Environmental Chemistry of Actinides - II

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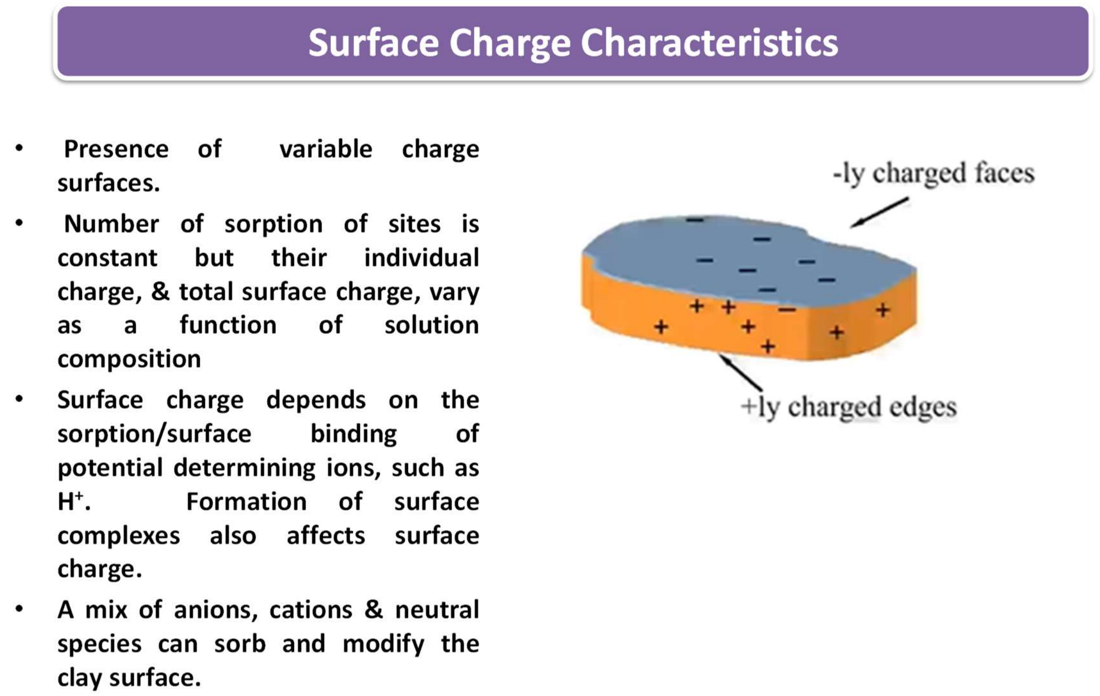
Week – 12
Lecture – 58



