Migration and Speciation of Uranium in Terrestrial Environment

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DECLARATION

I, hereby declare that the investigation presented in the thesis has been carried out by me. The work is original and has not been submitted earlier as a whole or in part for a degree/ diploma at this or any other Institution / University.

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List of Publications arising from the Thesis

Journal

1. Effects of CO_2 infiltration on Migration and Speciation of Uranium at Mineral–Water Interface, Sabyasachi Rout, P. M. Ravi, Ajay Kumar and R. M. Tripathi, J Radioanal Nucl Chem, 2017, 1709–1717.
2. Understanding the solid phase chemical fractionation of uranium in soil and effect of ageing, Sabyasachi Rout, Ajay Kumar, P.M. Ravi and R. M. Tripathi. Journal of Hazardous Materials, 2016, 317, 457–465.
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Sabyasachi Rout

DEDICATED

To my Beloved Parents

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Sabyasachi Rout

CONTENTS

Chapter 1

Introduction

Chapter 2

Experimental Methods and Techniques

Chapter 3

Behavior of Uranium at Soil- Water interface

Chapter 4

Chemical Fractionation of Uranium in Soil

Chapter 5

Effect of Salinity on Migration and speciation of Uranium at Soil-Water Interface

Chapter 6

Migration and Speciation of Uranium at Ore-water interface: Role of Ionic Strength, Humic Acid, pH and Carbonate

Chapter 7

Effects of Carbon Dioxide on Migration of Uranium

Chapter 8

Synopsis

Uranium is an important natural resource used in production of nuclear reactor fuel and nuclear weapons. It is lithophilic naturally radioactive element, chemically and radiologically toxic, and occurs in the earth's crust reaching an average concentration almost 0.0003% by mass. About 5% percent of all known minerals contain uranium as an essential structural constituent, as a result uranium minerals display a remarkable structure and chemical diversity [1]. The presence of uranium (U) in earth can be attributed to natural and anthropogenic sources. Natural U sources and its daughter products are present on the earth from the beginning of the formation of earth, presumably being formed in the course of nucleo-synthesis and are called primordial radionuclides.

In the geosphere, U chemical behavior is governed by redox reactions, complexation, colloid formation and interactions with soil mineral surfaces [2, 3]. Water is recognized as the dominant transport medium in the environment [4] and its chemical condition defines the oxidation state, the prevailing species and solubility of the radionuclides. The redox potential of the system influences the fate of uranium minerals, such as oxidation and dissolution leading to the growth of its concentration in meteoric as well as hydrothermal fluids. Most natural waters have low salinity, near neutral pH with a wide range of redox potentials (Eh) (from -300 to +700 mV) [5]. Under this natural condition of pH and Eh, U easily forms multiple oxidation states, which complicates the prediction of their behavior in environment in comparison to single oxidation state. Bicarbonate/carbonate and hydroxide are main inorganic complexing ligands present in aquatic system. Many other inorganic ligands such as phosphate, nitrate, fluoride, sulfate and silicate can also play a role by complexing with U. Organic chelating molecules present in the environment range from molecular citrate, oxalate, etc., to macromolecular, poly-electrolytic humic substances are important carrier of U in soil/mineral-water system. Uranium mobility in soil and its migration to groundwater also depends on soil properties like, pH, redox potential, particle size, soil mineralogy and amount of available water. Retention of U in soil is a result of several processes such as adsorption, chemisorption, ion exchange or their combinations [6]. The uranium sorption rate of soils with abundant clay, organic matter and iron content is generally high. Therefore, normally uranium does not reach the groundwater unless and until there is significant change in physiochemical properties of soil and water.

Recently it was observed that U concentration in drinking water sources of many countries round the globe is more than the drinking water standards. Incidentally, in many locations where U concentrations are high, salinity also was found to be high. High level of U has been reported in many states of India, among which U in ground water of Punjab was most highlighted in the year 2009-2010. Changes in soil environmental conditions over time, such as the degradation of the organic waste matrix, changes in pH, redox potential and soil solution composition, due to various remediation schemes or to natural weathering processes, also may enhance U concentration in soil and its migration to groundwater. In addition to this, long term climatic changes also has a great impact on soil and water chemistry which may leads to change in speciation of U and increased migration from soil/mineral to water. This leads to increased bioavailability of U in terrestrial environment. Therefore, from environmental protection and assessment point of view, it is very much important to study the migration of U in terrestrial environment especially at soil-water and mineral-water interface. These observations motivated us to carry out detailed studies on the speciation and migration of U from solid phase (soil and minerals) to solution (water).

The objective of the present work is to understand the change in migration behavior and speciation of U in terrestrial environment in response to changes in environmental conditions and to identify the complexities involved in the process. Laboratory experiments were carried out to understand the complex U behavior at soil-water and ore-water interface. An attempt has been made to quantify the factors influencing the processes and the energy released or absorbed during the process. At present increase in salinity is the major factor, while in future, increase in CO_2 partial pressure also may play important role on speciation and migration of U in ground water systems. Hence, in the present study, effects of these parameters on speciation and migration of U from soil/minerals to water were investigated.

The thesis has been divided into eight chapters and a brief description of each chapter is as follows:

Chapter 1: Introduction

In this introductory chapter, a detailed literature survey on geochemistry of U, occurrence of U in environment, its toxicology, its environmental chemistry, and sorption / desorption of U in natural systems and the parameters influencing speciation and migration of U has been carried out. The literature revealed that all U isotopes are radioactive, natural U is found in the environment at 99.27% ^{238}U, 0.71% ^{235}U and 0.005% ^{234}U by mass isotopic abundance and economic U ore deposits range in concentration from about 300 to over 5000 mg/kg. The principal ore minerals and their origin have been discussed in details [2]. Natural U is also found in water systems like surface water, oceans, groundwater, and in trace amounts in any material of terrestrial origin covering a wide range of oxidation states starting from +3 to +6. But out of these +4 and +6 are stable in aqueous medium at reduced and oxidized environment respectively. The U(VI) species, uranyl ion (UO_2^{2+}) is generally mobile and form strong complexes with PO_4^{3-}

and CO_3^{2-} whereas, in absence of carbonate or phosphate it forms hydroxyl complexes and responsible for contamination of ground water. On the other hand, U(IV) species concentration in water system is very low due to its low solubility. In the section, issues related to U in the world, possible sources of U contamination of soil and water systems, possible factors influencing contamination and case studies related to U contaminations in different environmental matrices were addressed. In addition to this, U in ground water of Punjab, India is also discussed. The gap area with respect to the understanding the mechanism behind the presence of U in ground water has been identified. This chapter also narrates how objectives of this study have been designed to address the gap areas.

Chapter 2: Experimental Methods and Techniques

Brief descriptions of methodology of the experiments and instrumental techniques which have been used during the present investigation have been provided in this chapter. The chapter describes the mechanistic aspects of the interfacial sorption process along with steps of batch sorption methodology used for kinetic, thermodynamic and equilibrium isotherms studies. Experimental procedures involved in soil and ore mineral characterizations namely mineralogical, particle size, elemental characterization, soil organic matter content, cation exchange capacity (CEC) are addressed in detail. An in-depth discussion is carried out in this chapter regarding analytical estimation of uranium in water and soil. Speciation of uranium in terms of chemical fractionation of uranium in soil, steps involved in sequential extraction for estimation of U in different fractions of soil prescribed by Scutz etal [7] are described. Working principles of the instruments namely, XRD, Particle Size Analyzer, CHNS-O analyzer, Ion-Chromatography, Voltammetry, Fluorimetry and X-ray Photo electron Spectroscopy are also discussed in this chapter. The chemical speciation models namely PHREEQC I and MEDUSA used for speciation studies of uranium in aqueous medium are also discussed in this chapter.

Chapter 3: Behavior of Uranium at Soil-Water Interface

This chapter gives a brief introduction followed by procedures used for the characterization of soil and studies related to kinetics, thermodynamics and equilibrium isotherms of U sorption onto soil. This chapter describes the effect of various parameters influencing the adsorption capacity of soil for U. It was observed that adsorption capacity of soil for U increases with Fe, Mn and naturally occurring organic matter (NOM) content in the soil. At circumneutral pH, effect of NOM on sorption capacity of soil is negligible in Fe-Mn dominated soil. Water parameters like pH, CO_3^{2-} and Ca^{2+} are sensitive parameters which influence U(VI) migration at soil water interface. Sorption followed pseudo-second order model with multi-step diffusion process irrespective of soil types and the rate-limiting step is chemisorption involving valence forces through sharing or exchange of electrons along with ion exchange. From the thermodynamic parameters derived, it could be inferred that sorption is spontaneous, endothermic in nature and follows dissociative mechanism. From these studies, it can be concluded that, the geological setup with high ferro-manganese content offer one of the candidate locations for waste disposal facilities or geological repository. Similarly, Fe or Mn enriched soils are effective as backfill to mitigate migration of U. The sorption parameters generated in these studies has potential application in predictive modeling of U transport in terrestrial environment.

Chapter 4: Chemical Fractionation of Uranium in Soil

Chemical fractionation of uranium or fractionation of uranium in different pools of soil along with effect of ageing has been reported in this chapter. When U come in contact with soil, it may go to one or several fractions/pools in soil such as; Exchangeable, Carbonate, Reducible fraction (Oxides and hydroxides of Fe, Mn), oxidizable fraction (Organic matter: OM), Acid leachable fraction (Secondary minerals) and Residual fraction (Primary minerals). Three soils of different origins were taken for the studies. Characterization of soil samples were carried out followed by amendment of soil samples with known concentration of uranium by batch sorption method. In order to study the impact of ageing on fractional distribution of U in different soil pools, sequential extraction of U was carried out as per standard protocol [7], by taking desired amount of sample from amended soil after one month and another one after 12th month. Characterization of amended soil samples such as, pH, Eh, mineralogy, CEC, organic matter, Fe, Mn and total U content were carried out in parallel to observe the effect of ageing on these parameters. Spectroscopic investigation using X-Ray Photoelectron Spectroscopy (XPS) was carried out to understand the governing mechanism behind the species distribution of uranium in soil matrix. The studies indicated that the fate of U in soil is initially governed by concentration of adsorbents (Such as carbonate, oxides of Fe/ Mn, OM etc.in respective fractions) but a significant rearrangement of U in these fractions of soil was observed due to aging. This leads to either increase or decrease in bioavailability of U. Further investigation using XPS revealed that a part of total U (VI) is converted to less mobile U(IV). Concentration of U in soil surface is mainly controlled by soil carbonates and organic matter content. Occlusion of U-Fe-Oxides (Hydroxide) in to amorphous silica has been considered as plausible mechanism which leads to decrease of U in reducible fraction. The bulk enrichment is due to fractionation of uranium in reducible and residual fraction.

Chapter 5: Effect of Salinity on Migration and Speciation of Uranium at Soil–Water Interface

This chapter focuses on the studies carried out on the effect of salinity on migration and speciation of uranium at soil-water interface. The studies indicated that U is present in the moderately reduced soil as a mixture of U(IV) and U(VI) with U(IV) as dominating (71%) state. Sequential extraction of soil samples showed that major fraction is bound to clay mineral (49.31%) followed by oxides and hydroxide of Fe/Mn (19.58%), organic phase (10.75%), exchangeable (10.41%) and remaining to carbonate phase (9.96%). UO_2CO_3, $(UO_2)_2CO_3\ (OH)_3$-, $UO_2(CO_3)_2^{2-}$, UO_2OH^+ and $UO_2(OH)_2$ has been reported as important species in the soil-solution at ambient condition. The effects of salinity induced by $CaCl_2$, $MgCl_2$, NaCl, $NaNO_3$ and Na_2SO_4 on the migration of U were studied. It was observed that the increase in salinity mobilizes U(VI) from soil exchangeable fraction, forcing it into solution. It is well known that the desorption capacity of cations are directly proportional to ionic radius ($Ca^{2+} > Mg^{2+} > Na^+$) and charge on cation ($Ca^{2+} \sim Mg^{2+} > Na^+$) which can be correlated to the high desorption of U induced by $CaCl_2$ followed by $MgCl_2$ and NaCl in chloride salts. Ion exchange mechanism is predominant in the desorption of U from soil in the case of $CaCl_2$, $MgCl_2$,NaCl, Na_2SO_4 systems, whereas ion exchange and oxidative dissolution of U(IV) seem to be the driving forces in $NaNO_3$ system. These results can be used, for predicting the migration behavior of trace uranium in soil and for impact assessment of the disposal of radioactive waste containing uranium.

Chapter 6: Migration and Speciation of Uranium at Ore-water interface: Role of Ionic Strength, Humic Acid, pH and Carbonate

This chapter describes the studies carried out on the role of ionic strength (IS) of the water in U migration from ore to water in contact and speciation in the ore water binary system.

Experiments were also carried out in ternary system (Uraninite-Water- Humic Acid) to investigate the composite impact of humic acid (HA) on mobility of uranium at different Ionic Strength (IS). Laboratory batch experiments were also carried out to investigate migration of uranium at varying pH and carbonate concentrations. The results of the study indicated that increase in the IS of the water accelerates the U migration from U bearing ore like uraninite at ore/mineral–water interface. In binary systems, high $Ca^{2+}$and NO_3^- concentration induces higher U mobility. Investigation of ternary system (Ore-Water-HA) revealed that presence of HA increases the U concentration in liquid phase at circumneutral pH, whereas presence of high Ca^{2+} ion content reduces the U concentration in solution. This is attributed to competition between Ca^{2+} ion with uranyl ion (due to similar ionic radii) for HA followed by formation of more stable Ca-Humato complex in comparison to U(VI)-Humato complex. As a result less number of Ca^{2+} ion is available in aqueous phase to induce the U desorption simultaneously less binding of U to humic acid causes drop in U concentration in aqueous phase. Increase in carbonate concentration of aqueous media induces migration of U irrespective of ore types but effect of pH depends on the type of host rock containing U minerals. The outcome of these studies can be used for predicting the migration behavior of uranium at mining, milling sites and for impact assessment of the disposal of radioactive waste generated from mines.

Chapter 7: Effects of Carbon Dioxide on Migration of Uranium

This chapter mainly focuses on the study of impact of CO_2 gas on migration of U at mineral (Uraninite)-water and soil-water interface including mechanism and change in speciation. This chapter describes the anticipated increase in concentration of CO_2 in atmospheric and hydrospheric environments consequent to the use of fossil fuels. This chapter also explains how the increase in CO_2 will affect the uranium speciation in soil –water and ore –water systems. Due to rapid industrialization, CO_2 concentration in the atmosphere has increased from 275 to 370 ppmv and by 2100 it is projected to be 750 ppmv [8]. Since aquatic system is in equilibrium with atmospheric gases, increase in atmospheric CO_2 level leads to increase in dissolve CO_2 in aquatic systems. This may cause change in physicochemical parameters of aquatic system which in turn leads to change in the aqueous speciation of dissolved U species. It may initiate various processes like, mineral dissolution, metal mobilization, and sorption/desorption and precipitations etc., at mineral-water or soil- water interface. For the study, a shaker incubator has been customized to carry out the experiment of infiltration of CO_2 gas at 1 atm for a period of 30 days. The result and discussion section describes the comparison of physicochemical properties of the system with respect to pre CO_2 exposure system. The study was carried out in a phased manner to understand the immediate impact and delayed impact. In Phase I experiment, sample aliquot removed after 24 hrs of exposure to CO_2 was analyzed while in phase II experiment, sample aliquot removed after 30 days of exposure to CO_2 was analyzed. Samples were also taken at different time intervals during the experimental period and analyzed for all the physicochemical parameters. Introduction of CO_2 leads saturation of water at mineral-water and soil-water interfaces with CO_2 which initiate various reactions. Initial increase in cation concentrations in aqueous phase suggest that mineral dissolution is driven by CO_2 which is in consistent with initial decrease in pH. The phase II experiment indicated an increase in cation concentration as compared to initial concentration. However the increase did not follow any correlation with time indicating influence of multiple parameters. In response to exposure of CO_2, U migration increases upto~150 times more than the pre exposed systems of ore-water system within 2–3 days and again start to fall and achieve equilibrium at the end of experiment. Observations were similar in soil-water system, where U concentration increased 325 times than pre-exposed system. The increase in mobility of U in soil -water system, consequent to the exposure to CO_2, is attributed to the release of U bound in different fractions of soil. Though the present studies present a trend on the effect of CO_2 exposure on soil-water system, it may be noted that amended soil was used in the present study, which may not represent quantitatively age old soil-water system. More studies are required to address this issue.

Chapter 8: Conclusions

In this concluding chapter findings of the thesis work have been summarized and finally presented all the result in a nutshell. The migration of U in terrestrial environment is very complex and also complexities increase due to human activities such as mining, processing and waste disposal practices along with issues like increased salinity and long term climatic change. The batch sorption studies of U onto wide variety of soil types revealed that sorption follows pseudo-second order kinetics with multi-step diffusion process irrespective of soil types. And the rate-limiting step is chemisorption involving valence forces through sharing or exchange of electrons along with ion exchange. Thermodynamically the process is endothermic in nature and follows dissociative mechanism for sorption. Sorption and migration of U in soil-water system is function of soil and water parameters among which soil Fe, Mn, OM content, water pH, CO_3^{2-}, Ca^{2+} are the most sensitive parameters. Chemical fractionation of U in soil initially depends on the sorbents responsible for sorption in different fractions but with ages a significant rearrangement takes place in different fractions and bioavailability decreases in soils containing high Fe content. Increases in salinity of aquatic system accelerate the U migration from soil and ore minerals to water in contact. Ca^{2+} and NO_3^- plays significant role in migration from solid phase to solution. NO_3^- is identified as dissolve oxidant for U. Case studies like, high level of U in ground water of Punjab, India along with high salinity, NO_3^- and pH can be correlated to the salinity induced migration. Change in climate or environmental conditions brought changes in terrestrial as well as subsurface aquatic systems like change in physicochemical properties of soil and water which leads to change in speciation and increases in the migration of uranium. Increased atmospheric CO_2 will directly or indirectly affect uranium migration to aqueous phase. Therefore all these parameters need to be taken in to consideration for development of remedial techniques and planning of disposal facilities such as Near Surface disposal Facility (NSDF) or Deep Geological Repository (DGR). This chapter also presents future scope for studies.

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List of Figures

List of Tables

CHAPTER 1

INTRODUCTION

Uranium (U) is ubiquitous throughout the environment as a primordial radionuclide. The concentration of uranium in soil varies greatly from location to location and is found in the earth's crust with an average abundance of 2.7 g/ton [1]. Uranium has 14 isotopes; the atomic masses of these isotopes range from 227 to 240. All uranium isotopes are radioactive. Natural uranium is found in the environment at 99.3% ^{238}U, 0.7% ^{235}U and 0.006% ^{234}U by mass isotopic abundance [2]. The half-lives of these isotopes are 4.51 x 10^9 y, 7.1x 10^8 y and 2.47 x 10^5 y respectively. Economic uranium ore deposits range in concentration from about 300 to over 5000 mg/kg [2]. Natural uranium is also found in surface water, oceans, groundwater, and in trace amounts in any material of terrestrial origin.

1.1 Chemistry of U

Uranium can exist in wide range of oxidation states starts from +3 to +6 oxidation states, of which the +4 and +6 states are the most common states found in the environment. Uranium in the +4 and+6 oxidation states exists in a variety of primary and secondary minerals. U(IV) minerals chiefly includes uraninite (UO_2 through $UO_{2.25}$) and coffinite ($USiO_4$) [3, 4]. Among U(VI) minerals carnotite [$(K_2(UO_2)_2(VO_4)_2$], schoepite ($UO_3.2H_2O$), rutherfordine (UO_2CO_3), autunite [$Ca(UO_2)_2(PO_4)_2$], tyuyamunite [$Ca(UO_2)_2(VO_4)_2$], potassium autunite [$K_2(UO_2)_2(PO_4)_2$] and uranophane [$Ca(UO_2)_2(SiO_3OH)_2$] are important minerals [3,4]. Secondary phases minerals which may form when sufficient uranium is leached from contaminated wastes or a disposal system and migrates downstream. A high level of uranium is also found in phosphate rock and lignite at concentrations that can be commercially recovered. In the presence of lignite and other sedimentary carbonaceous substances, U enrichment takes place as a result of uranium reduction from U(VI) to U(IV) to form insoluble precipitates, such as uraninite. All these mineral deposits are grouped under two main groups of deposits, those of igneous plutonic or volcanic association, including metamorphic deposits and those of sediment/sedimentary basin association (Table 1). On the basis of geological setting and in order of economic importance the classes of uranium deposits are: (1) Unconformity related, (2) Sandstone, (3) Quartz-pebble conglomerate, (4) Veins, (5) Breccia complex, (6) Intrusive, (7) Phosphorite, (8) Collapse breccia, (9) Volcanic, (10) Surficial, (11) Metasomatite, (12) Metamorphic, (13) Lignite and (14) Blackshale [5]. Deposits consist of a variable number of veins ranging in size from short and hair like stringers to those several kilometers long and as much as several meters thick. Vein uranium deposits typically pitchblende and coffinite, in fractures shear zones and stock works. The uranium minerals are either the sole metallic constituents in the veins or in poly-metallic veins, which are accompanied by other metals, such as Bi, Co, Ni, As, Ag and Cu. The deposits are hosted by: (i) granitic or syenitic rocks (intra granitic veins), (ii) rocks surrounding granitic plutons (per igranitic or per batholithic veins) or (iii) sheared or mylonitized, usually metamorphosed, sedimentary or igneous complexes (veins in shear and fault zones). Classification of the uranium vein deposits, based on their geological setting, takes into account structural and lithological controls in their localization.

Generally, uranium deposits worldwide contain daughter isotopes in disequilibrium with their parents due to change in chemical fractionations arises due to preferential leaching, selective solubility, adsorption and emplacement processes. Natural weathering along with anthropogenic induced disturbances such as: mining operations, land use and management cause leaching of U and contamination of terrestrial environment.

Table 1. Classification of uranium deposits

A Igneous Plutonic and Volcanic Association	1.Igneous Plutonic Association	1.1. Magmatic uranium deposits formed by different evolved uraniferous magmas	1.1.1. Alkaline complex deposits
		1.2 Formed as a result of high-to-low temperature hydrothermal activity associated with high-level granite magmatism	1.2.1. Granite associate-ed deposits including vein-type deposits
			1.2.2. Perigranitic vein deposits
			1.2.3. Metasomatite deposits
	2. Igneous Plutonic and Volcanic Association	2.1. Deposits associated with granite magmatism and acid volcanic and volcaniclastic sequences in anorogenic setting	2.1.1. Breccia complex deposits
	3. Igneous Volcanic Association	3.1. Formed as a result of high-to-low temperature hydro-thermal activity associated with high-level mainly felsic volcanics	3.1.1 Volcanic deposits
B. Metamorphic Association	1. Formed by metamorphic fluids probably	1.1. Synmetamorphic deposits	
		1.2. Vein deposits in metamorphic rocks	

	derived from igneous or sedimentary rocks previously enriched in uranium		
C. Sediment /Sedimentary basin Association	**1**. Continental	1.1 Associated with late post-orogenic sedimentary basins having mainly clastic fill -formed or modified in some	1.1.1. Quartz-pebble conglomerate deposits
			1.1.2. Unconformity-related deposits
			1.1.3Sandstone deposits
			1.1.4 Sediment-hosted vein deposits
			1.1.5.Collapse breccias
			1.1.6 Lignite deposits
		1.2. Penecontemporaneou with sedimentation or formed by surface weathering	1.2.1 Surficial deposits
	2. Marine	2.1. Oceanic deposits	Phosphorite deposits
		2.2. Epicontinental	Black shale deposits

1.2. Aqueous Chemistry of Uranium

Uranium can exist in the +3, +4, +5, and +6 oxidation states in aqueous environments. Dissolved U(III) easily oxidizes to U(IV) under most reducing conditions found in nature whereas U(V) aqueous species (UO_2^+) readily disproportionate to U(IV) and U(VI).

$$2UO_2^+ \rightarrow UO_2^{2+} + UO_2$$

Consequently, U(IV) and U(VI) are the most common oxidation states of uranium in nature. Uranium will exist in the +6 and +4 oxidation states, respectively, in oxidizing and more reducing environments. Both uranium species, UO_2^{2+} and U^{4+}, hydrolyze readily. The U^{4+} ion is more readily hydrolyzed than UO_2^{2+} as would be expected from its higher ionic charge. Langmuir calculated U(IV) speciation in a system containing typical natural water concentrations of fluoride (0.2 mg/L), chloride (10 mg/L), sulfate (100 mg/L) and phosphate (0.1 mg/L) [4]**.** He observed that below pH 3, UF_2^{2+} was the dominant uranium species. Above pH 3 dissolved U(IV) preferably form hydrolytic species such as $U(OH)_3^+$ and $U(OH)_4$(aq). Above pH 3 complexes with fluoride, chloride, phosphate and sulfate were not important. The total U(IV) concentration in solution is generally quite low between 3 and 30 µg/L, attributes to its low solubility [6,7]. Since Uranyl ions form polynuclear hydroxyl complexes, the hydrolysis of uranyl ions under oxic conditions is dependent on the concentration of total dissolved uranium. Most natural water system contains 0.1 to 10 µg/L dissolved uranium. This concentration may rise to ≥ 1,000µg/L in the vicinity of uranium mining sites. In a carbonate free U(VI)-water system, at pH values less than 5, $UO_2^{2+}$is the dominant species, $UO_2(OH)_2$ (aq) at pH values between 5 and 9 and $UO_2(OH)_3^-$ at pH values between 9 and 10. This was true for dissolved U(VI) concentrations in the range of 0.1 µg/L and 1,000 µg/L. Some poly-nuclear species such as $(UO_2)_3(OH)_5^+$ and $(UO_2)_2(OH)_2^{2+}$ are also dominated at dissolved U(VI) concentrations

≥1,000 µg/L [8]**.** In case of chemically more complicated systems, at pH values less than 5, the UO_2F^+ species dominates the system, whereas at pH values greater than 5, carbonate complexes [UO_2CO_3 (aq), $UO_2(CO_3)_2^{2-}$, $UO_2(CO_3)_3^{4-}$] and mixed hydroxo-carbonate complexes $(UO_2)_2CO_3(OH)_3^-$ are dominating in the system. These calculations clearly indicate the importance of carbonate chemistry on U(VI) speciation. UO_2^{2+} phosphate complexes [UO_2HPO_4 (aq) and $UO_2PO_4^-$] could be important in aqueous systems with a pH between 6 and 9 when the total concentration ratio $PO_4^{3-}/CO_3^{2-}> 0.1$ [9]. Complexes with sulfate, fluoride, and possibly chloride are potentially important uranyl species where concentrations of these anions are high. Therefore, natural water systems, complexes with chloride, sulfate and phosphate were relatively less important. However, their stability is considerably less than the carbonate and phosphate complexes [10]. Organic ligands will also play important role in uranium aqueous speciation. The un-complexed uranyl ion has a greater tendency to form complexes with fulvic and humic acids than many other metals with a double positive charge [11]**.** This has been attributed to the greater "effective charge" of the uranyl ion compared to other divalent metals. The effective charge has been estimated to be about +3.3 for U(VI) in UO_2^{2+}. This revealed that, relative concentrations of hydroxide, carbonate and dissolved organic material determine the aqueous speciation of U(VI) in ground water. Stability/ formation constant shows that tendency for U^{4+} to form humic or fulvic-acid complexes is less than its tendency to hydrolyze or form carbonate complexes [11]. Dissolution, precipitation and co-precipitation have a much greater effect on the concentrations of U(IV) than on the concentration of U(VI) in ground waters. In general, these processes are less effective in controlling the concentration of U(VI) in oxygenated ground waters far from a uranium source. Near a uranium source, or in reduced environments, these processes tend to become increasingly important and several (co) precipitates may form depending on the environmental conditions [3, 12]**.** Carnotite, a U(VI) mineral, is found in the oxidized zones of uranium ore deposits and uraninite, a U(IV) mineral, is a primary mineral in reducing ore zones [3]**.** The best way to model the concentration of precipitated uranium is not with the Kd construct, but through the use of solubility.

1.3. Sorption and Desorption of Uranium

Dissolved uranyl concentrations at solid (soil/ sediment/ Mineral/ clay)-water interface will likely be controlled by cation exchange and sorption processes. It may adsorb onto clays [13, 14] organics [15-17] and oxides [18, 19]. Sorption studies at different ionic strength indicate that sorption decreases with increase in ionic strength which attributes to competition between the uranyl ions with competing cations for exchange sites. Not only will other cations dominate over the uranyl ion in competition for exchange sites, but carbonate ions will form strong soluble complexes with the uranyl ion, further lowering the activity of this ion while increasing the total amount of uranium in solution [20].

Some of the sorption processes to which uranyl ion is subjected are not completely reversible. Oxides of iron and manganese act as a somewhat irreversible sink for uranium in soils [18, 19] Uranium bound in these phases is not generally in isotopic equilibrium with dissolved uranium in the same system, suggesting that the reaction rate mediating the transfer of the metal between the 2 phases is slow. Naturally occurring organic matter is another possible sink for U(VI) in soils and sediments. The mechanisms by which uranium is sequestered by organic matter have not been worked out in detail but plausible mechanism involves adsorption of uranium to humic substances through rapid ion-exchange and complexation processes with carboxylic and other acidic functional groups [17, 21-24]. These group scan form stable complexes coordinate with the uranyl ion by displacing waters of hydration. A process such as this probably accounts for a significant fraction of the organically bound uranium in surface and subsurface soils. In some cases sedimentary organics may act to reduce dissolved U(VI) species to U(IV) [25]. Uranium sorption to iron oxide minerals and smectite clay has been shown to be extensive in the absence of dissolved carbonate [13, 18, 26]. A substantial reduction in sorption takes place in the presence of carbonates and dissolved organic matters [18, 26]. Aqueous pH plays major role in U(VI) sorption onto solids by influencing sorption uranium speciation and modifying the surface of sorption medium. Most of the sorption studies reported in the literature are highly specific, such as sorption on clay minerals, iron oxides or any synthetic adsorbent, where study of different parameters effect are easy whereas study on heterogeneous surface such as soil is very complicated.

1.4. Uranium Toxicological Profile

Biological effects of uranium are very similar to other heavy metals (Pb, Hg, Cd) and identified as a nephrotoxine. Its nephrotoxic effects are more likely due to its chemical properties rather than its radioactivity, although ingested uranium may have a radiological effect on other tissues of deposition [27]. In general the chemical toxicity of soluble uranium compounds can even surpass the potential radiotoxic effects. The public may be exposed to low level of uranium by inhalation or through the diet. It may be also introduced into drinking water supplies through the mining and milling of uranium ores [28]. Along with chemical toxicity, bio kinetics and metabolism of uranium, including its toxic effects on kidney function, are well established. However, there is scarcity of published observations on uranium-induced reproductive and developmental toxic effects [29]. The latest experimental studies in mammals have demonstrated that during pregnancy, maternal stress may enhance the metal-induced adverse effects on embryo/fetal and postnatal development [30]. In addition to kidney brain could also be a potential target organ after uranium exposure. Central effects were observed, even though uranium levels in brain were very low [31]. Many isolated studies were published on the mechanism for the toxic effects of uranium at moderate to high acute doses on experimental animals. However, from the ethical point of view, only a few works were done on the bio-effects of chronic uranium intakes by human [32]. The radiological hazard of depleted uranium is less than that from natural and enriched uranium. Excess inhalation exposure to insoluble uranium compounds, can lead to increased cancer risk due to internal exposure to radioactivity. In contrast, insoluble compounds are poorly absorbed from the gastro-intestinal tract (GIT), hence generally have low toxicity [28, 33, 34]**.** The renal and respiratory effects from exposure to uranium by humans and animals are usually attributed to its chemical properties (chemotoxicity), whereas theoretically potential excess cancers are usually attributed to its radiation properties [35-37]. In general, large doses of ionizing radiation have the actual or theoretical potential of being teratogenic, carcinogenic and mutagenic. DNA has been found to be the most radiosensitive biological molecule, and ionizing radiation can damage individual chromosomes. The main result from low level ionizing radiation exposure is the potential damage of DNA or fragmentation. Practicable cells repair the damage but these errors can result in production gene mutation or chromosomal aberrations. However, animal studies indicate that there is no observable damage to the biological system below certain levels of exposure [38-40]. The recent studies on animals suggest that large exposure to ionizing radiation can both initiate and promote carcinogenesis, and interfere with reproduction and development [38-40]. The most sensitive indicator of uranium toxicity to mammals is nephrotoxicity. While acute high level exposure to uranium compounds can clearly cause kidney diseases in human beings, the evidence for similar toxicity as the result of long-term lower level occupational exposure have not noted an increase in deaths from uro-genital or renal diseases following occupational exposure to uranium [41, 42]. Most studies of respiratory diseases reported for uranium involve non cancerous damage of alveolar epithelium cell, characterized by interstitial inflammation of the alveolar epithelium leading eventually to serious diseases, which reduce respiratory function of lungs [37, 43]. Biogenetics of uranium mainly depends on the chemical form administrated or the route of exposure. On the other hand, its uptake and retention by the kidney and skeleton is a function of age, gender and the mass of uranium ingested [44]. The human body naturally contains approximately 56 μg of uranium, 32 μg (56%) are in the skeleton, 11 μg in muscle tissue, 9 μg in fat, 2 μg in blood and less than 1 μg in lung, liver and kidneys [45]. Absorption of uranium is low by all exposure routes (inhalation, oral and dermal). Absorption of inhaled uranium compounds takes place in the respiratory tract via transfer across cell membranes. The deposition of inhaled uranium dust particles in the lungs depends on the particle size and its following absorption used to be effected by its solubility in biological fluids. Estimates of systemic absorption from inhaled uranium-containing dusts in occupational settings based on urinary excretion range from 0.76 to 5%. Gastrointestinal absorption of uranium can vary from < 0.1 to 6% depending on the solubility of the uranium compound. Studies in volunteers indicate that approximately 2% of the uranium from drinking water and dietary sources is absorbed in humans. Another comprehensive review shows that the absorption is 0.2% for insoluble compounds and 2% for soluble hexavalent compounds [46-48]. Concerning dermal absorption, toxicity experiments in animals indicate that water soluble uranium compounds are the most easily absorbed ones. Once in the blood, uranium is distributed to the organs of the body. U in body fluids generally exists as the uranyl ion complexed with anions such as citrate and bicarbonate.

Uranium preferentially distributes to bone, liver and kidney. Half-times for retention of uranium are estimated to be 11 days in bone and 2 to 6 days in the kidney.

1.5. Issues Related to Uranium in World

There are strict regulatory policies for the management of radioactive waste, with international standards, guidelines and recommendations (from the International Atomic Energy Agency). However, during the early development civil applications of nuclear power and of military, statutory regulations were weaker and poor working practices resulted in the contamination of many sites of world. Controlled discharges and accidental leakage from plant buildings, waste storage vaults, underground tanks, shallow unlined burial trenches and nuclear weapon tests released radionuclides into the environment [49, 50]. Their subsequent migration through the surrounding environment has resulted in a significant legacy of ground waters, soils and sediments contaminated with complex mixtures of radionuclides [51]. Uranium is present in the environment as a result of discharges from the nuclear industries, leaching from natural deposits, releases from mill tailings, combustion of coal, other fuels and the use of phosphate fertilizers. U existing in soil can be dissolved in solution, or ion exchanged in reaction, complex with soil organics or precipitate as pure or mixed solids. They can move into the water, air and the food supply. The immobility of uranium in upper most soil layers represents a problem for environment and human health, since they can be easily integrated in the food chain. Consequently, the major part of radionuclides released into the environment will finally accumulate in either the upper layer of soils or interstitial system of sediments in aquatic systems. As a consequence, a risk for ecosystems, agro-systems and health could be induced. In particular, uranium mining and milling have caused enormous environmental effect by means of abandoned waste accumulation and improper disposal of the radioactive material, waste dump after uranium extraction, especially in the last 60 years. Large amounts of uranium-containing (both high and low-level) waste are generated from activities such as fuel fabrication, fuel reprocessing, research and development (R&D). All these negative impacts influenced the quality of the environment and affect mainly surface and ground waters, soils and simultaneously polluted great areas of land and endangered the catchments of drinking water. Uranium generates an important issue against public perception on the risk that the environmental contamination poses to the environmental and human health [52]. Therefore, it is strongly evident that the contamination caused by uranium has negative biological effects on important groups of the soil food web [53].The potential risk of uranium in soil contamination is a global problem about every country can be affected by one or more activities mentioned above. For a long period of time uranium was leached commercially in a large number of deposits using different *in situ* technologies [54-56], either alkaline leaching using solutions containing carbonate and bicarbonate, or acid leaching. The solubility of uranium in soil is dependent on several factors such as: pH, redox potential, soil texture, organic and inorganic compounds, temperature, moisture and microbial activities [57]**.** Several years ago, all commercial-scale operations for uranium leaching were stopped due to a complex of different political, economic and environmental reasons [58]. However, regardless of some preventive and remedial actions during the uranium recovery, many natural ecosystems were heavily contaminated with radioactive elements, mainly through the seepage of acid drainage waters [59-61]. Such waters are still a persistent environmental problem for many abandoned mine sites, while soils around the water flow path are polluted with radioactive elements becoming unsuitable for agricultural use. Countries (e.g. Canada, Germany) where the annual rate of precipitation is higher than the evaporation rate uranium tailing are frequently close to groundwater that connects with creeks, rivers and lakes. Therefore, leaching of uranium can contaminate large volumes of water followed by sediment. In countries with arid to semi-arid weather (e.g. Australia, western USA) groundwater contamination is a serious problem as well because of the limited quantities of water available for aquatic fauna, for irrigation and as drinking water [62]. Inappropriate conditioning and disposal of mill tailings waste permit the contamination to spread into soil, sediment, water bodies. Under aerobic and anaerobic conditions, dissolution or immobilization of uranium is affected or can be affected by one or more of the following processes:

a) Changes in pH and redox that result in changes of the speciation and/or oxidation state,
b) Complexation such as chelation by siderophore and other microbial products and by inorganic species such as carbonate and phosphate.
c) Change in soil and water quality parameters induced by climatic change is one of the challenging factors for today.

