Environmental Chemistry of Actinides - I

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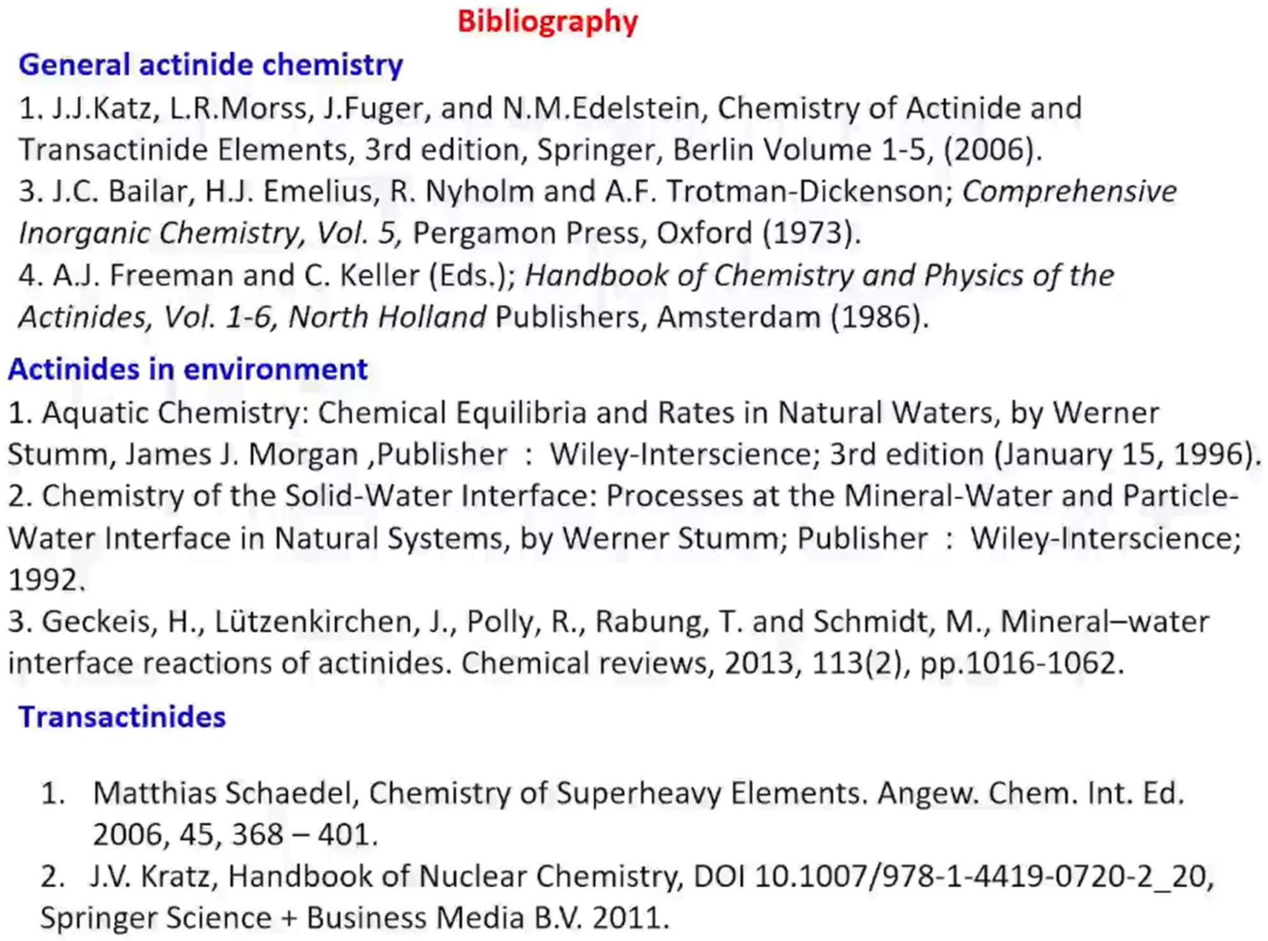
Week – 12
Lecture – 57



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Actinides in environment

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Transactinides

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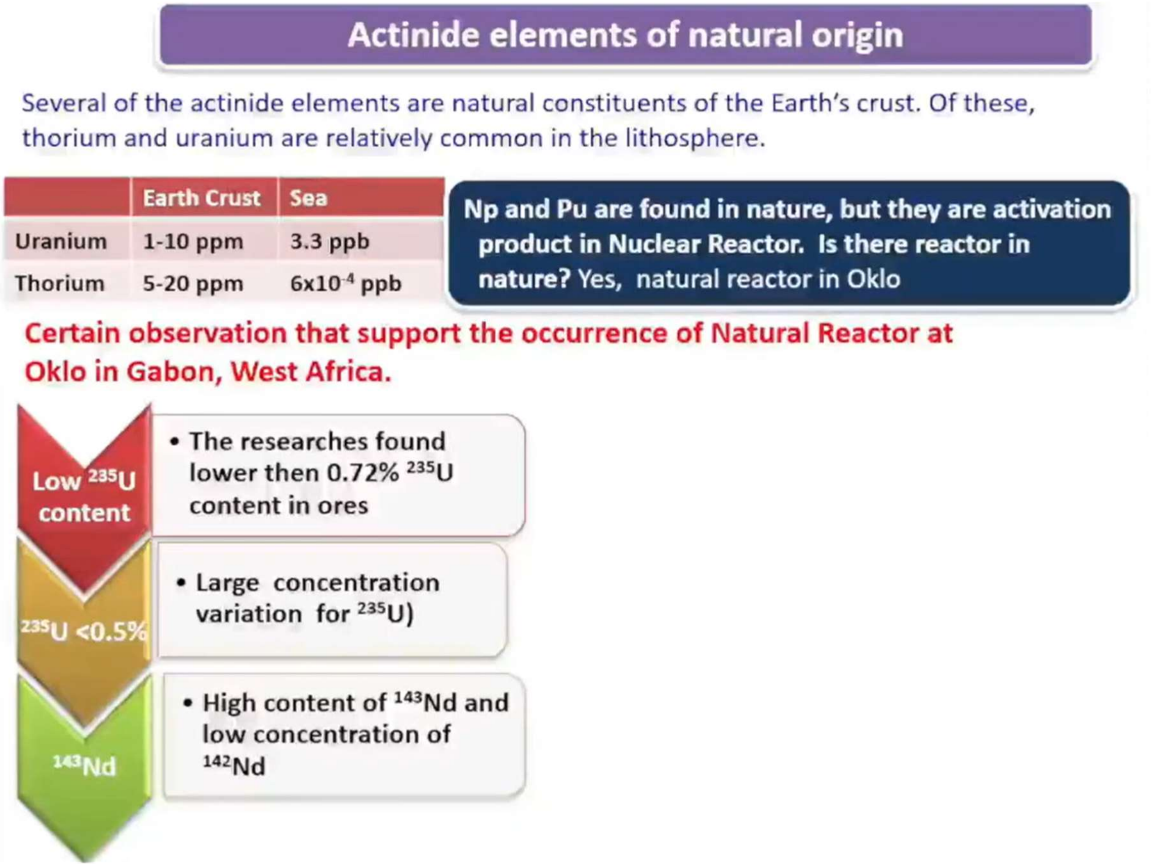
These are the references shown here for the actinide chemistry course including the general actinide chemistry, actinides in the environment as well as the transactinides. So, we have discussed actinide complexation and separation. Today we will be discussing actinides in the environment. In some of the previous lectures, we have discussed the factors that are responsible for this actinide in the environment. Today we will be discussing the factors in more detail about the actinides in the environment. Now there are several actinides we know in the earth's crust, already we have already discussed before like uranium, thorium to some extent actinium, and protactinium.

