surface complexation constant containing the correction factor (exponential term) is given as:

\[
K = \frac{[\equiv \text{SiOM}^{(n-1)+}][H^+]}{[\equiv \text{SiOH}][M^{n+}]} \exp(-\Delta z F \Psi / RT)
\]  \hspace{1cm} (2.13)

where, \(\Delta Z\) is the difference of surface charge produced on surface complexation. \(F\) and \(\Psi\) are the Faraday constant and surface potential respectively. \(R\) and \(T\) represent the gas
constant and temperature respectively. Expression of surface potential varies as per the EDL model employed.

Apart from these pH dependent sites, there is another type of surface site on clay surfaces. Clay minerals contain, structurally, silicon and aluminium oxides layers packed together by weak van der Walls interactions. Isomorphous substitution in these oxide layers produces residual charge on the clay surface. These charged sites participate in ion exchange reactions with the sorbing metal ions. SCM developed for clay surfaces should include therefore ion exchange and surface complexation reactions in modelling sorption reactions.

### 2.3.3 Simulation of sorption behaviour using SCM

FITEQL Software ver. 4.0 (Herbelin and Westall) was used to obtain the formation constant (logK) of the surface species. Formation constant was subsequently used to simulate the sorption behavior. FITEQL considers sorption by a multi-component chemical equilibrium model and operates by formulating the sorption model in a matrix or tableau format (Morel and Morgan, 1971; Morel, 1983; Dozambak and Morel, 1990, appendix B). In this format, every chemical entity is considered as a species in the sorption system, which can be written as the product of a reaction involving only the components. Components are entities which cannot be expressed as the product of an algebraic reaction involving only the other components. The components can, thus, be described as a linearly independent basis set spanning species space. Mass action equations are applied for each species while mass balance is taken into consideration for each component. Surface charge is accounted for by the Coulombic exponential term and is factored as a component in the tableau. Finally all the information is expressed in the form of a set of simultaneous equations. Next the equilibrium model is solved at each of the experimental data to
minimize the difference between values calculated from the model and values observed experimentally. This gives the optimized logK values. Details of running the optimization procedure and the best fit values can be found in the manual of FITEQL and chapter 3 of Dzombak and Morel (1990). Appendix 2 gives the FITEQL table produced while simulating Tc(IV) sorption on alumina in presence of humic acid.

2.4 Fluorescence Spectroscopy

Following excitation, the excited electronic state of a metal ion may come to the ground state by radiative decay process. Fluorescence spectroscopy uses this decay mode to determine metal ions speciation in its characteristic coordination environment. Three advantages associated with this spectroscopy make it important in this regard. These are characteristic excitation wavelength, characteristic emission wavelength (figure 2.3), and characteristic fluorescence.

![Energy-level diagram and characteristic fluorescence spectrum of Eu³⁺](image)

Figure 2.3 Energy-level diagram and characteristic fluorescence spectrum of Eu³⁺.
decay lifetime. The first two characterize the fluorescent probe by representing the energy levels and crystal field splitting of the species while the change in fluorescence lifetime reflects the effect of chemical reactions (such as hydrolysis, complexation, etc.) involving the probe atom. These advantages have been successfully employed to infer about the sorption mechanism.

2.4.1 Fluorescence measurement using chemical analogues

All the metal ions do not fluoresce significantly; actinides are generally less fluorescing than their lanthanide counterparts. Larger spatial expansion of $5f$ orbital and larger spin-orbital coupling in actinides causes smaller crystal field splitting leading to stronger non-radiative decay mode. In the fluorescence spectroscopic measurements reported in the present thesis, Eu(III) has been used to simulate the behaviour of Am(III). Choice of europium depends on its being the good fluorescent probe and chemical analogue of americium.

2.4.2 Instrumentation

Time resolved fluorescence spectroscopy (TRFS) measurements were carried out using Edinburgh F-900 time resolved fluorescence spectrometer consisting of CD-920 controller unit, a micro-second Xe flash lamp as excitation source and an optical multichannel analyzer coupled with M-300 excitation and emission monochromators. The data analysis was carried out using GEM-3 software supplied by M/s Edinburgh Instruments, UK.

2.4.3 Sample preparation and Data analysis

For fluorescence measurements, concentration of Eu(III) in alumina suspension (3 g/l) was fixed at $5.0 \times 10^{-5}$ M. Sample preparation method was similar to batch sorption experiment. After equilibration, the solid phase was mounted onto quartz plate for spectroscopic measurement.
Excitation wavelength was fixed at 230 nm and fluorescence emission was collected over 550 - 650 nm wavelength range. For recording the lifetime data, the emission wavelength was fixed at 620 nm. The temporal decay data were accumulated up to 4 milliseconds. Fluorescence intensity $I(\lambda, t)$ at wavelength $\lambda$ and time $t$ can be described as,

$$I(\lambda, t) = \sum_{j=1}^{n} I_j(\lambda, 0) \times \exp(-t/\tau_j)$$

where, $I_j(\lambda, 0)$ is the fluorescence intensity of the fluorescing species $j$ at time $= 0$ and $\tau_j$ is its lifetime. The factor $I_j(\lambda, 0)$ is a function of experimental set-up (optical path length $l$, excitation source intensity $I_0$, etc.), molar absorption coefficient and the fluorescence quantum yield of the species $j$, and its concentration in sample. The life time of the surface complexes was obtained by fitting the temporal data into the above equation.