However, uranium is known to occur at higher levels, frequently in smaller supplies. For example, uranium concentrations of up to 700 μg/L have been found in private supplies in Canada [63] Concentrations in excess of 20 μg/L have been reported in groundwater from parts of central Australia [64, 65] and New Mexico, USA [66]. In a case study of 476 Norwegian groundwater samples, about 18% had uranium concentrations in excess of 20 μg/L [67]. A study in Finland examined a population receiving drinking-water containing uranium with a median concentration of 28 μg/L [68]. In addition to this soil and sediment of most of the Department of Energy (DOE) site of USA are heavily contaminated.

Uranium Related issue in India: As discussed in previous sections uranium is a ubiquitous element, hence it is present in all environmental matrices such as water, soil, sediment, food materials and biota. On a global basis, its concentration in soil varies from 1-5 mg/kg while in water it varies from 1-3 µg/L. Major amount of uranium for Indian nuclear power is extracted from mining operations in Jharkhand and Andhra Pradesh. These mining operations are carried out safely as prescribed by the regulatory body ensuring that there is no damage to people or environment around the mining sites.

As per *Atomic Minerals Directorate (AMD)* of India groundwater of many part of India contains high level of uranium. Maximum uranium concentration was reported for Kadappa district (5.8 mg/L), Andhra Pradesh followed by Betul (5.2mg/L) of Madhya Pradesh and Sikar (5.1 mg/L) of Rajasthan. But Uranium in groundwater issue was highlighted for Punjab in the year 2009 and concentrations in excess (*in the range of* 2–644 µg/L with a mean value of 73.1 µg/L) have been reported in groundwater. About 42% of total water samples were observed to be beyond permissible limits (~60 µg/L) of India [69].

1.6. Missing Area in Literature

All over the world, plenty of literature are available related to uranium in environment and related issues covering, geochemistry of uranium, migration of uranium in geosphere and hydrosphere (specifically near mining sites), speciation of uranium in aqueous systems, sorption of uranium onto different minerals, determination of partition coefficient (Kd) of uranium in minerals and soil of local interest, case studies related to uranium in soil, water etc. Various remediation techniques specifically recovery of uranium from contaminated soils and water by bio-reduction, bio-accumulation, bio-sorption and phyto-remediation have been extensively discussed in literature [70-71]**.** In addition to this development of analytical techniques for estimation and quantification of uranium in different environmental matrices were also well reported in literatures [72]. In India very few studies were carried out with respect to uranium in environment, which mainly focused on speciation in ground water [69]**,** chemo toxicity and radio toxicity in terms of risk analysis [73], Uranium geochemistry study by isotopic ratio analysis [74] etc.

As mentioned earlier, the major concern in the country with respect to uranium is its natural existence as observed in Punjab and many other potential areas. It is reported that the source of uranium is geogenic in nature. The observation of uranium in specific locations needs further systematic investigation. Detailed lab studies need to be carried out to understand the migration of uranium in different soil / mineral-water systems. These studies will help in understanding the influential physico-chemical processes which leads to the leaching of uranium to the ground water. The quantification of various parameters will also help in predicting the potential areas of expected uranium contamination in other parts of the country. Physico-chemical properties of both soil and water in contact will influence the kinetics of leaching of uranium and the equilibrium concentration in water system. The properties of soil include the mineralogy, particle size, anionic / cationic content and organic content. The influential properties of water include pH, ionic strength and redox potential. The prediction also needs the information regarding the long term changes in the above mentioned parameters due to build up of CO_2 content, depletion of ground water, etc. These studies will also help in safety assessment of uranium waste disposal in Near Surface Disposal Facicities (NSDF) and Deep Geological Repositories (DGR).

From environmental protection point of view migration study of uranium from soil/ minerals to aqueous phase and speciation of uranium in both the phases in terrestrial environment is a major concern. Limited studies were reported regarding the migration of uranium along groundwater pathways in terms of transport modeling and restricted to mining sites only. No study was found regarding change in speciation and migration behavior of uranium with changing environmental conditions (or climatic change) and following questions are still unanswered.

a) What is the mechanism by which uranium will remain bound to the soil or mobilized from soil or from ore minerals?

b) What will happen to speciation and mobility of uranium in contaminated soil over time scale?

c) What will be effect of changing environmental conditions (increased salinity, CO_2, soil and water parameters etc.) on mobility and speciation of uranium at soil water and ore-water interface?

d) What are the important things to be included considering future environmental conditions in safety assessment of uranium waste disposal in Near Surface Disposal Facilities (NSDF) or Deep Geological Repositories (DGR).

1.7. Objective of study

From environmental protection and assessment point of view it is very much important to study the migration of uranium in terrestrial environment especially at soil-water and mineral-water interface. Uranium may behave differently with respect to different water types, soil types and mineral types. Therefore, any change in soil/ mineral and water parameters significantly affect the behavior of uranium in terms of speciation, mobility and toxicity. Current issue of climatic change also significantly affects the soil and water physicochemical parameters, which may accelerate or de-accelerate mobility of uranium in terrestrial environment. This contamination may leads to an uncontrolled source of uranium in future. Looking at the missing area of literature and considering current environmental scenario the research work was initiated *to understand the change in migration and speciation of uranium in terrestrial environment in response to change in environmental conditions and to identify the complexities involved in the process.* Lab experiments were carried out to reveal the complexities of uranium behavior at soil-water, ore-water interface in terms of mechanism of sorption and/or desorption, factor influencing the process, energy released or absorbed during the process. In short the thesis aims to fulfill missing area of the literature and answer the question.

1.8. Scope of the Study

The scope of this work encompasses a systematic study of the behavior of uranium in terrestrial environment namely soil–water and ore–water interface with main focus on migration and speciation. Though the laboratory study is site specific in nature, it has global application since the experiments were carried out on varieties of soil types, uranium ore minerals. The experimental results will be helpful for simulating migration of uranium in future environment also. The thesis comprises,

a) Behavior of uranium at soil-water and ore-water interfaces and factors affecting the migration and speciation at the interface.

b) Prediction of behavior of uranium at soil-water interface in terms of kinetics and thermodynamics of uranium sorption, sorption mechanism, effect of soil parameters and parameter sensitivity.

c) Speciation of uranium in contaminated soil and change in speciation with time.

d) Effect of salinity, CO_2 and other soil parameters on migration and speciation of uranium at soil-water interface.

e) Role of salinity, CO_2 and water parameters on migration and speciation of uranium at ore-water interface.

Chapter 2

Experimental Methods and Techniques

2.1. Introduction

Mechanistic description of migration of uranium from solid (Soil/ Minerals) to solution (Water) phase in terrestrial environment requires an understanding of physico-chemical behavior of uranium in environment. The parameters which are needed to be addressed in a terrestrial environment include:

a. Sorption studies of uranium in varying soil types including estimation of Kd, kinetics and thermodynamics of sorption, mechanism of sorption in terms of adsorption isotherms, impact of soil parameters and water quality parameters on migration of uranium from soil to water in contact.

b. Study of aqueous speciation of uranium at soil water interface and chemical fractionation in different soil fractions.

c. Studies on the factors affecting migration of uranium at ore-water interface and change in speciation at interface.

Fitting of sorption data to different kinetic models gives idea about kinetics of sorption, fitting to isotherm models reveals the sorption mechanism. Similarly fitting of sorption data at two or more temperatures reveals the thermodynamics of sorption, which is helpful for modeling the sorption kinetics and thermodynamics. Most frequently used methodology to study sorption kinetics and thermodynamics is batch sorption method and in this thesis work batch sorption method was adopted.

Study of speciation of uranium in aqueous medium can be performed both analytical method using advanced instrumental facilities and theoretical speciation modeling (analytical method in conjunction with chemical speciation model). Among analytical ‘techniques synchrotron based techniques such as; Extended X-Ray Absorption Fine Structure (EXAFS), Near Edge X-Ray Absorption Fine Structure (NEXAFS) spectroscopies and laser based fluorescence technique: Time Resolved Laser Induced Fluorescence (TRLIF) techniques are widely used. But the limitation of synchrotron based technique is it requires high concentration (×100 ppm) of analytes (Uranium) in sample. Therefore theoretical calculation using chemical speciation modeling is most suited one at lower concentration in aqueous medium and is used in this dissertation work.

Speciation of uranium in solid phase (soil/sediment/ minerals) can be performed: a) Chemical extraction (sequential extraction and bicarbonate extract for U specially) and b) analytical methods (especially spectroscopic techniques). In analytical techniques similarly, EXAFS, NEXAFS and X-ray Photo electron spectroscopy (XPS), TRLIF are widely used. But all these techniques are not successful at low concentrations except TRLIF. Here in this work chemical extraction method along with XPS was used in some cases.

All these studies required a complete characterization of soil (or solid phase) and aqueous medium (water). Characterization soils or ore minerals involve both physical and chemical characterization. Physical characterization comprises study of mineralogical composition by means of X-ray diffraction (XRD), Textural analysis by using particle size analyzer (PSA), measurement of pH, Eh, cation exchange capacity (CEC) of the soil and ore minerals. Chemical characterization involves the measurement of major elemental composition of interest by means of Atomic absorption spectroscopy, voltammetry, CHNO-S analyzer etc. Physico-chemical characterization of aqueous medium (water) mainly involves estimation of pH, Eh and major ions and metal of interest. Concentration of major ions can be estimated by Ion-Chromatographic techniques, carbonate and bicarbonate concentration by titrimetrically. Details of the techniques used for the study are discussed in following sections.

2.2. Techniques for Soil and Mineral Characterization

2.2.1. Mineralogical Study Using X-ray Diffraction (XRD): XRD is one of the most powerful non-destructive techniques for the study of crystal structures and mineralogical studies. It is based on constructive interference of monochromatic X-rays and a crystalline material. The following equation governed by Bragg's Law relates the wavelength of electromagnetic radiation (λ) to the diffraction angle and the spacing lattice in crystalline samples, which in turn used for identification of mineral phases:

$$n\lambda=2d \sin\theta \tag{2.1}$$

An XRD pattern obtained by scanning the sample through a 2θ angle-range contains all possible diffraction directions of the lattice due to the random orientation of the sample. Position of the diffracted peaks gives information about the atoms arrangement within the crystalline compound, intensity can be used to evaluate the type and nature of the atoms and the FWHM peaks is used to determine crystalline size and micro-strain in the sample. Quantitative analysis of crystalline phases can also be performed.

Sample preparation: Sample preparation is an important aspect of soil mineralogical analysis by XRD. Preparatory procedures must be judiciously selected according to the objectives. The simplest preparation procedure is to grind the soil "as is" into a powder fine enough to mount in the focal plane of the Diffractometer. The sample preparation of soil for XRD involves the removal of interfering factors namely salts, carbonates, organic matter and amorphous iron etc. The stepwise procedure used in XRD analysis of sample is as follows:

Take about 5g of milled/ grinded, homogenized soil sample in a centrifuge tube add 50 mL of deionized water with continuous shaking and proceeds stepwise as mentioned below:

a) Removal of salt: if the EC of soil solution is in the greater then 2d Sm^{-1} wash the soil with deionized water till the EC fall down to ≤ 1dS m^{-1}. Then centrifuge and take residual soil samples for next treatment.

b) Removal of Carbonate minerals: Add 50 mL of sodium acetate (1M) of pH 5 to the soil keeping it in a water bath and stir continuously. Check for effervescence to confirm destruction of carbonates. After the bubbling stops, place the bottle in the centrifuge and centrifuge at about 1500 rpm for 5 min. Decant and discard the clear supernatant fluid. Again wash the soil at least two times with deionized water and discard the washings after centrifugation.

c) Removal of organic matter: Add approximately 20 mL of water to the soil sample remaining in the centrifuge bottle. Heat the bottle to 80°C in a water bath or on a steam table. Add approximately 1 mL of H_2O_2 to the centrifuge bottle. When the oxidation of organic matter begins, as indicated by frothing, add a few drops of acetic acid or acetone and stir constantly. Continue addition of H_2O_2 and acetic acid with stirring till frothing subsided. Wash the soil with deionized water, centrifuge and discard washings.

d) Removal of Amorphous Iron: Add about 50 mL of citrate buffer solution and heat the bottle to 75 to 80°C in a water bath. Then add approximately 1 g of $Na_2S_2O_4$ to the bottle. Stir continuously for 1 min, and then occasionally for 5 min. Add a 2 g of $Na_2S_2O_4$ and stir as described above. After 10 to 15 min, remove the bottle from the water bath and cool. Place the bottle in the centrifuge and centrifuge at about 1500 rpm for 5 min. Decant and discard the clear supernatant fluid. Then wash the soil with deionized water, centrifuge and discard washings.

Now the sample is ready for XRD analysis. Mount the sample on sample holder and take diffraction pattern. Mineralogical identification can be carried out by comparing the pattern with the mineral data library *In the current research work, for characterization of soil and mineral samples APD 2000 PRO X-Ray Diffractometer (Make GNR, Italy) is used, in which Cu Kα is used as X-Ray source. Finally identification of mineral were carried out by comparing the diffraction pattern of sample with the ICDD mineral database*

2.2.2. Textural Analysis using Particle Size Analyzer (PSA)

Particle size information is extremely important for studying the sorption kinetics and thermodynamics. There are three techniques such as: a) low angle light scattering, b) dynamic light scattering and c) photo sedimentation are available till today for PSA. Among these techniques *low angle light scattering* also called laser diffraction is most commonly used technique. From instrumentation point of view, beam from continuous wave (CW) laser, usually He-Ne laser and fiber laser is collimated and passed through the sample, where scattering from particles occurs. The beam is then focused on a detector array where scattering pattern, shown in Fig. 2.1 as a diffraction pattern, is measured. The scattering pattern then analyzed according to theoretical models to give the particle size distribution. The combination of two optimized technologies (CILAS patent) enables the instrument to cover the whole range in one single measure, without any mechanical adjustment or optical realignment. The fine particles are measured by capturing the diffraction pattern, and applying *Fraunhofer or Mie theory*. The coarse particles are measured using a real time Fast Fourier Transform of the image obtained with a CCD camera equipped with a digital processing unit (DSP).

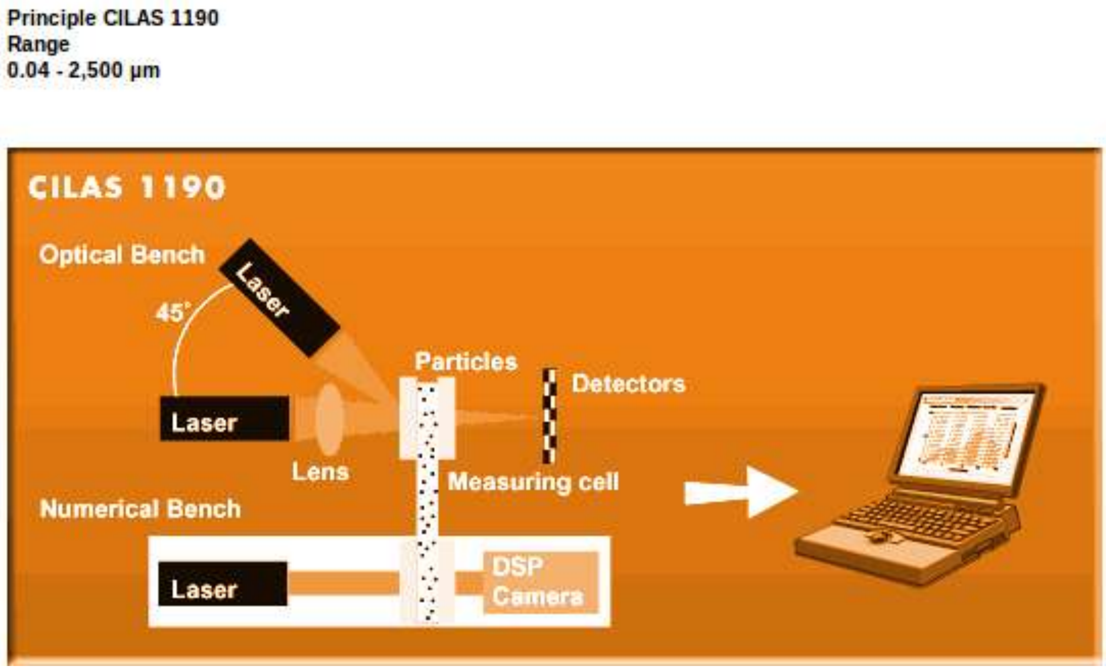


Figure 2.1. Block diagram of CILAS 1190 Particle Size Analyzer

The outcome of PSA is a particle size distribution, which nothing but the plot of the number of particles having particular value chosen quantity versus that quantity cumulative distribution representing the fraction of particles bigger or smaller than a particular size.

In this research work, Particle Size Analyzer-1190 (Make: CILAS, France) was used in liquid dispersion mode and the Fraunhofer diffraction principles were chosen for generation of particle size distribution.

2.2.3. Measurement of Soil Organic Carbon using CHNOS Analyzer

Measurement of soil organic carbon or mater (SOM) also known as natural organic matter (NOM) is very much important for sorption study. Most commonly used method for determination of organic carbon is Loss of Ignition (LOI), which involves heating the processed solid sample (soil) at 450 to 500^0 C for two hours and measure the mass loss. In the other way it can be estimated using CHNO-S elemental analyzer, which involves two steps:

a) Removal of inorganic carbon by acid treatment (1N HCl) followed by

b) Measurement of carbon using CHNOS elemental analyzer.

The analysis required high temperature combustion (900^0C) in an oxygen- rich environment, in the combustion 'C' is converted to CO_2. The combustion products are swept out of the combustion chamber by inert carrier gas such as helium and passed over heated (about 600^oC) high purity Cu. The function of Cu is to remove any oxygen not consumed in the initial combustion and to convert any oxides of nitrogen to nitrogen gas. The detection of CO_2 carried out by gas chromatographic separation followed by quantification using thermal conductivity detector (TCD).

2.2.4. Measurement of soil Cation Exchange Capacity (CEC)

The CEC of a soil is a measure of the quantity of *-ve* charged sites on soil surfaces that can retain +ve charged ions or cations by electrostatic forces. Cations retained electrostatically are easily exchangeable with cations in the soil solution so a soil with a higher CEC has a greater capacity to maintain adequate quantities of cations than a soil with a low CEC. It is one of the important soils parameter determines contaminate mobility. CEC is normally expressed in one of two numerically equivalent sets of units: meq/100 g (milli equivalents of charge per 100 g of dry soil) or cmolc/kg (centi-moles of charge per kilogram of dry soil). There are various methods are available in literature for soil CEC measurement, but method proposed by *Chapman, 1965 and Bower et al.,1952,* is most widely used [75,76]. Steps involved in CEC estimation is as follows.

a. Take 4 g of soil in a 50 mL falcon tube then add 33 mL of the 1M NaOAc (1 M, pH 7) shake in a mechanical shaker for 10 minutes and centrifuge it until the supernatant become clear.
b. Decant the supernatant and repeat the step ‘a’ at least two more times.
c. Add 33 mL of isopropyl alcohol to residue in the tube shake in a mechanical shaker for 10 minutes and centrifuge it until the supernatant become clear. Repeat the steps at least 2 times.
d. Add 33 mL of NHOAc solution, stopper the tube, shake it in a mechanical shaker for 5 min and centrifuge it until the supernatant liquid is clear. Decant the washing into a 100-mL volumetric flask. Repeat the steps for two more times.
e. Dilute the combined washing to the 100-mL mark with ammonium acetate solution and determine the sodium concentration by atomic absorption, emission spectroscopy, or an equivalent method

Where Na^+ is reported in mg (Na^+)/L:

$$\text{CEC (cmolc/kg)} = (\text{Na}^+ \text{ in extract}) / 23 \tag{2.2}$$

Cation Exchange Capacity (CEC) was calculated using following empirical relation described by *Breeeuwsma,* 1986 [77].

$$\text{CEC (meq/100g)} = 0.7\ (\%\text{clay}) + 3.5\ (\%\ \text{Organic carbon}) \tag{2.3}$$

2.2.5. Estimation of Fe and Mn

Fe and Mn play a major role in migration of uranium in terrestrial environment, hence it is very much important for sorption/ migration study. Various techniques are used for estimation of Fe and Mn in soil such as AAS, ICP-OES, ICP-MS and XRF etc. In the current research work AAS was used, which is a destructive techniques and require sample in liquid form. Hence estimation of Fe and Mn in soil involves two steps:

a) Acid Digestion of soil or minerals to bring it to liquid form

b) Analytical estimation

Conventionally digestion of soil or any mineral samples were carried out by taking soil in mixture of HNO_3, HF and H_2O_2 (3:2:1) heating on hotplate till complete digestion or destruction of matrix (Per chloric acid also used). After complete dissolution liquid aliquot need to be diluted to desired volume using 0.25% HNO_3 followed by analysis using either of the techniques discussed above. Now days Microwave assisted acid digestion is most widely used, since the technique is efficient, low chemical and least time consuming.

In the present study microwave assisted acid digestion was carried out using Mile stone s. r. l Ethos 1, followed by analysis using AAS calibrated for Fe and Mn.

2.3. Physico-Chemical characterization of Aqueous Phase

Physico-chemical characterization of water/aqueous phase in contact with soil/ minerals is very important since it controls the behavior of U or any metals at soil/mineral-water interface. The important parameters defines the physiochemical properties of aqueous phase are, pH, Eh, alkalinity major ions (Na^+, K^+, Mg^{2+} , Ca^{2+} , F^-, Cl^- , NO_3^-, SO_4^{2-} and PO_4^{3-}). In the present study pH and Eh of water samples were directly measured using Aquaread-1000 meter, whereas in case of soil and ore minerals, Soil/Mineral to water slurry 1:10(g/mL) was prepared followed by measurement of parameters. Major ions; Na^+, K^+, Mg^{2+} , Ca^{2+} , F^-, Cl^- , NO_3^-, SO_4^{2-}, PO_4^{3-} were estimated using ion-chromatographic techniques whereas alkalinity (CO_3^{2-} and HCO_3^-) was estimated titrimetrically using Auto tritrator (798 MPT Tritrino, Metrohm)

2.3.1. Ion chromatography technique for estimation of Na^+, K^+, Mg^{2+} , Ca^{2+} , F^-, Cl^- , SO_4^{2-}, PO_4^{3-}:

Ion chromatography, a form of liquid chromatography measures concentrations of ionic species by separating them based on their interaction with a resin (In column). Ionic species separate differently depending on species type and size. Sample solutions pass through a pressurized chromatographic column where ions are absorbed by column constituents. As an ion extraction liquid, known as eluent, runs through the column, the absorbed ions begin separating from the column. Based on retention time ions get separated and identified. Ionic concentrations in the sample estimated based on peak area of species.

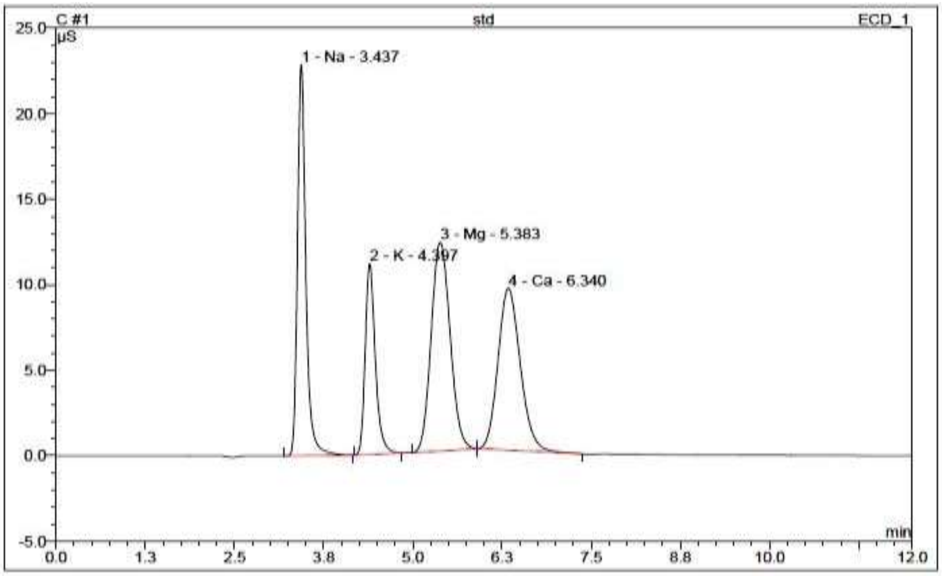


Figure 2. 2. Chromatogram of major cations using 5.0 mg/L of mixed cations standard solution

In the present work *Reagent Free ion chromatography system* (RFIC, DIONEX ICS-2100) was used. The major cations were estimated under following conditions:

a) Sample Volume: 25 µL Loop,

b) Column: Ion Pac CG17, CS17, 4-mm ,

c) Eluent and flow rate: 6 mM MSA, 1.0 mL/min,

d) Temperature: 30°C,

e) Detection: Cation Self-Regenerating Suppressor- ULTRA Auto Suppression - Recycle Mode,

The instrument was calibrated and standardized with the stock solution of ultra-pure Fluka (Switzerland) standards for cations (5 mg/L). A Typical chromatogram of major cations (Standard Concentrations 5.0.mg/L) is presented in Fig. 2.2.

The major anions were estimated under following conditions:

a) Sample Volume: 25 µL Loop,

b) Column: Ion Pac AG17, AS17, 4-mm,

c) Eluent and flow rate: 14 mM KOH, 1.0 mL/min,

d) Temperature: 30°C,

e) Detection: Anion Self-Regenerating Suppressor- ULTRA Auto Suppression - Recycle Mode

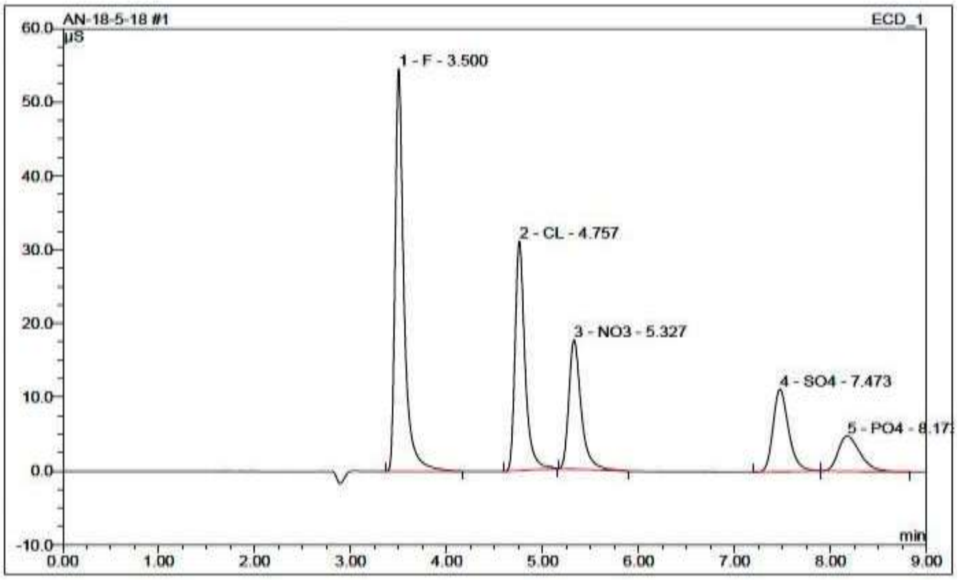


Figure 2. 3. Chromatogram of major cations using 5.0 mg/L of mixed cations standard solution

The instrument was calibrated and standardized with the stock solution of ultra-pure Fluka (Switzerland) standards for anions (5 mg/L). A Typical Chromatogram of major anions (Standard Concentrations 5.0 mg/L) is presented in Fig. 2.3.

2.3.2. Measurement of alkalinity titrimetrically

Alkalinity is the measure of how much acid it takes to lower the pH of a water sample enough to convert all bicarbonate (HCO_3^-) and carbonate (CO_3^{2-}) to carbonic acid (H_2CO_3). Although total alkalinity is equal to the stoichiometric sum of all bases in solution, it is mainly considered due to carbonates and bicarbonates. To measure alkalinity, water sample is titrated with an acid to an end point at which carbonate is converted to bicarbonate and bicarbonate is converted to carbonic acid. Based on equilibrium chemistry of CO_3^{2-} and HCO_3^- in natural water system CO_3^{2-} is the dominating species controlling the alkalinity of the system above pH 8.3 to 10, whereas 4.2 to 8.3 is due to bicarbonate. , volume (V1) of acid consumed to achieve pH 8.3 used for calculation of CO_3^{2-} concentration whereas, volume (V2) required to achieve pH 4.2 from 8.3 used for HCO_3^- calculation.

In the current study acid base (0.02N HCl) titration was carried out using Metrohm make auto-tritrator. Volume of acid consumed to achieve pH 8.3 (V1) and then 8.3 to 4.2 (V2) automatically registered, which is used for calculation of concentration of CO_3^{2-} and HCO_3^- using following equation

$$Alkalinity(mg/L)asCaCO_3 = \frac{\mathrm{T\,(V1/V2)} \times N \times E \times 1000}{V} \qquad (2.4)$$

Where,

T-Titre value in ml (V1: for Carbonate, V2: for Bicarbonate)

N - Normality of standard sulphuric acid (0.02N)

E - Equivalent weight of $CaCO_3$ (50)

V - Volume of sample taken in mL

2.4. Analytical method for Uranium estimation

Uranium is one of few naturally occurring radionuclides and can be determined by direct radiometric techniques. These techniques, however, are limited in their applicability due to the low specific activity and low concentrations at which it is typically found in nature. Among the most frequently used techniques belong: spectrophotometry, radiometric methods (α - spectrometry, γ- spectrometry), techniques of neutron activation analysis atomic spectrometric techniques (AAS - atomic absorption spectrometry, AES - atomic emission spectrometry, ICP - AES-inductively coupled plasma -atomic emission spectrometry, X - ray fluoresce), mass spectrometry and numerous electrochemical methods. ICP-MS is an interesting alternative method for uranium determination. This method has several advantages, e.g. short analysis duration, low detection limits (ng/L), low sample consumption and minimum of spectral interferences [78]. Voltammetric techniques are known to show unique advantages both economical (low initial and running costs) and strictly analytical (the ability to determine low levels of metal in different matrixes). In particular, stripping techniques are perfectly suited for trace and ultra-trace metal determination [79]. Adsorptive cathodic stripping voltammetry (AdCSV) is based upon adsorptive accumulation of metal ion complex with a suitable ligands (mordant blue, catechol, oxine, cupferron, chloranilic acid (CCA), aluminon, PAR and salicylidenimine) [80]. Determinations of uranium in solid matrix (soil) except γ- spectrometry and NAA are destructive techniques and require complete digestion of soil using acid (HF, HNO_3 and HCl). *In this work both Voltammetric and Fluorimetry technique were used for determination of uranium, voltammetric techniques preferable used for determination of uranium in digested soil and ore mineral sample.*

2.4.1. Voltammetric determination of U using chloranilic acid:

Uranium determination using chloranilic acid involves; pre-concentration of U(VI)-CCA complex at 50 mV at the hanging mercury drop electrode (HMDE) at a pH of about 1.8 to 2.4. The determination of uranium (VI) is specific and selective, as the positive deposition potential means that other metal-CAA complexes or organic matrix components of natural waters are either not adsorbed at all or hardly adsorbed on the HMDE. All measurements were carried out in the differential pulse (DP) mode using pulse amplitude ranged from −0.6 to −0.2 V, a pulse time of 30 ms and a potential step of 4 mV. The concentration of the chloroanilic acid solution was 1×10^{-4} mol/L. The pH of the sample in the reaction vessel was adjusted at 2 using supra-pure 8N HNO3 and the method can be used very complex matrices with low detection limit of 0.1 µg/L [80].

2.4.2. U determination using Fluorimetry:

Fluorimetry technique using fluran (or Phosphate buffer at pH 7) is also one of the best methods for determination of uranium in water samples and to achieve the low detection limits (detection limit of 0.1 µg/L). The technique involves following steps:

a) Addition of phosphate buffer (pH 7) leads to preferential formation of single species, uranyl phosphate.
b) This is excited by a light source in the range of 371 to 390 nm. The excited uranyl phosphate emits luminescence at 496, 516 and 540 nm.
c) Intensity of peaks determines the concentration of uranium in the solution.

In this work uranium analyzer UA-2 (Quantalase, Indor, India) was used for determination of uranium in water samples.

2.5. X-Ray Photoelectron Spectroscopy (XPS)

XPS is one of most advanced techniques used for surface speciation studies. However, interpretation of XPS spectra for uranium species requires a thorough understanding of the spectra. The U 4f peaks are the strongest and most resolved peaks in the XPS spectrum of U [81]. The U 4f peaks are commonly used to analyze the valence of U on the surface of materials, and, due to their intensity, play an important role in the characterization of adsorbed aqueous uranium species on the any surface [82-85]. The U $4f_{7/2}$ and $4f_{5/2}$ peaks occurs around 380 and 390 eV respectively. The spin–orbit interaction separates these two levels by around ~ 11.0 eV for uranium minerals. The U $4f_{7/2}$ peak position may vary as dictated by the crystal structure and under the influence of nearest-neighbor ions. The chemical shift of the U4f peaks due to the valence of uranium has been extensively described in the literature. Shake-up satellites are small peaks that are produced by photoelectrons that have lost part of their initial energy to a valence-band electron. When a core-level electron is expelled, an electrostatic potential is experienced by the valence electrons. They are excited to a higher empty orbital or are knocked off to the continuum almost at the same time. The energy difference between the ground state (g.s) and the higher orbital defines the difference in position between the satellite peak and the photoelectron peak. The positions of the satellite peaks are also function of the valence of the element and the number of its nearest-neighbor ions. For uranium, both U4f core-level peaks show satellites at higher binding energies: 6–7 eV for U^{4+} , 7.8–8.5 eV for U^{5+} and 4 and 10 eV for U^{6+} [81, 84, 86-88]. Some of the satellites of the $U4f_{7/2}$ peak are buried in the intense $U4f_{5/2}$ peak or may appear as a shoulder, which may lead to incorrect interpretation regarding the occurrence and fractions of the different bands. Hence, satellites of the U $4f_{5/2}$ peak and the U $4f_{7/2}$ peak are normally not considered for spectral interpretation, and one instead uses the satellites of the U $4f_{5/2}$ peaks and the shape of the $U4f_{7/2}$ peak for the determination of the U^{6+}, U^{5+} and U^{4+} bands.

In this work all XPS spectra were collected on an ESCA apparatus (Make SPECS GmbH) in constant analyzer energy mode. An Al Kα source of photons (1486.6 eV) was used for both survey and narrow scans. The powdered samples in form of pellets were fixed on sample holder with double sided carbon tape before being placed in the analysis chamber (10^{-10} mbar vacuum).

2.6. Sorption Study

2.6.1. Batch method:

Batch method is frequently used to study sorption kinetics and thermodynamics along with to study the equilibrium distribution of contaminant (radionuclides) between the solid phase and the aqueous phase under well-defined experimental conditions of temperature, pH, ionic strength and solid/liquid ratio.

The sorption percentage (S %) can be expressed as:

$$S\% = \frac{C_0 - C_e}{C_0} \times 100 \qquad (2.5)$$

Where, C_0 and C_e are initial and equilibrium concentration of contaminant in aqueous phase.

Partitioning is expressed by the distribution coefficient, Kd (L/kg), defined as:

$$Kd = C_S/C_L \qquad (2.6)$$

Or

$$Kd = \frac{C_0 - C_e}{C_0} \times \frac{V}{M} \qquad (2.7)$$

Where,

Cs is the concentration of the metal ion per Kg of the solid (mg/kg)

C_L is the concentration of the metal ion present per ml of the aqueous phase (mg/L)

C_0 and C_e are initial and equilibrium concentration of contaminant in aqueous phase.

V is volume of aqueous phase

M is mass of adsorbent (soil)

Another parameter which is more frequently used in sorption study is sorption capacity, which measure how much contaminant can hold by a particular adsorbent is known as sorption capacity (q_x) and defined as:

$$q_x = (C_0 - C_x) \times \frac{V}{M} \tag{2.8}$$

Where, ‘x’ can be t (Sorption capacity at particular time t), e (sorption capacity at equilibrium) and max (maximum sorption capacity).

Study of kinetics, even in homogeneous system is complex, so attempt to study in heterogeneous system such as soil and sediment, difficulties get magnified. This is largely due to complexities of soil or sediment which is made of mixture of organic and inorganic minerals and of different particle sizes. Both transport processes and chemical reactions can affect the reaction rates in subsurface environment. Transport process includes, a) transport in solution b) transport across a liquid film at the particle/liquid interface (Film diffusion) c) in liquid filled macropores, d) particle diffusion etc.

There are two important reasons for investigating the kinetics is;

a) To determine how rapidly reactions attain equilibrium and

b) To infer information on reaction mechanisms.

Determination of kinetics of sorption is a two-step process, first is monitoring the sorption at different time intervals then 2nd is fitting the sorption data with different sorption kinetic models. The kinetic model to which the data is fitted well is considered as the kinetics of sorption. As per time is concerned sorption can take place from micro- second to months, so fast sorption process (micro- scale process) can't be monitored by batch processes. In general sorption of metals on any solid sorbent follow either first order or second order reaction, since the sorption is expressed in terms of adsorption capacity (q_x), now days it is named as pseudo-1st order or pseudo-2nd order kinetics. The details of sorption kinetics are explained in chapter 3.

2.6.3. Thermodynamic of sorption

In order to evaluate the risks that may be associated with the contamination of soil with uranium disposal of waste, thermodynamic parameters of sorption need to be investigated. The thermodynamic parameters such as change in enthalpy (ΔH), free energy (ΔG) and entropy (ΔS) will provide idea about spontaneity of reaction, endothermic or exothermic along with predicting the mechanism of sorption also.

The most general equation for ΔG calculation is:

$$\Delta G=\Delta H-T\Delta S \tag{2.9}$$

For spontaneous reaction ΔG need to be negative and whether the reaction is exothermic or endothermic, that can be predicted from the ΔH of the reaction (exothermic: ΔH=-ve and endothermic ΔH=+ve). These thermodynamic parameters can be determined from the thermodynamic equilibrium constant, Kd (or the thermodynamic distribution coefficient) which is defined as:

$$K_d = \frac{a_s}{a_e} \tag{2.10}$$

Where, 'a_s' is activity of adsorbed U on soil and 'a_e' is activity of U in solution at equilibrium.

