Chapter 3
Sorption of fission products on mineral oxides:
Effect of humic acid
3.1 Introduction

Humic substances (HS) are important reactive fraction of natural organic matter present in soil, sediment, surface water and groundwater. They are polydisperse and heterogeneous mixture of organic molecules, and are formed as a result of the degradation of remains of the dead plants and animals (Stevenson, 1982). Presence of HS in the geosphere is dependent on many factors such as climate, pH, substrate material, topography and time (Stevenson, 1994). In soil, the humic content varies from 0 to 10% with still higher proportion in peat soil, while in water the dissolved organic carbon (DOC), may be as large as 50 ppm in dark water swamps. Samples from surface waters generally have DOC values from 0.1 to 8 ppm. In ocean waters, the DOC ranges from 0.5 to 1.2 ppm. In addition, organic matter is present in suspended sediments in lakes, rivers, estuaries and coastal seawaters. Majority of the DOC as well as the particulate and sorbed organic matter falls within the classification of HS (Choppin, 1988).

HS are divided into three groups based on their solubility in acid-base solutions; (i) fraction insoluble in aqueous medium is called Humin, (ii) the fraction soluble at all pH in water is known as the fulvic acid (FA) and (iii) the fraction soluble only above pH 3.5 in water is called humic acid (HA). A typical separation scheme is shown in figure 3.1. Specific details of HS separation from soil and water can be found in Tipping (2002). To a large extent, the procedures depend upon controlling the electrical charge of the humic matter. Higher the charge of the molecules, (e.g., at high pH), higher the solubility. Lower charge e.g., at low pH, promotes precipitation and adsorption to hydrophobic surfaces.
Unlike the simple organic complexants, the physicochemical properties of HA and FA are hard to define as the true nature of HS structures is still ill-defined despite many decades of research (Hayes et al., 1989). Origin, climatic conditions, pH, mineral surfaces and time cause variable degree of degradation of HS leading to the variable structure. Early concept (polymer model) envisaged humic substances as randomly extended macromolecules that had elongated shapes in basic or low ionic strength solutions, and coiled in acidic or high ionic strength media (Swift, 1999). Later informations gathered using spectroscopic, microscopic, pyrolysis, and soft ionization techniques gave a toss to the “polymer model” and a new concept of humic substances emerged, that of the supramolecular association, in which many relatively small and chemically diverse organic molecules form clusters linked by hydrogen bonds and hydrophobic interactions (Piccolo, 1999). Emphasizing molecular interactions

Figure 3.1 Separation scheme for humin, humic and fulvic acids
over molecular components has been the essence of the newer understanding of humic substance structure (Sutton et al. 2005). Amidst these structural ambiguities, distinguishing characteristics of humic and fulvic acids have been delineated. Fulvic acids are more aliphatic and less aromatic than humic acid and have lower molecular weight, 300 – 2000 amu, compared to 1000 to 5000 amu typical for aquatic humic acid. Main functional groups of humic and fulvic structures are carboxylic and phenolic groups along with minor presence of nitrogen based functional groups like amine, amide, etc. A hypothetical structure proposed for humic acid is shown in figure 3.2 (Stevenson, 1982).

![A hypothetical structure of humic acid](image_url)

**Figure 3.2 A hypothetical structure of humic acid**

Humic substances exhibit strong complexing affinity towards metal ions and significantly alter the metal ion speciation with their presence (Tipping and Hurley, 1992). They may also interact with mineral surfaces and thereby affect the sorption and migration of radionuclides in environment (Ticknor et al., 1996; Choppin, G., 1992; Maes, et al., 2006; Reiller, 2002). In an extensive evaluation of sorption of trace metals on natural sediments, Wang et al. (1997) concluded a correlation between sorption and hydrolysis of metal ions (termed as Linear Free Energy Relation) dependent on the proportion of total organic carbon and the mineral oxide component in the sorbent. Distribution coefficient ($K_d$) of Am(III) and Pu(IV) on Zeolitized tuff samples collected from the Rainier Mesa tunnel system, Nevada Test Site, were upto two
orders of magnitude lower in water with high DOM (15-19 mg C/L) compared to the same water with DOM removed (< 0.4 mg C/L) or in naturally low DOM (0.2 mg C/L) groundwater (Zhao et al. 2011). It is, therefore, pertinent that speciation and sorption of metal ion in presence of mineral surfaces and HS should be understood mechanistically and parameterized for predictive modelling.