## 2.5 X-ray Absorption Fine Structure Spectroscopy

This spectroscopy covers both Extended X-ray Absorption Fine Structure Spectroscopy (EXAFS) and X-ray Absorption Near Edge Spectroscopy (XANES), which have their origin in quantum interference effects. When X-ray of suitable energy impinges on a probe atom, electrons are produced in photoelectric absorption process. The outgoing electrons collide with the surrounding atoms and get scattered. Interference between the outgoing and scattered electron waves modulates the absorption coefficient, resulting in an oscillatory pattern above the absorption edge. The spectral region up to ~30 eV above absorption edge is defined for XANES while that beyond this limit is used for EXAFS data. Figure 2.4 depicts a typical spectrum obtained in the XAFS experiment. XANES can be used to determine the valence state and
coordination geometry, while EXAFS is used to determine the local molecular structure of a particular element within a sample. Details on XAFS can be found in standard texts, viz., Koningsberger and Prins (1988) and Bunker (2010). Sample preparation, data collection and analysis suitable for environmental samples have been discussed in details in monographs such as Kelly et al. (2008). A brief description of these aspects as applied in the present thesis work is given below.

2.5.2 Sample preparation and Data acquisition

The initial part of the XAFS sample preparation was similar to the sorption experiment, with the only exception of a larger (250 ml) suspension volume for the XAFS samples. After filtering the suspensions, the solid phase was vacuum dried in an oven at temperature below 40 °C. A
calculated amount (to get edge step ~ 1 in the Eu–L\textsubscript{III} X-ray absorption spectrum) of the dried powder was mixed with polyvinyl pyrrolidone and pelletized. Homogeneous mixing of binder and the solid powder in the pellet was ensured by thorough mixing and optical examination.

XAFS data were collected using the XAFS beamline at Elettra synchrotron facility. Storage ring was operating at electron energy equal to 2.0 GeV and beam current about 300 mA which decreased with a half life of 35 hours. XAFS spectra were recorded in transmission mode by placing the pellet in the path of the X-ray beam from the Synchrotron. Measurements were carried out with three ionization chambers, one each for initial X-ray intensity ($I_0$), intensity ($I$) after transmission through the sample and intensity ($I_m$) after the monitor foil (Fe) placed downstream of the second ionization chamber for simultaneous energy calibration. Harmonics of the beam were rejected by detuning the second monochromator crystal by 45%. Following Eu–L\textsubscript{III} edge energy (6977 eV), the spectra were collected over energy range 6700– 7600 eV, with a pre-edge energy step of 5 eV, 0.20 eV in the edge region and thereafter a constant ‘k’ step of 0.03 Å\textsuperscript{-1} in the extended XAFS region. Data acquisition was limited to 7600 eV as the Eu–L\textsubscript{II} edge lies just above this energy.

2.5.3 Data analysis

The Eu (L\textsubscript{III}) edge X-ray absorption spectra of the reference compounds and the samples were analyzed by the software package IFEFFIT. Philosophy of the analysis has been as follows: Determination of structural parameters (co-ordination numbers and distance of surrounding atoms around the probe atom) of a species by EXAFS basically involves the modelling of experimental data. A hypothetical model most suitable for the species to be characterized is proposed and a convergence between experimental data and the data generated for the hypothetical model is searched out. Data analysis is started with the data reduction step in
ATHENA software, where the plot of $\mu x$ vs. $E$ is corrected for background absorption and normalized for single absorption event. Next the modified plot is brought to momentum ($k$) space and subsequently Fourier transformed to radial ($R$) space. For the hypothetical structure, phase-shift and amplitude functions are generated by the theoretical multiple scattering calculations in FEFF program. These calculated functions with associated informations for the model in EXAFS equation (eq. 15) create $k$ and $R$ space data, viz.,

$$\chi(k) = S_0^2 \sum_{i=1}^{N_i} \frac{N_i F_i(k, R)}{R_i^2} e^{-2R_i/\lambda} e^{-2\sigma^2 k^2} \sin(2kR_i + \psi)$$

(2.15)

where, $\chi(k)$ is the measured EXAFS spectrum, and $k$ is the electron momentum. $N_i$ is the number of surrounding atoms in the $i^{th}$ coordination sphere, $R_i$ is the average radial distance to the $i^{th}$ coordination sphere, and $\sigma^2$ is the Debye Waller factor. $F_i(k,R)$, $S_0^2$, $\lambda$, and $\psi$ stand for backscattering amplitude, amplitude reduction factor, mean free path, and phase shift. Optimization of the calculated $k$ or $R$ space data to match the experimental data using non-linear least square fitting program is carried out in Artemis software. Hypothetical structures for the analysis of sorption samples have been based on the structure of oxide, hydroxide and silicate compound of Eu(III).