Now ΔG^0 (kJ mol^{-1}) at temperature T (in Kelvin) can be calculated as follows:

$$\Delta G^0 = -RT \ln K_d \tag{2.11}$$

Where, R is the gas constant (8.314 $Jmol^{-1}K^{-1}$), T is the temperature in Kelvin.

Moreover, since the adsorption isotherms have been measured at two temperatures, the heat of adsorption can be calculated. The temperature dependency of distribution coefficient (kd) obeyed the van't Hoff equation which can be written in the form of ΔH^0

$$\ln \frac{K_{d1}}{K_{d2}} = \frac{\Delta H}{R}\left[\frac{1}{T_2} - \frac{1}{T_1}\right] \tag{2.12}$$

Where, K_{d1} and K_{d2} are the distribution coefficients at two temperatures T_1 and T_2 (in Kelvin) respectively.

Standard entropy change, ΔS^0 (J mol^{-1} K^{-1}) can be calculated from following equation

$$\Delta S^0 = \left(\frac{\Delta H^0 - \Delta G^0}{T}\right) \tag{2.13}$$

2.6.4. Sorption Equilibrium and Isotherm

Sorption equilibrium (the ratio between the adsorbed amount with the remaining in the solution) is established when an adsorbate containing phase has been contacted with the adsorbent for sufficient time, with its adsorbate concentration in the bulk solution is in a dynamic balance with the interface concentration [89, 90].

In general, an adsorption isotherm is an invaluable curve describing the phenomenon governing the retention (or release) or mobility of a substance (Uranium) from the aquatic environments to a solid-phase (soil) at a constant temperature and pH [91, 92]. Typically, the mathematical correlation, which constitutes an important role towards the modeling analysis, operational design and applicable practice of the adsorption systems, is usually depicted by graphically expressing the solid-phase against its residual concentration.

Over the years, a wide variety of equilibrium isotherm models (Freundlich, Langmuir, Brunauer–Emmett–Teller, Dubinin–Radushkevich, Temkin, Toth, Koble–Corrigan, Redlich–

Peterson, Sips, Khan, Hill, Flory–Huggins and Radke–Prausnitz isotherm) have been formulated in terms of three fundamental approaches [93]. Kinetic consideration is the first approach to be referred. Hereby, adsorption equilibrium is defined being a state of dynamic equilibrium, with rate of adsorption and desorption are equal [94]. Whereas, thermodynamics, being a base of the second approach, can provide a framework of deriving numerous forms of adsorption isotherm models [95], and finally potential theory, is the third approach, usually conveys the main idea in the generation of characteristic curve [96]. However, an interesting trend in the isotherm modeling is the derivation in more than one approach, thus directing to the difference in the physical interpretation of the model parameters. Details of isotherm models used in the study are described in chapter 3.

2.7. Speciation study

2.7.1. Fractionation of uranium in soil and sequential extraction

In soil, uranium may be found in one or more of several "pools" of the soil, as follows:

a. Dissolved in the soil solution or occupying exchange sites on inorganic soil constituents *(Exchangeable Fraction)*
b. Specifically adsorbed on inorganic soil constituents *(Carbonate fraction)*
c. Associated with insoluble soil organic matter *(Organic fraction)*
d. Associated with oxides and hydroxide of Fe and Mn (*Fe/Mn-Oxide fraction*)
e. present in the structure of secondary and primary minerals *(Residual fraction)*

Sometimes the last fraction is again divided to two fractions in terms of bound to *secondary minerals* and *bound to primary minerals.* When metal introduced into the environment through human activities, metals are associated with the first four pools. Native metals may be associated with any of the pools depending on the geological history of the area. Metals bound to exchangeable fraction are most bio-available fraction. There are several methods available in literature for sequential extractions, but we followed method prescribed by Schultz et al. (1998), which involves following steps [97].

Exchangeable fraction: Take 2 g of processed, homogenized soil samples in a 50 mL centrifuge tube then add 20 mL of 0.4 M $MgCl_2$ and shake for 1 h followed by centrifuged at 3000 rpm for 10 min. Collect supernatant (F1) and take the residue for 2nd step after washing with 5 mL of $MgCl_2$. Add the washing with supernatant.

Carbonate fraction: Treat the residues from first step with 20 mL of 1 M NaOAc in 25 % acetic acid (pH=5). Shake for 2 h followed by centrifuged at 3000 rpm for 10 min. Collect the supernatant (F2) and take the residue for 3rd step after washing with 5 mL of 1 M NaOAc. Add the washing with supernatant.

Organic fraction: Treat the residues from 2nd step with 20 mL of 5-6% NaOCl and heat on a hot plate at about 80 degree for 3h with continuous stirring. Then cool it to room temperature followed by centrifuge at 3000 rpm for 10 min. Collect the supernatant (F3) and take the residue for next step after washing with 5 ml NaOCl.

Fe-Mn oxides fraction: Treat the residues from 3rd step with 0.04 M $NH_2OH.HCl$ (pH 2) and heat with continuous stirring for 5 h. Then cool it to room temperature, centrifuge at 3000 rpm. Then collect the supernatant (F4) and take the residue for next step after washing with 5 mL of 0.04 M $NH_2OH.HCl$ and add the washing with F4.

Acid leachable &Residual fraction: Treat the residues from 4th and carry out microwave assisted acid digestion followed by evaporation on hot plate. Finally collect the aliquots and dilute it to 25 mL using 0.25% nitric acid.

Note: All the supernatant collected in each steps along with washings were filtered using 0.45micron filter paper before analysis.

2.7.2. Aqueous Chemical Speciation

Chemical speciation is nothing but the distribution of an element (uranium in our case) amongst chemical species in a system and it is *very much important for understanding bioavailability, chemical toxicity, remediation, environmental fate and transport*. Despite the central importance of knowing the full speciation of a chemical in order to predict its behavior in a system, it is generally not possible to determine a speciation analysis using analytical techniques alone. Most techniques are focused on detection of free metal ion concentrations [98-100] or total metal concentrations [101]. Direct speciation measurement using traditional analytical methods requires significant complexity and generally hyphenated techniques [102-104]. As already discussed, because environmental concentrations of most metals of interest are low, and because many relevant forms of metals cannot be measured directly, analytical techniques often are not effective for determining overall speciation [105]. Thus chemical speciation determination generally based on utilizing analytical techniques in conjunction with chemical speciation models. Chemical speciation models rely on *mass balance* and *thermodynamics* to determine the concentration of each species that contains a given component. Chemical speciation is usually predicted with thermodynamic expressions, because the reactions involved take place in the bulk aqueous phase and are generally fast. Hence, these models rely on the local equilibrium assumption and on experimentally determined reaction constants. The local equilibrium assumption (LEA) states that, because aqueous-based reactions are reversible and generally rapid compared with other system processes, they may be assumed to reach equilibrium.

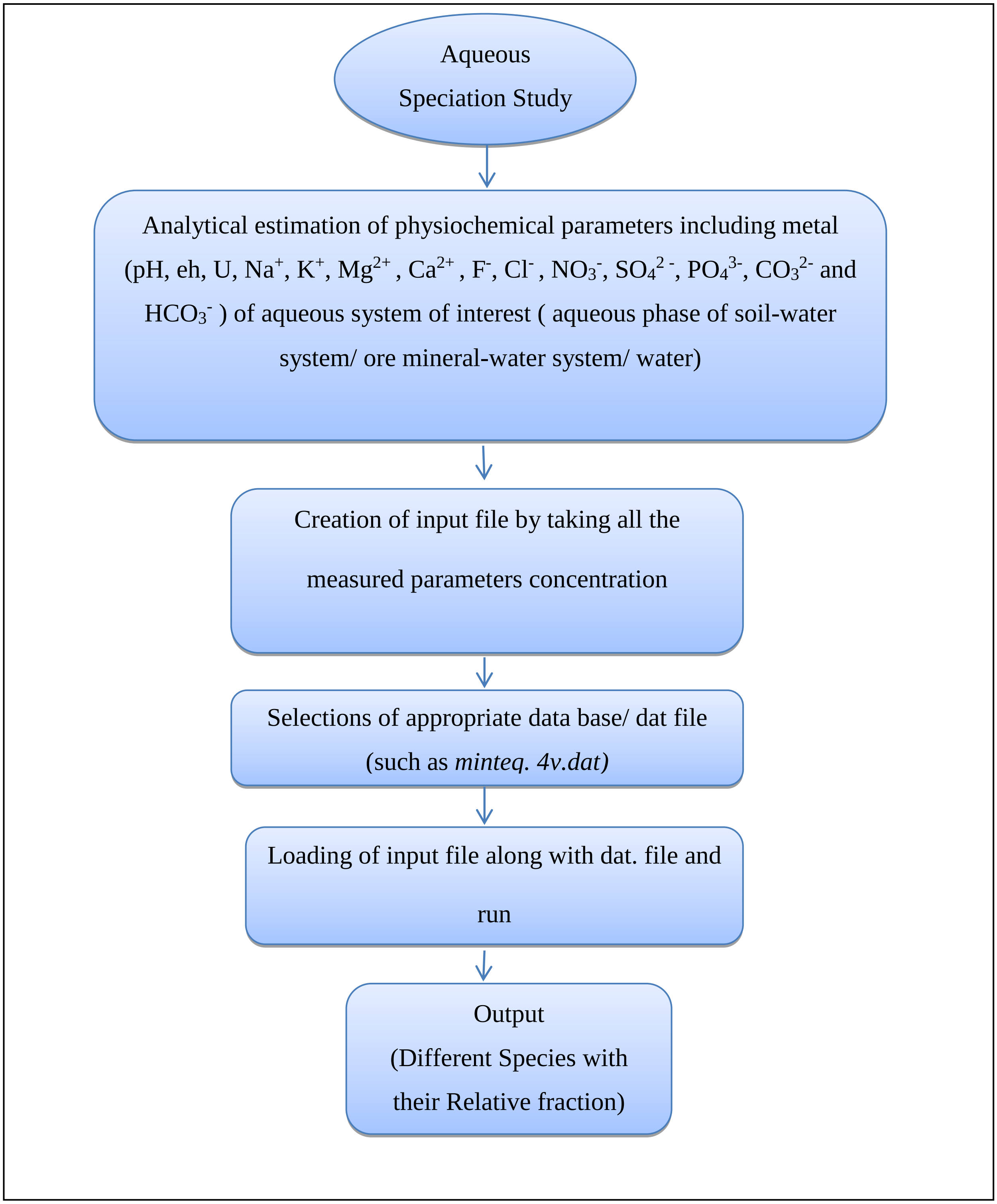


Figure 2.4. Steps involved in chemical speciation calculation

The thermodynamics of the system components will be predictive of the final state of the system [106]. However, speciation models using the LEA generally neglect reaction kinetics, and for some systems kinetics play a pivotal role [107-110]. There are various models are available for speciation calculations such as, *PHREEQC I*, *EQ3, MINEQL and MEDUSA* etc. all are based on one of these thermodynamic data base*; wateq4f.dat*, *minteq. 4v.dat*, *pitzer.dat, sit.dat*, *llnl.dat, iso.dat*, *amm.dat and phreeqc.dat.* In our study we used PHREEQC I and MEDUSA code for speciation calculation and the step involved presented in figure. 2.4.

Chapter 3

Behavior of Uranium at Soil- Water interface

3.1. Introduction

Like other metals, uranium at soil-water interface is also subject to movement with soil water, and may be transported through the vadose zone to ground water. Immobilization of uranium, by mechanisms of sorption and precipitation, will prevent movement of the metals to ground water. Like metal-soil interaction when uranium is introduced at the soil surface, either by natural or anthropogenic processes, downward transportation may not occur to any great extent unless the uranium retention capacity of the soil is overloaded. Changes in soil environmental conditions over time, such as the degradation of the organic waste matrix, changes in pH, redox potential, or soil solution composition, also may enhance uranium migration to soil solution**.** The extent of migration of U from soil to soil solution is directly related to the sorption kinetics and thermodynamics which in turn is a function of soil types and physicochemical properties of soil solution. Study of sorption of U(VI) onto soil is of great importance for the prediction of its fate at soil-water interface, which is prerequisite to the long-term performance assessment of nuclear waste repositories and migration of geogenic uranium from rocks to associated ground water system. As sorption processes depend on soil mineralogy and water chemistry [110,111] the physical and chemical properties of geological media (such clay minerals, soils and rocks) plays an important role in the evaluation of migration of uranium in the environment. The most important minerals in soil accelerate the retention of uranium are smectite, illite, vermiculite, allophone and imogolite as well as the oxides and hydroxides of silica, aluminum, iron and manganese [112]. Sorption of uranium by clay minerals has been extensively documented in the literature [113-118]. However, all these studied were carried out on individual clay minerals. But in natural environment clay minerals are one of component of the soil which composed of various other minerals and not necessary it’s a clayey soil. As different soil types possess different retention capacity, the soil type is also important to decide site for waste management and predict fate. It is therefore, understandable that the study of sorption kinetics, thermodynamics and isotherms is equally important as it provides valuable insights into the reaction pathways and into the mechanism of sorption reactions to understand the behavior of uranium at soil water interface.

3.2. Present work

In the present work, experiments were carried out to understand the behavior of uranium at soil water interface by kinetics and thermodynamics means. Sorption efficiency of four types of soil having different geological origin (from *metamorphic, sedimentary and igneous rocks) was estimated*. Sorption kinetic models were employed to analyze the kinetics and mechanisms of uranium sorption on the different soil types. Thermodynamic parameters of sorption were estimated. The best-fit equilibrium isotherms were determined by Freundlich, D-R and Langmuir isotherm models. The study also focused on evaluating how the process operation parameters of initial U concentration, adsorbent dosage (soil mass), natural organic matters (NOM) content, and change in soil water chemistry affect the adsorption capacity of the soil. This information will be useful for further applications in waste treatment or disposal facility special dealing with radioactive waste like uranium along with solving the issue of uranium contamination.

3.3. Materials and Methods

3.3.1. Materials

Four different soils (A, B, C and D) of different origin and chemical compositions were employed to study their U (VI) sorption capacity to remove uranium at soil solution interface.

Where, Soil A: *Metamorphic soil*, Soil B: *Sedimentary soil*, Soil C: Basaltic soil and Soil D: Basaltic saline soil. All soils were used as received without other treatment apart from drying at 100^0 C for 1 h to remove excess moisture and then kept in a desiccator until analyzed. A part of Soil samples from each soil types were heated at 550^0C($\pm10^0$C) for 2 hours in furnace to remove NOM. Working solution uranium as prepared by appropriate dilution of the stock solutions (10000 mg/L of Uranyl Nitrate, SEPEX Ltd.) immediately before use.

3.3.2. Characterization of properties of Natural Soil

Physico-chemical properties of each soil are given in Table 2.1. The soil texture analysis was carried out using CILAS Particle Size Analyzer 1109 (Range: 40nm-2500μm) in liquid Mode and the size distribution is presented in Fig. 3.1. X-ray diffraction (XRD) analysis was carried out to determine the phases of the clay minerals. The measurements were performed using GNR, APD 2000 PRO diffract meter (Cu-Kα X-rays:1.54 A^0) over the range of 5–50°, 2-theta for processed soil samples. The XRD pattern for all the soils are presented in Fig. 3.2. The natural organic content (NOM) was estimated using CHNO-S Analyzer (Flash EA-112, Thermo-Fischer), Fe and Mn content in soil was estimated by microwave acid digestion followed by spectro- photometric analysis using AAS (GBC, Avanta). Cation Exchange Capacity of soil was estimated by sodium acetate method as discussed in chapter 2 [76]

3.3.3. Sorption experiment

Adsorption of U(VI) on the different soil was carried out in a batch system. 5 g of soil added to 50 mL of known concentration of U(VI) solution. The mixture was agitated at160 rpm in a rotary shaker (*SK-300, JIOTECH*, Korea) at ambient temperature for 7 days. For kinetics study the samples were withdrawn at pre-determined time (1h, 2 h…168h) intervals until sorption equilibrium were achieved. Then the U(VI) solution was separated from the soil by centrifugation (Eppendorf Centrifuge 5430R, Germany) at 7000 rpm for 15min. The supernatants were then filtered using Millipore filter paper (0.45µm) to ensure the solutions were free from particles before measuring the residual U(VI) concentration. Adsorption isotherms study was carried out by varying initial conc. from 100.0, 500.0, 1000.0, 10000.0, 100000.0 µg/L. All experiments were carried out in duplicate and again the measurements were carried out in triplicate to ensure the repeatability in measurement. Finally, the average values were taken to minimize random error.

For determination of thermodynamic parameters, 5 g of each dried soil was added to 50 mL of 10mg/L uranium solution and batch equilibrium experiment was conducted at 25^0 and 50^0C in a shaker incubator. After 7 days of equilibration time the samples of each set were centrifuged, filtered through 0.45 µm filter paper and concentration of U in the equilibrium solution was determined using Uranium Analyzer UA2 (Quantalase Indore, India). The distribution coefficients of uranium in all the four soils were determined at different temperature.

3.3.4. Measurement of U(VI) concentration and removal capacity

U(VI) concentration was determined by Uranium Analyzer UA-2 (Quantalase, Indor, India) using phosphate buffer at pH 7 and standard addition technique was followed for quantification. The reliability of analysis was cross checked by inter comparison with Voltammetric technique. The sorption capacity at any time ‘t’ and removal rate/ sorption % of U (VI) *was* calculated using following relation:

$$q_t = (C_0 - C_t) \times \frac{V}{W} \tag{3.1}$$

$$S\% = \left(C_0 - C_t\right) \times \frac{100}{C_0} \tag{3.2}$$

Where,

C_0 is the initial U(VI) concentration (µg/L),

C_t is the concentration at any time (µg/L),

V is the volume of solution (mL), and

W is the weight of the adsorbents/ soil (g).

3.3.5. Theory of Adsorption isotherm

To optimize and model the adsorption, Freundlich, Langmuir and D–R isotherm isotherms [119] were used which explains U(VI)- soil interaction at soil solution interface.

Freundlich isotherm

Freundlich model allows for several types of adsorption sites on the solid and intermediate concentrations on heterogeneous surfaces can be defined by relation:

$$q_e = K_f C_e^{1/n} \tag{3.3}$$

Eq. (3.3) can be rearranged to obtain a linear form by taking logarithms:

$$Log(q_e)=log\ K_f +(1/n)log\ C_e \tag{3.4}$$

Where, q_e is the amount of U(VI) adsorbed per unit of adsorbent at equilibrium (µg/g), Ce is the concentration of U(VI) in solution at equilibrium (µg/L), K_f (µg$^{1-1/n}$L^n/g) and n are the called *Freundlich isotherm* constants, which are indicator of the extent of the adsorption and the degree of nonlinearity between solution concentration and adsorption respectively. K_f and 1/n values can be calculated from intercept and slope of the linear plot between log *Ce v's log* (q_e).

Langmuir isotherm

Langmuir isotherm is based on the assumption that a structure of adsorbent is homogeneous, where all sorption sites are identical and energetically equivalent. This means, each adsorption mono-layer coverage of U(VI) molecule on the outer surface of clay adsorbents. And it is valid for monolayer adsorption onto a surface containing a finite number of identical sites. The form of Langmuir isotherm can be represented by the following equation:

$$q_e = \frac{q_{\max} K_L C_e}{1 + K_L C_e} \tag{3.5}$$

The Eq.3.5 can be linearized to

$$\frac{C_e}{q_e} = \frac{1}{k q_{\max}} + \frac{C_e}{q_{\max}} \tag{3.6}$$

Where,

q_e is the equilibrium uptake (µg/g);

C_e is the equilibrium U(VI) concentration (µg/L)

q_{max} (µg/g) (saturated monolayer adsorption capacity) and

k (L/µg) (adsorption equilibrium constant) are the Langmuir constants.

Dubinin-Radushkevich Isotherm

The Dubinin-Radushkevich (D-R) isotherm model postulates that the mechanism for adsorption in micro-pores is that of pore-filling rather than layer-by-layer surface coverage. It is applied to the data in order to deduce the heterogeneity of the surface energies of adsorption and the characteristic porosity of the adsorbent. It is generally applied to express the adsorption mechanism [120] with a Gaussian energy distribution onto a heterogeneous surface [121]. The linear form of the D-R isotherm is given in as follows in Eq. 3.7.

$$\ln q_e = \ln q_{\max} - \beta \varepsilon^2 \tag{3.7}$$

Where,

ε is the Polanyi potential

β is the activity coefficient related to mean sorption energy (mol^2/kJ), which is equal to:

$$\beta = RT \ln\left(1 + {}^{1}\!/_{C_e}\right) \tag{3.8}$$

$$E=1/\sqrt{2\beta} \tag{3.9}$$

E (kJ/mol) is defined as the free energy change required transferring 1.0 mol of ions from solution to the solid surfaces and the magnitude of E is useful for estimating the type of sorption reaction.

3.3.6. Adsorption kinetics

In order to examine the controlling mechanism of adsorption processes such as mass transfer and chemical reaction, several kinetic models are used to test experimental data. A simple kinetic analysis of adsorption is the pseudo-first-order equation [122, 123] in the form;

$$dq/dt = k_1(q_e - q_t) \tag{3.10}$$

Where,

k_1 is the rate constant of pseudo-1st-order adsorption and

q_e denotes the amount of adsorption at equilibrium.

After definite integration by applying the initial conditions q= 0 at t= 0 and q= q_t at t = t equation (3.10) becomes:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \tag{3.11}$$

In addition, a pseudo-second-order equation based on adsorption equilibrium capacity [123, 124] may be expressed in the form:

$$dq/dt = k_2(q_e - q_t)^2 \tag{3.12}$$

Where,

k_2 is the rate constant of pseudo-second-order adsorption.

Integrating equation (3.12) and applying the initial conditions, we have

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \qquad (3.13)$$

It should be noted that, equation (3.13) has an advantage that k_2 and *qe* can be obtained from the intercept and slope of the plot of t/qt. vs. t and there is no need to know any parameter beforehand.

3.3.7. Adsorption mechanism

As the above two equations cannot give definite mechanisms, another simplified model is tested called Intra-particle diffusion model (IPD) which was proposed by Weber and Morris [125]. The effect of intra-particle diffusion resistance on adsorption can be determined by the following relationship

$$q_t = k_{id}(t)^{1/2} + I \qquad (3.14)$$

Where k_{id} is the intra-particle diffusion rate constant (µg /(g.h$^{1/2}$). To follow the intra-particle diffusion model, a plot of q_t against $t^{1/2}$ should give a linear line where a slope is k_{id} and intercept *I*. Values of *I* provides information regarding the thickness of boundary layer, i.e. the higher the '*I'* 'value the greater is the boundary layer effect.

3.3.8. Thermodynamic parameters

The thermodynamic parameters were determined from the thermodynamic equilibrium constant, K_d. Change in enthalpy was determined from distribution coefficient (K_d) at different temperatures (25 and 50 ^{0}C) using Van't Hoff equation as follows

$$\ln \frac{K_{d1}}{K_{d2}} = \frac{\Delta H}{R}\left[\frac{1}{T_2} - \frac{1}{T_1}\right] \qquad (3.15)$$

Similarly change in free energy calculated from distribution coefficient using Gibbs free energy equation,

$$\Delta G^0 = -RT \ln K_d \tag{3.16}$$

Finally the change in entropy can be calculated using following equation,

$$\Delta S^0 = \left(\frac{\Delta H^0 - \Delta G^0}{T} \right) \tag{3. 17}$$

3.3.9. Parameter Sensitivity

For sensitivity analysis, One-Factor-At-A-Time (OFT) direct approach was chosen and the results of the sensitivity analysis are presented in terms of metrics called the uranium ratio (UR) and the sensitivity index (SI_{UR}) and defined by following relation:

$$SI_{UR} = \frac{UR_{MIN} - UR_{MAX}}{UR_{Baseline}} \tag{3.18}$$

$$UR = \frac{U_{AQ}}{U_{Tot}} \tag{3.19}$$

Where,

U_{AQ}: Uranium concentration in aqueous medium

U_{Tot}: Total Uranium concentration (solid phase + liquid phase)

UR_{min} is UR at the minimum component concentration evaluated

UR_{max} is UR at the maximum component concentration evaluated

$UR_{baseline}$ is UR at the baseline for the system

(SI_{UR} >10%): those that had a significant effect; (1 < SI_{UR} < 10%): moderate effect; (0.1 < SI_{UR} < 1%): minor effect and (SI_{UR} <0.1%): no apparent effect.

Simulation was carried out using hydro-geochemical code *PHREEQCI ver.3* and *WATEQ4F* thermodynamic database to see the effect of water parameters on mobility of uranium at soil – water interface. Sorption controlled studies was carried out using Diffuse-*double layer* (DDL) model. And it is assumed that the ground water is in equilibrium with the soil containing hydrous ferric oxide mineral. Simulation was carried out by varying pH (5 to 10), CO_3^{2-} (0 to 6 mM), SO_4^{2-} (0 to 5mM), Ca^{2+}(0 to 10mM) and Na^{+}(0 to 25mM), Mg^{2+}(0 to 5mM) and K^{+}(0 to 1mM).

3.4. Results and Discussion

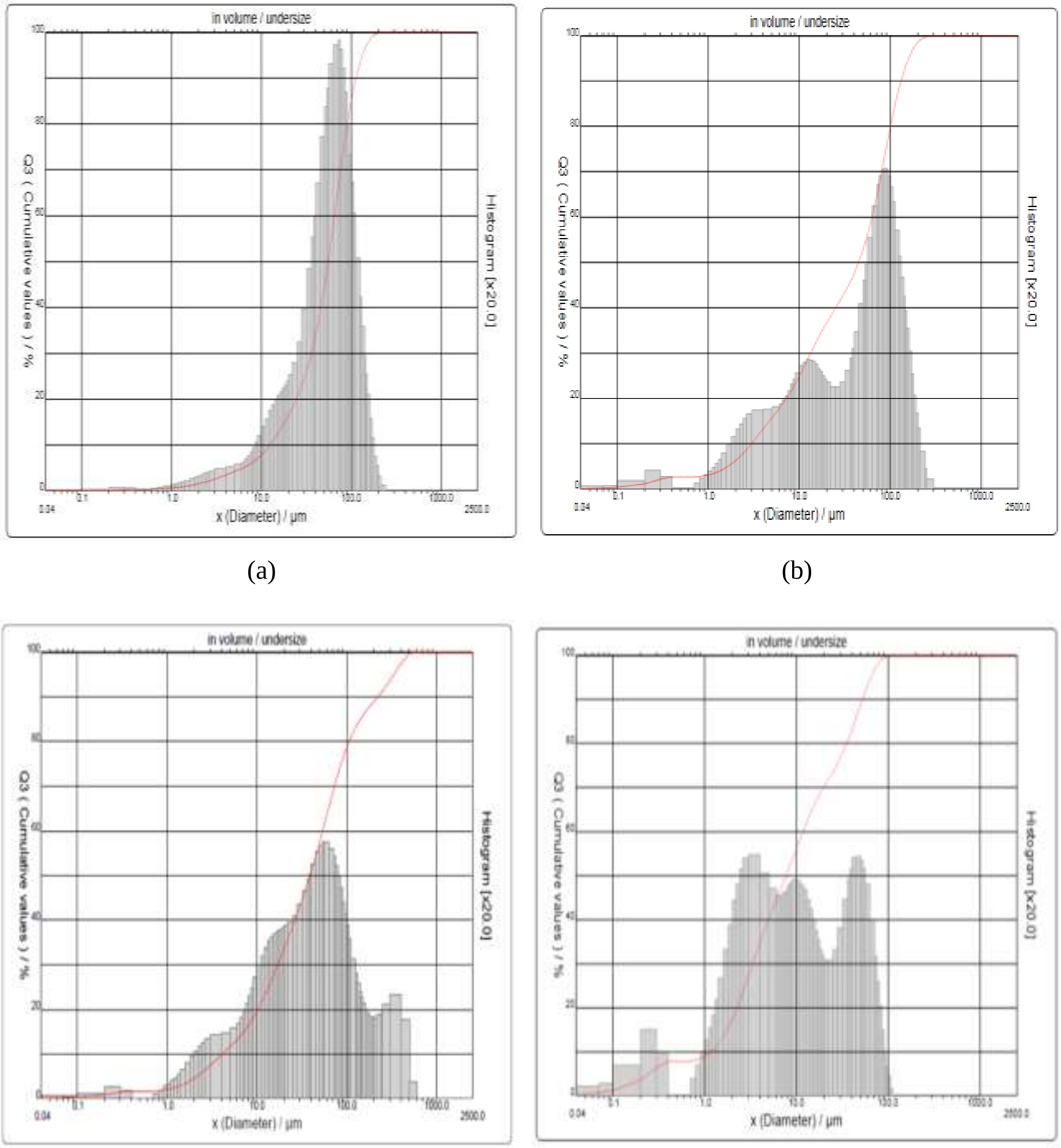
3.4.1. Characterization of Soils

Physico-chemical data with measurement uncertainties of all the four soil samples were presented in Table 3.1. Fig. 3.1(a, b, c and d) presents particle size (soil texture) distribution of all the four soils, it indicates that average soil textural distribution were in the order of B(90µm)>A(80 µm)> C (36 µm)>D(4 µm) although order of clay content is D> C>B>A. Analysis of total organic content in soil using CHNO-S analyzer revealed that Soil D contains maximum organic matter (2.04%) followed by C(1.44%)> B(0.15%)> A(0.06%). Fe and Mn content is maximum in soil C followed by D>A> B. Cation Exchange Capacity (CEC) indicates that Soil D exhibits highest CEC (meq/100g) followed by B>C> A. XRD is the basic technique to determine the bulk structure and composition of soil with crystalline structure. Fig 3.2 (a, b, c and d) presents XRD pattern of soil A, B, C and D respectively. Interpretation of mineralogical data indicates that soil A and B is dominated by quartz whereas C by plagioclase minerals and Soil D by calcite and dolomite. The method extraction efficiency and quality of analysis were checked against the certified reference material IAEA soil -7 for Fe and Mn with the recovery of 102 and 99 %, respectively at 95 % confidence interval.

Table 3.1. Physical and chemical properties of Natural Soil

Soil Type	pH	Sand	Silt	Clay	Max distribution (µm)	NOM (%) RSD (±0.2%)	Fe (%) RSD (±3%)	Mn (mg/Kg) RSD (±2.5%)	CEC (meq /100g)	Mineralogy Data Generated Using XRD
[1] A	7.5	42.25	56.16	1.59	80	0.058	2.6	245	5.60	Ilite, Chlorite, Quartz, K-Feldspar, Dolomite
[2] B	8.1	39.78	53.93	6.29	90	0.15	2.2	196	22.12	Ilite, Chlorite, Kaoline, K-Calcite, fedspar
[3] C	6.9	20.3	74.6	5.1	36	1.44	5.3	1852	18.85	Plagioclase, Smectite, Calcite, Quatrz
[4]D	7.6	5.55	77.13	17.31	4.0	2.04	4.9	502	62.04	Quartz, Calcite, Dolomite, Ca-Mont., Chlorite, Amphibole

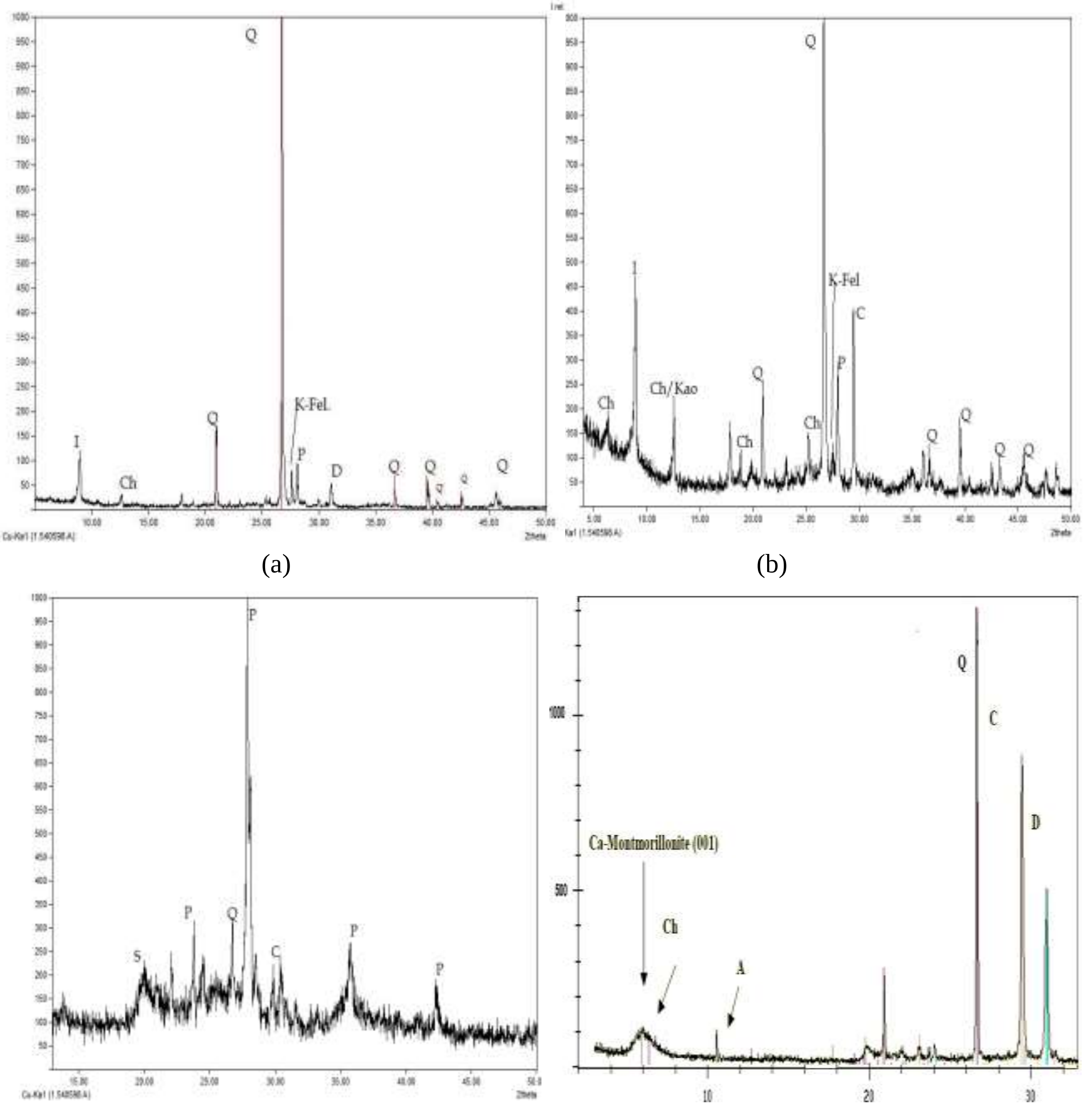
[1]Metamorphic origin, [2] Sedimentary origin, [3] Basaltic origin and [4]Basaltic origin (saline soil).



(a) (b)

(c) (d)

Figure 3. 1. Particle size distribution pattern of; a) Soil A, b) Soil B, c) Soil C and d) Soil D



(a) (b)

(c) (d)

Figure 3.2. X-ray diffraction patterns of: a) Soil A, b) Soil B, c) Soil C and d) Soil D

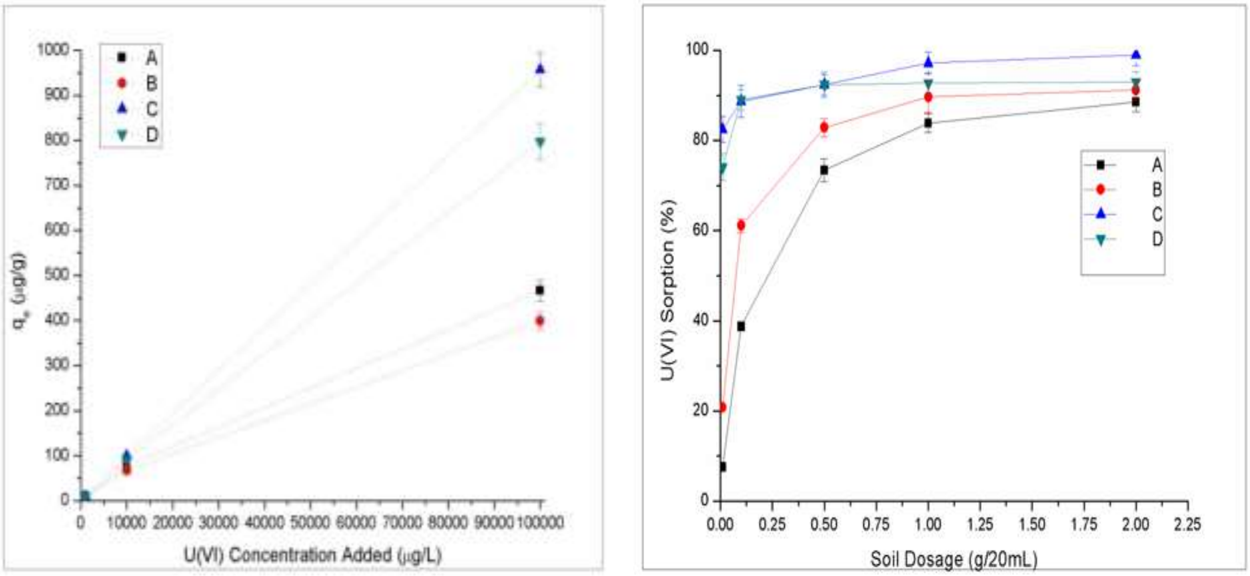
(Where S: Smectite, I: Illite, Q: Quartz , P: Plagioclase, C: Calcite, D: Dolomite, Ch: Chlorite, A: Amphibole and K-Fel: K-Feldspar)

3.4.2. Effect of U(VI) concentration

The effect of initial U(VI) concentration on the adsorption capacity of the soil was investigated under equilibrium conditions with 10mL/g (solution to soil ratio). Fig. 3.3a, presents sorption profile, where the sorption capacity increased with an increase in the U(VI) concentration. Thus it can be proposed that an increase in the U(VI) concentration leads to an increase in mass gradient between the solution and adsorbent, and thus acts as a driving force for the transfer of U(VI) molecules from bulk solution to the soil surface. The maximum sorption capacity attained 957.00 µg/g for soil C followed by Soil D (797.46 µg/g) > Soil A (466.5 µg/g)> Soil B (399.54 µg/g) respectively. The high sorption capacity of soil C is corresponded to its higher Fe and Mn content, when compared to other soils.