Interactions in ternary systems of metal ions - mineral surfaces - HS, are governed by metal ion interactions with mineral surfaces and humic substances, both dissolved and sorbed on mineral surface (figure 1.2). Formation of “ternary complexes” may result from interaction between any two binary systems namely, metal ions-HS, metal ion-mineral surface, and HS-mineral surface. There are generally two types of ternary complexes. In type 1, the humic molecule acts as the bridge between metal ion and mineral surface, whilst in type 2, the metal ion acts as the bridge. Interplay of these interactions results in variable sorption characteristics (Fairhurst et al., 1995). Dominance of different interaction modes has further been seen by changing the addition order of components in the ternary systems (Kar et al. 2011; Reiller, 2005). Existence of different ternary complexes has also been shown in spectroscopic results (Alacacio et al., 2001, Siato et al., 2005). Description of ternary systems in terms of these interactions is, however, simplistic as intrinsic characteristics of humic substances – polyelectrolyte material, heterogeneous mixture of organic molecules which undergo fractionation on sorption (Meier et al. 1999), electrostatic aspects – need to be considered in the framework of these interactions. In spite of functional groups similarity, differences observed in the effect of humic and fulvic acids on meal ion sorption have been attributed to their intrinsic characteristics. Fulvic acid having smaller molar mass behaves like simple inorganic ligand and is present near the surface layer during sorption on mineral surface whereas humic acid with higher molar mass/size extends away from the sorbent surface into diffuse layer around the mineral surface.
Metal ions interaction with humic substances

Metal ion interaction with humic and fulvic acid needs to deal with three aspects: site-specific binding, electrostatics and heterogeneity of the HS. Different predictive models have been developed ranging from conceptually simpler models (e.g., Mixture model, Triprotic acid model, Tipping, 2002), to operationally simpler models (e.g., Charge Neutralisation model, Kim and Czerwinski, 1996), to computationally involved models where all the three aspects have been included to reproduce the interaction behaviour (Model VI and NICA models, Tipping, 1998; Milne et al. 2003). The Model VI simulates the chemical heterogeneity with a finite number of discrete binding sites and the NICA model uses a continuous distribution approach. These two models have been successful specially in predicting metal ion binding to humic and fulvic acid largely independent of source and improved the understanding of mechanisms, such as denticity or coordination number in metal ion-humic acid complex.

Sorption of Humic substances onto mineral surfaces

Sorption of HS on surfaces such as Mn, Fe, Al oxides and clays has been studied using batch experiments. A number of mechanisms have been suggested for the binding of HS to inorganic surfaces (Lenhart and Honeyman, 1999): ligand exchange; cation/anion exchange; cation bridging; entropy driven physical sorption; hydrogen bonding and van der Waals / hydrophobic interactions. Chemical fractionation of HS has also been reported by several authors. Wang and Xing (2005) observed that the aliphatic fractions were preferentially adsorbed onto a kaolinite surface, while Feng et al. (2006) found that the aromatic components of a terrestrial humic acid are preferentially adsorbed onto montmorillonite. Varying fluorescence spectra of Eu(III) complexes in sorption of HS onto α-Al₂O₃ has been attributed to fractionation (Claret et al. 2005, 2008).
Metal ion interaction with mineral surfaces in presence of HS

Metal ion sorption on mineral surfaces in presence of humic substances is more than that expected based on the binary interactions (Bryan et al., 2012). This is so because binary interactions modify the response of the minerals surface and the humic acid towards metal ion.

Linear additive modelling (LAM) has been used to reveal interactions in ternary sorption systems. Here, the behaviour of the ternary systems is simulated just with the separate binary models. This has not been always successful. Bruggeman et al. (2010) found that sorption of Eu(III) in an illite/humic acid ternary system could be modelled by an additive approach using Tipping Model VI to simulate Eu(III)-humic acid interaction and a non electrostatic surface complexation model for the metal ion-mineral surface interaction. Interestingly in this study the humic substance was not interacting with the mineral surface. In sorption systems where the HS sorbs on mineral surface, there is also contrasting behaviour. Cd(II) sorption to humic acid-hematite systems was found to be more than the sum of the Cd(II) adsorptivites to individual component (Vermeer et al., 1999) with the difference increasing with the pH. Interaction of Ca(II) and fulvic acid at the goethite-water interface resulted in reduced sorption at lower pH values and enhanced adsorption pH at high pH (Weng et al. 2005). Warwick et al. (2006) studied the ternary systems of Cs(I), Cd(II), Ni(II) and Eu(III) with goethite, montmorillonite and kaolinite in presence of HS and successfully explained the data with the LAM approach. For modelling humic substances and metal ion speciation in ternary systems at equilibrium, the Ligand charge distribution (LCD) has been developed by van Riemsdijk et al (2006). It has also been used to simulate the ternary sorption systems. For example, in the case of Ca/goethite/fulvic acid ternary system, where the LAM does not work, the LCD was able to simulate the behaviour taking into account ternary complexes.
(Weng et al. 2005). Interestingly, the model predicted that the main interaction between Ca(II) and sorbed fulvic acid is electrostatic, and virtually all the sorbed Ca(II) is bound directly to the surface.