But neptunium and plutonium are also found in nature at very very minute concentrations. But we know that they are the activation products in the nuclear reactor. So, then how this neptunium and plutonium? we can say that they may be possible in the nature because of the natural reactor in Oklo that I have already mentioned in one of the previous lectures. Certain observations that support the occurrence of the natural reactor at Oklo in Gabon, West Africa are because of the low uranium 235 content.

Because we know that this natural uranium should have around 0.72% of uranium 235. But in the Gabon area this natural reactor whatever we call there the uranium 235 content was found to be lower than the 0.72% that is present in the ores. Then there is also this large concentration variation for this uranium 235 which is less than 0.5% it is seen., and this high content of neodymium 143, and low concentration of 142 neodymium that is its signature of some nuclear reaction was taking place at that point.



Actinide elements of natural origin

Several of the actinide elements are natural constituents of the Earth's crust. Of these, thorium and uranium are relatively common in the lithosphere.

	Earth Crust	Sea
Uranium	1-10 ppm	3.3 ppb
Thorium	5-20 ppm	$6x10^{-4}$ ppb

Np and Pu are found in nature, but they are activation product in Nuclear Reactor. Is there reactor in nature? Yes, natural reactor in Oklo

Certain observation that support the occurrence of Natural Reactor at Oklo in Gabon, West Africa.

Low ^{235}U content

- The researches found lower then 0.72% ^{235}U content in ores

^{235}U <0.5%

- Large concentration variation for ^{235}U)

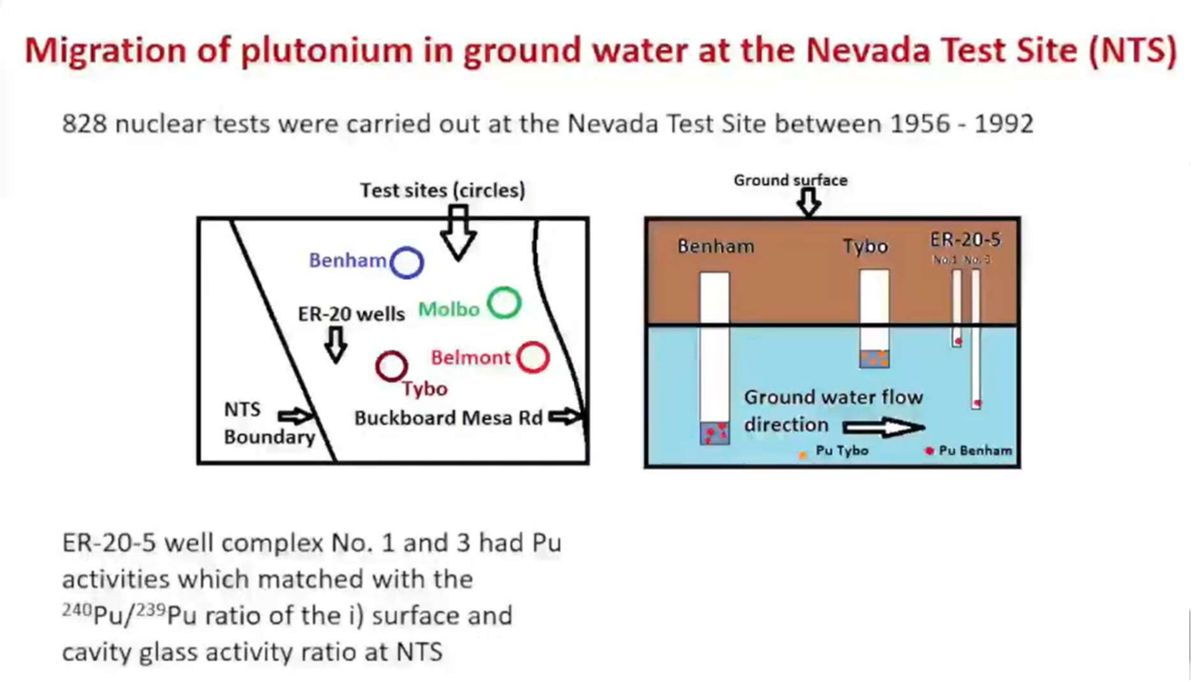
^{143}Nd

- High content of ^{143}Nd and low concentration of ^{142}Nd

Another factor which are responsible for the radionuclides in the environment, the sources are the nuclear test. Due to the nuclear test, nearly 4.5 tons of plutonium are released into the environment, and various activities in the nuclear fuel cycle also can have like reprocessing waste management can also contribute to the presence of plutonium, and other heavier actinides in the environment like neptunium.

There can also be accidental release. Some of the accidents I have mentioned here in this table below like the wind scale accident in 1957 in the UK, and there are some of these categories of these accidents which I have mentioned in the footnote of this table. That is number 5 category is accidents with wider consequences. Number 6 is a serious accident, and number 7 is a major accident. So, the former Soviet Union also there was an accident in 1957 that caused PISTIN, and it fell into category 6.

That is a serious accident. Three Mile Island in the USA in 1979 falls in category 5., and this Chernobyl reactor accident which is now in Ukraine in 1986. The accident took place, and it falls under category 7, and 2011 the Fukushima Daiichi nuclear reactor accident that is in Japan falls in category number 7.



Migration of plutonium in ground water at the Nevada Test Site (NTS)

828 nuclear tests were carried out at the Nevada Test Site between 1956 - 1992

ER-20-5 well complex No. 1 and 3 had Pu activities which matched with the ^{240}Pu/^{239}Pu ratio of the i) surface and cavity glass activity ratio at NTS

Now there was an interesting observation very close to the Nevada test site where a large number of nuclear weapons testing has been done. Around 828 nuclear tests have been conducted at the Nevada test site between 1956 to 1992. The left-hand side figure gives details of the test sites. We are aware the tests have taken place like this Benham test site, Molbo test site, Tybo test site, and Belmont test site. So, there are different testing sites where nuclear weapon testing has been carried out, and there are some wells that are away from this nuclear test site. So that is something called the ER-25 set of wells.

So, this well complex is there, and slightly away from these nuclear test sites like Benham, Typo, Belmont, and Molbo. So, in this well actually this drilling has been done, and the samples of plutonium have been detected, and they found that this signature of this plutonium that is a 242 to 239 isotopic ratio corresponds to that of the Benham test site. So which is much away from this well ER-20-5 that well complex number one, and number three well they were having these plutonium activities which matched with the 242 to 239 ratio of the surface, and the cavity glass activity at the nuclear test site at the Nevada test site of the Benham test site., and this shows here for the Benham how this testing has been done, and this has been modeled that probably there is some groundwater transport of this plutonium which is going here, and very close to the well actually this is the well complex where these samples have been taken well number one, and well number three, and the sample has taken few meters deep from the earth surface at the well number one., and at well number three at a deeper place, the sampling has been done, and both places they have found that even though the Tybo test site is very close to the place where drilling was done but the signature was that of the Benham nuclear test site that suggests that the plutonium from Benham test site has migrated to the well of the well number one as well as well number three. This is due to the typical mechanism of plutonium migration which will be discussed in the next lecture.