3.4.3. Effect of soil (adsorbent) dosage

The effect of adsorbent dosage were studied by changing the mass of soil and keeping the volume of solution constant in the range of 10 to 2000 mL/g on the removal of 100 µg/L of U(VI) is presented in Fig. 3.3b The removal of U (VI) increased with soil dosage for all type of soil. As the soil dosage increased, soil A, B, C and D demonstrated a gradual increase in sorption % of U(VI) from 7.6 to 88.5%, 20.8 to 91.18% , 82.66 to 97.18%, 74.08 to 92.98 % respectively. The study revealed that, the effect of soil dosages is not much important in case of soil C followed by D, this is due to high adsorptive capacity of soil C and D. This adsorptive enhancement is attributing to an increase in adsorption surface area and the availability of *adsorption sites* [126]. This investigation further confirmed that soil C demonstrated the highest adsorptive/ capacity.

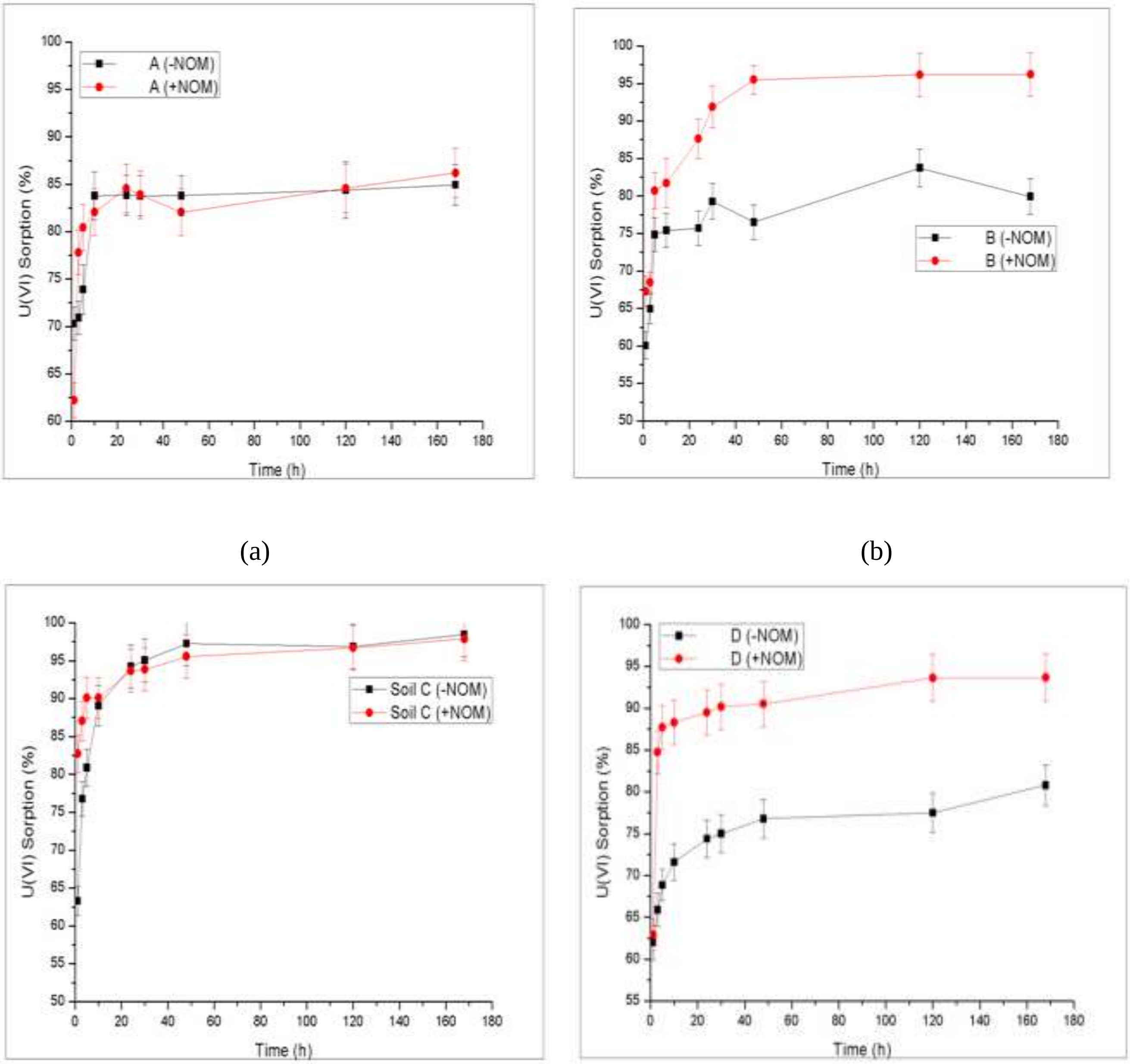


(a) *(b)*

Figure 3.3. Effect of (a) initial U(VI) concentration and (b) Adsorbent dosage (g of soil/20mL of Solution) on removal of U(VI) on all soil types (pH 7.2).

3.4.4. Effect of Natural Organic Matter Content (NOM)

Figure 3.4 (a, b, c and d) shows the U (VI) sorption on to soil in presence and absence of NOM (Soil heated at 550^{0}C for 2 h). It can be clearly seen that absence of NOM leads to significant reduction in sorption percentage in case of soil B and D, minor effect on soil A and almost no apparent effect on sorption capacity of soil C. At circumneutral pH which is the pH of studied soils, NOM remains adhere to soil surface by binding on positive charge site of soil and the strong complexation ability of surface adsorbed NOM with U(VI) leads to enhancement of the sorption. Removal of NOM by heating leads to reduction in sorption %. In case of soil A the % of NOM is negligible hence the presence and absence of NOM has minor effect on sorption.



(a)

(b)

(c)

(d)

Figure 3.4. Change in sorption % in presence (+) and absence (-) of NOM a) Soil A, b) Soil B, c) Soil C and d) Soil D

No change in soil sorption capacity in the absence of NOM in case of soil C revealed that, U(VI) sorption in soil is dominated by some other factors like oxides of Mn and Fe which is found in maximum in soil C out of all four soils. It's a well-known fact that, oxides of Mn and Fe are very good adsorbent by offering large surface area for sorption of uranium [127]. And the influence of the ternary complexes (U-NOM-Fe Oxide or U-NOM-Mn Oxide) decreases when oxides of Fe and Mn surface sites are in excess [128].

3.4.5. Adsorption isotherm

To describe how U(VI) molecules interact with the soil surface of different types, adsorption isotherm study was carried out. Adsorptive capacities of soil and adsorption isotherm parameter were determined by equilibrium studies. The Freundlich isotherm was employed to describe heterogeneous systems and reversible adsorption, which assumes the multilayer formations. Freundlich constants were used to determine whether the adsorption process is favorable or not. The value of K_f *is* indicative of the adsorption/ sorption capacity of the adsorbent, greater K_f value, indicates greater adsorption capacity. The value of '*n' (*Freundlich constant) *used* to verify types of adsorption, by measuring deviation from linearity [129].

For the Langmuir model, the effect of isotherm shape is used to predict a favorability of an adsorption system under specific conditions. The favorability of adsorption of Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor or equilibrium parameter R_L as described by Hall et al.[130].

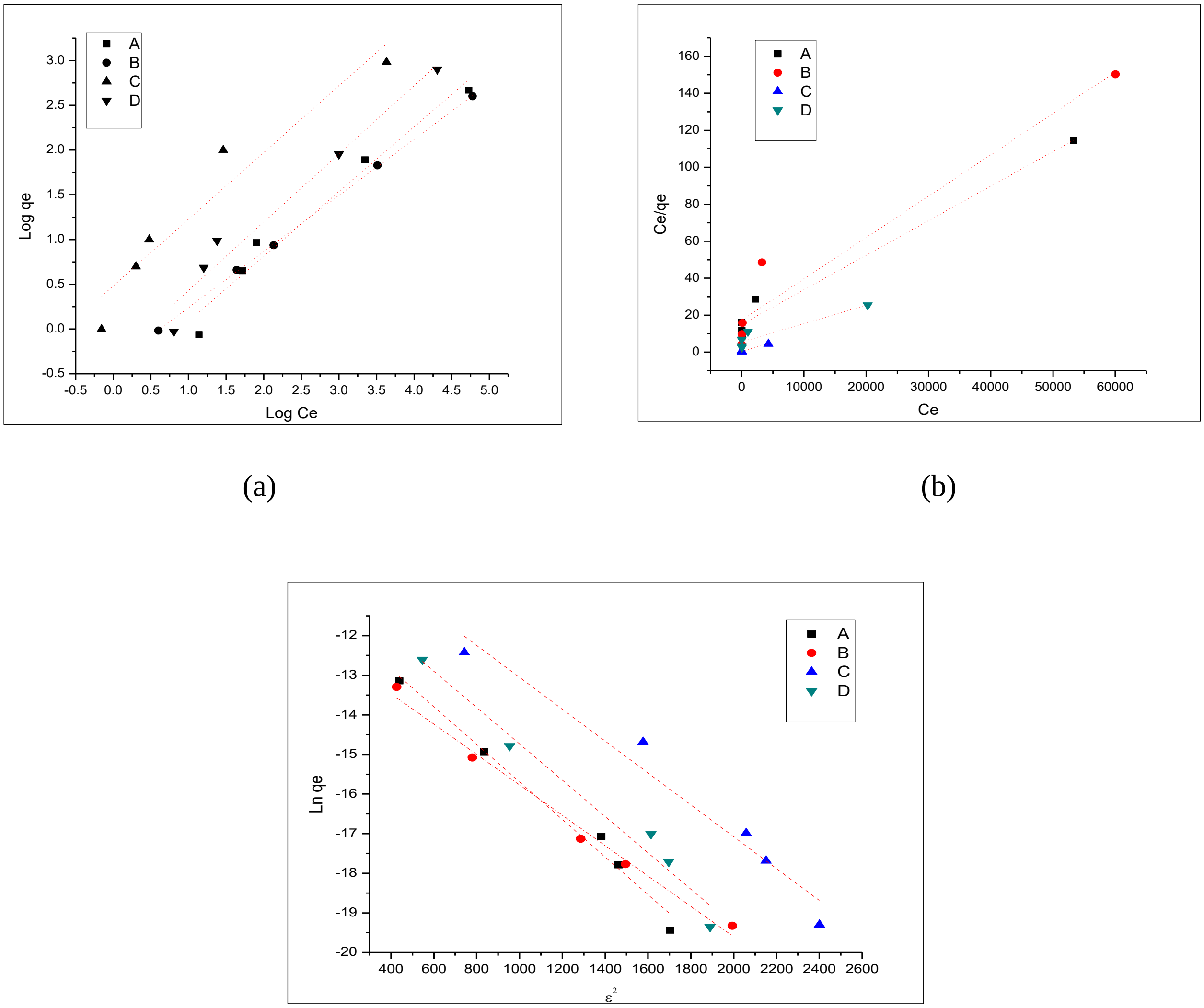
$$R_L = \frac{1}{1 + K_L C_I} \tag{3.18}$$

The values of the R_L are basically classified into four groups, indicating the shape of the isotherm as follows: $R_L>1$, adsorption is unfavorable; $0<R_L<1$, favorable; $R_L=1$ Linear and $R_L=0$, adsorption is irreversible. Table 3.2 presents the calculated values of Freundlich and Langmuir model's parameters. The n and R_L values indicate that the U(VI) adsorption on all the soil types is favorable for both adsorption isotherms under the experimental condition (27^0C).

Table 3.2 Adsorption parameter of isotherm for the adsorption of 100µg /L of U(VI) on Natural Soil

Isotherm Parameters	Soil A	Soil B	Soil C	Soil D
Langmuir				
q_{max}(mg/g)	0.535	0.446	1.055	1.013
K (L μg^{-1})	1.24×10^{-4}	1.30×10^{-4}	2.27×10^{-3}	1.76×10^{-4}
R^2	0.976	0.928	0.988	0.858
RL	0.99	0.99	0.81	0.98
Freundlich				
K_f (µg /g /(mol/L)$^{(1/n)}$)	0.230	0.410	3.030	0.464
n	1.381	1.594	1.342	1.310
R^2	0.959	1.000	0.905	0.954
D-R				
B (mol^2/kJ^2)	0.005	0.004	0.004	0.005
q_{max} (mg/g)	4.196	1.565	28.610	9.354
E (kJ/mol)	10.26	11.411	11.139	10.437
R^2	0.979	0.985	0.949	0.966

From Fig. 3.5 (a, b, and c) the U(VI) adsorption onto soil A, B C and D exhibits a reasonable fit to the Freundlich and D-R isotherm model (R^2> 0.95). However, a better fit to Langmuir model was observed for *Soil C* which was statistically confirmed by giving greater R^2 values closer to unity (0.98). This implies that the Freundlich and D-R isotherm model may better describe an adsorption isotherm for adsorbents (Soil A, B and D).



(a)

(b)

(c)

Figure 3.5. Adsorption isotherm for adsorption of U(VI) on Natural Soils (a) Freundlich and (b) Langmuir (c) D-R Isotherms

This adsorptive behavior indicates that the adsorption takes place on a heterogeneous surface for soil A, B and D, which may be attributed to the various active sites (Clay minerals, Oxides of Fe/Mn, NOM etc.) on soil having different affinities to U(VI) molecules. Adsorption on soil C is best described by Langmuir model which assumes monolayer adsorption which attributes to the dominant active site offered by oxides of Fe minerals. Both K_f and q_{max} values calculated from the Freundlich and Langmuir model (*Table 3.2*) supported the experimental results shown in previous sections, i.e., Soil C possess highest adsorptive capacity in comparison to other soils. R_L value of the isotherm for soil A, B and D were very close one indicating the linearity of the adsorption process whereas the R_L value of isotherms for soil C indicates favorable adsorption. E values obtained from D-R isotherms were 10.26, 11.41, 11.14 and 10.43 kJ/mol, for soil A, B, C and D. The typical range of bonding energy for ion-exchange mechanisms is 8–16 kJ/ mol, indicating that chemisorption or ion-exchange mechanism may play a significant role in the adsorption process. Soil offers various adsorption sites like adsorption on natural occurring organic matter (NOM), Fe/ Mn oxides, clay etc. which provides a heterogeneous surface U(VI) adsorption. Whereas with increase in Fe content probable U(VI) sorption is governed by Fe which provides a homogeneous surface, where U(VI) adsorb by forming both inner and outer sphere complex. This may leads to better fitting of U(VI) sorption on Soil C to Langmuir model. The sorption capacities q_{max} derived from the D-R model are higher than those derived from the Langmuir model this may be ascribed to the consideration of different assumptions in the formulation of the isotherms.

3.4.6. Kinetics of Adsorption

The kinetics of U(VI) sorption was studied using pseudo-first order (PFO) and pseudo second order (PSO) kinetics. The calculated Kinetic parameters with the equilibrium adsorption capacities of the all the four soils are given in Table 3.3.

Table 3.3. Comparison of Kinetics of U(VI) sorption onto soil by Pseudo-First Order and Pseudo-Second Order kinetic models for of 100µg /L of U(VI)

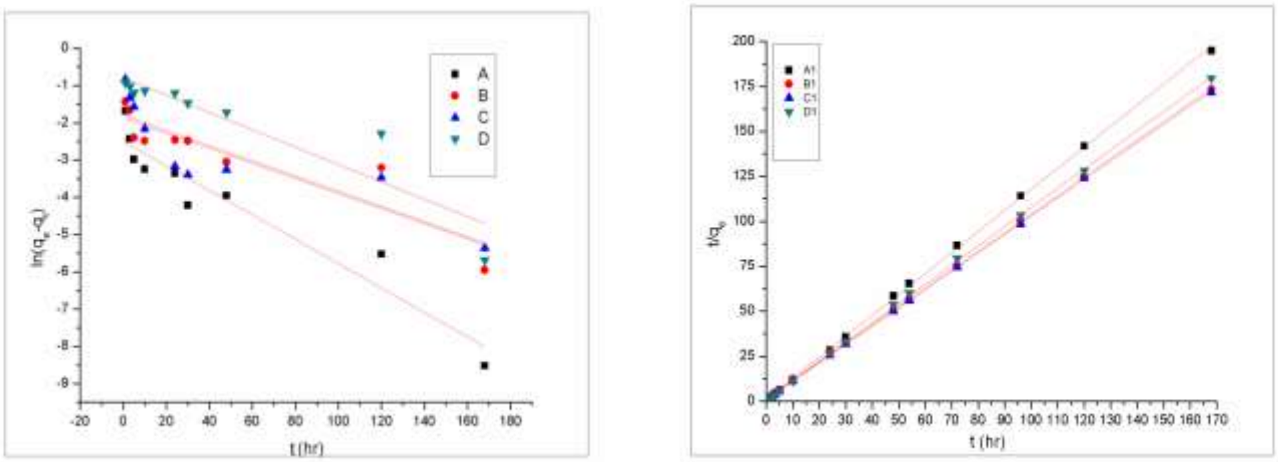
Soil	Pseudo-Second Order Model					Pseudo-First Order Model		
	Cep (µg/L)	Qe(µg/g) Theoretical	Qe(µg/g) Experimental	K_2 (µg/g.hr)	R^2	Q_e	K_1	R^2
[1]A	13.8	0.86	0.862	1.42E+00	0.999	0.31	0.006	0.421
[2]B	4	0.98	0.96	7.28E-01	0.999	0.55	0.024	0.972
[3]C	1	0.98	0.98	1.45E+00	1	0.36	0.011	0.813
[4]D	6.4	0.943	0.936	1.25E+00	0.999	0.35	0.013	0.598

[1]Metamorphic origin, [2] Sedimentary origin, [3] Basaltic origin and [4]Basaltic origin (saline soil).

The kinetic parameters and R^2 indicates that the sorption kinetics follows second order kinetics irrespective of soil types. Fig. 3.6 a presents the first order kinetic curves of all adsorbents, investigation of figure revealed that, the plot dose not exhibits any linearity. This disagreement is corroborated by lower R^2 value. This clearly envisage that adsorption of U(VI) on these soils did not follow pseudo-first order model. On the contrary, the result shows an ideal fit to the second order kinetic irrespective of soil types with the extremely high $R^2 > 0.99$ (Fig. 3.6b, Table 3.3). The linearity also followed at higher concentration level as shown in Table 3.4. This clearly envisage that adsorption of U(VI) on these soils did not follow pseudo-first order model. On the contrary, the result shows an ideal fit to the second order kinetic irrespective of soil types with the extremely high $R^2 > 0.99$ (Fig. 3.6b, Table 3.3 & Table 3.4).

Table 3.4. Comparison of Kinetics of U(VI) sorption onto soil by Pseudo-First Order and Pseudo-Second Order kinetic models at different U(VI) concentrations.

C0 (μg/L)	Soil	Qe(μg/g) Experimental	PFO			PSO		
			Qe(μg/g) Theoretical	K_1	R^2	Qe(μg/g) Theoretical	K(μg/g.hr)	R^2
500	A	4.48	0.528	0.005	0.032	4.54	5.38E-01	0.99
1000		9.2	0.851	0.005	0.063	10	1.06E-01	0.99
10000		77.75	4.055	0.014	0.844	83.3	3.27E-03	0.99
100000		466.5	8.870	0.018	0.811	476.2	7.23E-04	0.99
500	B	4.56	0.376	0.002	-0.06	4.762	1.10E+00	0.99
1000		8.64	0.856	0.009	0.346	8.696	2.70E-01	0.99
10000		67.36	3.643	0.016	0.814	71.429	5.44E-03	0.99
100000		399.54	11.674	0.024	0.647	500.00	6.67E-05	0.86
500	C	4.98	0.206	-0.01	0.322	5.00	2.67E+00	1.0
1000		9.97	0.359	0.009	0.832	10.00	1.49E+00	1.0
10000		99.71	0.703	0.008	0.724	100.00	3.39E-01	1.0
100000		957.06	9.666	0.024	0.660	1021.45	1.37E-04	1.0
500	D	4.84	0.510	-0.01	0.737	4.854	8.37E-01	1.0
1000		9.76	0.870	0.011	0.578	9.80	2.77E-01	0.99
10000		90.0	2.077	0.013	0.519	90.90	2.02E-02	0.99
100000		797.46	13.654	0.019	0.522	1000.0	5.00E-05	0.92



(a) (b)

Figure 3.6. Adsorption kinetic for adsorption 100.0 µg/L (a) Pseudo-first order and (b) Pseudo-second order

A good agreement between the experimental adsorption capacity at equilibrium and theoretically calculated value using PSO model for all soil types also supports that kinetics follows PSO. The best fit to the pseudo-second order kinetics revealed that the adsorption mechanism depends on the adsorbate (Concentration of U (VI)) as well as adsorbent (Amount of Soil), and the rate-limiting step may be chemisorptions involving valence forces through sharing or exchange of electrons.

3.4.7. Adsorption Mechanism

Adsorption is usually governed by either the liquid phase mass transport rate or the intra-particle mass transport rate. In this study, the Intra-particle diffusion model was used to identify the diffusion mechanism of the U(VI) adsorption onto the natural soil. Fig.3.7 revealed that the non-linearity of adsorption over the whole time range. But the whole range can be break into a few linear regions.

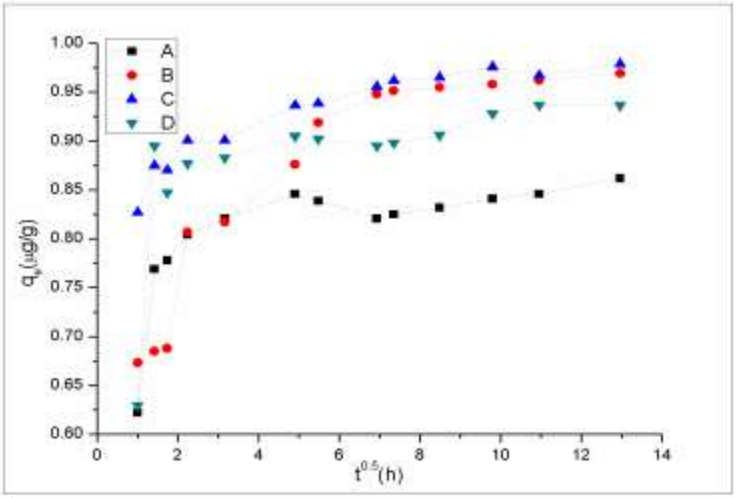


Figure 3.7. Intra-particle diffusion kinetic for adsorption of U(VI) on soil A, B, C and D

This indicates that there are two or three stages of adsorption are taking place. This multi-linearity stages arises due to following reasons: a) Initial portion can be attributed to external surface adsorption that the U(VI) diffuses through the solution to the external surface of the soil or the boundary layer diffusion of U(VI) molecules, where the adsorption rate is high, b) The second portion illustrates the gradual adsorption stage, where intra-particle diffusion rate is rate-controlling and c) The last portion refers to the final equilibrium stage in which the intra-particle diffusion starts to slow down and level out as the extremely low U(VI) concentration remains in the solution or maximum adsorption was attained. Generally, when adsorption steps are independent of one another; two or more intercepting lines encounters when plotting, q_t against $t^{1/2}$ which depends on actual mechanism involved [128,131].

The plot indicates that although a multiple linear relationship exists for all the soil types, none of the lines passed through the origin (intercept ≠ 0). This revealed that the rate limiting step of sorption involved intra-particle diffusion as well as some other mechanisms such as complexation or ion-exchange [129, 122]. Critical review of the literature indicates that, oxides of Fe and Mn act like a bi-dentent binuclear surface species which forms of inner sphere complex with U(VI) [133-136]. U (VI) also forms inner-sphere bi-dentate binuclear complexes with silica and ϒ-aluminum oxide surfaces [137,138]. The work can be extended to study the mechanism at molecular level using EXAFS.

3.4.8. Thermodynamic Parameters of Sorption

The determination of the thermodynamic parameters (ΔH^o, ΔS^o and ΔG^o) for U(VI) as given in Table 3.5 can provide mechanism insights into U(VI) adsorption onto soils. The values of the standard enthalpy change (ΔH^o) were positive in a soils, indicating that it is an endothermic process for U adsorption onto soils. One possible interpretation for the endothermic process is that U(VI) ions are well solvated in water. In order to be adsorbed onto soils, U (VI) ions are denuded of their hydration sheath to some extent and this dehydration process needs energy. It is assumed that the needed energy for dehydration exceeds the exothermicity of the ions attaching to soil surfaces. The implicit assumption herein is that the adsorbed U(VI) ions are less hydrated than those in solution. The removal of water molecules from U(VI) ions is essentially an endothermic process and the endothermicity of the de-solvation process exceeds the enthalpy of sorption to a considerable extent [139-141].

The values of the Gibbs free energy change (ΔG^o) were all negative at two temperatures studied herein as expected for a spontaneous process under our experimental conditions. The higher the reaction temperature, the more negative the value of ΔG^o, indicating that the adsorption reaction is more favorable at elevated temperatures [141]. At higher temperature, U(VI) ions are readily dehydrated and thereby their sorption becomes more favorable. The ΔG^o values were observed to be relatively higher for undisturbed soils at both temperatures which might be due to high silt and clay content and low moisture content.

Table 3.5. Thermodynamic parameters for U sorption onto soils

Soil	ΔG^0(KJ/mol)		ΔH^0(KJ/mol)	ΔS^0 (J/mol.K)	
	25^0 C	50^0 C		25^0 C	50^0 C
[1]A	-19.32	-20.22	16.31	119.56	113.10
[2]B	-23.53	-25.23	10.21	113.22	109.72
[3]C	-20.15	-22.35	12.21	108.59	107.00
[4]D	-25.23	-26.83	10.32	119.30	115.02
[1]Metamorphic origin, [2] Sedimentary origin, [3] Basaltic origin and [4]Basaltic origin (saline soil).					

However, the values of the standard entropy change (ΔS^o) in soils were all positive for U(VI) sorption onto soils, which indicates that during the whole adsorption process, some structural changes occurs on soils surface and thus leading to an increase in the disorderness at the soil-water interface. In addition, whether or not a surface adsorption reaction is an associative or dissociative mechanism, strongly depends on the value of ΔS^o. When the value of ΔS^o is higher than −10 kJ $mol^{-1}K^{-1}$, a dissociative mechanism controls adsorption [139, 141]. The large ΔS^o values at the two temperatures herein suggests that a dissociative mechanism is responsible for U(VI) adsorption onto soils. Furthermore, the decreased ΔS^o values at elevated temperature in all soil types indicate increase in temperature leads to more efficient sorption.

3.4.9. Role of Soil Parameters on Sorption

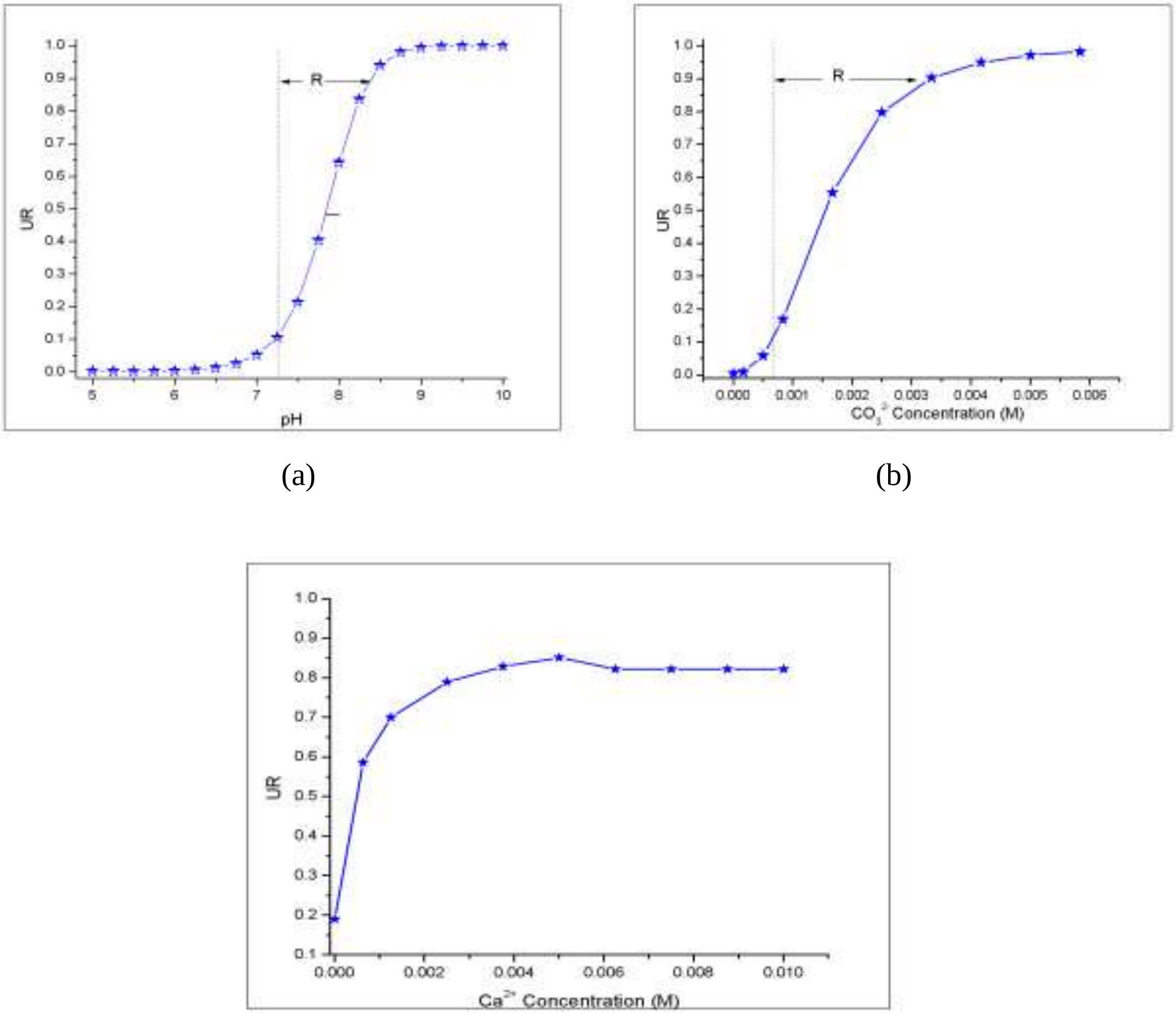
To study the relationship between the *soil parameters (at near neutral pH) with sorption capacity (q)* multi-correlation analysis was carried out between the adsorption capacity (q_{max}), Fe, Mn, Clay, NOM contents and CEC. The correlation matrix is presented in the Table. 3.6.

Table 3.6. Correlation matrix of soil parameters and sorption capacity

	q_{max}	Clay	Mean P.S	NOM	Fe	Mn	CEC
q_{max}	1.00						
Clay	0.54	1.00					
Mean P.S	-0.93	-0.79	1.00				
NOM	0.94	0.79	-0.99	1.00			
Fe	1.00	0.51	-0.91	0.93	1.00		
Mn	0.74	-0.09	-0.44	0.51	0.78	1.00	
CEC	0.55	1.00	-0.80	0.80	0.52	-0.07	1.00

3.4.10. Role of Water parameters on Mobility of uranium

Figure 3.8 (a, b, c) elucidates the effect of pH, CO_3^{2-} and Ca^{2+} on mobility of U(VI) from mineral surface to aqueous phase (water) in contact, whereas effects of SO_4^{2-} and Na^+ are not discussed since it does not exhibit any significant variation on UR. Variation of pH (Fig. 3.8a) indicates that range of pH from 7.25 to 8.5 is the most critical range where, there occurs an abrupt change in UR value. U(VI) ion starts to mobilize from surface above pH 7.25 because at higher pH negative surface dictate at the same time the predominant species of U are negative complexes; $UO_2CO_3^{4-}$, $UO_2CO_3^{2-}$, $UO_2(OH)_3^-$ etc., this leads to repulsion between mineral surface and U species causing increase in UR or desorption. Similar trend was observed when CO_3^{2-} concentration varies in the range of (R) 6.5×10^{-4} M to 3.4×10^{-3} M, which is the critical range where rapid increase in UR was observed.



(a) (b)

(c)

Figure 3.8. Variation of UR with change in; a) pH, b) CO_3^{2-} and c) Ca^{2+} of system

Increase of Ca^{2+} concentrations in solution increases the UR and decreases above 0.004M. Increase in UR indicates that, presence of Ca^{2+} competes with U(VI) for sorption on hydrous ferric oxide mineral as well as due to formation of stable complex of $Ca_2UO_2(CO_3)_3$. Decrease in UR above 0.004M Ca^{2+} concentration attributes to precipitation of Ca^{2+} as *calcite* and *aragonite* in this typical case which in turn accelerate sorption of U(VI) on mineral surface. The results of the sensitivity analysis is presented in terms sensitivity index (SI_{UR}) and it was found that, SI_{UR} for pH, CO_3^{2-}, SO_4^{2-} Ca^{2+} and Na^+ are -1.55,-1.43,-0.001,-0.85 and -0.02, respectively.

This shows pH and CO_3^{2-}extremely affecting followed by moderately by $Ca^{2+}$and affected up to miner level by Na^+ and SO_4^{2-}. The –ve sign indicates that with increase in the concentrations of the said parameters UR increases i.e., aqueous U(VI) increases due to competitive sorption on hydrous ferric oxide mineral surface as well as due to formation of stable soluble complexes.

3.5. Summary

The study of uranium behavior at soil-water interface is highly complex. Sorption study revealed that adsorption/sorption capacity of soil for uranium, increases with Fe, Mn and NOM content. The Fe-Mn controlled sorption system is least affected by organic content (NOM) at circumneutral pH. Among water parameters pH, CO_3^{2-} and Ca^{2+} are sensitive parameters which influence U(VI) mobility at soil water interface. Sorption followed pseudo-second order model with multi-step diffusion process irrespective of soil types and the rate-limiting step is chemisorptions involving valence forces through sharing or exchange of electrons along with ion exchange. The Freundlich and D-R isotherm model were found to be the best describe the adsorption of U(VI) onto soil A, B and D whereas Langmuir model describe the adsorption of U(VI) on soil C. Presence of High Fe and Mn content provides a homogeneous surface which accelerate the monolayer sorption. Thermodynamic parameters infer that sorption is spontaneous, endothermic in nature and follows dissociative mechanism. The study also revealed that geological setup with high ferro-manganese content is best location for waste disposal facilities or geological repository. Thus the Fe or Mn enriched soils can be used as backfill to mitigate migration of U.

Chapter 4

Chemical Fractionation of Uranium in Soil

4.1. Introduction

U concentrations can be found in all environmental matrices, inevitably leading to the exposure of human and non-human biota. From chapter 3 it is clear that geochemical behavior of soil plays important role as it immobilizes the uranium in different soil pools till not subjected to any natural or anthropogenic disturbances. To better assess the environmental impact of U, more information relating to its migration and bio-availability in soils is necessary. U may be present in soil as precipitated, sorbed, complexed and reduced forms, which impact its mobility and fate in the surface as well as subsurface soil environment. Behavior and bioavailability of U in a soil is a function of U speciation/ association in soil which in turn depends on soil properties. Important soil properties that influence the chemical and physical behavior of U includes pH, oxides (and hydroxides) of Fe, Mn, Al and Si, carbonate minerals and organic matter (OM) contents [142-146]**.** It is already discussed that, when U comes in contact with soil it may go to one or several fractions/pools in soil such as, *Exchangeable*, *Carbonate, Reducible fraction (Oxides and hydroxides of Fe, Mn), Oxidizable fraction (Organic matter: OM), Acid leachable fraction (Secondary minerals) and Residual fraction (Primary minerals)*. And the mobility and bioavailability of U in the environment depend not only on total concentration but also on their association with the solid phase (fractions) to which it is bound. It is very important to study the solid phase chemical fractionation of U in soil. In addition to this if there is a chance of rearrangement of the U within different pools of soil with time, this may lead to another question on safety of radioactive waste management. There are many research articles on the solid phase chemical fractionation of uranium in soil, which encompass mainly, case studies for pollution status enquiry and development or modification of analytical methods for sequential extraction only [147-149]. What will happen to the bound uranium with time is not found in literature.

4.2. Present Work

Work was carried out to understand the chemical fractionation of U in soils from different origin and impact of ageing on chemical fractionation. This study integrated batch experiments of U(VI) adsorption to soil, study of U in different soil fractions, ageing impact on fractionation of U and spectroscopic investigation of adsorbed U(VI) using X-ray Photoelectron Spectroscopy (XPS). This integrated approach of studying both wet chemistry and spectroscopic investigation will come out with valuable information, which may be helpful to predict the bioavailability of U in soil and design of remediation technique.

4.3. Methodology

4.3.1. Soil sample and its Characterization

For the study, soil A (Metamorphic origin), B (Sedimentary origin) and C (Igneous Basalt origin) were chosen. Physico-chemical characteristic of the pre-amended soil is already discussed in chapter 3 (Table 3.1, Sec 3.4). Further soil characterization was carried out in amended soil, just after amendment, after one month and after twelve months to investigate any change in soil physico-chemical parameters. U content in soil was estimated in digested samples using voltammetry.

4.3.2. Preparation of amended soil

To investigate the effect of ageing on fractionation of U in different soil fractions it is necessary to know the initial date of contamination, which can be only possible by taking amended soil. For the study all the three soils were amended with the water containing 100mg/L of U(VI) in the ratio of 1:10 (g/mL: soil to solution). The mixture was agitated at 160 rpm in a rotary shaker (SK-300, JIOTECH, Korea) at ambient temperature for 7 days. The 7 days of equilibration time fixed based on our previous experience [147]. After 7 days the supernatant was removed by centrifugation and the soil was allowed to dry at room temperature. Then soil samples were kept as such undisturbed in the falcon tubes with regular opening, in order to provide an ambient environment. The characterization of the soil samples was carried out as described in previous section in order to monitor any change in properties of amended soil but no noticeable change was observed except the U was detected in the amended soil.