**Literature Studies on fission products sorption in presence of HS**

Though extensive studies have been performed for the effect of HA on the sorption of actinides and europium on oxides surface, there are very few studies devoted to investigate such effect in the sorption of fission products. This could be due to the relatively short life of fission products and/or their chemistry. For example, the mono and divalent metal ions are weakly interacting with HS while a longer half life fission product such as technetium is anionic. A few studies have been carried out on sorption of $^{137}$Cs on clays, such as montmorillonite (Dumat et al., 2000) where HA was found to decrease the sorption of Cs on the clay at pH 7. In another work on sorption of $^{137}$Cs by silica gel, no effect of HA was observed (Hakem, et al., 2004). In oxic conditions and under neutral pH conditions, Tc exists as TcO$_4^-$ and interacts very weakly with mineral surfaces and HS (figure 3.3) (Kumar et al. 2007, 2011). Tc(VII) may, however, be reduced to Tc(IV) under reducing condition and by

![Figure 3.3 Effect of humic acid on Tc(VII) sorption on hematite and alumina](image)

Figure 3.3 Effect of humic acid on Tc(VII) sorption on hematite and alumina
reductants like Fe(II) and Mn(II) present on various solid sorbent, thereby enhancing its interaction with HS. Maes et al (2003) observed Tc(IV) associated with HS enhancing solubility up to the order of $2 \times 10^{-6}$ M. Evidence for the aggregation of Tc(IV) colloids with humic substances has been obtained in EXAFS and XANES studies (Maes et al., 2004; Geraedts et al. 2002). Artinger et al. (2003) carried out extensive studies on humic colloid mediated transport of Tc(IV) in Gorleben ground water and found the presence of humic substances enhancing the transport rate of Tc(IV). Tc(IV)-humic complexes have been suggested to be the dominant chemical species in deep groundwater containing humic substances, and the complexation reaction may control the mobility and fate of Tc under reducing environments (Sekine et al. 1997). While Cs(I) interacts with mineral surface and HS weakly, Tc(IV) interacts with both of them strongly. It is therefore important to study the effect of HS in their sorption on mineral surface.

Present Study

In the present work, the role of humic acid on the sorption of Cs(I) and Tc(IV) on mineral oxides has been investigated. Mineral oxides chosen for the study are silica and alumina. Silica is an important naturally occurring mineral oxide, originating basically from various weathering actions on rock, clays and sediments. Though alumina does not exist in nature in its pure phase; it has been of research interest due to following reasons: (1) alumina is structurally similar to iron oxides, such as hematite, magnetite. Iron oxides are produced in aquatic system by the corrosion of iron/steel containers and have been found interacting significantly with environmental radioactivity; (2) Unlike iron oxides, they are amenable to spectroscopic techniques such as TRLFS.

Among the binary interactions, there exists stronger interaction between Cs and mineral surfaces while Tc(IV) interacts strongly with humic acid. Studies of the present chapter aim
to investigate the sorption of Cs(I) and Tc(IV) on oxide surfaces in presence of humic acid and thereby understand the role played by HA in deciding the sorption behaviour of ternary systems.