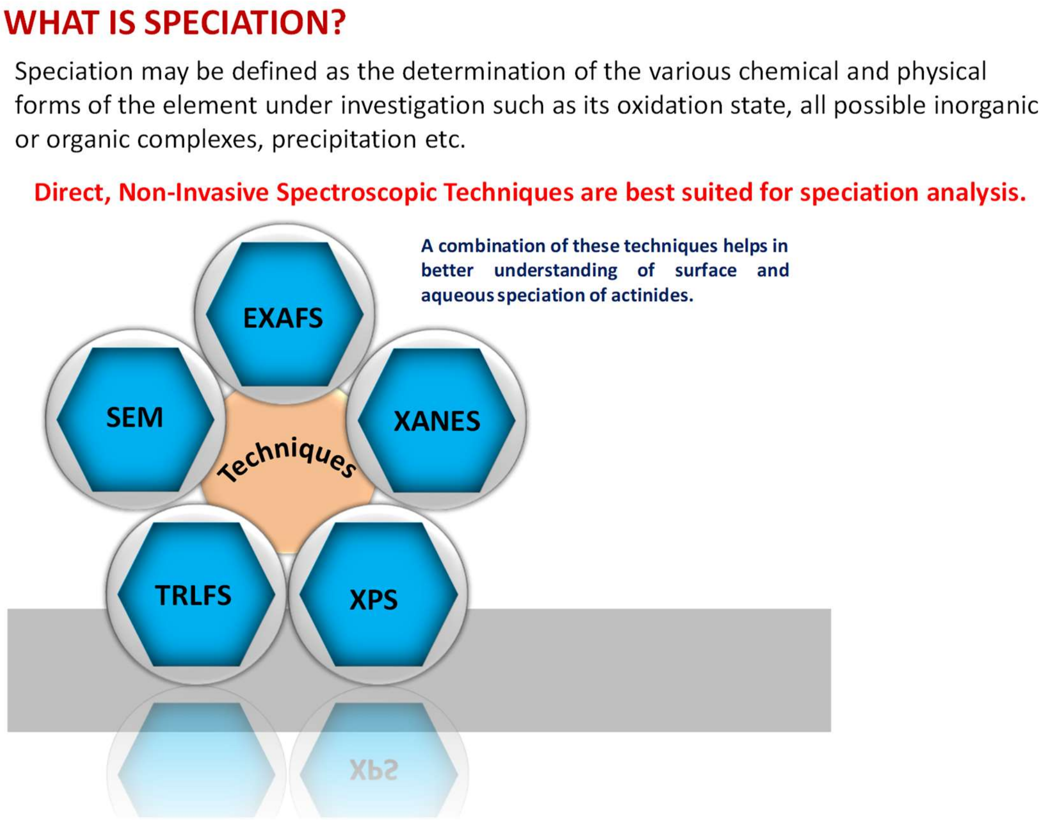
Actinide in the Environment

The great number of interdependent parameters has to be taken into account, in order to understand the behaviour of actinides in the environment properly

- **Oxidation state:** function of the redox potential (Eh)
- **Hydrolysis:** depends on the oxidation state and pH,
- **Complex formation** (other than hydroxo complexes): depends on the presence of complexing agents and on their concentration,
- **Solubility:** depends on the kind of solid formed, on complex formation and on colloid formation,
- **Colloid formation:** depends on [An], presence of carrier colloids and sorption of the actinides on these carrier colloids,
- **Sorption:** depends on the actinide species present in the water (ionic species, complexes, colloids),
- **Filtration effects:** depend on the size of particulate matter carrying the actinides and the size of the pores in the sediment.

Most of the above parameters can be controlled, if we know the **SPECIATION** of the actinides under a given condition

Now what are the factors that are deciding these actinides in the environment? The first thing is of course the oxidation state which is also considered as the Eh value, and the hydrolysis which depends on the oxidation state as well as the pH value. We know that this groundwater pH can be different, in different places. Same also with seawater, seawater has a different pH. Now another factor which are also relevant is the complex formation. We know that if it is hydrolyzing then the complex formed is the hydroxo complex but apart from that if there is any other complexing agent which is present in the groundwater system or the environment, and their concentration. If the concentration is large then the fraction of plutonium or the actinide that is present in the complex form will be relatively larger, and if the complexation constant is higher than the plutonium or the actinide in the complex species will be large. Next of course is the solubility. Now what is the solubility of this complex which is strong, whether this complex is soluble in the groundwater system or this complex is precipitating? These also matter. If it is a soluble complex form then it can go in the flow of this groundwater, and the migration can be a relatively longer distance., and there can be another thing which is called the complex formation, and colloid formation. There can be the colloid formation of this plutonium or other actinides which are present in the environment, and this colloid formation depends on the pH hydrolysis constant as well as the amount of the actinide present., and there can be also these colloids which are formed they can act as carriers, and they can also serve other actinides. So, this is called colloids which I will be discussing subsequently., and then another factor is the sorption. This depends on the actinide species which is present in the groundwater system. Also, it depends on the ionic species, and what are the complexing ions present, and the colloids that are present in the groundwater system. Finally, there is a filtration effect that depends on the size and particulate matter that is carrying the actinides, and on the rock surface, it can get filtered. That is how the actinides in the particulate matter can be immobilized on the rock surface., and all these factors are part of the speciation of the actinides which depends on the environmental conditions. Now what is the speciation?



WHAT IS SPECIATION?

Speciation may be defined as the determination of the various chemical and physical forms of the element under investigation such as its oxidation state, all possible inorganic or organic complexes, precipitation etc.

Direct, Non-Invasive Spectroscopic Techniques are best suited for speciation analysis.

A combination of these techniques helps in better understanding of surface and aqueous speciation of actinides.

The speciation may be defined by the determination of various chemical, and physical forms, the element in this case the actinide, and the investigation, such as its oxidation state, all possible inorganic or organic complexation, and the precipitation, etc. There are methods by which the speciation can be understood, and you can find out the nature as well as the amount of the species that are formed involving the actinides, and the techniques are SEM, EXAFS, XANES, TRLFS, and XPS. So, these are the techniques that are used. These techniques give a better understanding of the surface as well as aqueous speciation of the actinides. Now why do we study this speciation?

WHY STUDY SPECIATION?

As we know that, the presence of actinide in our food chain is harmful because of the associated radiotoxicity and chemical toxicity of the actinides. The chemical properties such as solubility, mobility, bioavailability and in fact toxicity of the actinides are governed by its speciation under given set of chemical conditions and a thorough knowledge of speciation is required to prevent or minimize the bioavailability of actinides.

Speciation of actinides decides

- **Solubility**
- **Mobility**
- **Bioavailability**
- **Toxicity**

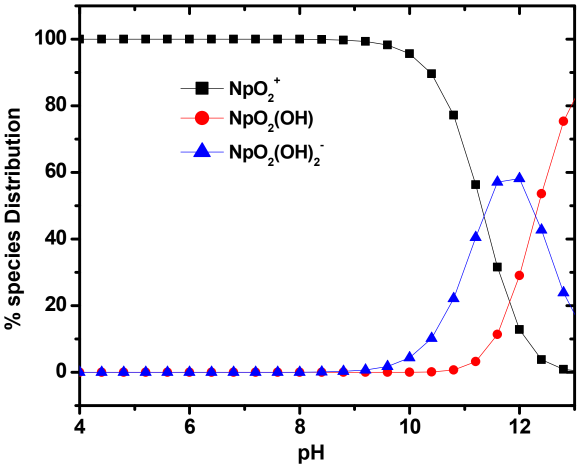
As we know the presence of actinides is dangerous if it goes into our food chain because its radiotoxicity is high. Also, the actinides and the heavier elements have very high chemical toxicity. In both these factors, this radiotoxicity, as well as the chemical toxicity, is going to be harmful to living beings, and these chemical properties of these actinides, and their complexes besides the migration of actinides. So, what are the important factors here? The first of course is the complexation which also includes the hydrolysis of the actinides. Then whatever these complexes are formed, whether they are soluble in the groundwater system or not, then their mobility.

The mobility can be as such also but if it is not forming a colloid then naturally the mobility is going to be much much less. So that is why the colloid formation is going to be an important factor in this migration of the actinides. We will be discussing these colloids in detail subsequently in this lecture. Finally, the bioavailability of this whatever radionuclides are for example plutonium. If it is migrating in the groundwater system it is also available in the aquatic system like the fish and other marine living species which are there.