4.3.3. Sequential extraction

Sequential extraction for U was carried out two times, at an interval of one month and 12 months. For extraction, processed homogenized soil samples (2 g) were subjected to a sequential extraction method optimized for the quantification of actinides bound to soil to determine the soil fraction to which U is bound [97] with little modification in method as discussed in Chapter 2 (Section 2.7.1). Total U was measured by complete digestion of the same samples. A solution/sample ratio of 10 (mL/g) was used for extraction in each step. After extraction, the leachate was separated from the solid residue by centrifugation at 3000 rpm for 20 min. Before next step, the residue was rinsed with deionized water (18.2 MΩ cm^{-1}) with a water/sample ratio of 5 (mL/g) under stirring for 10 min, then the washing water was combined with leachate after centrifugation. The combined solution was filtered through 0.45 µm Millipore filter paper to remove the small particles. The remaining solid on the membrane was combined with the residue for the leaching of next step. All reaction steps were done in duplicates and aliquots from each step were analyzed for U using voltammetry.

4.3.4. Methodology for XPS Analysis

XPS analysis of 12th month aged samples was carried out to have a better understanding of rearrangements of U in different soil fractions. All XPS spectra were collected on an ESCA apparatus (Make SPECS GmbH) in constant analyzer energy mode. The powdered samples in form of pellets were fixed on sample holder with double sided carbon tape before being placed in the analysis chamber (10^{-10} mbar vacuum). As the studied compounds were electric insulators, the obtained spectra were corrected from the charge effect using as internal reference the *C 1s* line from adventitious aliphatic carbon (284.6 eV). The recorded lines in the spectral regions corresponding to U 4f, Fe 2p and C 1s were fitted using the XPSPEAK 3.0 program after subtraction of the background (Shirley baseline).

4.4. Results and Discussion

As the physiochemical parameters of soil and the interaction of U with various soil components determines the dynamics and chemical fractionation of U in the soil, important characteristics were determined in all the three soils after amendment. The physicochemical parameter data generated were compared with the physicochemical parameters of pre-amended soil which were discussed in chapter 3 (Table 3.1, Sec. 3.4). Study revealed that, there is no change in soil properties after amendment except the U was detected in amended soil. The total U content was found to be maximum in soil C (797.5 mg/kg) followed by 466.5 mg/kg in A and 399 mg/kg in B. The highest adsorption capacity of C can be correlated to its properties, such as high content of OM, Fe and Mn as well as minimum particle size distribution. The lower adsorption capacity of B in comparison to the A although both are chemically not significantly different attributes to higher pH (8.2) which decreases the adsorption of U(VI) on soil during the equilibration period. In amended soil, particle size distribution indicates that average soil textural distribution were in the order of 36 µm for soil C followed by 80 and 90 µm for A and B respectively. The highest organic content was measured for C (1.44%) followed by B (0.15%) and A (0.06%). The Fe and Mn content in the soil were found to be maximum in C (Fe: 5.3% and Mn: 1852 mg/kg), A (Fe: 2.6% and Mn: 246 mg/kg) and B (Fe: 2.2% and Mn:196 mg/kg). The highest cation exchange capacity was evaluated for B (22.12 meq/100g) followed by C (18.8 meq/100g) and A (5.6meq/100g) respectively. The mineralogical data generated by XRD revealed that C dominated by minerals from the family of plagioclase and mica, whereas B and A mainly dominated by quartz with a small percentage of carbonate and mica mineral family.

4.4.1. Chemical Speciation of U

When studying the solid phase chemical fractionation of U in different fractions or pools of soil samples using sequential extraction after one month (Table 4.1), it was observed that U is not uniformly distributed in all fractions. The first fraction (F1) extracted (Exchangeable) is the water soluble and exchangeable fraction which contains water soluble species such as the free uranyl ion and weakly adsorbed U species. As such it represents the most mobile and potentially most available U species in the environment and for the soil C and A, a very small portion (<5%) of total uranium associated with this phase, whereas in case of B which is alkaline in nature about 54 % is associated to exchangeable fraction (F1). The Second fraction (F2), which contains U in carbonate, shows that about 32.19 % of total U exists in this phase for B followed by 17.51% in A and 4.52% in C. Formation of these complexes is dependent on the pH and increases the solubility and availability of U [146, 148]. The association of U to this fraction may be attributed to the high carbonate content which favors the formation of stable Uranly – carbonate complex [145]. An attempt was made to find correlations of the percentage U extracted by the exchangeable fraction (F1) with the clay content or with the CEC of the three soils. This was done based on the *Pearson and Spearman* correlation coefficients, but no dependence was observed (r^2~0.62). For the percentage U extracted by the carbonate fraction (F2), a good correlation was found with the $CaCO_3$ content of the soils (r^2~0.82). The third fraction (F3) is the reducible fraction which includes the oxides of Fe and Mn. Uranium can be scavenged by these oxides through adsorption and/or co-precipitation [149]. The highest relative amounts of U associated with reducible fraction (F3) is for soil C (61.1%) followed by B (6.35%) and A (4.13%). The relative amount of U extracted by the reducible fraction can however be related to the total Fe and Mn content of the soils (r^2~0.98). According to Schultz the fourth fraction (F4) comprises the U associated to soil organic matter which is called as oxidizable phase. The highest U associated to oxidizable phase for C followed by A and B. The correlation between the relative U content and OM was found to be 0.83. The last fraction (F5) which consists of both acid leachable and residual was extracted by complete digestion and it was found that about 69.0 % of total U bound to this fraction in A followed by 23.74 in C and 5.72 in B.

4.4.2. Rearrangement in Chemical Fractionation with ageing

Comparison of physiochemical properties of soil after an interval of 12 months indicates that there is no significant change in any parameters, any change in the parametric value attributes to the measurement uncertainty. But a very interesting result was observed when chemical fractionation of U obtained by sequential extraction were compared (Table 4.1). The comparison of the chemical fractionation of U in between one and 12 months aged soil samples revealed a significant rearrangement occurred among the different fractions, where total U concentration is remained unaltered (Fig. 4.1 a, b and c). This is expected as its closed system no chance of removal of uranium from the system.

Table 4.1. Comparison of physiochemical parameters and Uranium fractionation in different fractions of soil in the interval of One and 12 months

	After One Month			**After Twelve Months**		
	A	**B**	**C**	**A**	**B**	**C**
pH	7.5	8.1	6.9	7.65	8.0	7.0
Particle Distribution (Max)	81	90	35	81	90	35
Fe (%)	2.6	2.2	5.3	2.45	2.25	5.2
RSD	(±2)	(±2)	(±2)	(±2)	(±2)	(±2)
Mn (mg/Kg)	245	196	1852	244.5	195	1855
RSD	(±1.5)	(±1.5)	(±1.5)	(±1.5)	(±1.5)	(±1.5)
SOM (%)	0.058	0.15	1.44	0.62	0.16	1.38
RSD	(±2)	(±2)	(±2)	(±1.6)	(±1.6)	(±1.6)
CEC (meq/100g)	5.6	22.12	18.85	5.6	22.12	18.85
RSD	(±2.5)	(±2.5)	(±2.5)	(±2.5)	(±2.5)	(±2.5)
Total U (mg/Kg)	466.5	399	797.5	455.8	382	799
RSD	(±2.5)	(±3.2)	(±5.1)	(±3)	(±4)	(±4)
		% of Total U				
Exchangeable	4.85	53.96	2.92	5.54	2.35	0.15
RSD	±0.04	±1.8	±0.07	±0.19	±0.07	±0.003
Carbonates	17.51	32.19	4.52	21.28	50.68	8.03
RSD	±0.17	±1.0	±0.1	±0.31	±1.2	±0.27
Oxides of Fe/Mn	4.13	6.35	61.08	8.04	1.2	5.42
RSD	±0.13	±0.20	±1.5	±0.16	±0.03	±0.10
Organic	4.51	1.88	7.79	16.82	14.33	15.74
RSD	±0.16	±0.07	±0.194	±0.67	±0.38	±0.47
Acid Leachable and Residual	69.0	5.72	23.74	48.31	31.44	70.71
RSD	±3.61	±0.28	±0.59	±1.49	±1.0	±3.5

Comparison revealed that there is increase in the U concentration in carbonate phase (F2) in all the soil types and organic phase (F4) whereas decrease in the concentration of U in F3 (Oxides of Fe and Mn). Comparison of U exchangeable fraction revealed that there is major decrease in case of C and B, whereas a slight increase in case of A, which can be neglected considering uncertainty in measurement.

Study of change in F5 (Acid leachable and residual) with ageing indicates that, there is an increase in this fraction for C and B whereas decrease for A from 69% to 48%. This variation in different soil types plausibly arises due to variability in mineralogical compositions: soil B and C compose of smectite and illite respectively as important constituents whereas it's a miner constituent in case of soil A. And U(VI) forms structurally more bound (inner-sphere) complexes with smectite and illite. Interestingly no correlation was derived between the U concentration in different fraction and properties of that fraction except in F2, i.e., there exist a good correlation between concentration of U in F2 and carbonate concentration. Looking at this significant rearrangement of U in different fractions we assume a complex interplay between various soil properties is going on with ageing and following assumptions were derived.

a) Decrease in the exchangeable fraction attributes to formation of more stable complex of U with carbonates and organic matter or adsorption/co precipitation of U on oxides of Fe and Mn.

b) Decreases in F3 (oxides of Fe and Mn) may be attribute to mobilization U in reducible fraction due to re-oxidation [150] and this can be accelerated by carbonate, bicarbonate complexation [151] and/ or occlusion of U-Fe(oxides/hydroxide) complex on amorphous silica [152]**.** However, soil re-oxidation may not lead to complete removal of U from this fraction because, during U mobilization from Fe-rich soil limited by sorption of U(VI) to the secondary Fe(III) mineral [153]. But possibility of change in surface sites of Fe(III) minerals with ages resulting U release from binding site can't be ignored [154]. As per occlusion is concerned it arises due to different in reaction time i.e., U adsorption to Fe-(oxides/hydroxides) is relatively rapid, occurring within minutes to hour while, the observed precipitation of silica occurred over several weeks or months. This sequence of reaction (Uranium adsorption to iron bearing mineral such as ferrihydrite, followed by precipitation of silica coating on ferrihydrite) leads to occlusion.

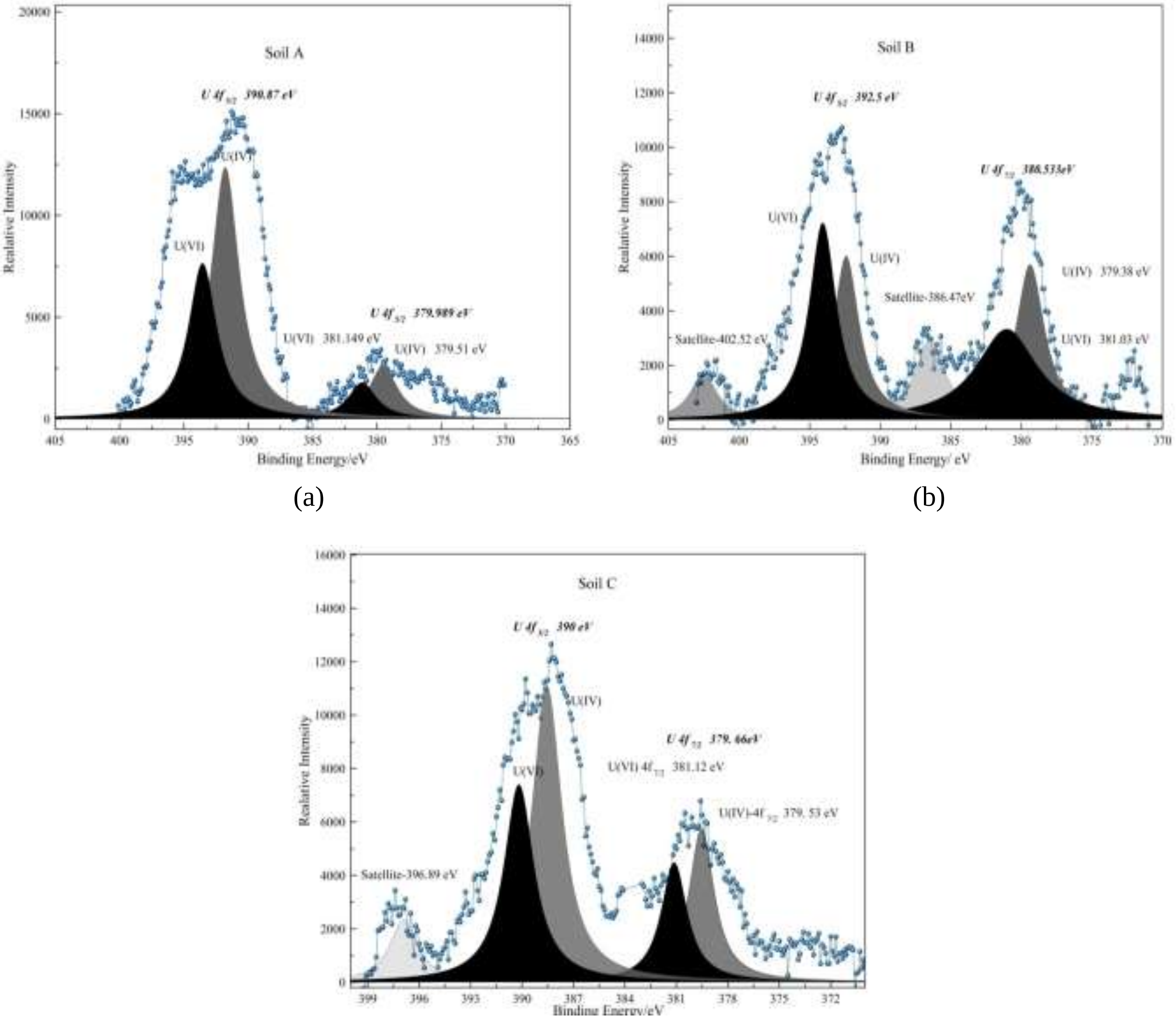
c) Increase in relative percentage of U in F4 (OM) attributed to micro-pore diffusion which follows slow kinetics hence increases over period of time [155].

d) Increase in U concentration in the F5 (Acid leachable and Residual) may be correlated to the occlusion of U to silica or increase in complexation (Inner sphere) with clay mineral [156]. Decrease in case of A is probably from acid leachable fraction because the U trapped in residual fraction only removes by complete destruction of alumino-silicate structure.

4.4.3. Spectroscopic Study

The XPS study of 12th month soil samples were carried out to understand the process occurred with ages. The overall XPS Spectrum of soil samples for U4f spectra is illustrated in figure 4.1**.** The U $4f_{7/2}$ and $4f_{5/2}$ peaks occur around 380 and 390 eV, respectively. The spin–orbit interaction separates these two levels by ~10-12 eV for U. The peak position varies in a narrow range as it is dictated by the crystal structure, the influence of which is due to the nearest-neighbor ions. Shake-up satellites are small peaks that are produced by photoelectrons that have lost part of their initial energy to a valence-band electron. When a core-level electron is expelled, an electrostatic potential is experienced by the valence electrons. They are excited to a higher empty orbital or are knocked off to the continuum almost at the same time. The energy difference between the ground state and the higher orbital defines the difference in position between the satellite peak and the photoelectron peak. The satellite peak position also depends on the valence of the element and the type and number of its nearest-neighbor ions. Literature data show that for uranium, both U4f core-level peaks show satellites at higher binding energies: U(IV) 6–7 eV , U(V) 7.8–8.5 eV and U(VI) exhibits two satellite peaks at 4 and 10 eV [157-162]. Some of the satellites of the U4f$_{7/2}$ peak are buried in the intense U4f$_{5/2}$ peak. Hence, satellites of the U 4f$_{7/2}$ peak and the U 4f$_{5/2}$ peak are normally not considered for spectral interpretation, and one instead uses the satellites of the U 4f$_{5/2}$ peaks and the shape of theU4f$_{7/2}$ peak for the determination of the U(VI), U(V) and U(IV) bands. The presence of two peaks separated by about 10-12 eV clearly indicates the presence of U in the surface of soil. Deconvolution of the parent peaks and peak fitting conclude that U exists in both oxidation states of +4 and +6. This means a part of the +6 get reduced to +4.

Curve fitting results indicates that in soil A about 60% of total U in +6 and 40% in +4 states, In case of B 55% in +6 and 45% in +4 state whereas in case of C 45% in +4 and 55% in +6 states. This is in line with the our study i.e., major fraction of U exists in carbonates (F2) and organic fraction (F4) in case of B, where U supposed to be remain in +6 state whereas in case of C and B major fraction bound to reducible (oxides hydroxides of Fe/Mn) and F5(Acid leachable and residual) fraction. In addition to this presence of satellite peak at about 10.02 eV apart from U4f$_{5/2}$ in case of B confirms the dominancy of the U(VI) species, whereas in case of C presence of satellite peak about 6.89 eV apart from U4f$_{5/2}$ confirms the dominancy of U(IV) species.



(a)

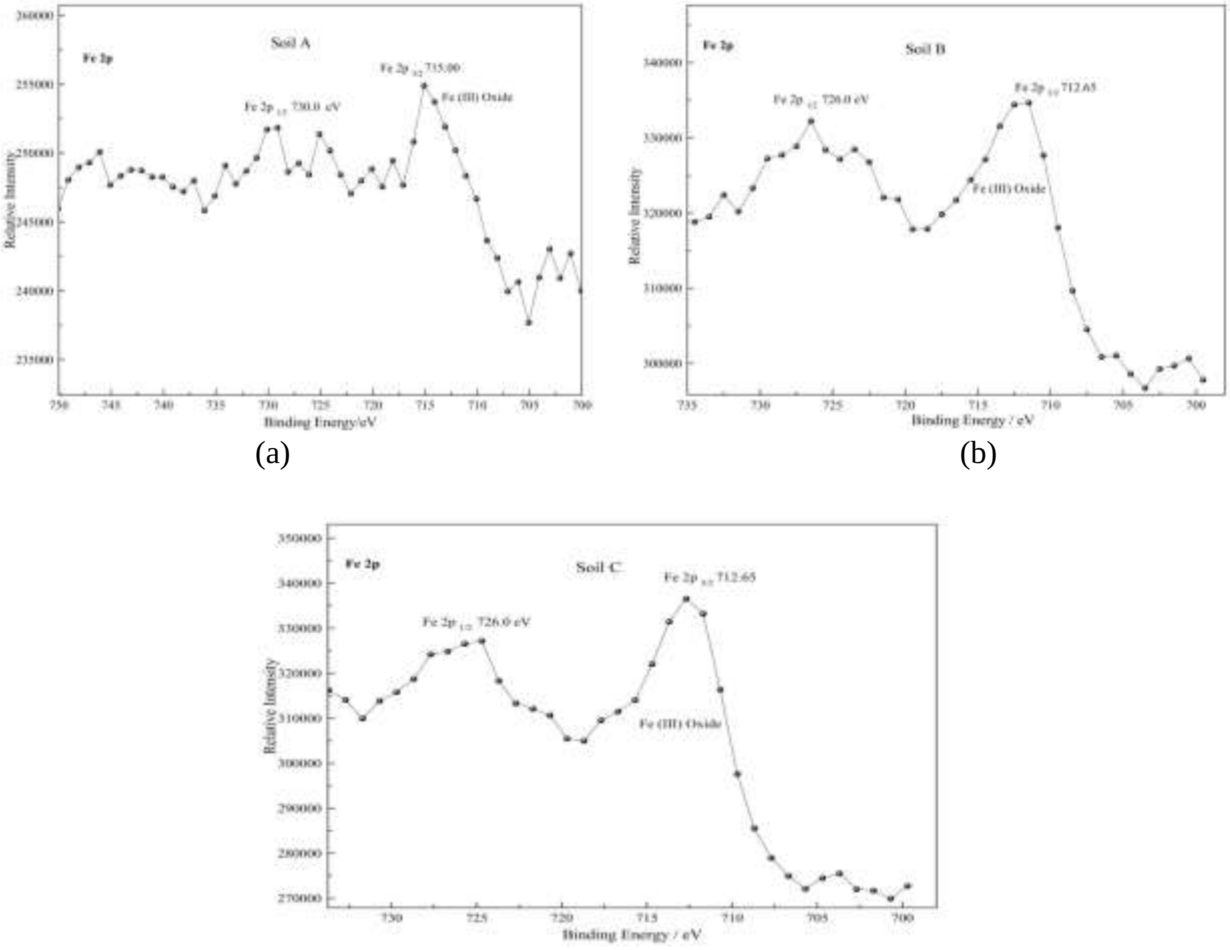
(b)

(c)

Figure 4.1. Deconvulated XPS spectrum with original Spectrum in The U 4f region for Soil: a) A (Metamorphic), b) B (Sedimentary) and c) C (Igneous Basalt)

If we compare the spectrum of all the three soil types, the best resolute peak is observed in case of B followed by C and A , although the order of U content in soil is something different (B<A<C). This indicates that there occurs surface depletion (bulk enrichment) of U in case of C and A and maximum in A, whereas contrary is true for B. As Fe-oxides and hydroxides offer

binding sites for U complexation, the Fe 2p binding energy region was studied for all the three soils and presented in figure 4.2.



(a)

(b)

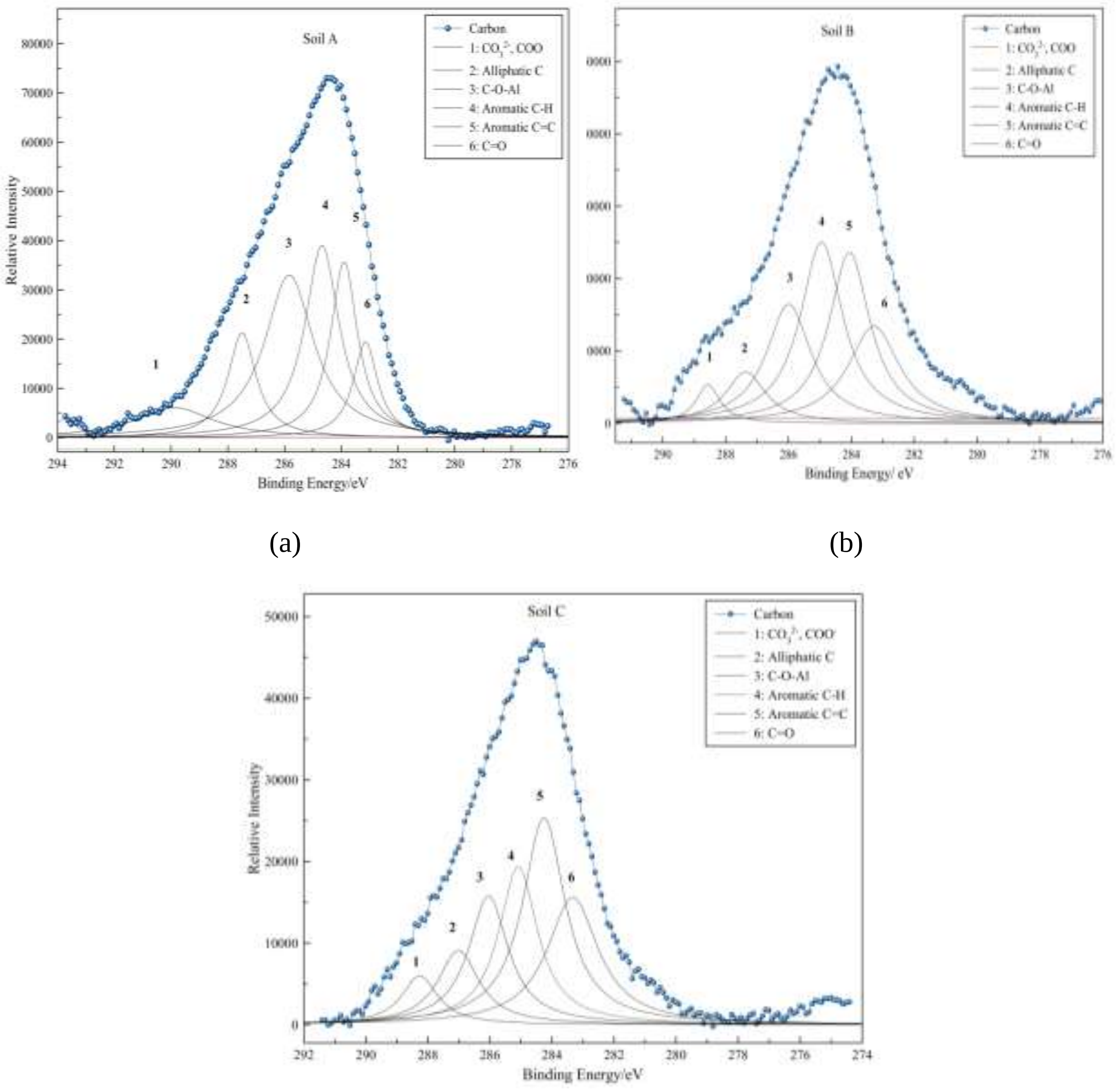
(c)

Figure 4.2. Deconvulated XPS spectrum with original Spectrum in The Fe 2p region for Soil: a) A (Metamorphic), b) B (Sedimentary) and c) C (Igneous Basalt)

The figure 4.2 a, b and c confirm the presence of Fe as surface species. The position of the Fe $2p_{3/2}$ peak at ~712eV is indicative of Fe(III), which may be present in any one of several possible species including, magnetite (Fe_3O_4), hematite (Fe_2O_3) or hydrated ferric oxide (FeOOH). It is difficult for XPS to differentiate between these three Fe(III) containing species. A small fraction of Fe(II) may be present in Fe coupon but was not identified by deconvulation. Very weak Fe 2p peak in case of soil A indicates depletion of surface Fe. Dominancy of Fe(III) ion on surface indicates that our assumption of re-oxidative may not be the case, whereas occlusion of U-Fe(oxides/hydroxide) complex on amorphous silica may be responsible for decrease in the U level in reducible (F3) fraction.

Study of carbon binding region is also important, as both organic (COO^-) and inorganic carbon (CO_3^{2-}) form stable complexes with U in carbonate (F2) and oxidizable (F4) fractions of soil. Unfortunately it is difficult to deconvulate the carbon spectrum for inorganic and organic C in soil like complex matrix, as both the peak lies in the range of 288-290eV.

Figure 4,3, peak at ~286 eV (-C-O-Al) i.e., binding of OM on aluminum oxides of soil, with the supporting peaks of aliphatic and aromatic carbon confirms that soil is coated with organic matter and provides binding sites for sorption of U. Presence of carbonate minerals were confirmed by the XRD spectrum and presence of U in carbonate fractions confirms the U association with the soil carbonate. The deconvulation of $U4f_{7/2}$ peak of C and B does not produce any peak correspond to U(VI)-SiO_2 (not presented here) whereas it is identified for A at 383.33 eV which is in line with XRD data of A. The spectroscopic as well as wet chemistry study revealed that the U fractionation between surface and bulk of soil, where surface concentration is governed by carbonate, organic matter and uncoated or exposed site of oxides of Si and Al, whereas bulk concentration is mainly controlled by oxides of Al, Si. Enrichment of Oxides of Fe/ Mn in surface or bulk phase decides the fate of U in reduced fraction, to be in surface or in bulk soil.



(a) (b)

(c)

Figure 4.3. Deconvulated XPS spectrum with original Spectrum in The C 1s region for Soil: a) A (Metamorphic), b) B (Sedimentary) and c) C (Igneous Basalt)

4.5. Summary

The first aim of this study was to investigate the solid phase chemical fractionations of U in different pools or fractions of soil from different parent rocks. Secondly it was aimed to observe the effect of ageing on these chemical fractionations and spectroscopic study to predict the mechanism involved. It can be concluded that although the fate of U in soil initially governed by concentration of adsorbents (Such as carbonate, oxides of Fe/ Mn, OM etc.in respective fractions) but with ageing there occurs a significant rearrangement of U in these fractions of soil. This leads to either increase or decrease in bioavailability of U, which depends on soil properties as well as environmental conditions. Spectroscopic investigation envisage that a part of total U (VI) is converted to less mobile U(IV), Concentration of U in soil surface is mainly controlled by soil carbonate and organic matter content and up to some extend by exposed site of oxides and hydroxides of Si, Al.   Decrease in U in reducible fraction was due to occlusion of U-Fe-Oxides (Hydroxide) in to amorphous silica rather than the mobilization due to oxidation. Hence U in reducible (F3) and residual (F5) are responsible for U enrichment in bulk soil and may be considered as the irreversible sink for U in soil. Although U associated with the oxidizable fraction of the soil are assumed to remain immobilized for longer periods, they can become available through decomposition processes.

Chapter 5

Effect of Salinity on Migration and speciation of Uranium at Soil-Water Interface

5.1. Introduction

The ground water level has considerably sunk due to the increased demand for drinking, and agricultural uses and reduced re-charging consequent to climate changes. This led to increased salinity of inland ground water system due to low-recharge and intrusion of saline water to ground water system at coastal areas. This may lead to increased leaching of minerals from rocks in contact with the ground water. Elevated levels of uranium and heavy metals were observed in Punjab. This prompted us to study the impact of salinity on the leaching of uranium from soil. Simulation studies using PHREEQC I revealed that pH, CO_3^{2-} and Ca^{2+} ions are critical water parameters influencing uranium migration at mineral-water interface. Effect of salinity or ionic strength on migration and speciation of uranium at mineral water interface are also very important. The increased salinity may induce increased migration from soil to water in contact due to: (a) competition of cations present in the solution with positively charged U species for sorption sites on the solid phase and (b) competition of anions present in the solution for complexation sites with anionic uranium species.

5.2. Present Study

From the above it is evident that fate of uranium and soil is complicated and also sensitive to salt content. The objectives of present work to investigate effect of salinity on migration and speciation of uranium at soil-water interface. These results can be used, to quantify the change in migration behavior of uranium from soil to soil solution due to the increased salinity of soil solution. This has application to assess the environmental impact assessment in natural migration of uranium from soil to water as well as in migration of uranium from nuclear waste disposal sites.

5.3. Experimental

5.3.1. Soil sample and its characterization:

Five contaminated soil samples of same geo-referred location were chosen. Physicochemical characterization was carried out as per standard protocols. Natural organic matter (NOM) content was estimated by loss of ignition technique by heating the soil at 550^0 C (±100 C) for 2h in muffle furnace. Clay mineralogy study of composite soil sample was carried out using X-ray diffract meter over the range of $5–50^0$ 2θ as per standard protocol discussed in chapter 2. The textural analysis of undisturbed composite soil was carried out using particle size analyzer (make CILAS 1109, France, range: 40 nm to 2500 µm) in liquid mode. pH and Eh of soil solutions (10:1 mL: g) were measured using aqua-meter with aqua probe-1000 (UK) , whereas major ions (Na^+, K^+, Ca^{2+}, Mg^{2+}, Cl^-, NO^{3-} and SO_4^{2-}) were estimated by using Ion-Chromatography (ICS 2100, Dionex RFIC, USA).

Soil samples (0.2g) were subjected to microwave assisted complete digestion using HNO_3, HCl and HF in a ratio of 3:1:1. Total U in digested solution was determined by voltammetry (Metrohm Auto Lab, Switzerland) using dropping mercury electrode (DME), whereas total Fe and Mn content were analyzed using AAS (GBC Avanta, France). The method extraction efficiency and quality of analysis were checked against the certified reference material (IAEA-312) for U and IAEA soil-7 for Fe and Mn with the recovery of 98%, 102% and 99% respectively at 95% confidence interval.

5.3.2. Extraction of soil U(VI) by bicarbonate solution

To quantify the U(VI) and U(IV) content in the soil, a bicarbonate extraction was performed. Bicarbonate extraction of U(VI) was carried out under both aerobic and anaerobic conditions as described by Zhou and Gu., [163] to see the effect of oxygen on extraction of U(VI). For anaerobic extraction homogenized soil samples (2g) was handled in the anaerobic chamber (95% N_2/5% H_2) and treated with 20 mL of anoxic 1M $NaHCO_3$ in falcon tubes. The samples were placed in a shaker and vigorously stirred for 7 days in anaerobic conditions. For aerobic extraction, experiment was carried out in open environment. After 7 days both the tubes were centrifuged and supernatant were filtered (using 0.45 µm Celulose acetate Millipore filter) and filtrate was taken for U analysis using voltammetry. Since U(VI) is extracted by bicarbonate extract (both in aerobic and anaerobic condition) the measured U in filtrate represents total U(VI) present in soil. The amount of U(IV) present in the soil was estimated by taking difference of total U (estimated by complete digestion) and U(VI).

5.3.3. Sequential extraction

Dried, homogenized soil samples (2g) were subjected to a sequential extraction method optimized for the quantification of actinides proposed by Schultz et al (1998) with small modification [97]. Total U was measured by complete digestion of the same samples as described above. A solution/sample ratio of 10 (mL/g) was used for extraction in each step. After extraction, the leachate was separated from the solid residue by centrifugation at 3000 rpm for 20 min. The residue was rinsed with deionized water (18.2 MΩ•cm-1) with a water/sample ratio of 5 (mL/g) under stirring for 10 min., then the washing water was combined with leachate after centrifugation. The combined solution was filtered through 0.45 µm Millipore filter paper to remove the small particles. The remaining solid on the membrane was combined with the residue for the leaching of next step. Aliquots from each step were analyzed for U using voltammetery.

5.3.4. Desorption experiment

Na^+, Ca^{2+}, Mg^{2+}, Cl^-, SO_4^{2-} and NO_3^- are the predominant ions present in soil solution. Hence study of salt induced U desorption from soil was carried out at different levels of salinity induced by NaCl, $CaCl_2$, $MgCl_2$, Na_2SO_4 and $NaNO_3$. Desorption studies were carried out at low salinity (0.006 M), medium salinity (0.03 M) and high salinity (0.3 M). For reference, pure water leachability of U was also studied by extracting soluble fraction using double distilled water. 5g soil and 25 mL salt solution (ratio 1:5) was added to a falcon tube. The tubes were shaken on an orbital shaker (200 rpm) for a week at ambient temperature (27^0 C). The suspensions were then centrifuged at 3000 rpm for 15 min, passed through a 0.45 µm filter and analyzed for uranium using Voltammetric (Incase of high saline samples) and fluorimetric technique. The amount of U desorbed were calculated based on the concentrations of U in the desorption solution. All analyses were performed in triplicate and included a blank sample as a control sample. The measurement uncertainties were within the 5% of RSD.

5.4. Results and Discussions

5.4.1. Physicochemical characterization of soil

Figure 5.1 presents the particle size distribution of the composite soil samples, which shows that soil, compose of clay (4.55%), silt (61%), sand (30.45%) and most abundant particle size distribution is 55µm. The major elemental compositions are listed in Table 5.1 along with soil pH, Eh and NOM. pH and Eh data indicates that the soil is near neutral and is moderately reduced. U concentration varies between 21.2- 36.5mg/kg. The presence of any uranium mineral phase could not be detected by the XRD analysis (Fig.5.2) because uranium is only a minor component (or contaminant) in this soil. XRD analysis revealed that soil is enriched with felsic clay minerals (smectite, albite, labradorite and quartz) and calcite.