3.2 Experimental details

3.2.1 Characterization of mineral oxides

Nanometre sized silica and alumina powders were purchased from AEROSIL and Degussa India Ltd respectively, and were used without purification. X-ray diffraction based characterization showed that silica was amorphous in nature while alumina was present in its γ-phase. Both the sorbents were found free from any other structural phase impurities. Specific surface area and porosity of these solid particles were determined using N₂ gas based BET analysis. The surface area was found to be 180 and 203 m²/g, for silica and alumina respectively. Pore volumes obtained in BET analysis are 0.269 and 0.067 cc/g for silica and alumina, respectively, indicating insignificant porosity. Zeta potential of the silica and alumina suspensions prepared by suspending particles in 0.01 M NaClO₄, was measured at varying pH values using a Malvern zetasizer (4.0 mw He-Ne laser at 633 nm). The instrument measures electrophoretic mobility of the particles using dynamic light scattering data and obtains the zeta potential by putting velocity data into Henry’s equation (eq. 3.1).

\[ U_E = \frac{2 \varepsilon z f(K_a)}{3 \eta} \]  

(3.1)

where, \( U_E \), \( \varepsilon \), \( z \), \( \eta \) stand for electrophoretic mobility, dielectric constant, zeta potential, viscosity and \( f(K_a) \) is Henry’s function. Its value is 1.5 under Smoluchowski approximation. The iso-electric points, that is, pH corresponding to zero potential, were found to be 2.4 and
8.9, for silica and alumina respectively, which are in agreement with the PZC (point of zero charge) values available in literature (Silva and Nitsche, 1995).

Site density (≡AlOH) and hydrolysis constants of sites present on alumina surface were determined by titrating alumina suspension (strength 7.5 g/l in 0.1 M NaClO₄) in N₂ environment with 0.1 M HCl and NaOH solutions and modeling the titration data using FITEQL V. 4.0 software. A constant time interval (2 min.) was provided between the consecutive titrant additions.

### 3.2.2 Humic acid characterization

Humic acid (HA) in the sodium form was procured from ACROS, Belgium, and was purified by repeatedly dissolving in alkali followed by precipitation in perchloric acid medium. Purified HA was characterized for elemental composition using CHNS-O (EA-1110) elemental Analyser, Radiochemistry Division, BARC and the values compare well with the literature reported values (Table 3.1) (Kim et al., 1990).

<table>
<thead>
<tr>
<th>Element</th>
<th>% Obtained</th>
<th>Literature value (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>48.82</td>
<td>50-60</td>
</tr>
<tr>
<td>H</td>
<td>4.415</td>
<td>4-6</td>
</tr>
<tr>
<td>N</td>
<td>0.82</td>
<td>2-6</td>
</tr>
</tbody>
</table>

The UV-Visible spectrum of humic acid (100 mg/l solution of humic acid in 0.05 N NaClO₄) was recorded using the JASCO V-530 UV/VIS spectrophotometer. The spectrum showed a featureless continuum without recognizable peaks. A slight hump at ~ 250 nm was, however, observed in the UV region. The ratio of absorbance at 465 and 665 nm (E₄/E₆), which is an indication of the humification or the condensation of aromatic humic constituents
(Kim et al., 1990), was found to be 5 and was comparable to that for Gorleben HA (Kim et al. 1990). The IR spectrum of humic acid in Nujol medium was obtained with Philips PU-9500 IR spectrophotometer. Prominent peaks in the 1600-1650 cm\(^{-1}\) wave number region characterize carboxylate group present in HA (figure 3.4). Fulvic acid shows a reduced absorption compared to humic acid in this region.

![Figure 3.4 IR spectrum of humic acid](image)

The proton exchange capacity (PEC) for HA was determined by potentiometric titration (4.6 ± 0.1 meq/g) and by the Baryta method (4.8 ± 0.1 meq/g) (Stevenson, 1994). Baryta method is based on the complete neutralization of HA with excess Ba(OH)\(_2\), followed by titration of the unused base with a standard acid. pK\(_a\) values for HA functional groups were obtained in the framework of triprotic acid model (discrete 3-sites (HL\(_i\); i=1-3) for proton affinity (Tipping, 2002) using potentiometric titration and modelling of the titration data in FITEQL. During this titration, pH of the HA solution (0.04 g HA in 0.1 M NaCl) was first
brought to 2.97 by adding 0.1 M HCl dropwise and then the titration was continued with the successive addition of 0.2 ml of the base (0.02 N NaOH + 0.08 M NaCl) up to nearly 10 ml.