Then it enters the food chain, and that is how this becomes toxic to the human being. So basically, we must evaluate all these factors solubility, mobility, and bioavailability but in this lecture, we will be mostly talking about solubility and mobility. This bioavailability and toxicity are not going to be covered in this lecture.

FACTORS DECIDING SPECIATION

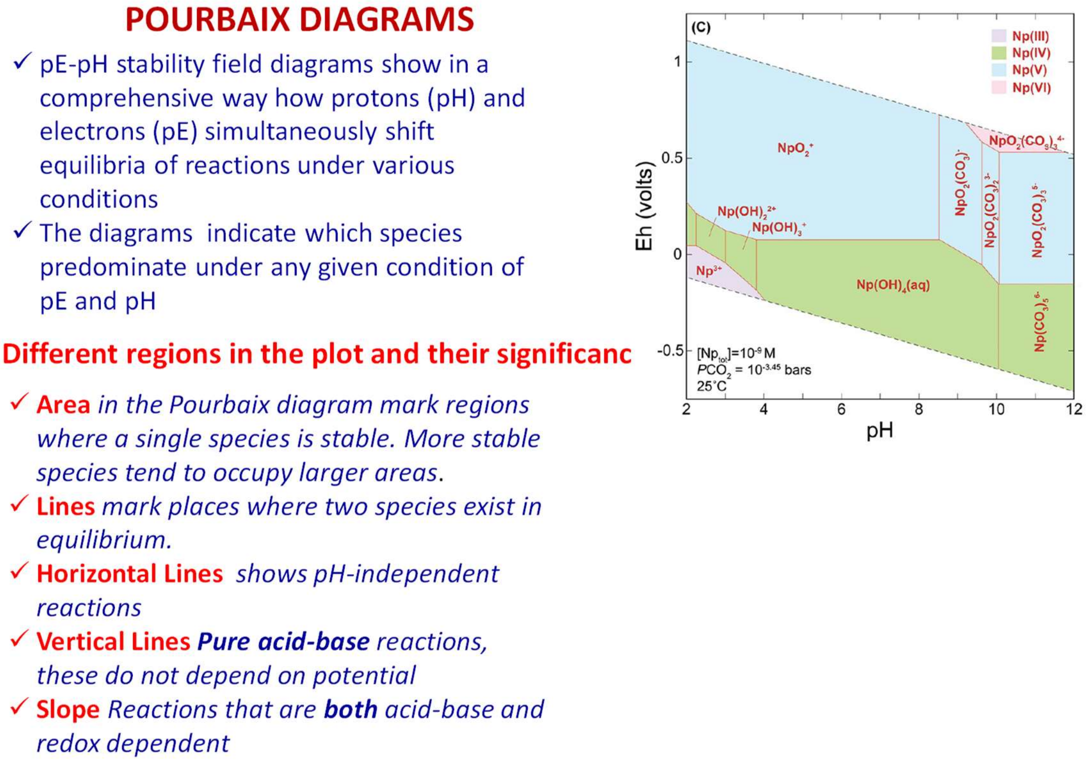
The three main factors that govern the chemical speciation of actinide are pH, oxidizing/reducing condition (Eh) & the presence of inorganic/organic complexing agents



Speciation Diagram of Np(V) as a function of pH ([Np]: 10^{-7}M). The predominance of Np as NpO_2^+ can be seen up to pH 9, later hydrolysis starts.

Now the factors that are deciding speciation are pH which exists in nature that is particularly in the groundwater system, the marine conditions. Then oxidizing, deducing conditions termed as the Eh, and the presence of inorganic, and organic complexing agents. So these are the main factors that are the pH, Eh, and the complexing agents that decide the speciation of the actinides. In this case, we have taken an example of NpO_2^+. NpO_2^+ as you know, exists as the NpO_2^+ as the ionic species, and this is the most mobile of the other neptunium species, ionic species like Np(IV), Np(III) or Np(VI) this is the neptunium hexavalent, neptunyl ion. So compared to all these species the NpO_2^+ species is more mobile, and that is why we are considering here the NpO_2^+ speciation. We give the distribution of the NpO_2^+ species as a function of the pH, and the concentration of neptunium taken here is 10^{-7} molar.

You can see here that at low pH values, you get this NpO_2^+ species which is the black line which is showing here up to pH around 9 or so you can find this NpO_2^+ that is NpO_2^+ species is predominant. Beyond that, it is going to undergo hydrolysis, and there is a possibility of the formation of NpO_2OH which is a neutral species, or $NpO_2(OH)_2^-$ that is anionic species. So, you find that first this NpO_2OH species, which is forming, and then subsequently it is forming the $NpO_2(OH)_2^-$ species. So that is how at pH>12 you get the anionic species of neptunium. Now this Eh-pH diagram is also called, the Pourbaix diagram which was already discussed in one of the previous lectures, and this shows the stability of the species under a given pH and atmospheric conditions.



POURBAIX DIAGRAMS

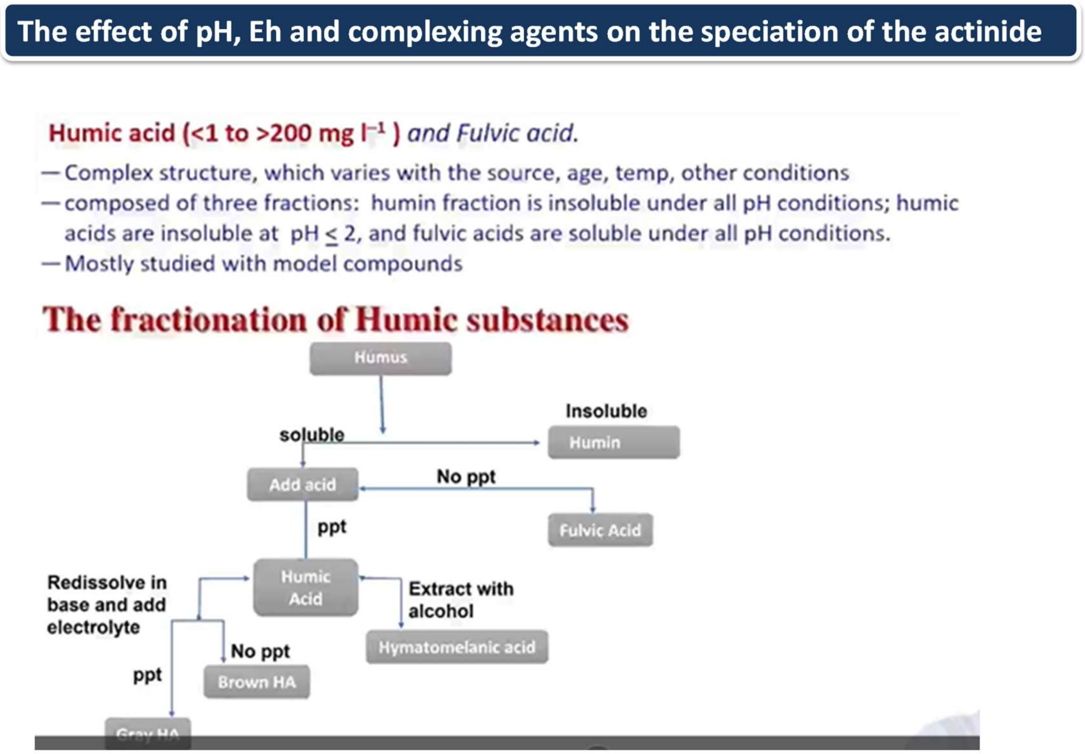
- ✓ pE-pH stability field diagrams show in a comprehensive way how protons (pH) and electrons (pE) simultaneously shift equilibria of reactions under various conditions
- ✓ The diagrams indicate which species predominate under any given condition of pE and pH

Different regions in the plot and their significanc

- ✓ **Area** *in the Pourbaix diagram mark regions where a single species is stable. More stable species tend to occupy larger areas.*
- ✓ **Lines** *mark places where two species exist in equilibrium.*
- ✓ **Horizontal Lines** *shows pH-independent reactions*
- ✓ **Vertical Lines** ***Pure acid-base** reactions, these do not depend on potential*
- ✓ **Slope** *Reactions that are **both** acid-base and redox dependent*

So this diagram indicates which species predominate under any given environmental condition of pE, and pH. So, this side figure shows the neptunium again, and you can see here this is the area in this Pourbaix diagram. This marks the region where a single species is stable very clearly shown here. This is the area that is demarcated in this, and this is where the NpO_2^+ species is stable., and that is how further subsequently also for the other areas. this is marked by how these species are stable in which area.