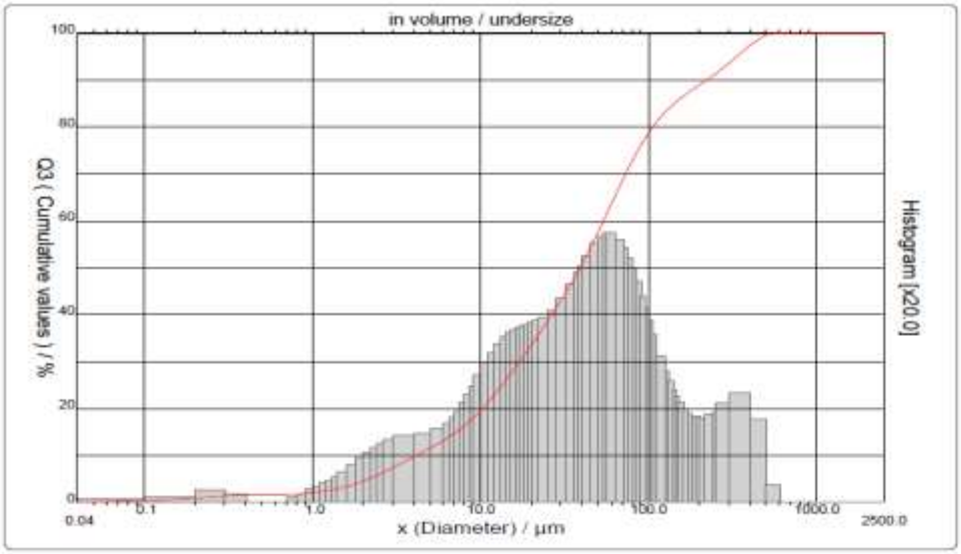


Figure 5.1. Particle size distribution of composite soil sample

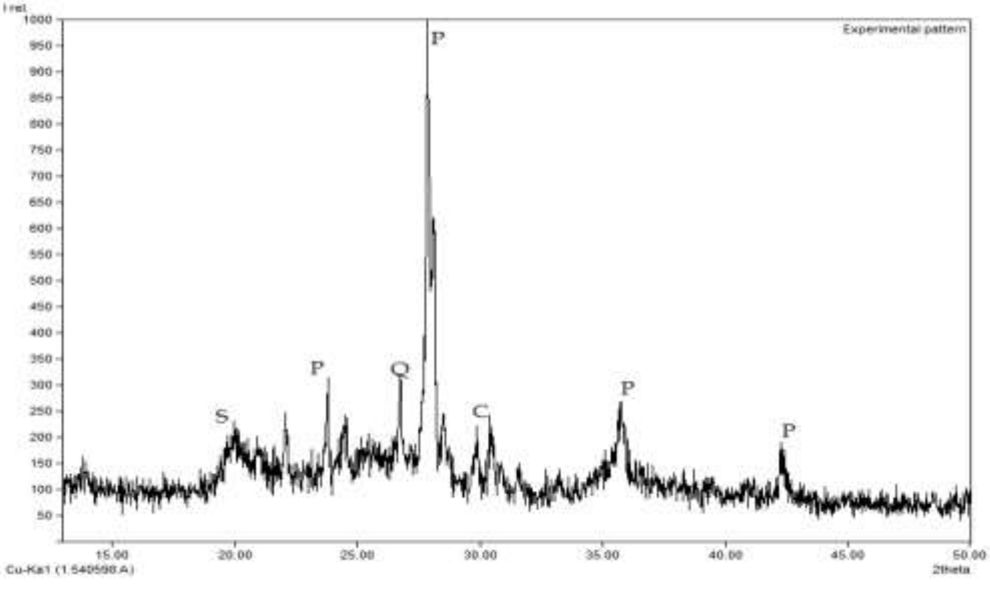


Figure 5.2. X-ray Defractrogram of clay mineralogy present in soil where, S: Smectite, P: Plagioclase (Albite& Labradorite) and Q: Quartz, C: Calcite

Table 5.1. Chemical Composition of the soil with measurement uncertainties

Soil	**Na (%)**	**K (%)**	**Mg (%)**	**Ca (%)**	**pH**	**Ev (mV)**	**U (mg/kg)**	**U(VI) (mg/kg)**	**NOM (%)**	**Fe (%)**	**Mn (mg/kg)**
S-1	2.17 (±3.0%)	0.40 (±3.7%)	0.74 (±2.0%)	5.01 (±4.0%)	7.02	395.0	22.25 (±2.5%)	7.00 (±2.2%)	6.20 (±1.5%)	1.98 (±2.5%)	546.70 (±2.0%)
S-2	1.78 (±2.5%)	0.31 (±3.0%)	0.83 (±4.0%)	6.7 (±1.5%)	7.45	405.0	36.5 (±4.0%)	9.50 (±1.5%)	8 (±1.2%)	2.80 (±2.5%)	554.17 (±2.0%)
S-3	1.47 (±2.5 %)	0.28 (±3.0%)	1.12 (±2.5%)	4.9 (±3.7%)	7.02	395.0	28.75 (±3.5%)	7.90 (±3.7%)	6.70 (±1.2%)	2.57 (±2.5%)	550.80 (±2.0%)
S-4	1.34 (±3.5%)	0.22 (±3.0%)	0.68 (±3.2%)	5.26 (±3.5%)	7.3	399.97	30.55 (±2.0%)	7.60 (±2.8%)	7.20 (±1.2%)	2.78 (±2.5%)	562.30 (±2.0%)
S-5	1.54 (±3.0%)	0.25 (±2.5%)	0.86 (±3.5%)	5.14 (±3.5%)	7.05	380.95	21.2 (±3.0%)	7.40 (±2.5%)	5.80 (±1.2%)	1.97 (±2.5%)	542.000 (±2.0%)

Elemental composition was determined after acid digestion of the soil in duplicates, and the Natural organic carbon content was determined by loss of ignition (LOI) method.

Measurement uncertainties presented in terms of RSD inside the parenthesis.

Soil carbonate and bicarbonate was estimated in 10:1 soil solution by titrimetric method. The soil composition data also revealed that there exists a good correlation between total uranium content with total Fe ($r = 0.99$) and with NOM ($r = 0.94$) content. This indicates U may be preferentially bound to oxides of Fe and NOM. This indicates U may be preferentially bound to oxides of Fe and NOM.

5.4.2. Uranium extraction and speciation in moderately reduced (+395mV to +400.5mV) soil

The results of analysis of speciation of uranium in soil are presented in the Table 5.2. Result indicates that about 29% (Range: 25-35%) of the total U exist as U(VI) and remaining exists in reduced state (U(IV)), whereas under anaerobic condition about 23% of total U extracted as U(VI). Although there is no significant difference between extraction under oxic and anoxic conditions the increases in U(VI) extraction under aerobic condition could not be denied. Leaching of U(VI) by carbonates appears to involve processes like:

a) dissolution of U(VI) bound to soil mineral phases,

b) dissolution of U(VI) bound to NOM at high pH,

c) and oxidation of U(IV) under oxic conditions followed by leaching with bicarbonate solution.

All these three processes may act concurrently or independently. Since first two processes are independent of oxic or anoxic conditions, the third process attributed to the slight increases in U(VI) concentration in aerobic condition in comparison to anaerobic condition.

U bound to different chemical fractions of soil estimated by sequential extraction is presented in table 5.2.The sequential extraction data revealed that maximum (49.7%) uranium exists in acid leachable and residual fraction and remaining U exists in the following order:

Bound to oxides/ hydroxides of Fe or Mn (19.58%) > organic phase (10.89%)> Exchangeable (10.56%)> Carbonate phase (10.13%).

U(VI) which is more mobile and soluble species in the soil–water system preferentially associated to exchangeable phase by ion exchange mechanism. But comparison of the results of both sequential extraction and bicarbonate extract revealed that U(VI) also adsorb to other phases otherwise it could have released with first treatment with $MgCl_2$ (which is used for extraction of exchangeable fraction). This is in line with the previous studies; the uranyl ion and its complexes adsorb onto clays [13, 14], organics [16, 17 22] and oxides [17, 19]. This binding of uranium is controlled by both ion exchange and chemisorptions mechanism which depend upon the soil pH, as lowering of pH reduce the number of exchange sites on variable charged surfaces, such as iron-oxides, aluminum-oxides, and natural organic matter.

Table 5.2. U bound to different fraction of contaminated soil

U in different Fractions	**Reagent used for extraction**	**Average % of total U(±SD) (N=5)**
Exchangeable	0.4 M $MgCl_2$	10.41(±0.48)
Carbonate bound	1 M NaAc in 25 % Acetic acid	9.96 (±0.57)
Fe/Mn oxides	0.04 M NH_2OH_HCl; pH 2	19.58(±2.84)
Organic	5–6 % NaOCl	10.75±(0.42)
Acid Leachable & Residual	H_2O_2, HNO_3, HF, H_3BO_3 , (Concentrated)	49.31±(2.69)
U(VI) Extracted Under Aerobic and Anaerobic Conditions		
U(VI) -Oxic		28.45 (±0.96)
U(VI) -Anoxic		22.78 (±1.00)

5.4.3. Speciation of uranium in soil Solution-Modeling approach.

Chemical speciation of uranium in soil solution (10:1 mL/g, water to soil ratio) was theoretically calculated using speciation code MEDUSA. The chemical speciation of uranium in aqueous system is a function of U concentration, major ions concentration, pH and Eh (since U is a redox sensitive element). Since in the ambient condition U(IV) is not present in soil solution the estimated U in soil solution is considered as U(VI). For U(VI) speciation concentration of major ions (CO_3^{2-}: 0.22mM, Cl^-: 0.52mM, NO_3^-: 2.32mM, SO_4^{2-}: 0.82mM, Na^+: 0.33mM, K^+: 0.12mM, Mg^{2+}: 0.64mM and Ca^{2+}: 1.40 mM), U(VI): 40.8nM), pH and Eh of the soil solution was taken as input. The detail of steps involved in speciation calculation is already discussed in the chapter 2.

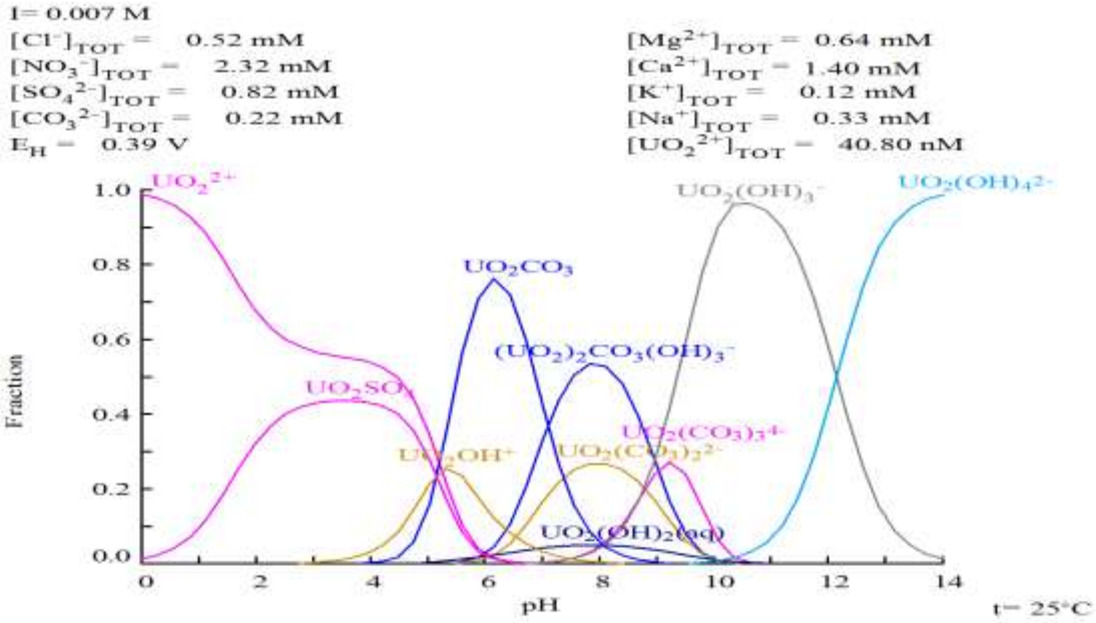


Figure 5.3. Speciation of U(VI) in soil solution

Outcome of the speciation calculation is presented in Fig. 5.3, which indicates that, U(VI) in soil solution exists predominately as UO_2CO_3 followed by $(UO_2)_2CO_3(OH)_3^-$, $UO_2(CO_3)_2^{2-}$, UO_2OH^+ and $UO_2(OH)_2$ species at the specified pH (7) and Eh (0.39V) of soil solution This indicates that in ambient condition U exist predominately as uranyl carbonate and mixed carbonate-hydroxo complexes.

5.4. 4. Effect of ionic strength on Uranium migration

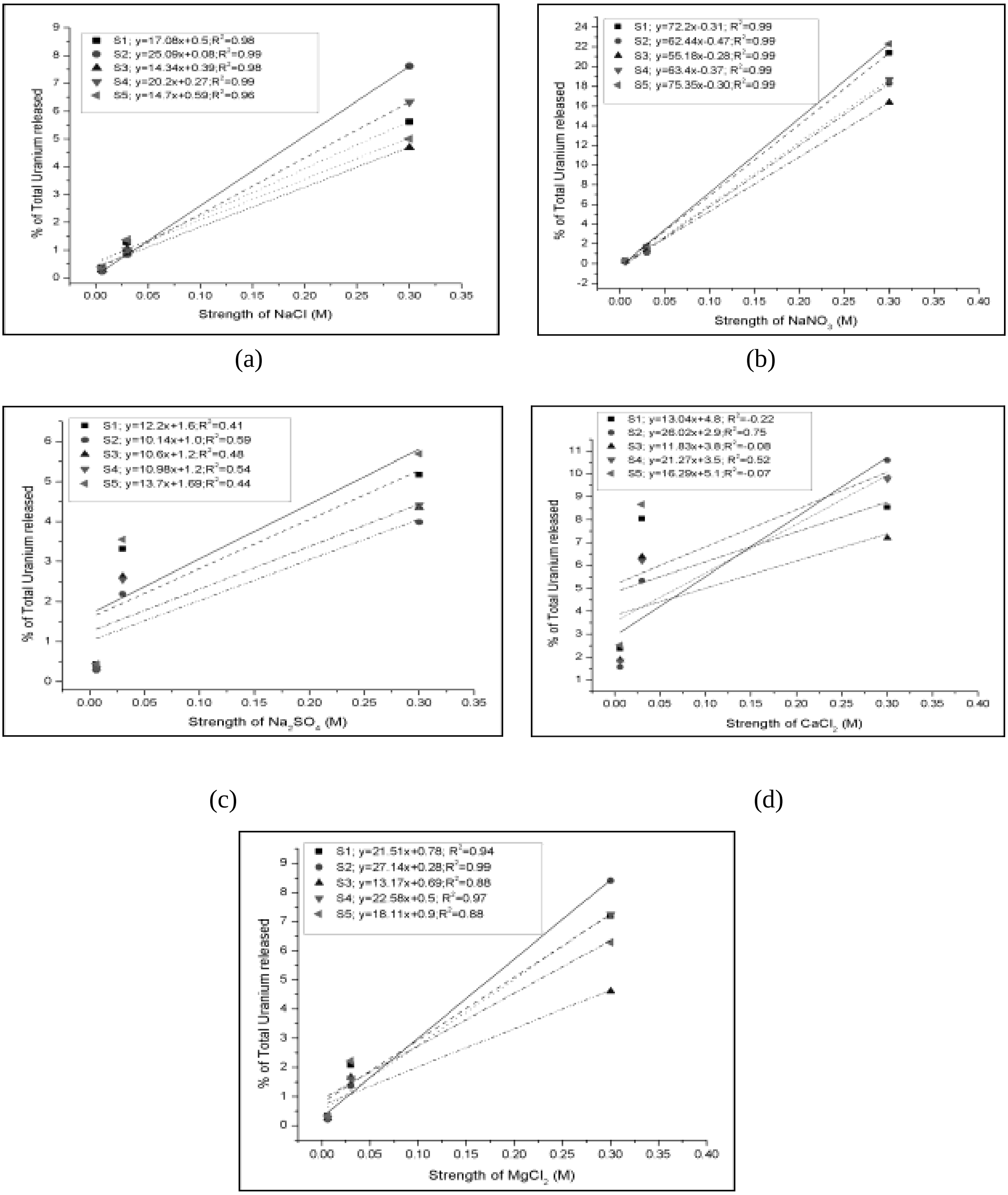
Fig. 5.4 a, b, c, d & e shows the percentage of uranium brought into soluble form when extracted with $MgCl_2$, $NaNO_3$, NaCl, $CaCl_2$ and Na_2SO_4 solutions respectively of different ionic strengths. It can be see that there occurs a significant release of U from soil with increasing the ionic strength of the salt solution and a strong linear relationship ($r2 \approx 0.9$) exist between amount of U desorbed and ionic strength of salt solution except in the case of $CaCl_2$ and Na_2SO_4. The % total U desorbed from soil matrix as a function of salinity is presented in fig. 5.5. Investigation of the figure revealed that at different level of salinity, U migration follows the order as shown below.

Low salinity (0.006M); $CaCl_2 > MgCl_2 > Na_2SO_4 > NaCl > NaNO_3$

Medium Salinity (0.03M); $CaCl2 > Na_2SO_4 > MgCl_2 > NaNO_3 > NaCl$

High salinity (0.3M); $NaNO_3 > CaCl_2 > MgCl_2 > NaCl > Na_2SO_4$

Effect of cations: For the same anion (Cl^-), the migration of U from soil phase to aqueous phase, induced by cations, are in the order of: $Ca^{2+} > Mg^{2+} > Na^+$. Same trend was observed for low salinity (0.006M), medium salinity (0.03M) and at high salinity (0.3M). This can be attributed to the double charge of Ca^{2+} and Mg^{2+} compared with the single charge of Na^+. However, the difference between Ca^{2+} and Mg^{2+} induced migration was likely due to differences in size and atomic mass of these cations; Ca^{2+} is heavier and larger than Mg^{2+}. This trend is followed at all the three salinity level for chloride salts. At low and medium salinity level Na_2SO_4 induces more U desorption than NaCl and $NaNO_3$,this attributes to high ionic strength of Na_2SO_4 in comparison to NaCl and $NaNO_3$, whereas at high salinity level Na_2SO_4 induces least desorption of U although the ionic strength is the same as ionic strength of Ca and Mg salt (0.9 M).



(a) (b)

(c) (d)

(e)

Figure 5. 4. Effect of salts: a) NaCl, b) $NaNO_3$ c) Na_2SO_4 d) $CaCl_2$ and e) $MgCl_2$ on uranium migration, from soil to solution (each point is the average of the five soil samples)

Investigation of Fig. 5.5 shows that $NaNO_3$ exhibits most surprising behavior in U migration, at low and medium salinity it induces least migration (Comparable to NaCl) in comparison to all other salts. This can be justified on the basis of ionic strength and ionic radii of Na^+ ion. But at high salinity it induces highest U migration to solution in comparisons to other salts. The above study also indicates that as the ionic strength of salt solution increases concentrations of ions increases and displace the U(VI) from soil exchange sites forcing it in to solution. Uranium mobilized to solution by increasing ionic strength of salt. process to which uranyl ion is subjected are not completely reversible i.e., it is not affected by increasing strength of the solution. Sorption to oxides of Fe/Mn and OM may be the possible irreversible sinks which immobilize the U(VI) in soil. This is in line with the previous studies which confirmed that, iron oxides (i.e., hydrous ferric oxyhydroxide, lepidocrocite, and goethite) serve as sinks for U(VI) by forming predominantly bidentate surface species [19,133-135]. U(VI) also form inner-sphere bidentate binuclear complexes with silica and ϒ-aluminum oxide surfaces [137,138]. U(VI) also bind to smectite surface which is among the predominate mineral of the contaminated soil (XRD, Fig. 5.2) both by ion exchange and chemisorptions [8, 14, 138, 165,166].

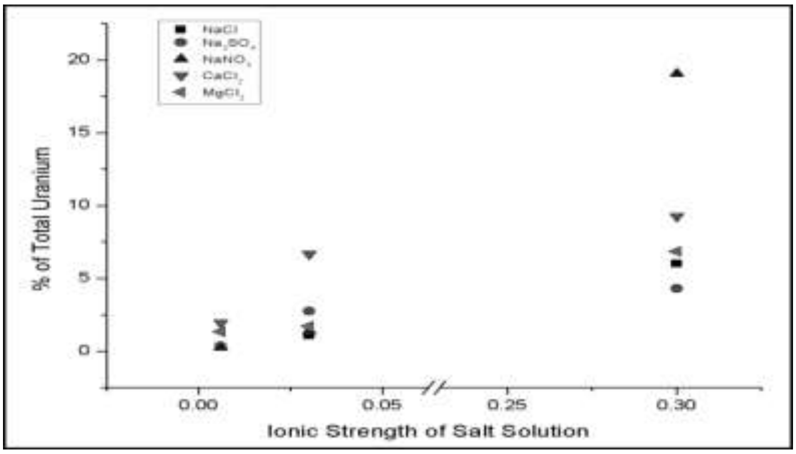


Figure 5.5. Percentage of total Uranium migration as a function of strength of salt solution (M)

5.4.5. Migration of U in relation to the total uranium at exchangeable sites of soil

Above studies revealed that Uranium desorption from soil is independent of total uranium concentration in soil. Experimental outcomes of effect of salinity or ionic strength on U desorption indicates that increase in salinity leads to increase in U desorption. It was also observed that the degree of desorption varies with salt types (Since $NaNO_3$ exhibits anomalous behavior at higher salinity). This indicates that some other factors are also there which controls the migration of U from soil to solution. Therefore, study was carried out to find out the relation between percent of U mobilized as a function of U at exchangeable fraction and presented in Fig. 5.6.

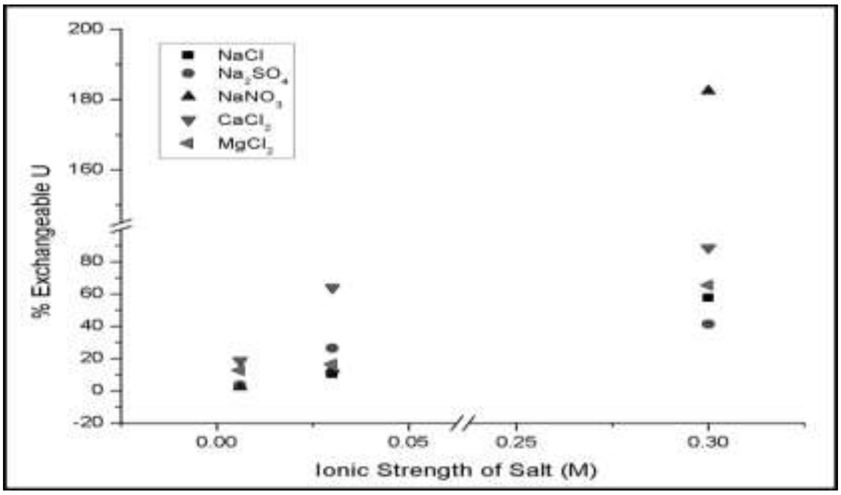


Figure 5.6. Percentage of exchangeable U migration as a function of strength of salt solution (M)

The figure revealed that all the salt follows same order as discussed earlier in fig.5.5. At high salinity Ca^{2+} salt cause a maximum of 89% of desorption of uranium from exchangeable site followed by Mg salt (65.5%)> NaCl (57.5%) > Na_2SO_4 (41.2%). The plausible mechanism involved is ion exchange mechanism only otherwise it could have mobilized the U bound to other fractions (and desorbed percentage could have more than 100% when comparing with only exchangeable fractions only) From the above observation it may be predicted that U in contaminated soil bound to other fractions (Fe/Mn –Oxides, Organic phase etc.) by surface complexation preferably rather than by ion-exchange mechanism only. The maximum desorption of uranium by calcium salt is attributed to its high ionic radii followed by formation of stable aqueous complex like $Ca_2UO_2(CO_3)_3(aq)$ at circumneutral to alkaline pH conditions which accelerate desorption. The nonlinear relation between ionic strength of $CaCl_2$ and U desorption discussed in previous section arises because of limitation of Ca ion to desorb the uranium by ion exchange mechanism only. Fig 5.6 presents that at high salinity $NaNO_3$ induces U migration about 182.5% of exchangeable fraction which is not possible. This clearly envisages that at high ionic strength, $NaNO_3$ has ability to mobilize the U associated with other fractions. This may be attributed to its oxidizing properties which leads to uranium migration occurred concomitant with nitrite formation, suggesting nitrate-dependent, iron-accelerated oxidation of U(IV) to U(VI) [167, 168]. The migration of organically bound U(VI) by decomposition of OM induced by nitrate can't be denied. Hence the degree of migration of U, upon addition of five salts under study revealed that ion exchange mechanism is the prime mechanism. However, in the case of $NaNO_3$ mechanism seems different.

5.5. Summary

The above study revealed that salinity increases U migration from solid to solution phase. The extent of increase in migration depends upon both speciation of uranium in soil as well as the type of salt responsible for the increase in salinity. In moderately reduced soil, major fraction of uranium exists in U(IV) state. It is observed that exchangeable uranium as well as uranium bound with NOM and Fe/Mn gets leached into solution when treated with 1M sodium carbonate solution in aerobic condition. This study indicates that, U migration from soil by salts ($CaCl_2$, $MgCl_2$, Na_2SO_4 and NaCl) is independent of the total U content of soil rather it is depends upon % of total U in exchangeable sites. $NaNO_3$ induced uranium migration involves ion exchange as well as oxidative dissolution of U(IV) bound to Fe/Mn-oxides and NOM. Migration study also indicates that the fraction of U(VI) bound to Fe/Mn-oxides and NOM by some mechanism other than ion exchange. The study provides an important message that high level of NO_3^- in ground water is potential to mobilize the soil U(VI) by changing the redox potential of environment. The comparatively higher levels of uranium present in ground water, including those in Punjab, should be viewed in the light of present studies.

Chapter 6

Migration and Speciation of Uranium at Ore-water interface: Role of Ionic Strength, Humic Acid, pH and Carbonate

6.1. Introduction

The geogenic uranium present in mineralized rock may migrate to water in contact. The migration rate depends upon the pH and redox condition of the ore water binary system, the contact time and water quality parameters of water in contact. The observed high concentration of uranium in ground water from Punjab area can be attributed to the migration from mineralized rock surfaces. The study of the process of migration of uranium from ore to ground water will help in locating potential areas of uranium in the country which in turn is important in regulatory point of view. The study of ore-water system is limited in literature and almost no data available in Indian conditions. Changes in environmental conditions and water quality due to various remediation schemes, natural weathering processes and due to climate change also may enhance uranium migration form mineral to water system in contact. Uranium minerals in different host rocks behave differently with these changing conditions. Previous chapter elucidate that increase in the salinity at soil-water interface highly influence the migration of uranium along with speciation. This may influence migration and speciation of uranium at ore-water interface also. In addition, change in carbonate concentration, pH and temperature also influence migration of uranium

6.2. Present Work

The work is focused on the role of ionic strength of the water in uranium migration from ore mineral to water in contact and speciation in the binary system (ore-water). Experiments were also carried out in ternary system (Uraninite-Water- Humic Acid) to investigate the impact of humic acid on migration of uranium at different ionic strength. Laboratory batch experiments were also carried out to investigate migration of uranium at varying pH and carbonate concentration.

6.3. Materials and Method

6.3.1. Characterization of Ore and binary phase:

Mineralogical study using XRD: For the study, two representative ore samples were collected from the different mining site differing in host rocks (Ore A: Quartz based, Ore B: Carbonate based). The samples were air dried, ground, homogenized and sieved through a 2 mm sieve and immediately sealed in plastic bags for future experiments. Mineralogy study of both the ores was carried out using GNR (Italy) APD 2000 PRO X-ray diffractometer as per standard procedure discussed in chapter 2.

Elemental Analysis: Powdered ore samples (0.2 g) were subjected to microwave-assisted complete digestion using HNO_3, HCl and HF in a ratio of 3:1:1 with few drops of H_3BO_3. Total U in digested solution was determined by voltammetry (Metrohm VA Stand 663 Auto Lab, Switzerland) using dropping mercury electrode (DME), whereas total Fe, Pb, Cu content were analyzed using AAS (GBC Avanta, France). The method extraction efficiency and quality of analysis were checked against the certified reference material (IAEA-312) for U and IAEA soi-7 for Fe, Pb, Cu content.

Extraction of U(VI) by bicarbonate solution: In order to study the speciation of uranium (U(VI)/U(IV) in the ore, a bicarbonate extraction was performed under anoxic conditions as described by Zhou and Gu., 2005 [157]. Homogenized ore samples (2 g) were treated with 1 M $NaHCO_3$ and shaken for 24 hours in a shaker in a special reactor in which anaerobic atmosphere is maintained by passing a mixture of gas (95 % N_2/5 % H_2). Subsequently, the leachate was separated by centrifugation and filtered using 0.45 µm cellulose acetate filter paper. The filtrate was analyzed for uranium using voltammetry, which represents total U(VI) concentration. The amount of U(IV) present in the ore was obtained by taking difference between total U and U(VI).

Chemistry of Binary Phase (Ore-Water): An ore-water binary system was prepared by mixing ore with synthetic water (IS. 0.0001M) in the ratio of 1: 10 (g/mL). The mixture was shaken for 24 hours at room temperature followed by separation of leachate by centrifugation. The pH and Eh of leachate were measured using aqua-meter with aqua probe-1000 (UK). The major ions (Na^+, K^+, Ca^{2+}, Mg $^{2+}$,, Cl^-, NO_3^- and SO_4^{2-}) were estimated using ion chromatography (ICP2100, Dionex, RFIC, USA). The carbonate and bicarbonate in the solution were measured titrimetrically using Metrohm Auto- tritator (Tritrino).

6.3.2. Effect of variation of pH

To study the effect of variation of pH on migration of uranium from ore to water, batch experiment was carried out in ore-water system (1:10 g/mL). Solutions with pH ranging from3, 4, 5,6,7,8 and 9 were prepared using ultrapure HCl (1M) and NaOH (0.5 M) with continuous agitation. The solutions were equilibrated for seven days, pH being monitored every day to check any change in pH due to buffering action of minerals in host rock. After 7 days, samples were centrifuged, aliquots from the supernatant were taken and U concentration measured using voltammetry.

6.3.3. Effect of Carbonate

To study the effect of variation of CO_3^{2-} concentration, batch experiment was carried out for both the ore types at four different concentrations, 0.05, 0.1, 0.5 and 1M of Na_2CO_3 at same ore to water ratio (1: 10g/mL). After seven days of continuous shaking, solutions were separated by centrifugation followed by filtration using Millipore filter paper. Uranium concentration in the leachate (Aqueous Phase) was measured using voltammetry.

6.3.4. Desorption Experiments using water of different ionic strength

Desorption experiments of uranium from both the ores (A and B- using synthetic water made of three different salt and at four different ionic strengths (total 24 no of sample in batch) were carried out. Synthetic water of different ionic strengths (0.001, 0.01, 0.1 and 1.0M) were prepared in deionized water (18.2 µS/cm, TKA Smart 2 pure, Germany) and salts $CaCl_2$, $NaNO_3$ and NaCl (99.9% assay, Merck, Mumbai). Prepared synthetic water was kept in anaerobic chamber (under Nitrogen Atmosphere) for future experiments. 4 g of powdered ore was added to 40 mL of synthetic water in falcon tubes and the tubes were agitated at 160 rpm in a rotary shaker (SK-300, JIOTECH, and Korea) at ambient temperature for 7 days. The leachate was separated from the ore by centrifugation (Eppendorf Centrifuge 5430 R, Germany) at 4000 rpm for 15 min followed by filtered using Millipore filter paper (0.45µm) to ensure the solutions were free from particles. The U concentration in the supernatants was analyzed using voltammetry in DPAdCSV mode. The pH, Eh, concentrations of major ions of each leachate was also measured concurrently. Each experiments and measurements were carried out in duplicate.

6.3.5. Desorption Experiment in ternary system (Uraninite-Water- Humic acid)

A stock solution of Humic acid (200mg/L) was prepared by taking required weight of Humic acid and diluting it in a 100 mL standard flask. Then 3 mL of humic acid (from stock solution) was spiked to each tube so that the final concentration of humic acid in each tube is 15mg/L and solid (Ore) to solution (water) ratio 1: 10 (g/mL) maintained. The mixture was agitated at 160 rpm in a rotary shaker (SK-300, JIOTECH, Korea) at ambient temperature for 7 days. Then the solution was separated from the ore by centrifugation (Eppendorf Centrifuge 5430 R, Germany) at 4000 rpm for 15 min. The supernatants were then filtered using Millipore filter paper (0.45 µm) to ensure that solutions were free from particles before measuring the U concentration. Level of uranium in the leachate was analyzed using Voltametry in

DPAdCSV mode. Each experiments and measurements were carried out in duplicates. The chemistry of each leachate was also studied by measuring pH, Eh, major ions.

6.4. Results and Discussion

6.4.1. Physio-Chemical Characterization of Ore

The initial chemical composition of both the ore (A and B) and Ore-water binary phase is presented in the Table 6.1.

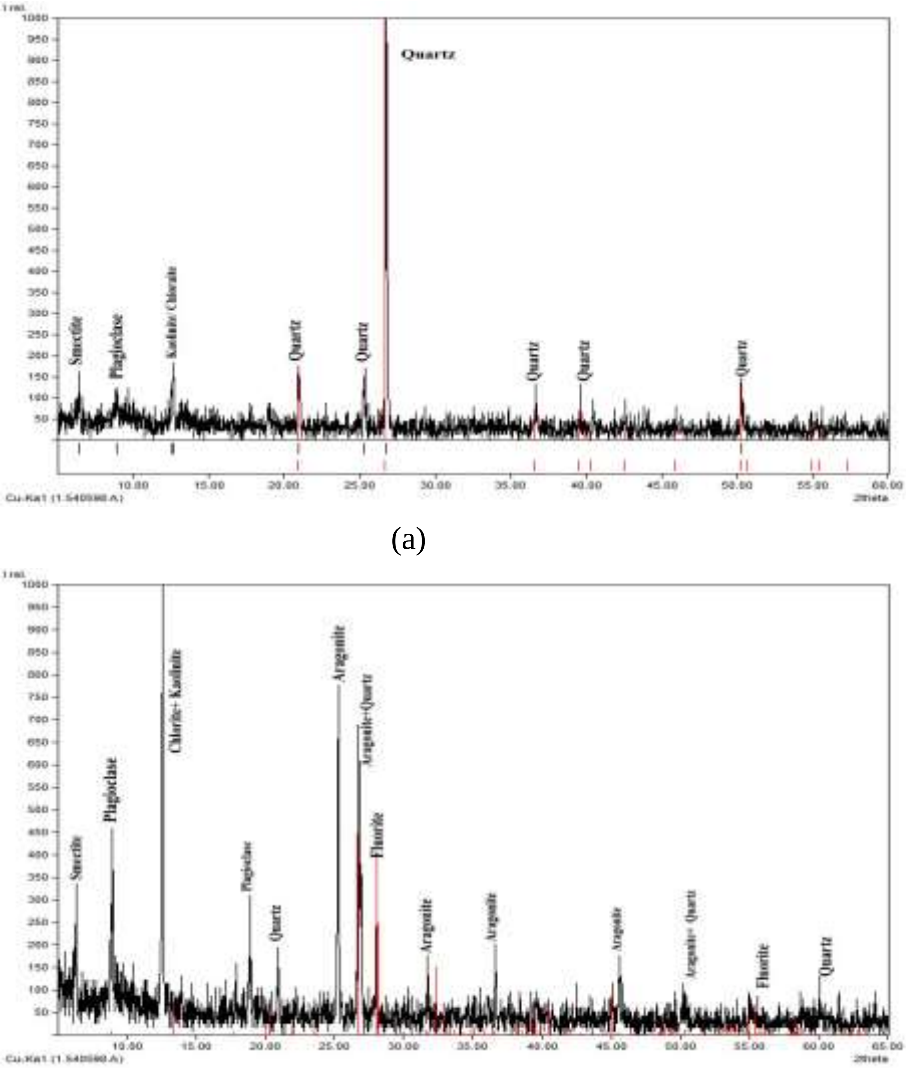
Table 6.1 Physico-Chemical Characteristics of the Ore and Ore -Water Extract with Measurement Uncertainties

Sample	**Cu**	**Pb**	**Fe**	**U (Total)**	**U(VI)**
Unit	**(mg/kg)**				
Ore-A	1107.95 (±22.18)	124.65 (±2.5)	59135.48 (±1214)	721.0 (±43)	35.41 (±2.1)
Ore-B	1770.43 (±35.4)	57.52 (±1.2)	63526.32 (±1270.5)	385.85 (±17)	39.38 (±2.0)

Ore –Water Extract

Sample	pH	Eh	U	F^-	Cl^-	NO_3^-	SO_4^{2-}	HCO_3^-
Unit		V	µg/L	mg/L				
Ore-A	7.34	0.395	2.94	1.20	58.79	131.81	0.55	47.82
Ore-B	7.53	0.405	29.01	0.53	57.14	121.15	22.26	50.00

The concentration of Cu, Pb, Fe, U in Ore A are 1107.9(±22.18) mg/kg, 124.6 (±2.5) mg/kg 59135.5 (±1214) mg/kg, 721 (±43) mg/kg respectively whereas in Ore B, 1770.43 (±35.4) mg/kg, 57.52(±1.2) mg/kg 63526.32 (±1270.5) mg/kg, 385.85 (±17)mg/kg respectively. The bicarbonate extraction studies of ores revealed that Ore A consists of 35.4 mg/kg of U(VI) which is about 5.0 % of total U and Ore B consists of 39.4mg/kg which is about 10.2% of total Uranium



(a)

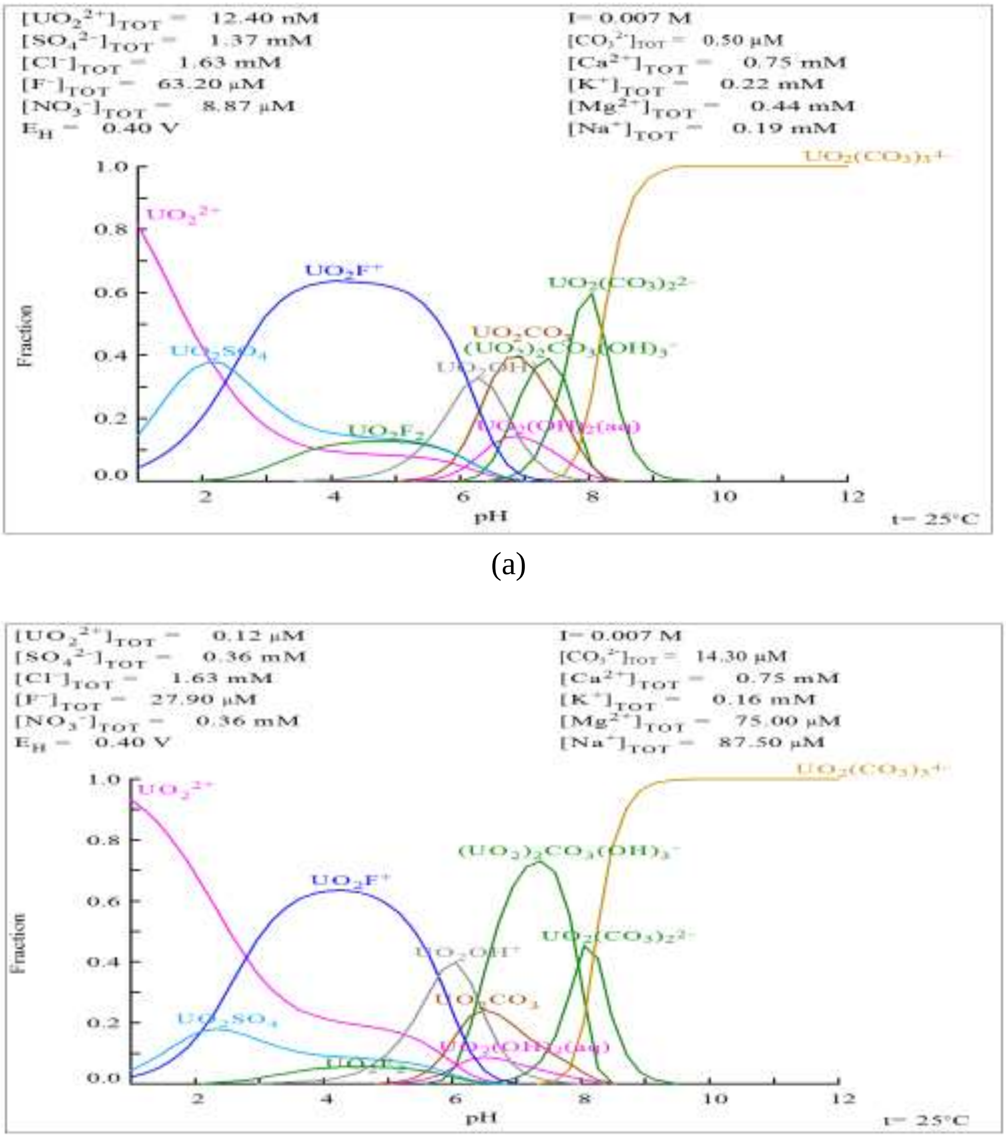
(b)

Figure 6.1. X-ray diffractogram of ore minerals: a) Ore A and b) Ore B

The mineralogical study of Ore A and B is presented in figure 6.1 a & b respectively. Study revealed that. Ore A is dominated with quartz, followed by chlorite, kaolinite and smectite, whereas Ore B is dominated with carbonate mineral (Aragonite) followed by plagioclase, quartz, kaolinite and smectite,. Mineralogical data revealed that both ore are differing in host rock minerals; ore A is quartz based and ore B is carbonate based.