### 3.2.3 Determination of stability constant of Cs(I)-HA

The average stability constant for Cs-HA system in 0.05 M NaClO₄ medium was determined using Schubert’s ion exchange method (Lenhart et al. 2000). Schubert’s method is based on measuring the distribution of metal ion between the solution phase and a cation exchange resin, in the presence and absence of a metal complexing ligand. If \( \lambda_0 \) and \( \lambda \) stand for the distribution ratio in absence and presence of humic acid, respectively, relationship between distribution ratios and ligand concentration as per the Schubert’s method can be expressed by eq. 3.2.

\[
\left( \frac{\lambda_0}{\lambda} - 1 \right) = \frac{\beta_{1,n} [L]^n}{\Pi}
\]  

(3.2)

Where, \( \beta_{1,n} \) stands for stability constant of mononuclear metal ion complex with \( n \) number of ligands. The term \( \Pi \) accounts for metal ion reactions with ligands present in the system other than HA, e.g., OH\(^-\). \( \log \beta_{1,n} \) can be determined from a plot of \( \log \{(\lambda_0/\lambda)-1\} \) versus \( \log [L] \).

The conditions necessary for the application of Schubert’s method include, excess concentration of ligand over the metal ion concentration, so that the ligand concentration can be treated as constant even after some of it is complexed with the metal ion. Dowex-50W×8, a strong cation-exchange resin, was converted into the sodium form and used in the metal ion distribution experiment. HA concentration was varied in the range of 0-100 mg/l. pH of the experiments (4.0 and 6.5) was adjusted using sodium acetate-acetic acid buffer and dilute HClO₄/NaOH solutions. The ion exchange capacity (2.7 ± 0.1 meq/g) of the resin employed in the study was measured titrimetrically. The mass of the resin in each sample was fixed at 0.03 g. The equilibration time of 48 hr for the ion-exchange experiment was based on
the preliminary kinetic experiment. Control experiments were also conducted to determine the sorption of HA onto the resin.

3.2.4 Sorption experiments and Modelling exercises

Details of sorption experiments and the modelling protocol followed in the present work have been discussed in chapter 2. Specific details pertaining to this chapter are as follows. Both silica and alumina suspensions used in the experiment have solid to liquid ratio 5 g/l. During sorption 24 hrs was given for metal ion equilibration with mineral surfaces while 48 hrs equilibration was employed when HA was present in the sorption system. In ternary sorption system, HA was equilibrated with mineral surface before metal ion addition. To reduce Tc(VII) to Tc(IV), Sn(II) (10^{-6} M SnCl2 in suspensions) was used in acidic condition and reduction was ensured by Tetraphenyl arsonium chloride (in chloroform) based solvent extraction procedure, wherein TcO_4^- gets extracted to organic phase while Tc(IV) species remain in aqueous phase.

Humic acid sorption on silica and alumina was separately studied over pH 3-10 in NaClO_4 medium (0.05 and 0.1 M, respectively). 2 mg/l HA was contacted with the suspensions at different pH for 48 hours. On equilibration, the suspensions were centrifuged and assayed using UV visible spectroscopy to measure HA sorption.

In surface complexation modelling, constant capacitance model (C = 1.2 F/m^2) was used for surface electrostatics. In order to determine the protonation / deprotonation constants and concentration of alumina surface sites (≡Al-OH), potentiometric titration of the alumina suspension (7.5 g/l) in 0.1 M NaClO_4 was carried out with the continuous addition of either 0.1 M HNO_3 or 0.1 M NaOH under N_2 gas environment. A constant time interval (2 min.) was provided between the consecutive titrant additions. Potentiometric data was modelled
using FITEQL and optimized protonation/deprotonation constants were kept constant during
the modelling of the Tc(IV) sorption data.

3.3 Results and discussion

3.3.1 Acidity of silica and alumina surface sites

Figure 3.5 shows the zeta potential of silica and alumina suspensions in 0.01 M NaClO₄
medium. Silica becomes negatively charged above pH 2.3 while alumina is positively
charged up to pH ~ 8.9. In absence of any specifically sorbing cation, SCM postulates the
formation of surface charge as due to protonation/deprotonation reactions of the surface sites.
Negatively charged silica surface thus can be attributed to the deprotonation reaction which
in turn is promoted by the higher electronegativity of Si atoms in comparison to Al atoms.
Figure 3.6 shows the potentiometric titration data of γ-alumina with 0.1 M HCl and NaOH
along with its surface complexation modelling under 2-pK formalism for surface complexation and constant capacitance model for electrostatics. Modelling results of potentiometric data is shown in table 3.2. Comparing deprotonation constant of alumina with that of silica (log K = -7.60 ± 0.05; Marmier et al., 1999) higher isoelectric point for alumina (pH = 8.9) is obvious.