Also, these lines indicate two species are coexisting together. These vertical lines also mention this is a purely acid-base reaction, and this does not depend on the pH value. the horizontal lines on the other hand show that these are pH-independent reactions, and, they are not dependent on the Eh values, the potential whatever is prevailing under the condition. Now the slope of the lines suggests that both the acid-base and the redox-dependent reactions are considered in this case or both are prevailing.



The effect of pH, Eh and complexing agents on the speciation of the actinide

Humic acid (<1 to >200 mg l^{-1}) *and Fulvic acid.*

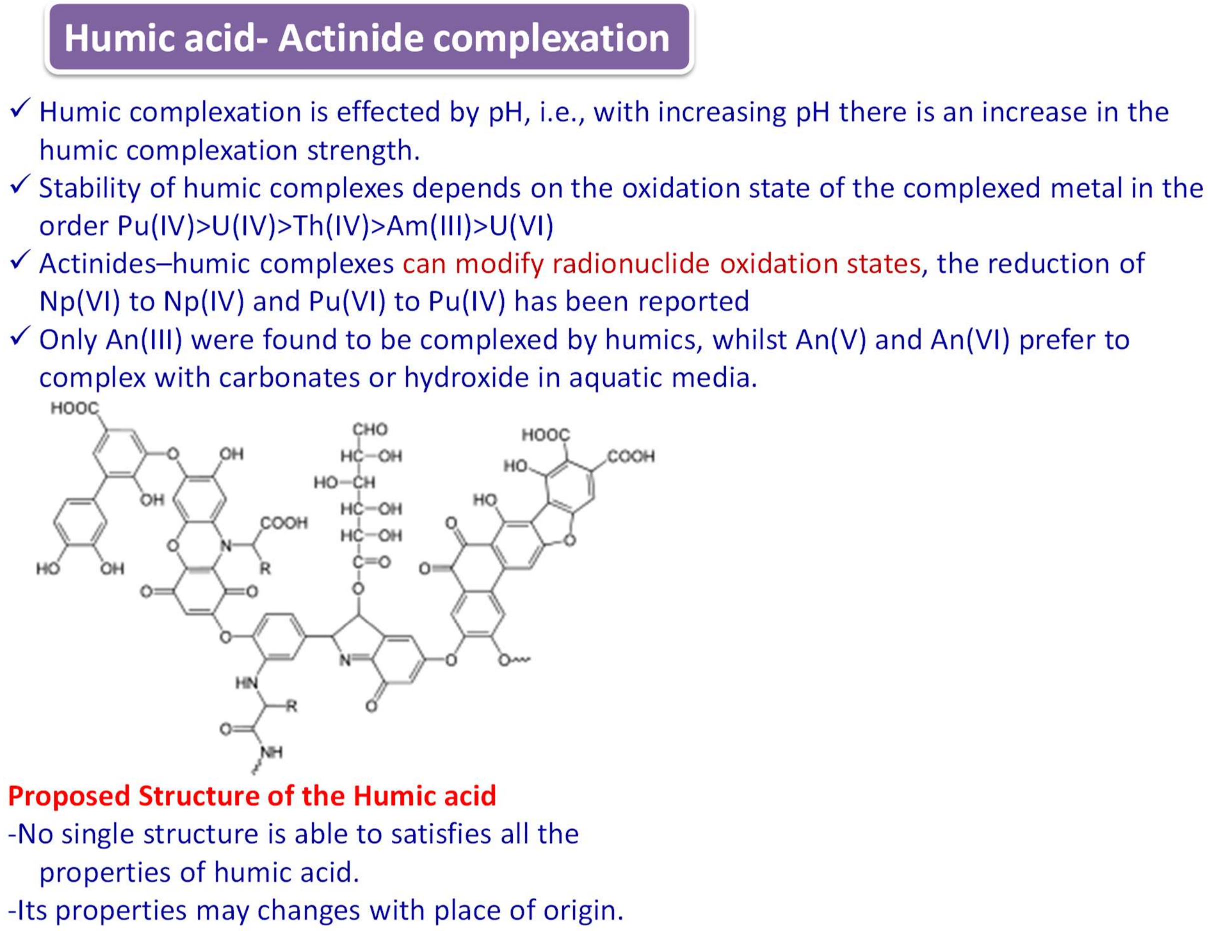
— Complex structure, which varies with the source, age, temp, other conditions
— composed of three fractions: humin fraction is insoluble under all pH conditions; humic acids are insoluble at pH ≤ 2, and fulvic acids are soluble under all pH conditions.
— Mostly studied with model compounds

The fractionation of Humic substances

Now we also see this effect of pH, Eh, and complexing agents on the speciation of the actinides. Now, what are the complex agents? Mostly under the groundwater condition, we have this humic acid and the fulvic acid.

Humic acid is a plant-origin acid that after many years is transformed into humic substances. Now these humic substances have a very complex structure, and this varies the source, age, and temperature as well as other conditions. This is composed of different fractions the human fraction is insoluble under all pH conditions, and the humic acid is insoluble at a pH value less than 2. Whereas the fulvic acids are soluble under all pH conditions. So mostly because the humic acids are very complex structures so the studies with the actinides are with the model compounds which mimic part of the humic substances.

Here I have shown a schematic of how this humus is first you can extract it with alkali, which is insoluble and is termed as a humin, and which is soluble that if it is treated with acid, and precipitated that is termed as the humic acid fraction, and which is not precipitated that is the fulvic acid, and then it can re-dissolve the humic acid, and you can again add electrolyte, and you get precipitation which is something called a grey humic acid, and which is not precipitated it is called the brown humic acid.



Humic acid- Actinide complexation

- ✓ Humic complexation is effected by pH, i.e., with increasing pH there is an increase in the humic complexation strength.
- ✓ Stability of humic complexes depends on the oxidation state of the complexed metal in the order Pu(IV)>U(IV)>Th(IV)>Am(III)>U(VI)
- ✓ Actinides–humic complexes can modify radionuclide oxidation states, the reduction of Np(VI) to Np(IV) and Pu(VI) to Pu(IV) has been reported
- ✓ Only An(III) were found to be complexed by humics, whilst An(V) and An(VI) prefer to complex with carbonates or hydroxide in aquatic media.

Proposed Structure of the Humic acid

-No single structure is able to satisfies all the properties of humic acid.

-Its properties may changes with place of origin.

This is the representative structure of the humic acid is given here. Now this humic complexation is affected by controlling the pH. Now that by increasing the pH there is an increase in the strength of this humic acid complexation that is because some of the functional groups like it has the carboxylic acid as well as the phenolic type of groups are there this gets deionized, and you get COO^- or O^- type of functional groups which are taking part the complexation with the metal ion or in this case the actinide ions, and that is only possible if you increase the pH to very high values. So, basically humic acid will have a number of pKa values if it is whether it is a carboxylic acid functional group or a phenolic functional group the phenolic group will be at a higher pH value it will be dissociating, and there is no single structure which can satisfy all properties of the humic acid, and its properties may change with the place of origin of the humic acid.