6.4.2. Speciation of Uranium in Ore and Binary Phase:

The concentration of uranium (total) and U(VI) in both the ores is presented in the Table 6.1 Study indicates that about 5.0% of total Uranium exist as U(VI) in ore A and remaining is in U(IV) state, whereas in Ore B, about 10.2% of total Uranium exist as U(VI) and remaining in U(IV) state. The chemical speciation of U(IV) in binary phase in both the systems is presented in the figure 6.2 a and b.



(a)

(b)

Figure 6.2. Speciation of Uranium in Binary phase: a) Ore-A- Water, b) Ore-B –Water

Chemical speciation of uranium in binary system (Ore-water ; 10:1 mL/g, water to ore ratio) was theoretically calculated using speciation code MEDUSA. The chemical speciation of uranium in aqueous system is a function of U concentration, major ions concentration, pH and Eh (since U is a redox sensitive element). Since in the ambient condition U(IV) is not present in aqueous phase the estimated U in aqueous phase is considered as U(VI). The detail of steps involved in speciation calculation is already discussed in the chapter 2. Speciation study revealed that, for the binary system A at the pH of 7.34 Eh of 0.4V and specified ionic composition, uranyl species namely $(UO_2)_2CO_3(OH)_3^-$, UO_2CO_3, $UO_2(OH)_2$, UO_2OH^+ and $UO_2(CO_3)_3^{4-}$ were present out of which aqueous $(UO_2)_2CO_3(OH)_3^-$ is predominating species followed by UO_2CO_3. In case of system B, $(UO_2)_2CO_3(OH)_3^-$, $UO_2(CO_3)_2^{2-}$, $UO_2(CO_3)_3^{4-}$, UO_2CO_3, $UO_2(OH)_2$, and UO_2OH^+ were present and $(UO_2)_2CO_3(OH)_3^-$ is the predominating species followed by $UO_2(CO_3)_2^{2-}$ at pH 7.53 and Eh 0.4V. This indicates that, U(VI)-carbonato and mixed hydroxyl-carbonate species are responsible for uranium concentration in aqueous phase.

6.4.3. Role of Ionic Strength

Figure 6.3 (a, b and c) and 6.4 (a, b and c) shows that there is an increase in U desorption from both the Ore A and B with increase in ionic strength of the synthetic water in ore-water system. The ionic strength induced desorption is more in case Ore B than Ore A, which can be attributed to the larger amount of U(VI) in the ore B as compared to Ore A.

It can be seen from figures that

An increase in ionic strength of NaCl from 0.001M to 1.0 M leads to

1. An increase in concentration of U in aqueous phase from 0.24 µg/L to 4.18 µg/L, in the case of Ore-A.

2. An increase in concentration of U from 12.4 to 62.82 µg/L in aqueous phase, in the case of Ore-B.

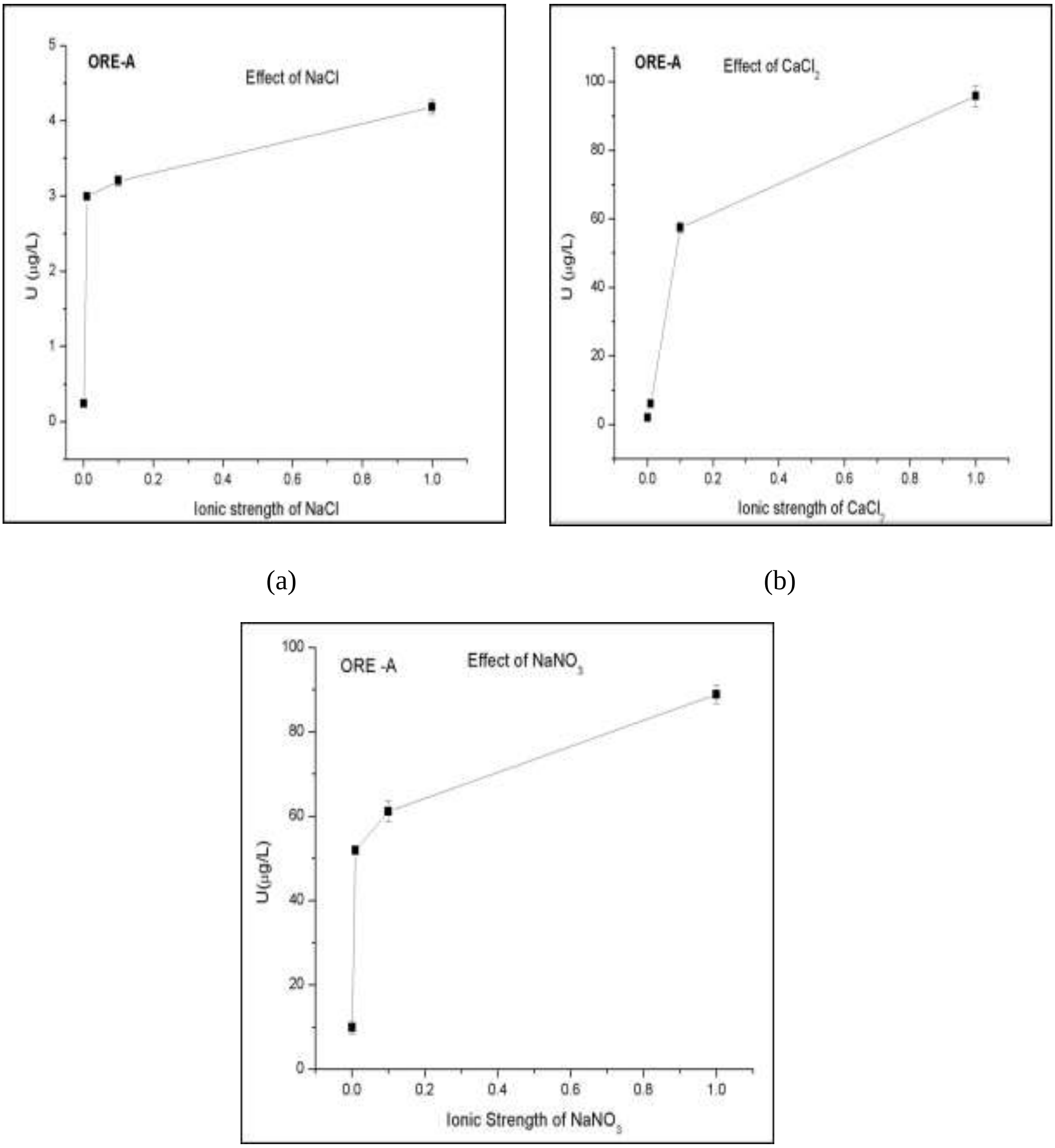
An increase in ionic strength of $NaNO_3$ from 0.001 M to 1M leads to

1. An increase in concentration U in aqueous phase from, 8.9 µg/L to 88.8 µg/L, in the case of Ore-A.
2. An increase in concentration of uranium in aqueous phase from 10.95 to 96.27 µg/L, in the case of Ore-B.

An increase in ionic strength of $CaCl_2$ system from 0.001 M to 1M, leads to

1. An increase in concentration of U in aqueous phase from 1.98 to 95.8 µg/L, in the case of Ore-A.
2. An increase in concentration of Uranium in aqueous from 19.52 to 521 µg/L in the case of Ore-B.

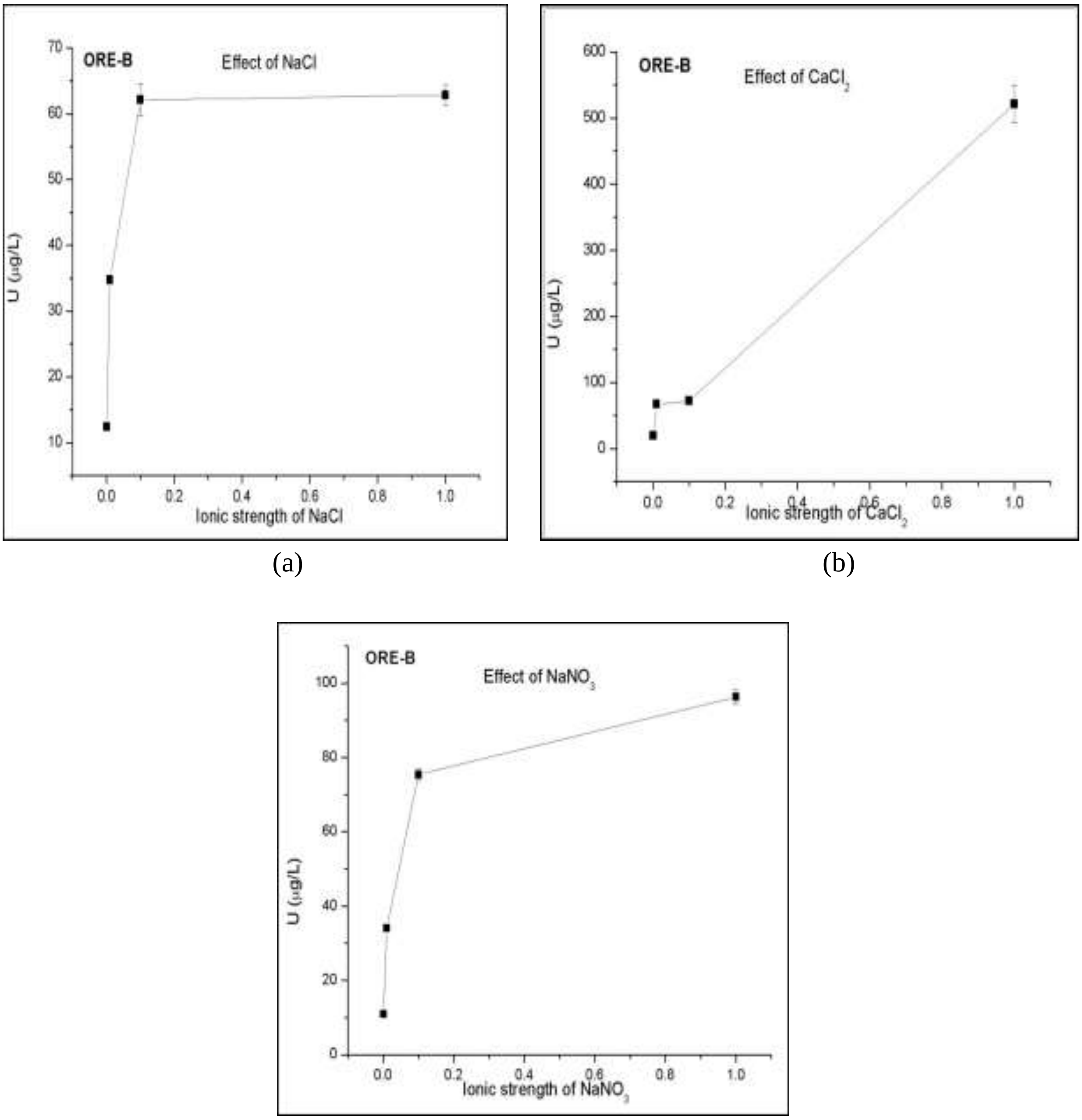
The migration of uranium from Ore to solution phase may be attributed to the ion exchange mechanism. i.e., the U (VI) bound to the exchangeable fraction of the minerals present in the ore get replaced by the competing cations Na^+ and Ca^{2+}. The efficient capacity of the Ca ions to replace Uranyl ions in comparison to Na^+ ions can be attributed to its higher ionic potential which in turn depends upon ionic radii and ionic charge. Close observation of the figures indicates, in both the cases (Ore A and Ore B), that NaCl induced desorption of Uranium achieved the saturation almost after 0.1M I.S. Whereas desorption of uranium from ore follows almost a linear relationship with the I.S of $NaNO_3$ and $CaCl_2$ systems. Higher desorption of U in case of $NaNO_3$ in comparison to NaCl is clearly not understood. Literature survey was carried out to understand the anomalous behavior of the $NaNO_3$ and it was found that nitrate Salt has potency to oxidize the reduced U biotic as well as abiotic way [167, 168]. Hence it may be due to oxidative dissolution of U(IV) in Uraninite. This study also indicates that with increase in ionic strength of salt solution, concentration of ions in the aqueous phase increases, which displace the U(VI) from exchange sites forcing it into solution



(a) (b)

(c)

Figure 6.3. Effect of I.S of ; a) NaCl, b) $CaCl_2$ and c) $NaNO_3$ on desorption of Uranium from Ore in Ore-water system A



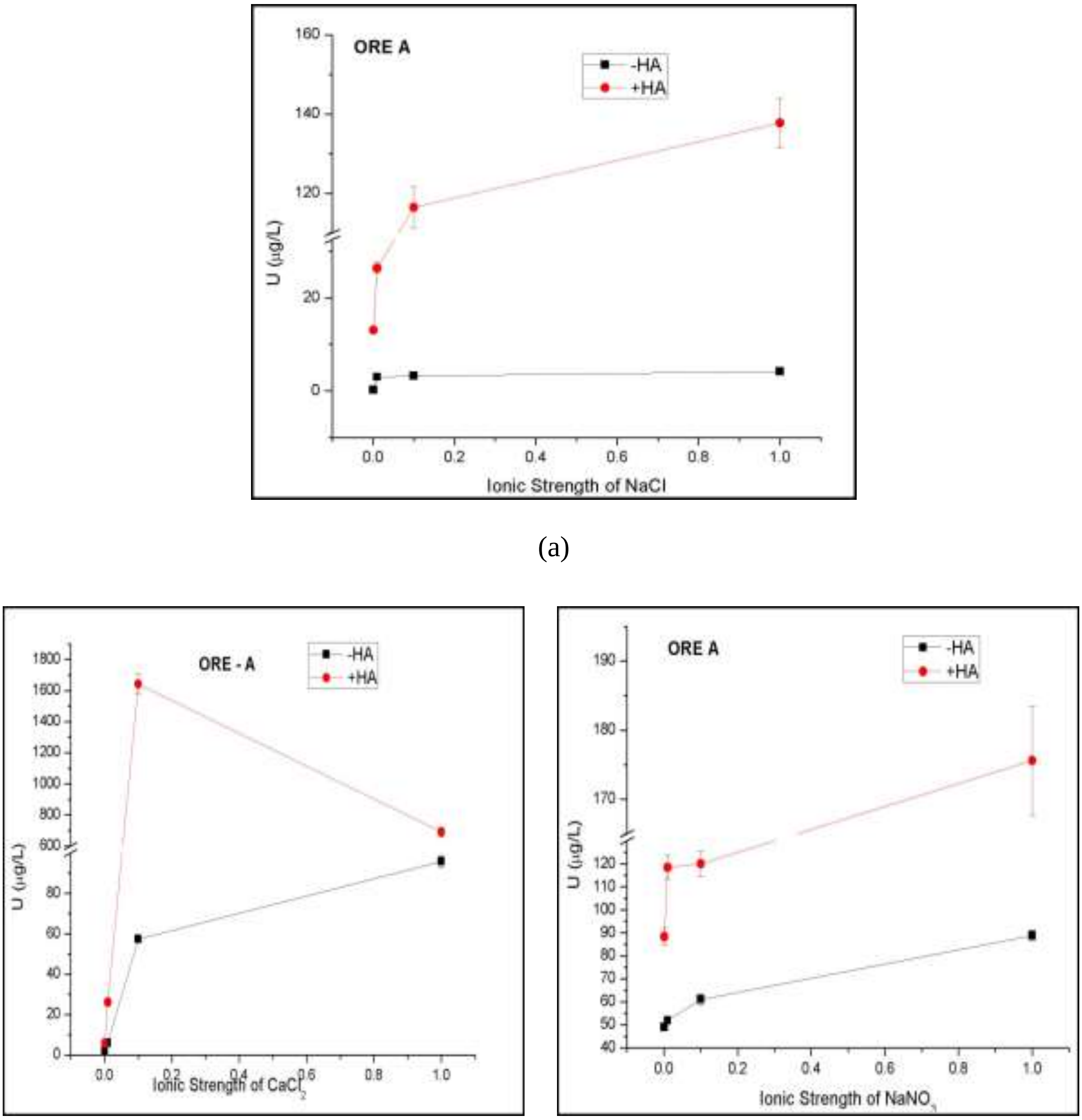
(a) (b)

(c)

Figure 6.4. Effect of I.S of ; a) NaCl, b) $CaCl_2$ and c) $NaNO_3$ on desorption of Uranium from Ore in Ore-water system B

6.4.4. Study of Ternary System:

Role of Humic acid is extensively studied in soil-water system, but no literature was found on the role of humic acid on migration of uranium from Uraninite (ore) in Uraninite-water System. Here we have studied the migration of uranium in the ternary system due to presence and absence of humic acid (Presented in figure 6.5. a, b and c; Ore A and Figure 6.6. a, b and c: Ore B)

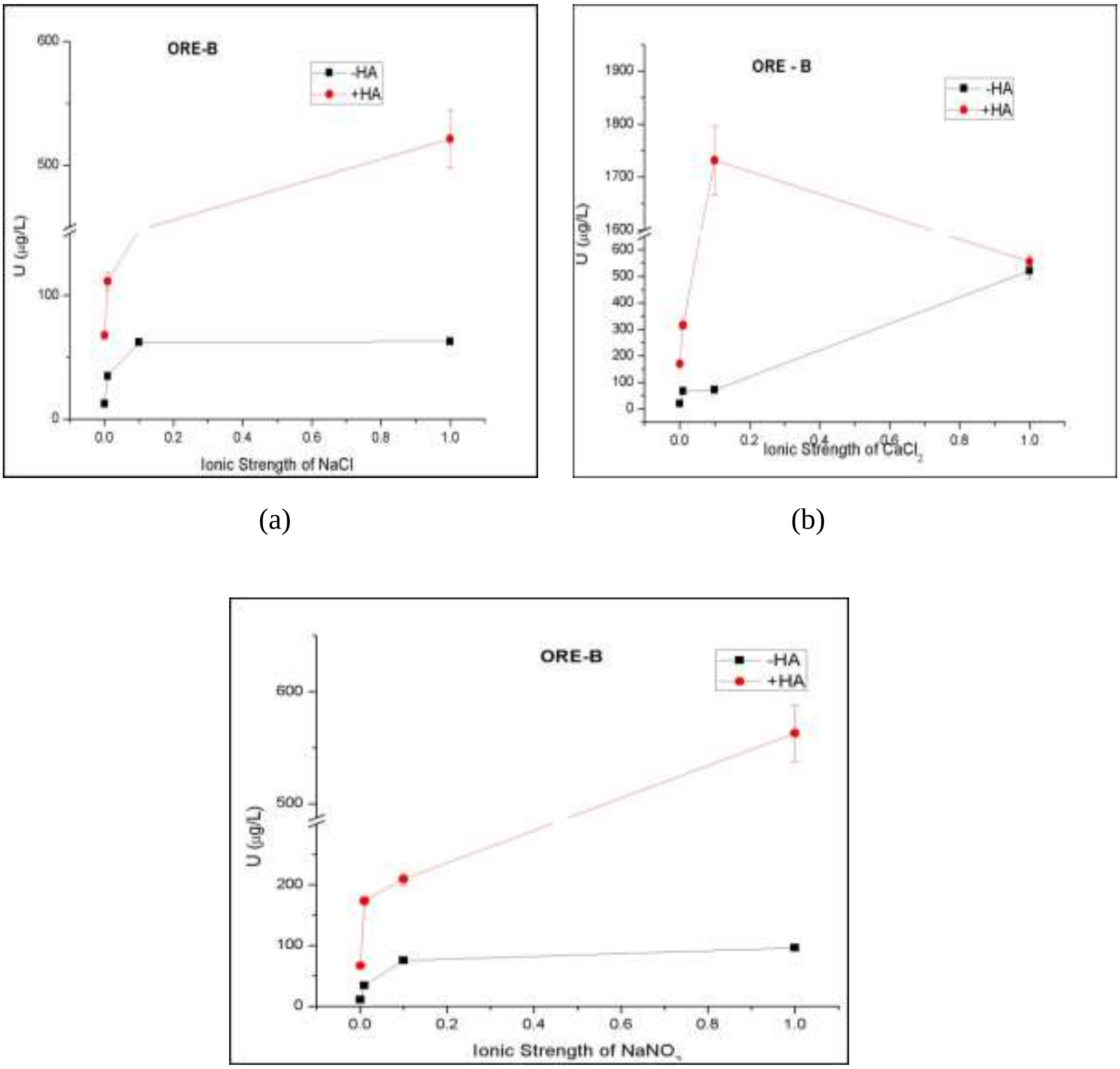


(a)

(b)

(c)

Figure 6.5. Variation of U concentration in aqueous phase due to variation of I.S of: a) NaCl, b) $CaCl_2$ and c) $NaNO_3$ in presence (+HA) and absence (-HA) of humic acid in Ore(A)-water system



(a)

(b)

(c)

Figure 6.6. Variation of U concentration in aqueous phase due to variation of I.S of: a) NaCl, b) $CaCl_2$ and c) $NaNO_3$ in presence (+HA) and absence (-HA) of humic acid in Ore (B)-water system

Figure elucidate that in both the cases (Ore A and Ore B) presence of humic acid lead to more desorption of uranium from solid phase (ore) to liquid phase (Synthetic water) for all salt types and at all different ionic strength in comparison to absence of humic acid. Increases in uranium desorption in presence of Humic Acid can be attributed to affinity of the uranium for humic acid which forms more stable aqueous Uranyl–Humato complex.

The figure also revealed that uranium concentration in aqueous phase increases with increase in I.S of salt solution of NaCl and $NaNO_3$, whereas it decreases for $CaCl_2$ irrespective of Ore types. This indicates with increase in the Ca^{2+} ion concentration of ternary system in presence of constant humic acid concentrations desorption of uranium decreases. This is attributed to competition between Ca^{2+} ion with uranyl ion (due to similar ionic radii) for HA followed by formation of more stable Ca-Humato complex in comparison to U(VI)-Humato complex. As mentioned in literature size of Ca^{2+} ion is comparable to size of U(VI) and theirs is an competition between the Ca^{2+} and uranyl ion to form complex with the humic acid. As Ca-Humato complex is more stable than Uranyl humato complex with increase in concentration of Ca^{2+} with increase in ionic strength, no. of Ca^{2+} ion increases which suppress the formation of Uranyl –humato complex and leads to decrease in U(VI) ion concentration in aqueous phase of ternary system.

6.4.5. Effect of pH and CO_3^{2-}

Effect of pH and carbonate on migration of uranium from ore to water is presented in Fig. 6. 7 and 6.8 respectively. Fig. 6. 7 shows that an increase in pH from 3 to 9 leads to a decrease in U concentration in aqueous phase in ore A system. In the case ore B system, increase in pH leads to an initial fall in uranium in aqueous phase, followed by increase at higher pH. It may be noted that uranium mineral in ore A is in quartz based host rock having less buffering capacity in comparison to the ore B system which is dominated with aragonite i.e., carbonate based. At high pH, uranium migration in ore B system is higher than ore A, which can be correlated to the carbonate concentration in aqueous phase of ore B system which in turn is higher than that of ore A system.

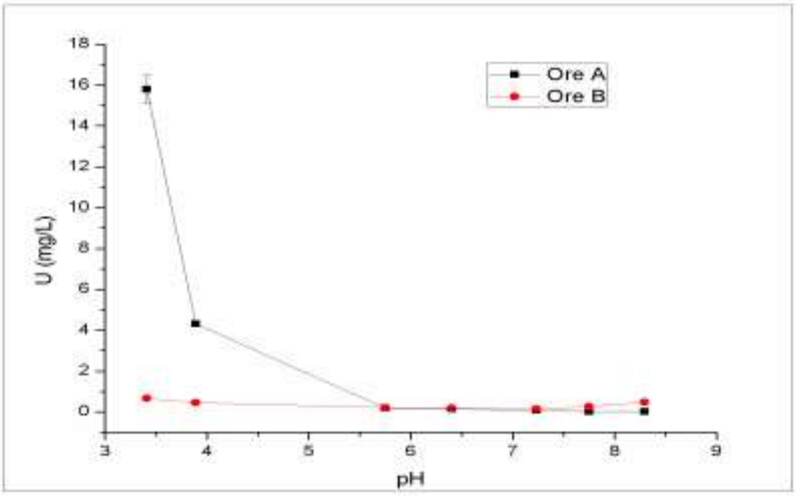


Figure 6.7 Effect of pH on migration of U at ore-water interface

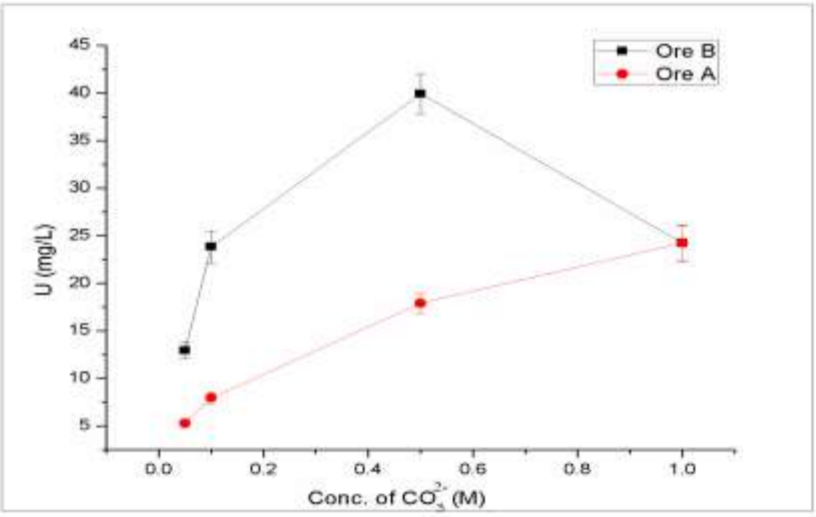


Figure 6.8. Effect of CO_3^{2-}on migration of U at ore-water interface

Figure 6.8 presents the effect of carbonate concentration on uranium leachability or migration from different ores to aqueous phase in contact. The increase in carbonate concentration from 0.05 to 1 M led to a significant migration of U from solid phase (ore) to aqueous phase in both the systems. The increasing trend was in consistent with increase in the carbonate concentration in case of Ore A system, whereas in case of Ore B, concentration U initially increases to 40 mg/L with increase in carbonate concentration upto 0.5M later on decreases to

22.5mg/L. The decrease in U concentration in aqueous phase may be attributes to the precipitation of dissolved U as $Na_2U_2O_7$ due to saturation of aqueous phase with U and saturation concentration of U in the Ore-bicarbonate binary system is above 40 mg/L at ore to water ratio of 1:10 g/mL.

6.5. Summary

The above study revealed that increase in the ionic strength of the water accelerates the uranium migration from uranium bearing ore like, Uraninite at Ore –Water interface to water. The extent of migration depends upon various factors like the type of host rock, speciation of uranium in the ore, type of salt dominated in the aqueous phase, temperature and also presence of any humic like substances. In general, an increase in ionic strength led an increase in migration from solid (ore) phase to aqueous phase. Ca^{2+} ion was found to have more potency to desorb the uranium from the ore as compared to sodium ion. . Nitrate concentration also accelerated the uranium desorption by presumably acting as a dissolved oxidant. In ternary system of ore-water- humic acid, presence of humic acid increases the uranium concentration in liquid phase. However, a competitions between Ca^{2+} ion and uranyl ion retarded the desorption at higher concentrations of $Ca^{2+.}$ Increase in carbonate concentration accelerates migration of uranium irrespective of ore types but effect of pH depends on the type of host rock containing uranium minerals. The results will be extremely useful in predicting the uranium migration from mineralized ores to ground water and subsequent impact assessment. The results also will be useful in impact assessment of disposal options of uranium.

Chapter 7

Effects of Carbon Dioxide on Migration of Uranium

7.1. Introduction

Climate modeling studies and long term observations have indicated that the concentration of carbon dioxide (CO_2), one of the main greenhouse gases, is mainly responsible for global warming [169]. From the era when the industrial revolution began, CO_2 concentration in the atmosphere has increased from 275 to 370 ppm and by 2100 it is projected to go up to 750 ppm [170]. An increase in atmospheric CO_2 level may also lead to an increase in dissolved CO_2 in aquatic system which may cause changes in physicochemical properties of aquatic system. This may also trigger a change in pH and aqueous speciation of dissolved species. It may initiate various processes like, mineral dissolution, metal mobilization, sorption, desorption and precipitations etc., at mineral-water or soil-water interface. In an attempt to control CO_2 emissions into the atmosphere, researchers have been trying to identify different ways to collect and store/dispose of CO_2 in geological systems, such as deep ocean waters, sediments, and aquifers. One of the consequences of this option is the possibility of some fraction of the stored CO_2 being leaked into overlaying aquifers. Thus, attention in evaluating the environmental impacts of CO_2 leakage into potable aquifers should focus on the secondary effects, namely the geochemical changes caused by the increased CO_2 dissolution in these systems. Dissolved into groundwater, CO_2 increases the concentration of total carbonate, including H_2CO_3 (aq), HCO_3^- and CO_3^{2-} which may cause a decrease in pH. Such acidic condition can affect the dissolution and sorption processes which in turn may cause detrimental effects on groundwater quality by enhancing dissolution and/or desorption of potentially hazardous trace metals [171]. A number of studies were reported in the literature on the mobility of metals at sediment-water interface; Mobilization of the metals Al, Fe, Zn, Co, Pb and Cu increases with acidifications [172]. Trace metal mobilization is already been observed during experiments on the controlled release of CO_2 from saline and freshwater aquifers [173, 174]. The mobilization of trace elements can result from the dissolution of carbonates, sulphides and iron oxy-hydroxide minerals, by adsorption/desorption reactions at the sediment–water interface and by ion exchange processes [173]. However, detailed information about the impacts of CO_2 leakage is essential for risk assessments; the consequences of such incidents are still largely unknown for mineral-water interface.

7.2. Present Study:

The objectives of this study includes the assessment of the impact of CO_2 on migration of Uranium at mineral (Uraninite)-water interface and soil-water interface to determine what processes affect these changes and over what time scale they might occur. To this end, we tried to investigate the change in speciation of U due to CO2 infiltration and geochemical indicator to identify the CO2 infiltration.

7.3. Methodology:

7.3.1. Materials

To study the impact of CO_2 infiltration to ore-mineral-water system, milled U ore (Ore A and B) were collected from two different mining sites differing by their host rock compositions. Detailed compositions of ore samples are discussed in chapter 6 (Table 6. 1 and Fig. 6.1a&b). Natural rock samples were chosen because it allows for a realistic prediction of reactions when CO_2 comes in contact with natural systems. This study is focused to understand the changes in physicochemical parameters of water in contact with ore with time and to interpret mobility and speciation of U during experimental period.

Similarly for study of impact of CO_2 at soil-water interface, soil amended with U (total U content: 797mg/Kg) was taken.

For this study, synthetic water was used in order to reduce the corrosiveness of the DI water which was prepared by amending DI water with 2mg/L of NaCl.

7.3.2. Experimental approach

For the study 20 g of milled, unwashed samples of ore A, B and soil sample taken in reactors (Duran Bottles having hose connection) in duplicates and were equilibrated with 200 mL of synthetic water (solid to water; 1: 10 g/mL). To minimize microbial influences in the reaction vessels, glassware and fittings were acid cleaned and then heated to 250 °C for 5 h. Amber color bottles were chosen for reactor to minimize photo sensitive reactions. The experiment was conducted in two steps.

Step I (Pre exposure period): Reactors containing the ore mineral and water were kept inside the shaker incubator at 25^0C for two weeks to allow water–mineral and water -soil systems to approach equilibrium with respect to major elements and U. At the end of the 2nd week, 4 mL of water were collected from each reactor.

Step II (Exposure period): 2nd week onwards, a stream of 99.8% pure CO_2 was bubbled at atmospheric pressure through each bottle using flow-regulated channels at a constant flow rate for 30 days. Each channel is coupled to the bottle through a double holed rubber stopper. One hole is used to deliver the CO_2 into the bottles via a plastic bubble diffuser while the other hole in the stopper is connected to an exhaust tube leading from the headspace of each incubation bottle. Each bottle has an independent CO_2 delivery and exit system. The schematic diagram of experimental setup is presented in Fig. 7.1. To maintain gas pressure, two cylinders were connected in parallel with an auto-changeover and pressure was monitored continuously using pressure gauge.

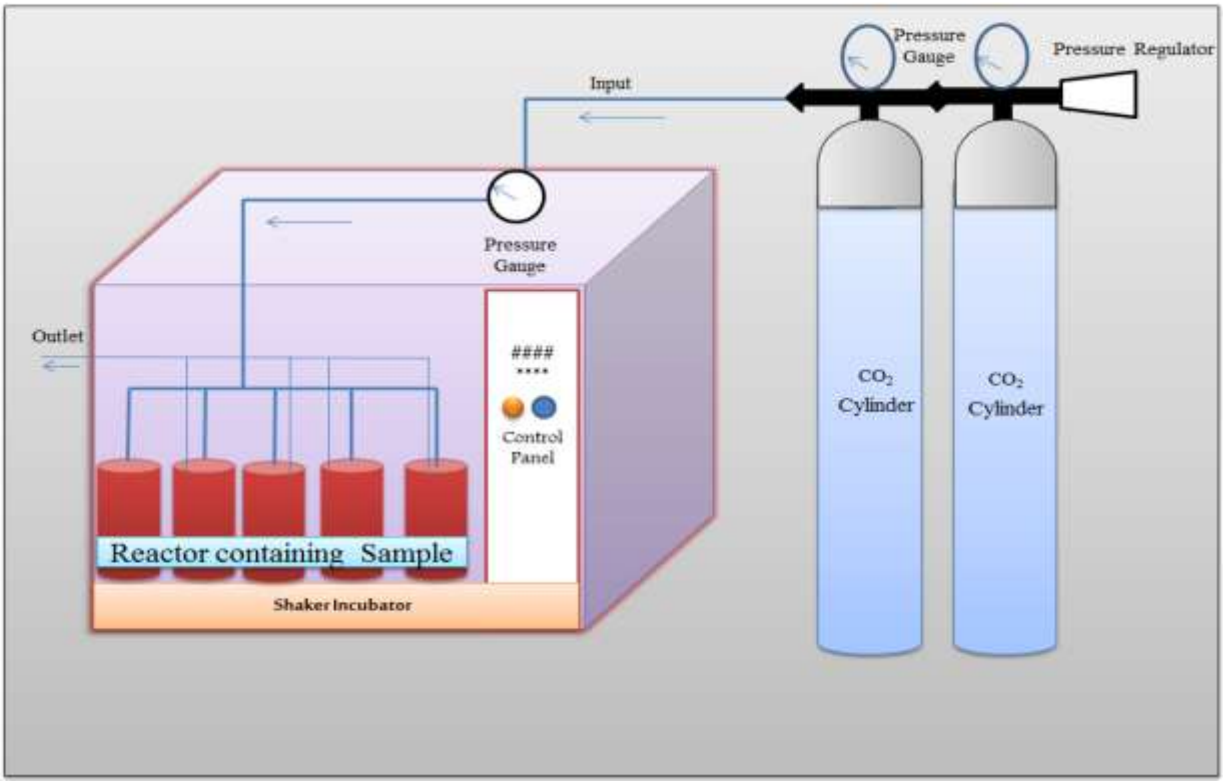


Figure 7.1. Experimental Setup for CO_2 gas exposure

The reactors were placed in continuous shaking (20rpm) mode with 5 min stop at every 90 hr. The temperature was maintained at 25^0C. 4 mL of water samples were collected at the different time intervals, initially at 0.5 hr, 1hr, 3hr, 5hr, 7hr and 9hr, then at the end of 1st , 2nd , 3rd , 7th , 14th , 21st and 30th day. During the sampling, the incubator chamber is flushed with CO_2 gas to ensure that there is no interaction with the outer atmosphere.

Samples collected in 1st and 2nd step were centrifuged, filtered using 0.41-micron syringe filter and analyzed for:

a) Major ions (Na^+, K^+, Mg^{++}, Ca^{++}, F^-, Cl^-, NO_3^-, SO_4^{2-}) using ion-chromatography (RFIC ICS 2100, Dionex), Bicarbonate titri-metrically using autotritrino (798 MPT Tritrino, Metrohm).

b) For U with voltammetry (Metrohm VA Stand 663 Auto Lab, Switzerland) by dropping mercury electrode (DME) and Differential Pulse Adsorptive Cathodic Striping Mode.

Some of the samples were analyzed for uranium using an independent fluorimetric technique to ensure the analytical reliability.

c) pH and Eh was measured using Aqua-meter.