![Figure 3.6 Potentiometric titration of alumina suspension. Solid line refers to surface complexation modelling of the titration data.](image)
Table 3.2. Details of potentiometric titration of alumina suspension and SCM fitting

<table>
<thead>
<tr>
<th></th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Log K ($\equiv$AlOH + $H^+$ $\leftrightarrow$ $\equiv$AlOH$_2^+$)</td>
<td>$7.2 \pm 0.2$</td>
</tr>
<tr>
<td>Log K ($\equiv$AlOH - $H^+$ $\leftrightarrow$ $\equiv$AlO$^-$)</td>
<td>$-9.1 \pm 0.1$</td>
</tr>
<tr>
<td>Alumina concentration</td>
<td>7.5 g/l</td>
</tr>
<tr>
<td>Ionic strength</td>
<td>0.1 M NaClO$_4$</td>
</tr>
<tr>
<td>Specific surface area</td>
<td>203 $\pm$ 5 m$^2$/g</td>
</tr>
<tr>
<td>Specific capacitance</td>
<td>1.2 F/m$^2$</td>
</tr>
<tr>
<td>Surface sites ($\equiv$SOH)</td>
<td>$1.022 \times 10^{-3}$ mol/l</td>
</tr>
<tr>
<td>WSOS/DF (weighted sum of squares per degree of freedom)</td>
<td>29.5</td>
</tr>
</tbody>
</table>

3.3.2 Proton affinity of HA functional groups

Potentiometric titration data of HA is shown in figure 3.7 (a). The curve exhibits characteristics typical of a polyelectrolyte where the continuous ionization of the functional
groups creates the pattern devoid of any sharp transition. Derivative of this plot (figure 3.7 (b)) indicates two maxima attributed to the ionization of two broad groups of functional groups with nearly 2 and 5 ml of titrant (NaOH) addition. These peaks have been considered to be represented by carboxylic and phenolic groups, respectively.

Modelling of HA potentiometric titration data was, however, carried out using three discrete sites model (Triprotic model), corresponding to carboxylic, amine and phenolic groups. As the concentration of metal ion (Tc) involved in the study was very small compared to that of HA, only the higher affinity (carboxylic) sites are expected to participate in metal binding. Hence determination of the concentration and affinity constant of this type of site with greater precision was considered necessary and three sites model was adopted for the modelling of potentiometric data. Results of this exercise are listed in table 3.3.

<table>
<thead>
<tr>
<th>Site</th>
<th>Concentration (M)</th>
<th>Log K</th>
<th>WSOS/DF</th>
</tr>
</thead>
<tbody>
<tr>
<td>HL₁</td>
<td>$5.107 \times 10^{-4}$</td>
<td>-3.602</td>
<td></td>
</tr>
<tr>
<td>HL₂</td>
<td>$3.715 \times 10^{-4}$</td>
<td>-5.885</td>
<td>7.39</td>
</tr>
<tr>
<td>HL₃</td>
<td>$2.108 \times 10^{-4}$</td>
<td>-8.118</td>
<td></td>
</tr>
</tbody>
</table>

3.3.3 Humic acid sorption on oxide surfaces

Sorption of humic acid on silica and alumina surfaces is shown in figure 3.8. The plot shows the typical behaviour of an anion sorbing on oxide surface; higher sorption percentage at lower pH values and decreasing sorption at increasing pH. However, there is difference in the absolute sorption percentage at these two surfaces; percentage sorption is higher for alumina than that for silica at lower pH values. This observation indicates the involvement of ligand exchange as the predominant reaction mechanism, as silica being negatively charged.
over the studied pH range should have shown negligible sorption of HA. This is further substantiated with the fact that humic acid sorption on silica surface does not change with increased ionic strength (i.e., 0.1 M) (figure 3.14). However, electrostatic factor can not be ruled out entirely as alumina with its positively charged surface sorbs higher proportion of humic acid compared to silica. Participation of other mechanisms such as hydrophobic binding, van der Waals interactions, etc., however, cannot be ruled out in defining the sorption behaviour.