Now while considering the stability of these humic acid complexes as already mentioned before the tetravalent actinides will be forming much stronger complexes than the trivalent and the hexavalent, and in the set of tetravalent actinide ions, you find that which has higher ionic potential that forms a stronger complex. So, Pu(IV) forms a stronger complex with the humic acid compared to uranium-4 which in turn forms a stronger complex than thorium-4, and thorium-4 forms a stronger complex than americium-3 or other trivalent actinide ions which in turn forms a stronger complex than the uranium-6 ion that is the uranyl ion., and this actinide humic acid complexation this can modify the radionuclide oxidation state that is the reduction of Np(VI) can go to Np(IV), and Pu(VI) to Pu(IV) this has been reported as has been mentioned in the previous Nevada Test Site report also even though we are expecting plutonium-5 to put that has been reduced to Pu(IV) that is how the plutonium concentration has been much less.

Why study actinide sorption and migration behaviour?

This is as an application part of whatever you have learned till now for actinide speciation. In any unfortunate scenario if there is some leak of the radionuclides to the environment, the first thing it encounter is the soil, which is basically composed of clay minerals, and/or a complex assemblage of different oxides in different proportions. The movement of radionuclide to the clay/oxide can lead to interaction between the two, that interaction we need to study. This will help in understanding of the migration or the movement of the radionuclide form one place to other. This information is essential in many aspects such as

- ✓ To avoid the radionuclide from becoming the part of our food chain.
- ✓ Choosing better buffer back fill material for the deep geological repository
- ✓ Remediation of any radioactive contaminated sites etc..

Before going to see the interaction between the radionuclide and the clay/oxide surface lets see some properties of oxide/clay surface in aqueous media.

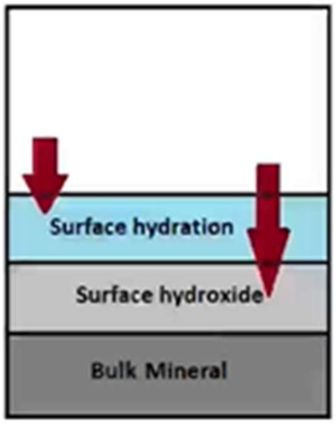
Now why study the actinide sorption and migration behavior? This is an application part, and we have already studied the actinide speciation as well as the complexation. In any unfortunate scenario if there is some leak of the radionuclide into the environment as I have already mentioned by accidents or from the vitrified waste blocks which are there under the deep geological repository from there also if there is some leakage of the radionuclide then finally of course if from the nuclear weapon testing, there is a lot of actinides are there.

Because of that, we try to understand this actinide substance and migration behavior, and this will help us understand this migration and movement of the radionuclide from one place to the other. This information is essential, to avoid the radionuclide becoming part of our food chain, choosing a better buffer backfill materials in case of the deep geological repository, and the remediation of any radioactive contaminated site. Before going to see the interaction between the radionuclide, and the clay or oxide surface let us see some of the properties of the oxide clay surface in the aqueous medium.

How does the oxide/clay surface look like in the aqueous solution?

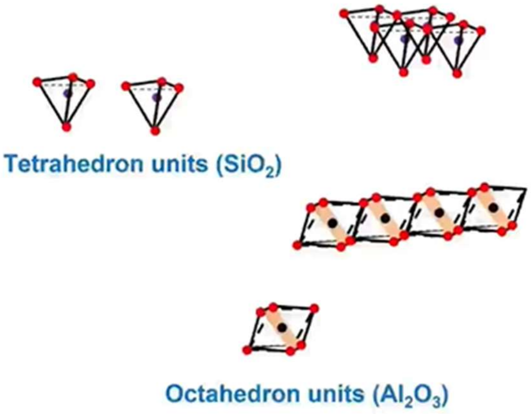
The surface of oxide/clay has surface -OH group or more correctly hydrated hydroxyl groups.

The clays also have surface hydroxyl groups like oxide but in addition to the oxides Clay minerals have a sheet-like structure and are composed of mainly tetrahedrally arranged silicate and octahedrally arranged aluminate groups. Depending upon the arrangement of silicate and aluminates clay can be divided in several groups such as **smectite, kaolinite** etc…



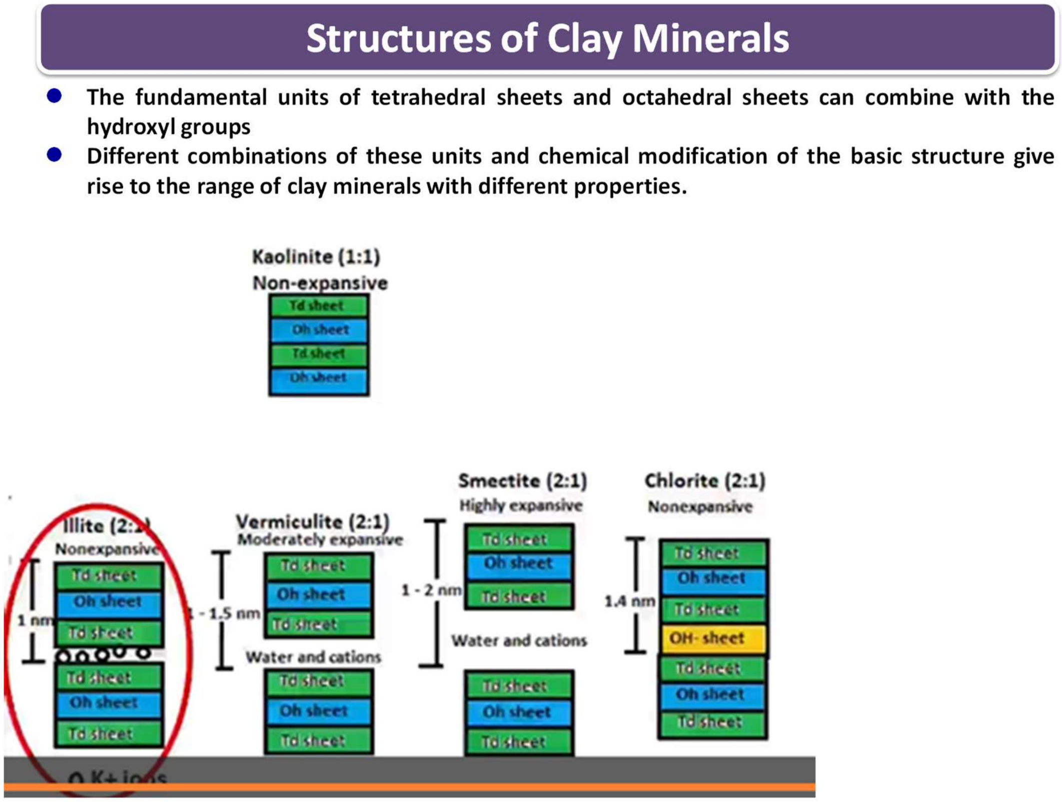
Now how does the oxide at the clay surface look like in the aqueous solution? The surface oxide and clay have a surface OH group as I have shown here you have some of these OH groups mentioned here which form a bond with this water molecule here. The many places you have the surface OH group which forms a bond with the water molecule here, and that is how it is responsible for forming the complexes with the actinides, we also have these clay minerals which have the surface hydroxyl groups I will be showing in the next few slides how these are acting, and the oxides also are present like we have the silica and alumina but they also have replaceable hydrogen ions some sort of hydroxyl groups are there, and that is how this complexation is taking place.

These clay minerals also have a sheet-like structure and are composed of mainly tetrahedrally arranged silicates and octahedrally arranged aluminate groups, depending upon the arrangement of the silicates, and aluminates the clay can be divided into several groups such as the smectite, kaolinite etcetera it comes in the next few slides.