7.4. Results and Discussion:

The X ray difractogram for both the ore A and B is already presented in chapter 6, in (Fig. 6.1 (a, b)) and that of soil is presented in chapter 3 (Figure 3.2c). The mineralogical study revealed that Ore A is dominated with quartz, followed by chlorite, kaolinite and smectite, whereas Ore B is dominated with carbonate mineral (Aragonite) followed by plagioclase, quartz, kaolinite and smectite, Mineralogical data revealed that both ore are differing in host rock minerals. In soil (S), Plagioclase, Smectite, Calcite and Quartz were the main minerals observed. Change in physicochemical parameters mineral- water and soil- water interface due to exposure to CO_2 is shown in Table 7.1 and 7.2 respectively for pre and post exposure (after 24 h & 30th day) period. The role of CO_2 was investigated in two phases in terms of fast change /reaction (Phase I: assuming change in 24hour duration) and slow change/ reaction (Phase II: for the period of 30 days). In all the three cases pH falls rapidly within the 30 min (for Ore A: 7.34 to 4.35, for Ore B 7.54 to 4.47 and in case of soil (S) from 7.1 to 4.6) then slowly increases to 4.51, 4.55 and 5.65 respectively in the next 24 hours, similarly the Eh of the system fall from ~ 0.4V (partially oxidized) to 0.105V (partially reduced) for both the systems. All alkali and alkaline metal concentrations were found to be higher than the pre exposure system. Na concentration in CO_2 exposed system-A, B and S shows 8.7, 15 and 6 times higher than pre exposure systems respectively. Similarly, concentration of K in aqueous phase was increased by 2.39, 1.7 and11 times with respect to pre-exposure period for A, B and S respectively in first 24 hours. Mg concentration in aqueous phase was increased by 4, 5.77 and 21times with respect to pre-exposed system for A, B and S respectively. Similarly, Ca concentration in aqueous system increased by 2.39, 1.7 and 4 times with respect to pre-exposure systems for A, B and S respectively in the first 24 hours.

Table 7.1. Change in Physico-chemical parameters of water in mineral-water system

Parameters	Prior exposure to CO_2 Ore A	Prior exposure to CO_2 Ore B	Post exposure to CO_2 Ore A		Post exposure to CO_2 Ore B	
			Phase I (24 h)	Phase II (30th day)	Phase I (24 h)	Phase II (30th day)
pH	7.34	7.53	4.51	5.41	4.55	5.81
Eh (V)	0.395	0.40	0.105	0.105	0.105	0.105
Na (mg/L)	4.43	2.01	38.64	49.88	30.18	58.27
K(mg/L)	8.27	6.39	19.8	16.69	11.09	14.46
Mg(mg/L)	10.5	1.8	41.99	27.49	10.4	34.15
Ca(mg/L)	14	29.78	33.4	70.21	51.25	80.76
F(mg/L)	1.2	0.53	1.36	1.85	0.63	0.42
Cl(mg/L) (	58.79	57.14	94.5	269.49	61.22	125.89
NO_3^-(mg/L)	131.81	121.15	143.03	212.15	71.38	105.58
SO_4^{2-}(mg/L)	0.55	22.26	2.89	1.85	8.61	6.72
HCO_3^-(mg/L)	47.82	50	34.2	422.7	35.8	670
U(µg/L)	2.94	29.01	123.6	210	114	78.3

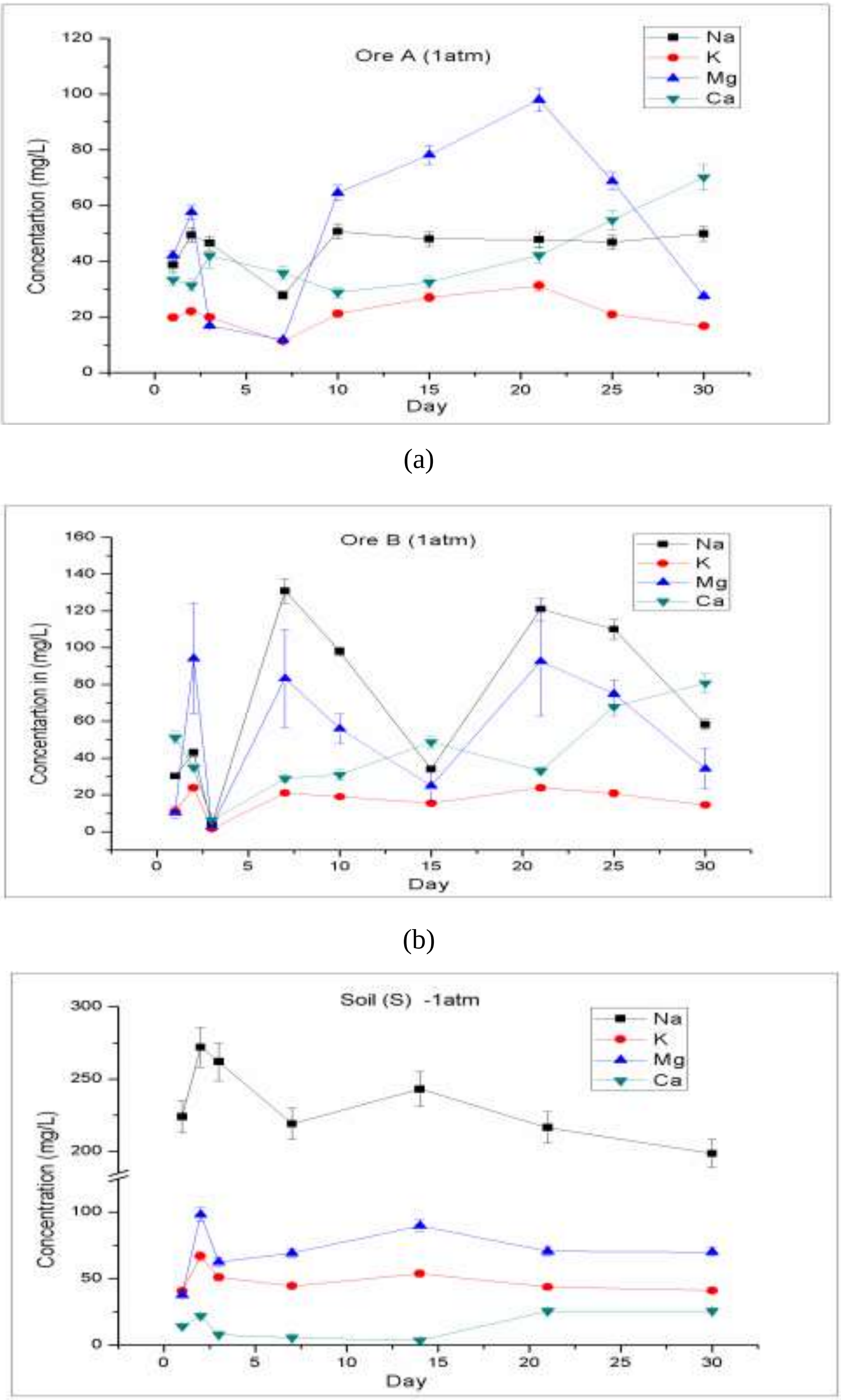
Table 7.2. Change in Physico-chemical parameters of water in soil-water system

Parameters	Pre CO_2	Post CO_2	Post CO_2
	Soil	Soil Phase I (24 h)	Soil Phase II (30th day)
pH	7.1	5.65	6.24
Eh (V)	0.385	0.112	0.110
Na (mg/L)	36.94	224	198.5
K(mg/L)	3.44	40.72	41.03
Mg(mg/L)	1.78	37.58	70.05
Ca(mg/L)	3.51	14.06	25.57
F(mg/L)	1.2	0.53	1.36
Cl(mg/L)	153.58	146.6	97.25
NO_3^-(mg/L)	24.41	47.3	28.22
SO_4^{2-}(mg/L)	9.55	9.54	9.54
HCO_3^-(mg/L)	47.82	337	600
U(µg/L)	48.72	3716	15840

The increase in the metal ion concentration attributed to the dissolution of minerals induced by dissolved carbonic acid and plausible mechanism is as follows:

$$\text{Feldspar } (K^+, Na^+, Ca^{2+}) + H_2O + CO_2(g) \longrightarrow (K^+, Na^+, Ca^{2+}) + \text{Kaolinite} + 2SiO_2\,(aq) + HCO_3^-$$

$$(Ca^{2+}/Na^+/\,Mg^{2+})\,CO_3 + H_2O + CO_2\,(g) \longrightarrow HCO_3^- + Ca^{2+}/Na^+/\,Mg^{2+}$$



(a)

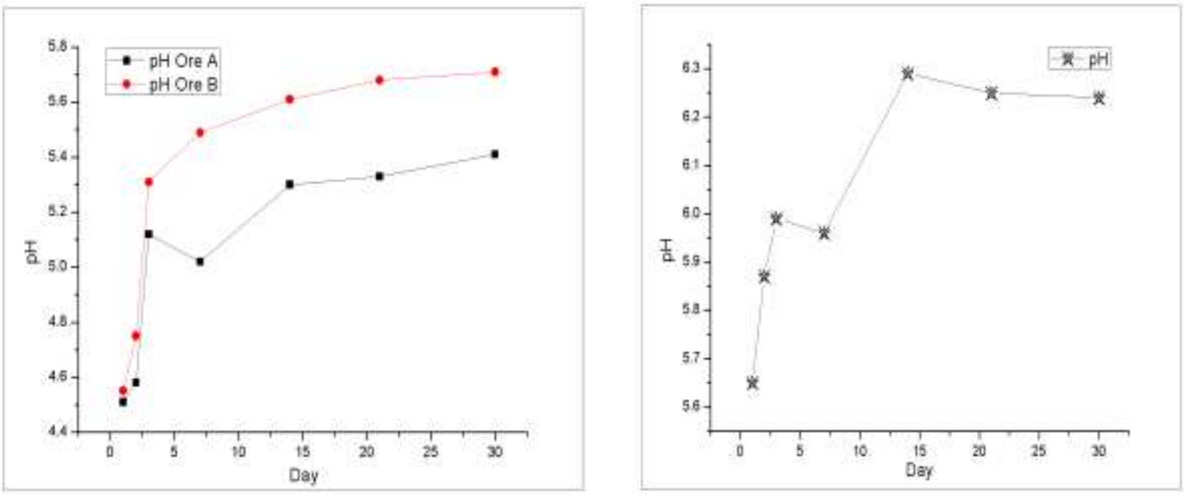
(b)

(c)

Figure 7.2. Variation of major cations at a) Ore A-water, b) Ore B-water and c) Soil-water System

The long term change in concentrations of different cations in aqueous phase after exposure to CO_2 attributed to the complex processes involving desorption from solid phase due to dissolution of minerals, ion exchange or formation of soluble anionic complexes with carbonate ion along with precipitation. The long term changes (Phase-II) in aquatic parameters of Ore-A, Ore-B and soil (S) systems after exposure to CO_2 for a period of 30 days are presented in the figure 7.2, 7.3 and 7.4 respectively.

Figure 7.2 shows that, among the major cations, K^+ achieved equilibrium at the end of experiment in both the ore- water system A and B, whereas Na^+ achieved equilibrium in case of the system- A only. Concentrations of Ca, Mg in both the system and Na in system- B had not achieved equilibrium till the end of experiment. These fluctuations may be arise due to continues sorption and desorption reaction occurring at the mineral water interface. Since system B (Ore B) is dominated by carbonate minerals the pH buffering leads to continuous dissolution and precipitation of carbonate bearing minerals (Na/Ca/Mg-CO_3) which attributes to the fluctuation in concentrations of these counter cations. In soil-water system all the cations achieved the equilibrium at the end of 30th days other than Na^+ ion, which exhibits slight fluctuation.



(a) (b)

Figure 7.3. Variation of pH with time a) Ore-water System and b) Soil-water System

Initial decrease of pH in Phase I followed by slight rebound and eventual stabilization at levels up to 5.4, 5.8 and 6.24 in system A, B and S respectively (fig 7.3 a &b). Higher equilibration pH of system B in comparison to A due to high buffering capacity of system B, which is in line with the mineralogical data of Ore B, i.e., Ore B dominated with carbonate minerals. In case of soil system pH raised to 6.24 attributed to high buffering capacity of soil in comparison to the ore minerals

Speciation of CO_2 is presented in Fig. 7.4 which is very much important since it control the water chemistry hence mobility of metals. At the set temperature of 25^0C and 1 atm P_{CO2} dominating species are H_2CO_3, HCO_3 and CO_3^{2-} along with OH- whereas at ambient atmospheric condition (where $pCO_2$is 0.0004 atm) CO_3^{2-} was not expected to exist.

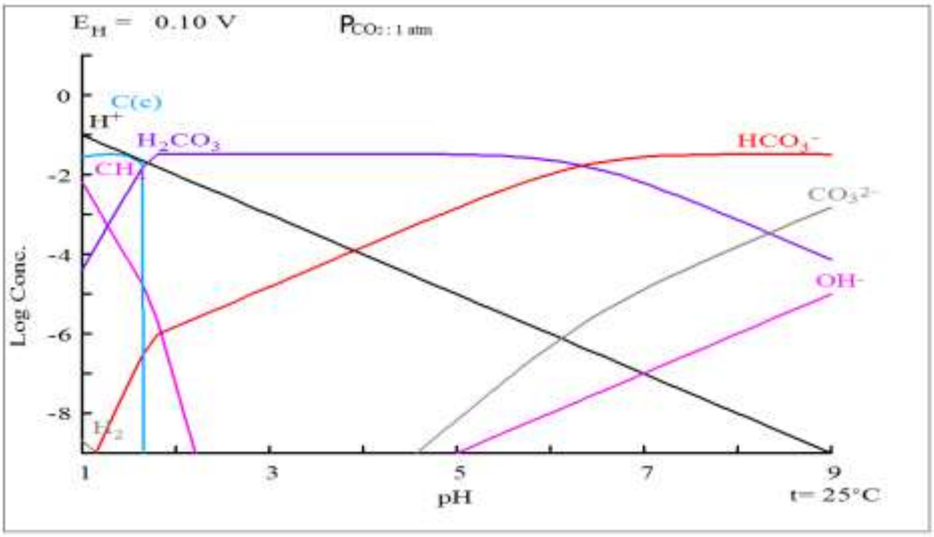


Figure 7.4. Speciation of C(IV) in aqueous medium in equilibrium with 1 atm CO_2

Possible speciation equation is as follows:

$$CO_2(g) \leftrightarrow CO_2(aq)$$

Subsequent hydration and dissociation reactions:

$$CO_2(aq) + H_2O \leftrightarrow H_2CO_3 \leftrightarrow HCO_3^- + H^+$$

$$HCO_3^- \leftrightarrow CO_3^{2-} + H^+$$

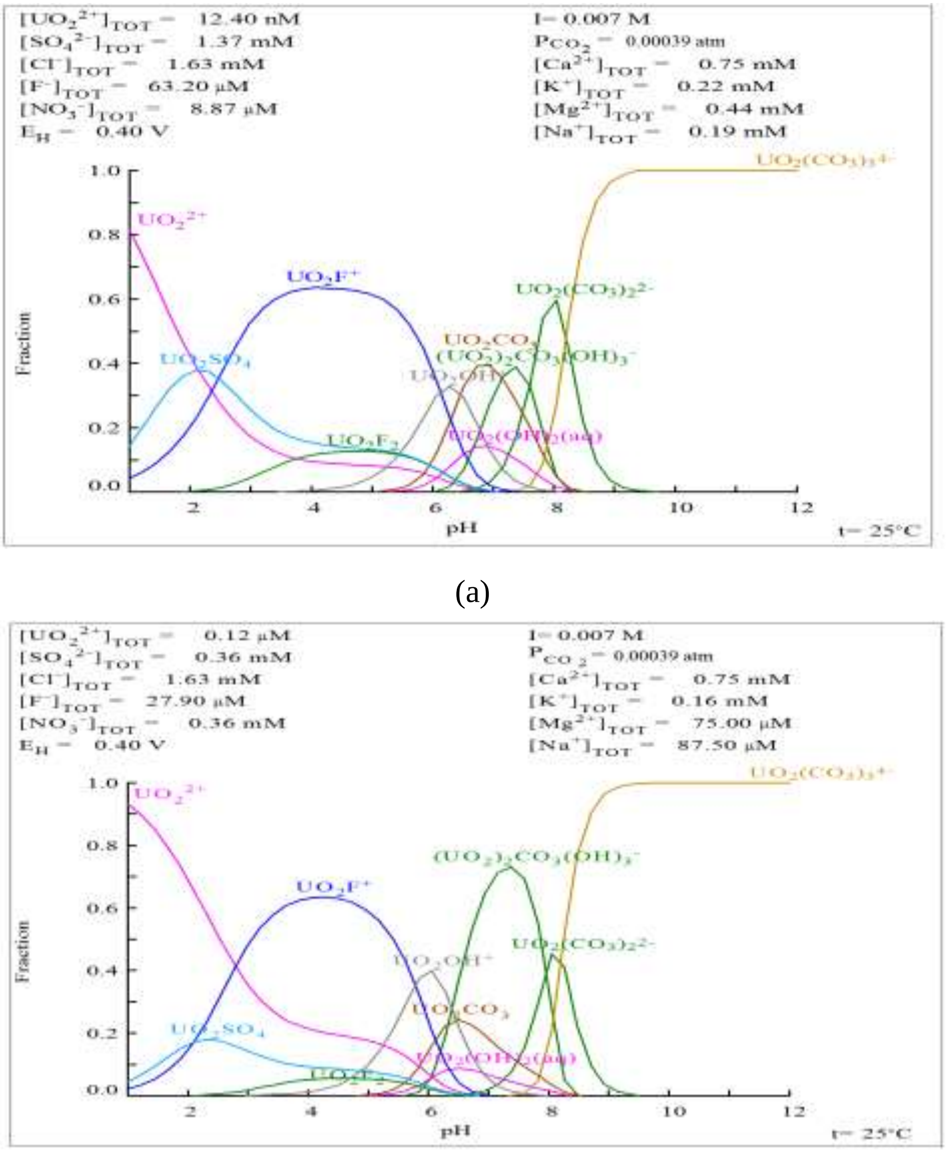
Anions concentrations measured showed no significant increases after introduction of CO_2, suggesting that the increase of cation concentrations following introduction of CO_2 was mainly balanced by an increase of HCO_3^-, which would occur with the dissolution of CO_2.

7.4.1. Migration of Uranium at Mineral water interface:

In response to exposure to CO_2 for duration of 30 days, there occurs a rapid increase in U in all the systems within 2 to 3 days. On further exposure, uranium concentration was found to decrease with time and became erratic at the end of 30 days. At the end of the experiment it was found that the U level in system A was about 210µg/L, in system B about 78.0 µg/L and in Soil (S) about 16 mg/L. With the dissolution of CO_2 into water, pH rapidly decreased in all reactors which accelerate desorption/leaching of U. The fluctuation in concentration may be due to complex mineral assemblages that had varying buffering capacities. The decrease in U solubility may be arises due to two reasons precipitation of dissolved U along with the carbonate and/ or with decrease in Eh of the both the system. Decrease in Eh leads to formation of sparingly soluble U (IV) species. High concentration of U in aqueous phase of system A in comparison to aqueous phase of system B can be attributed to low buffering capacity of ore A mineral. The increase in mobility of U in soil -water system, consequent to the exposure to CO_2, is attributed to the release of U bound in different fractions of soil. Though the present studies present a trend on the effect of CO_2 exposure on soil-water system, it may be noted that amended soil was used in the present study, which may not represent quantitatively age old soil-water system. More studies are required to address this issue.

7.4.2. Speciation of Uranium at mineral water interface

Figure 7.5 and 7.6 presents the speciation of uranium (+6) in both the system for pre CO_2 and post CO_2 exposure period.



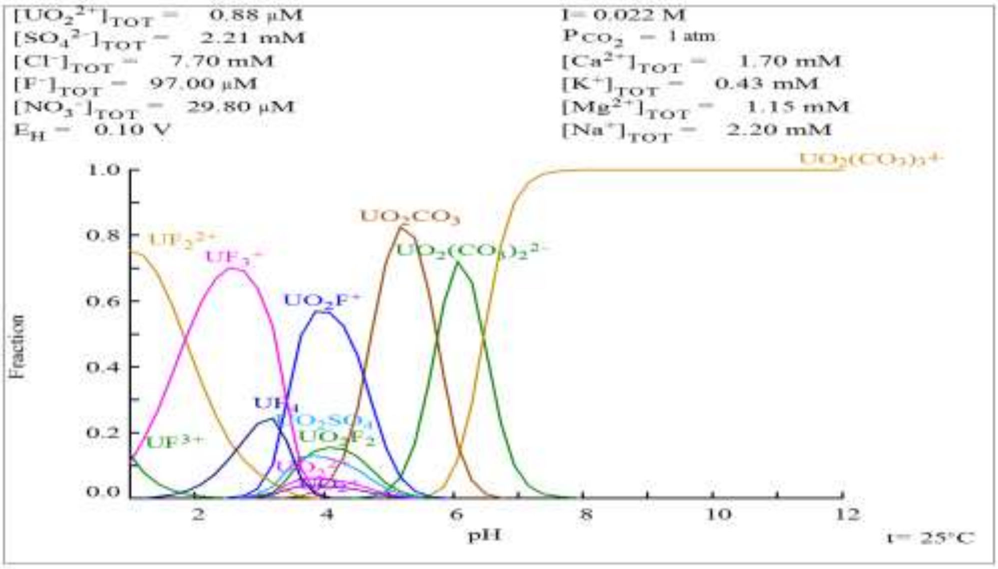
(a)

(b)

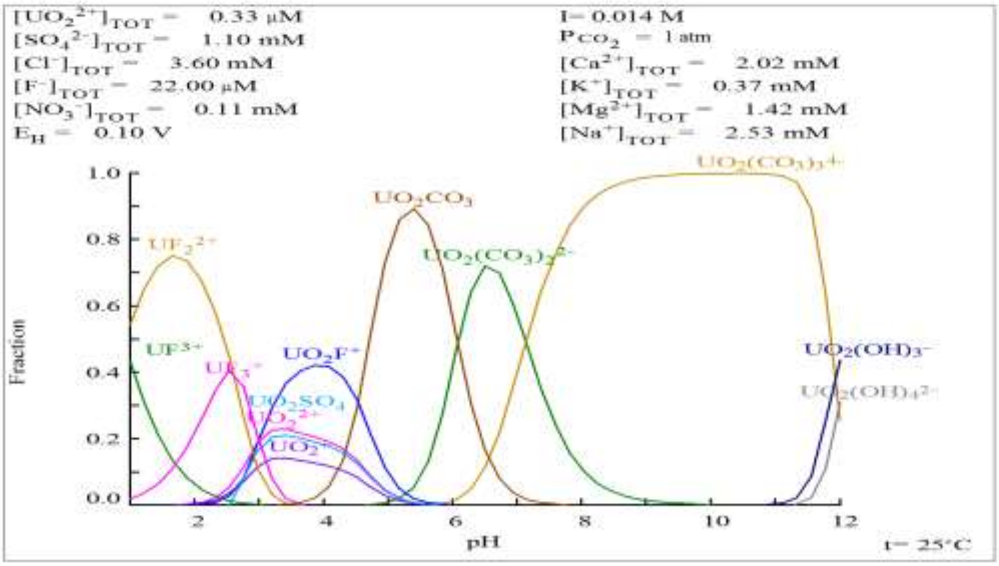
Figure 7. 5. Aqueous speciation of U(VI) during pre-exposure period at mineral-water system; a) Ore A-Water, b) Ore B-Water

Based on equilibrium concentration of different dissolved species, uranium, pH and Eh of systems the speciation diagram was drawn. In pre exposure study, figure revealed that for the binary system of A at the pH of 7.34 Eh of 0.4V and specified ionic composition, uranyl species namely $(UO_2)_2CO_3\ (OH)_3^-$, UO_2CO_3, $UO_2(OH)_2$, UO_2OH^+ and $UO_2(CO_3)_3^{4-}$ were present out of which aqueous $(UO_2)_2CO_3(OH)_3^-$ is predominating species followed by UO_2CO_3. In case of system B, $(UO_2)_2CO_3(OH)_3^-$, $UO_2(CO_3)_2^{2-}$, $UO_2(CO_3)_3^{4-}$, UO_2CO_3,

$UO_2(OH)_2$, and UO_2OH^+ were present and $(UO_2)_2CO_3(OH)_3^-$ is the predominating species followed by $UO_2(CO_3)_2^{2-}$ at pH 7.53 and Eh 0.4V.



(a)



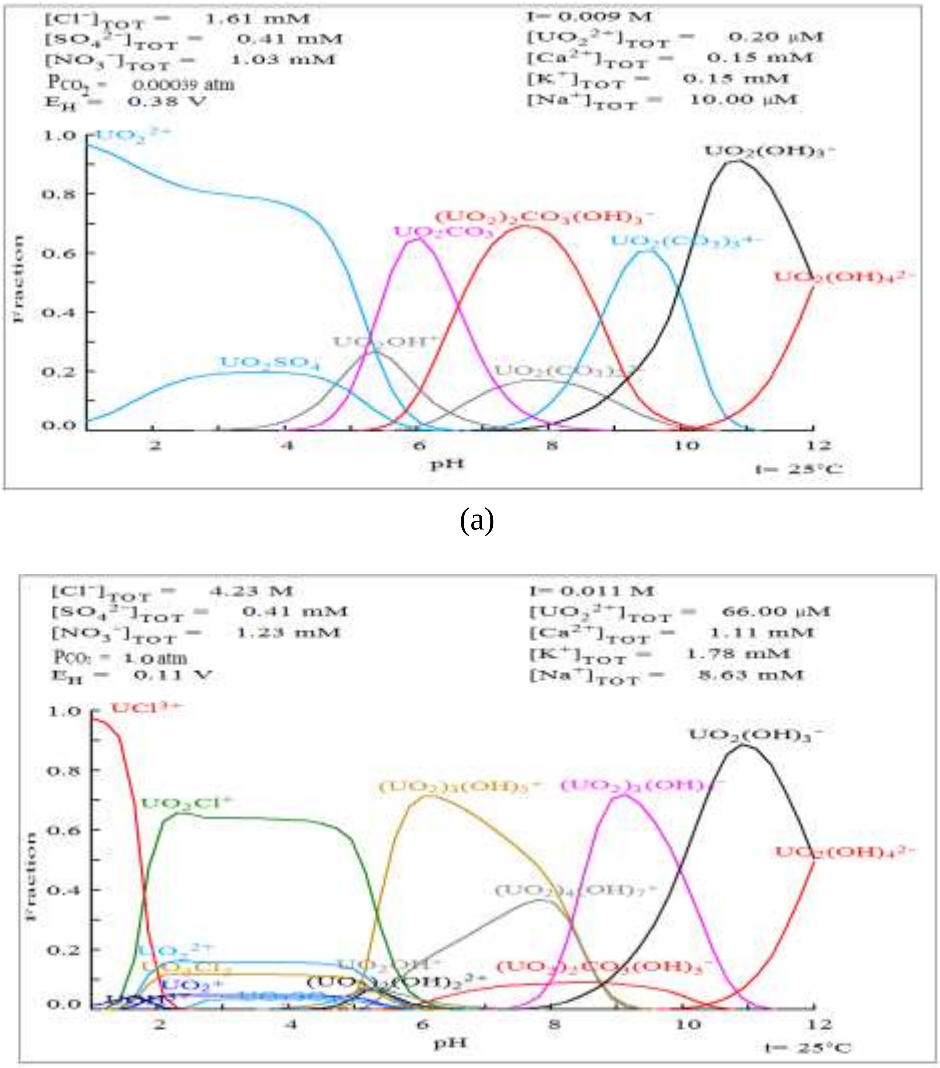
(b)

Figure 7.6. Aqueous speciation of U(VI) during post-exposure period at mineral-water system a) Ore A-Water, b) Ore B-Water

Speciation of U(VI) in post exposure system is presented in figure 7.6. a &b, figure shows that there is a significant change in speciation due to CO_2 infiltration. The change in speciation is attributed to the change in the water chemistry induced by CO_2 exposure. For Ore A system at the system pH: 5.41, Eh: 0.1V and set ionic compositions, UO_2CO_3,

$UO_2(CO_3)_2^{2-}$, UO_2F^+, UO_2^{2+}, UO_2SO_4 and UO_2F_2 are the species identified. In system B; similar species were identified at the system equilibrium pH: 5.81 and Eh: 0.1V.

This reveled that in the pre exposure system the anionic species of U(VI) such as mixed hydroxyl carbonate species, carbonate species are responsible for U mobility where as in post exposure system neutral and cationic species of U(VI) such as UO_2CO_3, UO_2F^+, UO_2^{2+}, UO_2SO_4 and UO_2F_2 are responsible for U mobility.



(a)

(b)

Figure 7. 7. Aqueous speciation of U(VI) at soil-water interface in a) pre- exposure system and b) post- exposure system

7.4.3. Speciation of Uranium at soil water interface

Figure 7.7 (a) revealed that in pre exposure period at the pH of 7.1 $(UO2)_2CO_3(OH)_3^-$ is the predominate species followed by UO_2CO_3 and $UO_2(CO_3)_2^{2-}$ whereas, after CO_2 exposure (Fig 7.7 b) the speciation significantly changed and positive uranium species became dominated out of which $(UO2)_3(OH)_5^+$ is dominating species followed by $(UO_2)_4(OH)_7^+$ due to change in system pH to 6.24 , Eh: 0.1V and ion chemistry of system.

U(IV) is not considered for speciation calculation in both ore-water and soil-water system since the concentration of U(IV) is negligible in comparison to U(VI) in the above systems.

7.5. Summary

Introduction of CO_2 into ore water and soil water binary systems leads to saturation of water at mineral/soil-water interface with CO_2. Initial elevated cation concentrations suggest that mineral dissolution was driven by CO_2 which is consistent with initial decreases in pH. The phase II experiment documented increase, stabilization, and/or decline of concentrations with fluctuation. In response to exposure of CO_2, U solid to aqueous phase mobility increases 15 times more than the pre exposed systems of A and B within 2–3 days, subsequently the mobility starts to fall and achieve equilibrium at the end of 30 days. The trend was same in soil-water system, where U concentration increased 325 times than pre-exposed system. The higher degree of mobility of uranium in soil water system can be attributed to U bound in different fractions of soil whereas in ore minerals it is mainly residual fraction. pH and HCO_3^- can be used as geochemical indicator for CO_2 induced metal/ U mobility. Though the reaction rates in laboratory-batch experiments tend to be higher by orders of magnitude than those in field conditions, use of natural ore samples may help represent more realistic reaction timescales.

Chapter 8

Conclusions

The issue of high-level of U in drinking water sources of many countries round the globe as well as in many states of India is one of the important environmental concerns. This increase in migration of U from geological system (soil and minerals) to aquatic systems in terrestrial environment may be due to long-term change in environmental condition of soil/minerals and ground water systems. The migration of U depends upon several complex parameters such as water quality, soil (and mineral) characteristics, U speciation in solid phase and redox potential of the system etc. A detailed study of these parameters is essential for understanding the mechanism of migration from solid to solution in geological systems. This motivated us to carry out detailed studies on the speciation and migration of U from solid phase (soil and minerals) to solution (water) in terrestrial environment. This study also will be useful in carrying out environmental impact assessment of waste disposal sites. As part of the dissertation work, batch sorption and desorption experiments, aqueous and solid phase speciation studies and spectroscopic investigations were carried out to explore migration behavior of uranium in terrestrial environment with special focus on soil-water and mineral-water systems. Aspects delineated in these studies were (1) sorption kinetics and thermodynamics along with studies of sorption isotherms to understand behavior of U at soil-water interface, (2) Speciation of uranium in contaminated soil and effect of ageing on its bio-availability and speciation, (3) effect of salinity on migration of uranium at soil/mineral-water system and (4) effect of CO_2 on solid to aqueous phase migration of uranium in mineral-water and soil-water binary systems. The major findings and conclusions from this work are summarized below.

a) The batch sorption studies of U in wide variety of soil types revealed that sorption follows pseudo-second order kinetics with multi-step diffusion process irrespective of soil types. The rate-determining step is chemisorption involving valence forces through sharing or exchange of electrons along with ion exchange sites. Soil parameters like Fe, Mn and Organic Matter (OM) were found to increase the U sorption to the solid phase. Soil with high iron and manganese content showed high adsorption capacity for uranium. Change in soil organic content did not exhibit significant change in sorption capacity of such soils at circumneutral pH. Fe and Mn rich soils followed Langmuir sorption isotherms in comparison to other type of soil which followed Freundlich and D-R isotherms. Among water parameters pH, CO_3^{2-} and Ca^{2+} were found to be the sensitive parameters influencing solid to aqueous phase mobility and aqueous phase speciation of U at soil water interface. Thermodynamic parameters derived from the experimental data, indicated that the sorption is spontaneous, endothermic in nature and follows dissociative mechanism. The study also revealed that geological setup with high ferro-manganese content offers least mobile environment for Uranium. Such geological set up offers candidate sites for waste disposal facilities or geological repository of uranium. Fe or Mn enriched soils can also be used as a backfill to mitigate migration of U. This opens a wide scope for research in modified materials and selection of natural matrix for immobilization of U.

b) The study on speciation of uranium in soil of different types revealed that, in moderately reduced soil, major fraction of uranium exist as completely immobile U(IV) state whereas in aerobic condition it sparingly soluble to sodium bicarbonate solution due to partial oxidation of U(IV) to U(VI). The increase in bicarbonate in soil/mineral water system in aerobic environment leads to mobilization of bound

U(IV) from soil exchangeable sites as well as from OM due to formation of soluble uranyl carbonate complexes.

The sequential extraction experiments were carried out to understand the chemical fractionation uranium in soil matrix and change in chemical fractionation with ageing. Spectroscopic investigation (using XPS) was also carried out to understand the process involved during ageing. The study revealed that, even though the fate of U in soil initially governed by concentration of adsorbents (Such as carbonate, oxides of Fe/ Mn, OM etc. in respective fractions) but with change in time there occur a significant rearrangement of U in among all the fractions However there was no difference in total uranium in soil matrix before and after aging process. Spectroscopic investigation envisages that, surface speciation of uranium is mainly controlled by soil carbonate and organic matter content. A significant decrease of U in reducible fraction was observed after aging. The apparent decrease in concentration of reducible U in soil matrix with aging can be attributed to the occlusion of U-Fe-Oxides (Hydroxide) in to amorphous silica. The study can be extended to see the effect of ageing on uranium speciation in different environmental condition which will be helpful for predicting long term behavior of U in terrestrial environment.

c) Study of effect of salinity on migration of uranium from solid to solution at soil-water and mineral-water interface conclude that increase in salinity induced increased uranium migration from solid phase to aqueous phase. Study in soil-water system revealed that, extent of mobilization depends upon both speciation of uranium in soil as well as type of salt. This study indicated that, U mobilization from soil by salts ($CaCl_2$, $MgCl_2$, Na_2SO_4 and NaCl) is independent of the total U content of soil rather it depends upon % of total U in exchangeable sites. This indicates that the migration process of U induced by these salts is driven by ion exchange mechanism. The present study indicated that $NaNO_3$ mobilizes the larger fraction of U (VI) from solid phase. This may be because of fact that $NaNO_3$ induced uranium mobilization involves ion exchange as well as oxidative dissolution of U(IV) bound to different fractions of soil. Study of effect of salinity on mineral-water indicated that, the extent of mobilization depends upon various factors like the type of host rock, speciation of uranium in the ore, type of salt dominated in the aqueous phase and also presence of any humic like substances. Like soil-water system, water dominated with Ca^{2+} ion has more potency to desorb the uranium from the ore and water with high nitrate concentration also accelerate the uranium desorption. In ternary system of ore-water- humic acid, presence of humic acid increased the uranium concentration in liquid phase. However, in presence higher concentration of Ca^{2+} ion uranium desorption was suppressed due to formation of more stable Ca-Humato complex in comparison to Uranyl-Humato Complex. Increase in bicarbonate concentration accelerated mobility of uranium irrespective of ore types but effect of pH was found to depend on the type of host rock containing uranium minerals. The outcome of study opens a scope for research in the field of nitrate induced abiotic oxidative dissolution of U(IV) to U(VI).

d) Experiments were carried out to investigate the effect of infiltration of CO_2 to mineral/soil-water interface initiates various reactions. The studies were carried out in a carbonate based ore water system, quartz based ore water system and a soil water system. A rapid decrease in pH was observed consequent to CO_2 to mineral water and soil water systems. This triggered dissolution of rock minerals and soil minerals leading to an increase in cation concentrations at soil/mineral-water interface within 24 hour. In response to exposure of CO_2, U mobility increases up to maximum ~150 times more than the pre exposed mineral-water systems within 2–3 days and again started to fall and achieve equilibrium at the end of 30 days. . The extent of mobilization was found to depend upon the type of host rock containing uranium minerals. Similar observations were made in soil-water system, where in U concentration in aqueous phase increased by 325 times than pre-exposed system. The increase in migration of U in soil -water system, consequent to the exposure to CO_2, is attributed to the release of U bound in different fractions of soil. Though the present studies present a trend on the effect of CO_2 exposure on soil-water system, it may be noted that amended soil was used in the present study, which may not represent quantitatively age old soil-water system. More studies are required to address this issue. pH and HCO_3^- can be used as geochemical indicator for CO_2 induced metal/ U mobility. The study can be extended to see the effects CO_2 infiltration on the mobility and speciation of heavy metals at mineral-water and soil water system as well as effect of CO_2 on.

In a nutshell study of migration of uranium in terrestrial environment is very complex and also complexities increase due to human activities such as mining, processing and waste disposal practices along with current issue of climatic change. Change in climate or environmental conditions and wrong human practices directly or indirectly brought changes in terrestrial as well as subsurface aquatic systems like change in physicochemical properties of soil and water which increases the uranium (any metal also) migration from soil/mineral to water in contact. Case studies like, high level of uranium in ground water of Punjab, India along with high salinity and pH can be correlated to the salinity induced mobilization. Study of speciation of uranium in soil or minerals are very much essential to assess its migration behavior. Uranium associated with residual fraction are least or not affected by any change in physicochemical properties of soil/mineral–water system. Increased in atmospheric CO_2 will directly or indirectly affect uranium migration. The present study gives a basic insight to the process of migration of uranium to aqueous stream from ore and soil system. This knowledge will be extremely useful in carrying out the assessment of long term impact of uranium waste disposal facilities such as Near Surface disposal Facility (NSDF) or Deep Geological Repository (DGR). The knowledge also will be useful in predicting the salinity induced migration of uranium and other heavy metals from rocks to drinking water systems.

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