Surface complexation modelling (figure 3.9) of humic acid sorption on alumina using 3-sites model for HA and 2-pK approach for surface complexation on alumina surface, could quantitatively explain the sorption profile reasonably. The optimized surface species (table 3.4) is an outer sphere complex of HA on alumina surface sites (≡AlOH.HL₁).
3.3.4 Cs(I) and Tc(IV) complexation with HA

$^{137}$Cs activity left in the supernatant after equilibration with the fixed amount of cation-exchange resin was found to be constant, irrespective of varying pH, ionic strength, and HA concentration. A typical plot of $\log(\lambda_0/\lambda - 1)$ vs. $\log[HA]$ at pH 6.5 and 0.05 M ionic strength is shown in figure 3.10. Concentration of HA has been converted into eq/l using carboxylic acid content in HA and the amount of HA used in the experiment. The results indicate weak interaction of cesium ($\log \beta = -1.86 \pm 0.23$) with humic acid.

Tc(IV) shows strong interaction with humic acid and a conditional constant ($\log \beta$) value of 5 obtained by Maes et al. (1999) has been used in the present work for modelling exercise.
3.3.5 Cs(I) sorption on silica in presence of humic acid

Cs(I) sorption on silica in absence and presence of HA is shown in figure 3.11. In absence of HA, sorption percentage is insignificant till pH 7, above which it increases and attains ~30% value by pH 10. With HA, the sorption percentage at lower pH values shows enhanced profile while there is no difference at higher pH values. Increase at lower pH values has a convex shape with maximum sorption in the pH range of 4 to 6.

Cs(I) sorption on silica has strong competition from Na(I) of the background electrolyte. Further, with lesser ionic potential, it behaves like a weak Lewis acid and therefore, as per the
hard acid-hard base concept, shows weak interaction with strong Lewis base like oxygen of silica surface. Metal ion sorption on oxide surface starts with the formation of outer sphere complex with surface sites and subsequently converts into inner sphere when complexing behaviour of metal ions has increased, such as at higher pH. Cs(I) sorption profile at lower pH can thus be attributed to suppression of outer sphere complexation while the increasing sorption with pH above 7 is due to increasing ionic interaction with ≡SiO− group like with hydroxyl ion in Cs(OH) ionic compound.

Increased sorption percentage of Cs(I) at lower pH values in presence of HA indicates stronger binding of Cs(I) with HA sorbed silica surface. As per the formulation of linear additive model:

Figure 3.11. Sorption of Cs(I) on silica in presence and absence of humic acid. The solid line represents the linear additive modelling of the ternary system.
additive model (eq. 2.10), there should be no such enhancement (i.e., $K_d = K_d^0$). To reproduce the sorption percentage, LAM was modified to include the different binding ability of surface bound HA and dissolved HA. Eq. 2.10 gets modified to eq. 3.3 where $\beta_1$ and $\beta_2$ stand for the Cs(I) stability constant for surface sorbed and dissolved HA.

$$K_d = \frac{K_d^0 + (V/W)f_{HS} \beta_2 [HS]}{1+(1-f_{HS}) \beta_1 [HS]} \quad (3.3)$$

In an iterative fitting of the sorption data of the ternary system in eq. 3.3, $\beta_2$ value was varied in step of 0.1 unit from $\beta_1$ value. Log $\beta_2$ value of 4.6 was found to reproduce the ternary sorption profile. This value is significantly different from stability constant of dissolved HA and substantiate the stronger binding behaviour in the ternary system.

SCM defines sorption as the result of surface complexation and the electrostatic factors. Though interaction ability of HA and surface oxygen atoms with Cs(I) should not change due to sorption, presence of HA on surface could present a cloud of negative charge causing enhanced electrostatic attraction for Cs(I). This is evidenced by the fact that zeta potential of HA-sorbed-silica changes significantly from that of bare silica and comes closer to that of HA (figure 3.12).

Cs(I) is thus present on HA-sorbed-silica surface as counter ion condensate around the polyelectrolyte (HA), wherein Cs(I) can be considered as forming outer sphere complex with HA. This conclusion is substantiated by the facts that Cs(I) sorption on HA-sorbed-silica decreases significantly with increased ionic strength (0.1 M from 0.05 M NaClO$_4$) whereas the same for binary sorption systems do not change with ionic strength (figure 3.14). Similar conclusion was derived in an LCD model application to Ca(II) sorption by goethite surface in presence of FA where, with the enhance capability of the model, the authors could delineate
the interaction between Ca and FA at the surface of goethite as mainly due to the electrostatic effects (Weng et al. 2005).