2:1 silica / alumina: Illite
3 layer 2:1: Smectite

So, this is the tetrahedral structure of the silicate structure, and this is the octahedral aluminate structure or aluminum oxide structure, and you have these layered structures where you have these tetrahedral layers, and the octahedral layers, and another tetrahedral layer so they form a structure like this, and finally you have a structure like this which is given here. So, you have the silica to alumina ratio if it is 2 to 1 then it can be Ilite or if a 3 layer 2 is to 1 it can be smectite as is given in the next slide.



Structures of Clay Minerals

- **The fundamental units of tetrahedral sheets and octahedral sheets can combine with the hydroxyl groups**
- **Different combinations of these units and chemical modification of the basic structure give rise to the range of clay minerals with different properties.**

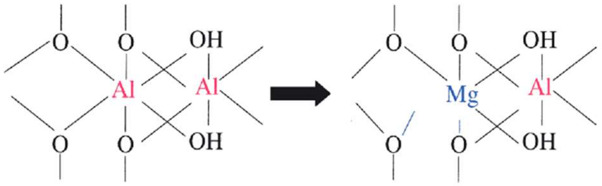
So, the structure of the clay minerals is given here you have this tetrahedral sheet or the octahedral sheet, and you can have another tetrahedral another octahedral sheet this is how the stacking can be done. For example, we take this Illite so, in this case, we have a 3 layer structure showing a tetrahedral octahedral and a tetrahedral sheet, and this dimension is around 1 nanometer, and this Illite actually is a non-expensive type of structure so where this part is actually having distance is very very less where you have the potassium ions embedded between these 2 types of this sheet structures whatever are there you have for Vermiculite or which is moderately expansive, and you have this distance is around 1 to 1.5 nanometers for smectite is highly expansive. you have around 1 to 2 nanometers this distance on water molecules, and cations can be there between the 2 layered structures given here. Similarly, for the chlorite structure you do not have a non-expensive system, and you do not have anything in between these layers. Kaolinite which is at the top as a non-expensive 1 is to 1 structure.

Types of charge in clays

Permanent Charge

- Due to isomorphous substitution
  - the replacement of one ion for another of similar size within the crystalline structure of the clay).
  - Al^{+3} by Mg^{+2} in octahedral sheet and Si^{+4} by Al^{+3} in tetrahedral sheet

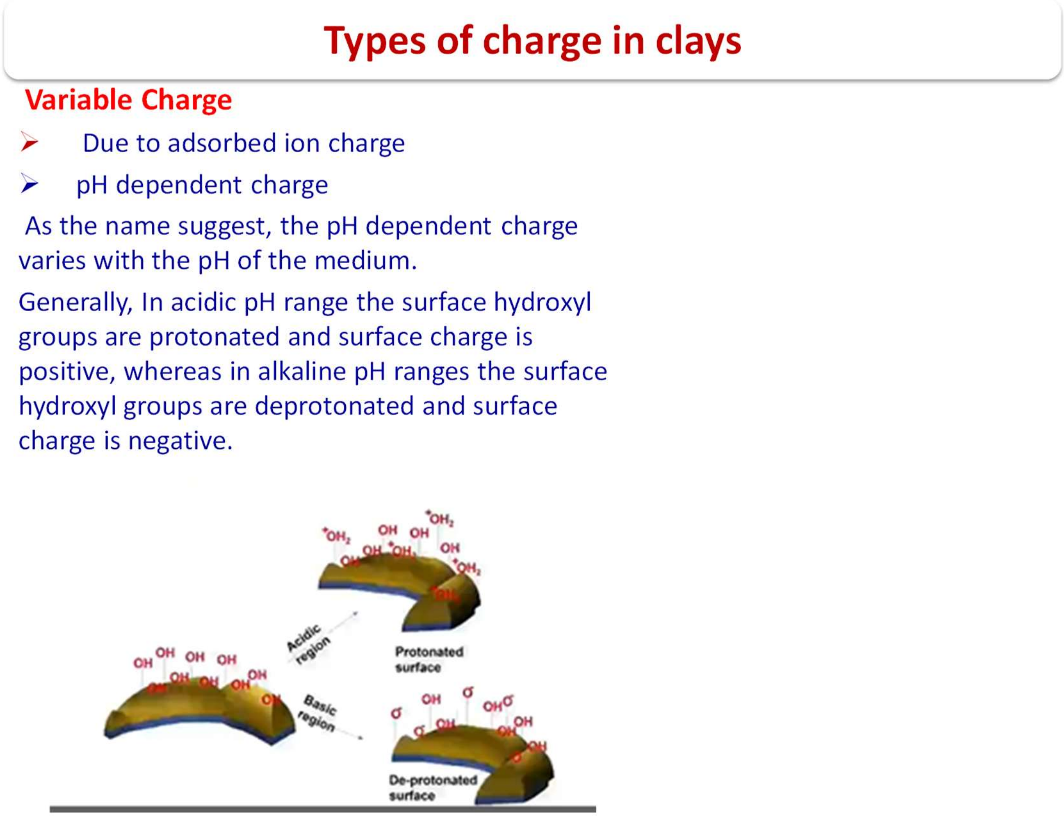
- Due to isomorphous substitution



Neutral Octahedral sheet Net negatively charged

Now the type of charge in the clay so there are some permanent charges due to the isomorphous substitution in the replacement of one ion for another one, this can be like we have one set of ions there, which is replaced by another set of ions which are having similar size within the crystalline structure. For example, we have this aluminum 3 plus which is replaced by magnesium 2 plus in the octahedral sheet or we have this silicon 4 plus by aluminum 3 plus in the tetrahedral sheet in these cases you have this replacement of the charge, and that is how you can have also permanent charge is there in the structure of the clay minerals as I have shown.

It also can have isomorphous substitution, and it is shown here in the scheme given here that all this aluminum is substituted by magnesium, and that is how you have permanent charges present in this structure. So, you have the neutral octahedral sheet which where you have the aluminum ions now there is a net negatively charged octahedral sheet where you have this magnesium is replacing the aluminum. So, this is due to the isomorphous substitution.



Types of charge in clays

Variable Charge

- Due to adsorbed ion charge
- pH dependent charge

As the name suggest, the pH dependent charge varies with the pH of the medium.

Generally, In acidic pH range the surface hydroxyl groups are protonated and surface charge is positive, whereas in alkaline pH ranges the surface hydroxyl groups are deprotonated and surface charge is negative.

Now the type of charge in the clays can be also a variable charge so this is due to the adsorbed ion also this is pH dependent charge you can show these examples here. Adsorbed ion means some ion is adsorbent to this clay mineral, and there will be different charges will be there also depending on the pH as shown in this scheme below you can see that you have this hydrated alumina whereas, at a lower pH value, you get this type of structure where these hydrogen ions are there but if you have a higher pH value then you find that these hydrogen ions are now removed so you have the O^- ions are there so that is how you have the developed the surface charge that is O^- charges present in the surface, and that can form the complex.

Point of zero charge (PZC)

The pH at which the surface charge is zero varies from one clay/oxide to other (see table below, Iso electric point (IEP)). the suspension (oxide/clay in water) pH at which the surface has a zero net charge is known as Point of zero charge (PZC) .