Figure 3.12 Zeta potential measurements of humic acid, silica and humic acid equilibrated silica
3.3.6 Tc(IV) sorption on alumina in presence of humic acid

Tc(IV) sorption on alumina both in absence and presence of HA is shown in figure 3.14. Sorption in absence of HA remains low (~10-20 %) over the pH range 4 – 11 which is distinctly different from the high sorption percentage expected for tetravalent metal ions (Reiller et al. 2005). Tc in its IV oxidation state exists as TcO$_2^{2+}$ at lower pH values and hydrolyses to TcO(OH)$^+$ and TcO(OH)$_2$ with increasing pH (figure 3.15). Hydrolysed Tc species thus carry lesser effective ionic charge and this decreases the interaction affinity leading to reduced sorption percentage.

Figure 3.13 Effect of ionic strength in Cs(I) and humic acid sorption systems.
Sorption of Tc(IV) in presence of HA greatly increases at lower pH values compared to that in absence of HA, reaches quantitative value in the pH range 5-6 (figure 3.14) and decreases at higher pH values. Sorption profile in the ternary system follows the trend of HA sorption on alumina (figure 3.9) indicating that HA sorption by alumina governs Tc(IV) sorption characteristics. LAM of the ternary systems (figure 3.16) considering different metal binding characteristic of dissolved and surface sorbed HA (eq. 3.3) reproduces the sorption profile. The inset in figure 3.17 shows the variation of log $\beta_2$ (5.3-6.9) with pH. Considering the effective charge of TcO$_2^+$ and trivalent actinides/lanthanides, log $\beta_2$ value stands in conformity for the value (~ 4.7 - 7) reported in Am(III)/Cm(III) sorption on

Figure 3.14 Effect of humic acid on Tc(IV) sorption on alumina. Solid lines stand for surface complexation modelling of sorption systems
hematite in presence of humic acid (Samadafam et al. 2000). The variation does suggest the role of HA in governing the sorption. However, the participation of interactions other than those present in binary systems, governing sorption is also clear as Tc(IV) interaction constants with dissolved and surface sorbed HA are different.

SCM of the Tc(IV) sorption on alumina in absence and presence of HA is shown in figure 3.14 and the modelling result is listed in table 3.4. Modelling of Tc(IV) sorption on alumina indicates the formation of two Tc(IV) surface species while ligand bridged Tc(IV) surfaces species forms on alumina sites in ternary system. The log K value obtained for ternary system matches closely with maximum value of log $\beta_2$ observed in LAM. Predominance of ligand bridged ternary complex (type 1) in characterising the ternary sorption system seems justified

Figure 3.15 Eh-pH predominance diagram of technetium aqueous speciation
in view of weak Tc(IV) interaction with mineral surface and stronger interaction of Tc(IV) with HA.

Table 3.4 Surface Complexation modeling of Tc(IV) binary and ternary sorption systems

<table>
<thead>
<tr>
<th>Equilibrium reactions</th>
<th>Species optimized</th>
<th>Log K</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Tc(IV)-Alumina</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>≡AlOH + TcO^{2+} → ≡ AlOTcO^{+}</td>
<td>≡ AlOTcO^{+}</td>
<td>5.80</td>
</tr>
<tr>
<td>≡AlOH + TcO^{2+} + H_{2}O → ≡ AlOTcO(OH)</td>
<td>≡ AlOTcO(OH)</td>
<td>-1.01</td>
</tr>
<tr>
<td><strong>HA-Alumina</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>≡AlOH + HL_{1} → ≡ AlOHL_{1}</td>
<td>≡ AlOHL_{1}</td>
<td>4.44</td>
</tr>
<tr>
<td><strong>Tc(IV)-HA-Alumina</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>≡AlOH + TcO^{2+} + HL_{1} → ≡ AlOL_{1}TcO</td>
<td>≡ AlOL_{1}TcO</td>
<td>6.79</td>
</tr>
</tbody>
</table>

Figure 3.16 Linear additive modelling of Tc(IV) sorption on alumina in presence of humic acid. Inset shows the variation of log β₂ over the pH range of sorption
3.4 Conclusion

Presence of humic acid was found to strongly modify the sorption of Cs(I) and Tc(IV) on mineral oxide surfaces. Though the general pattern of HA effect - enhanced metal ion sorption at lower pH values and suppressed sorption at higher pH compared to that in absence of HA – is same, the role played by humic acid varies. In case of Cs(I), it alters the electrostatics at the oxide-water interface while strong Tc(IV) interaction with HA causes the formation of ternary complex in Tc(IV)-HA-alumina system. Complexing behaviour of humic acid governs the sorption in ternary sorption system of Tc(IV)-HA-alumina.