Mineral	PZC	Mineral	PZC
SiO_2	2-2.5	Hematite	7.0-8.8
Kaolinite	3.0-4.6	δ-MnO2	2.8
Goethite	7	β-MnO2	7.2-8.7
α-Al_2O_3	8.3-9.4	Albite	2.0

For any surface
If pH (of suspension) < PZC, the surface is positively net-charged
If pH > PZC, the surface is negatively net-charged

Now one important parameter that is considered in the case of the clay minerals is the point of zero charge commonly known as the PZC will be discussed in this slide. So what is the point of zero charge? that is the pH at which the surface charge is zero it is neither a positive charge nor a negative charge so the charge at that point is called a point of zero charge. It varies from one clay or oxide to another one thrown a table here, and see this point of zero charge for silica it is 2 to 2.5 kaolinite 3 to 4.6 goethite is around 7 alpha alumina is 8.3 to 9.4 delta manganese dioxide is 2.8 beta manganese dioxide 7.2 to 8.7, and albite it is 2 hematite 7.0 to 8.8 so like that then for different minerals or the clay minerals we can have the different PZC values. Now for any surface the pH of the suspension is less than that of the PZC then the surface is net positively charged, and if the pH>PZC then naturally the hydrogen ions are removed, and the surface is net negatively charged.

Some Useful Terms with their unit

Specific surface area : m^2/g
Clay concentration (s/l) : g/l
Surface concentration : mol/g
Surface Density : mol/m^2
CEC : meq/g
Surface Charge : C/m^2
Faraday constant : 96490 C/mol

Some conversions

$$\text{Surface concentration(mol/m}^2\text{)} = \frac{\text{Surface concentration(mol/g)}}{\text{specific surface area (m}^2\text{/g)}}$$

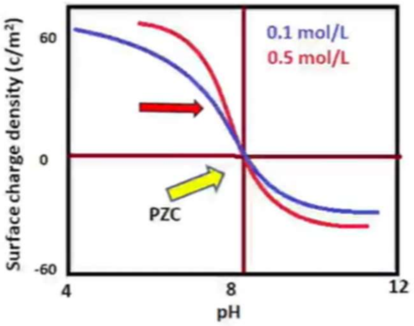
$$\text{Surface concentration(mol/l)} = \frac{\text{Surface concentration(mol/g)}}{\text{Clay concentration (g/l)}}$$

$$\text{Surface charge (C/m}^2\text{)} = \frac{\text{Surface concentration(mol/g) x Faraday constant (C/mol)}}{\text{specific surface area (m}^2\text{/g)}}$$

So some of the important terms that are necessary for this understanding of the clay mineral complexation with actinides are defined in this transparency as the specific surface area this is the unit is meter square per gram clay concentration it can be grams per liter surface concentration can be moles per gram surface density moles per meter square, and cation exchange capacity can be milliequivalent or the CEC is considered the milliequivalent per gram surface charge can be coulombs per meter square, and Faraday constant is 96490 coulombs per mole. So that is how these are defined, and some conversions of the surface concentration. The moles per meter square is a surface concentrate moles per gram divided by the specific surface area meter square per gram surface concentration in moles per liter can be surface concentration divided by the clay concentration surface charge we define all the surface concentration multiplied by Faraday constant divided by the specific surface area.

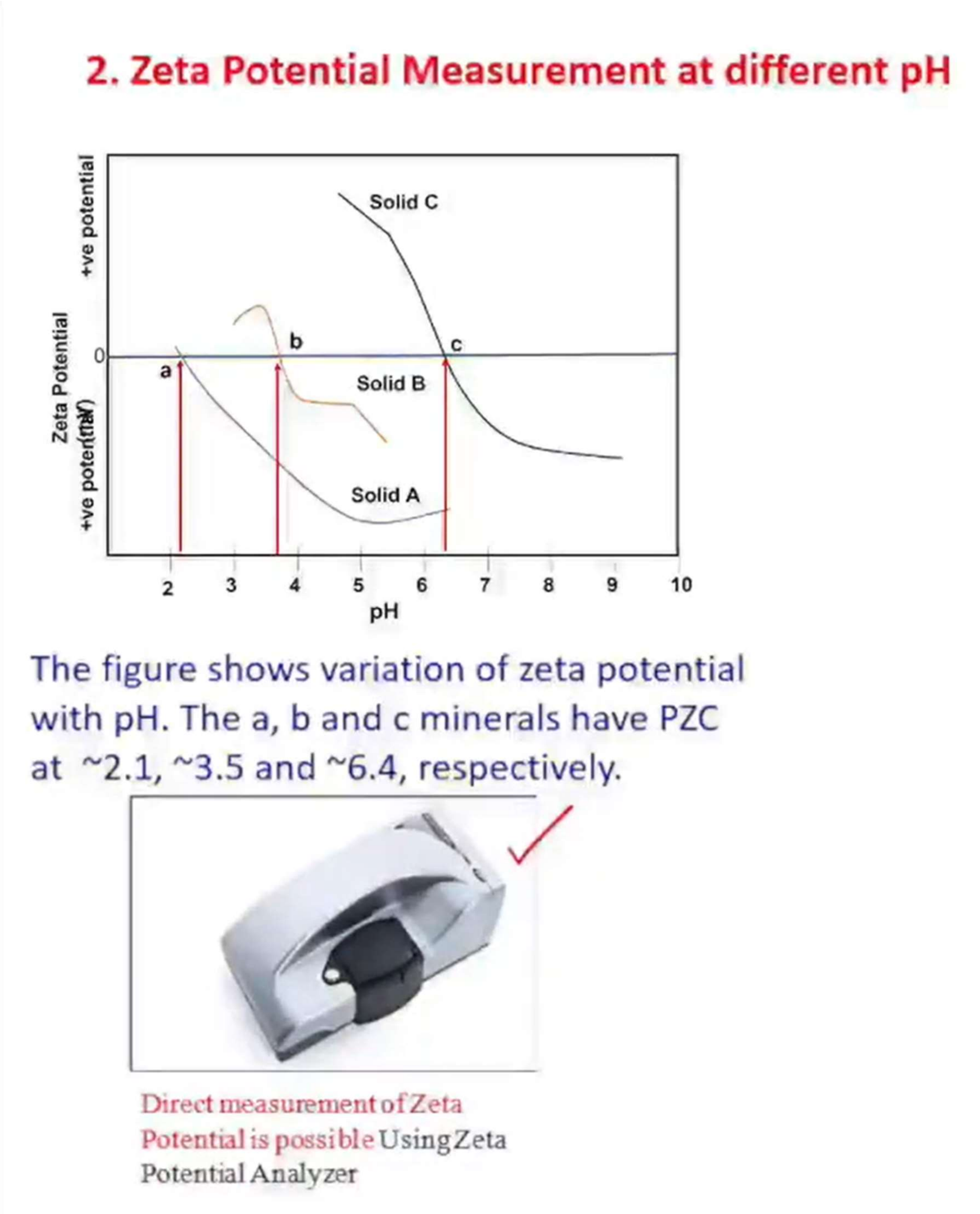
How to Measure Surface charge/ Potential

1. Potentiometric titration



After the titration, the surface charge density was calculated and plotted against the pH of suspension to get the PZC.

Now how to measure the surface charge of the potential can be done by potentiometric titration. So, you see here all these different pH values, you can get the surface charge density, and that is how it will be varying initially, and then when it comes down you get this pH value where you have this value is zero. So that is the charge density is zero which is called the PZC. So PZC can be measured by potentiometric titration. It can also be done by using an instrument that measures the zeta potential and the different pH values.



2. Zeta Potential Measurement at different pH

The figure shows variation of zeta potential with pH. The a, b and c minerals have PZC at ~2.1, ~3.5 and ~6.4, respectively.

Direct measurement of Zeta Potential is possible Using Zeta Potential Analyzer

So this is the photograph of this zeta potentiometer which is used in the laboratories. So, in this case, automatically you get as a function of pH the zeta potential values, and you can find out for substances like A, B, and C you get these are the point of zero charge where the profile is like this for A, this is for B, and this is for C. So, this is how you can get the zeta potential.

Thank you.