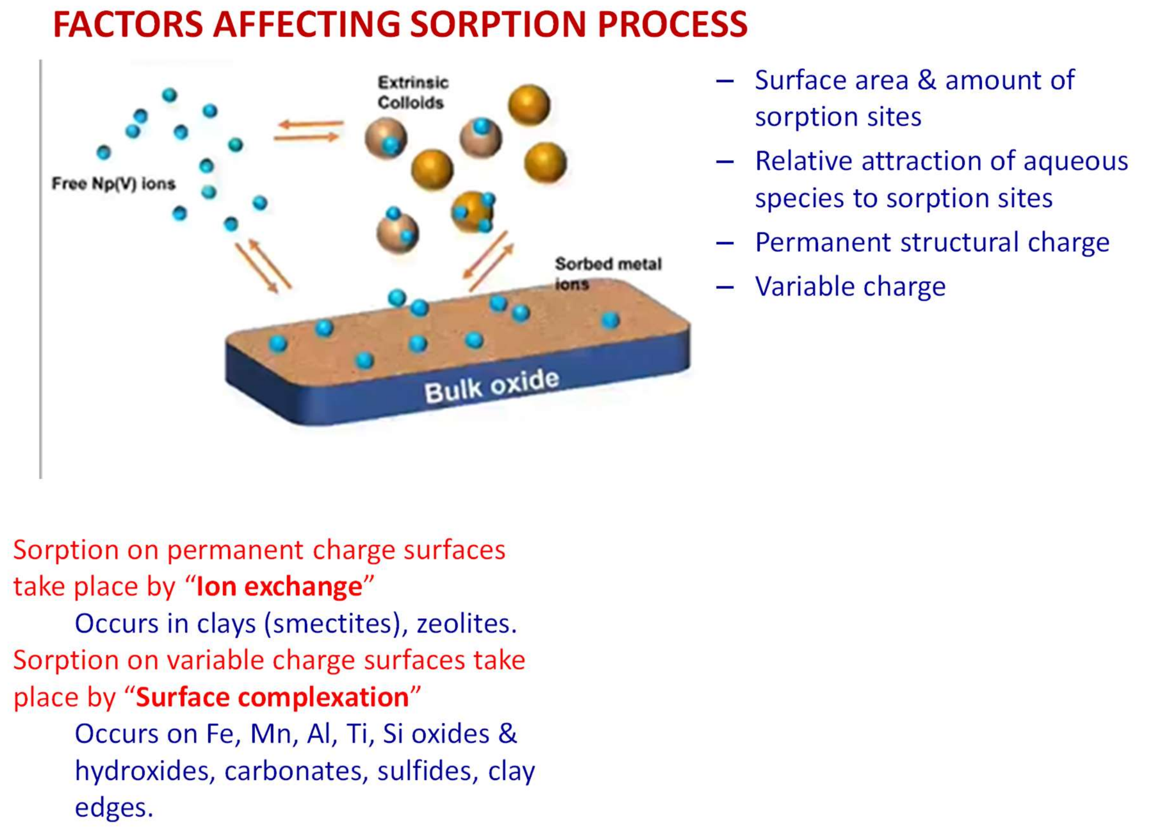
Surface Charge Characteristics

- Presence of variable charge surfaces.
- Number of sorption of sites is constant but their individual charge, & total surface charge, vary as a function of solution composition
- Surface charge depends on the sorption/surface binding of potential determining ions, such as H^+. Formation of surface complexes also affects surface charge.
- A mix of anions, cations & neutral species can sorb and modify the clay surface.

We have already discussed the point of zero charge, how it has to be determined experimentally, the potentiometric titration or by zeta sizer, which gives the zeta potential determined as a function of the pH values., and from that, we can find out the point of zero charge, the PZC value. Now as I've already mentioned that depends on the pH values, and the PZC of this sorbent or the clay mineral whatever we are talking about. So based on that the metal ion uptake can be decided. For example, if the PZC value of a particular clay mineral is around seven then at pH value lower than seven, will exist in the protonated form. So naturally the uptake of the protonated species will not be there on this mineral surface.

But if we increase the pH value to higher than that of the PZC, then these hydrogen ions are dissociated or removed from the surface of this clay mineral., and we have the O minus or negatively charged species at the surface of this clay mineral., and then will be forming the complex with the cationic species, if present in the aquatic system. If it is forming a complex or if it is forming anionic species, the actinide ion, then it will naturally not form a complex at the pH value higher than that of the PZC.

Now coming to the surface charge characteristics of these minerals, the figure shows how you have this negatively charged in the phases you have, and also the positive charge edges are there. So they will be actually binding with the cationic as well as the anionic species. That is the cationic species will be binding with the phases, and the anionic species will be binding with this. Now in this case, when the presence of the variable charged surfaces as shown here, the number of surface sites is constant, but their individual charge and the total surface charge will vary as a function of the solution composition. The surface charge depends on the sorption, surface binding of the potential determining ions, the charge of hydrogen ions, and the formation of the surface complex also affects the surface charge. A mix of anion, cation, and neutral species can sorb, and modify the clay.



FACTORS AFFECTING SORPTION PROCESS

- Surface area & amount of sorption sites
- Relative attraction of aqueous species to sorption sites
- Permanent structural charge
- Variable charge

Sorption on permanent charge surfaces take place by “**Ion exchange**”

Occurs in clays (smectites), zeolites.

Sorption on variable charge surfaces take place by “**Surface complexation**”

Occurs on Fe, Mn, Al, Ti, Si oxides & hydroxides, carbonates, sulfides, clay edges.

Now what are the factors that are affecting the sorption process? Number one is the surface area and the amount of sorption sites. We have a very large surface area that is the same mineral if you have finer particles, it will have a very large surface area for a particular weight of the clay mineral. So in that case, the surface area has increased naturally which will also have higher uptake of the actinide ions or the metal ions, and also the amount of sorption sites that is the density of the sorption sites in the mineral surface. As shown here, you have this bulk mineral phase which is shown here.

Now how many sites are there that are binding in the metal ion that also is dependent on the amount of actinide or the metal ion which is taken up by the mineral phase or the bulk mineral phase? Then the relative attraction of the aqueous species to the sorption sites. Some other species are present in the aqueous phase which are also going to the sorption sites. Then permanent structural charge, and also variable charge. These are the factors which are deciding the sorption process.

Now the mechanism of this can be two ways. First is the ion exchange which is happening in case of the clay minerals like smectite, and zeolites. So in this case, we have this example which is given here that you have the neptunium ions are there. So the charge is not given but you can consider suppose neptunium plus 5 state that is neptunyl ion is there. So then how it will form complexes with the bulk mineral phase or it will be transported as such.

So as shown here some of this neptunium will be forming of course directly it will be forming complex on the surface of this bulk mineral phase. Then it can also bind with some of the mineral colloids with these bigger size species which is shown here. This is a mineral colloid which is there. Now what is the colloid? that I will be discussing subsequently in this lecture. So is this by this neptunium binding to this mineral colloid which is there, and this also can move.

There is a transport of this can be there. Neptunium can as such it can be transported but then it will be less. The magnitude of transport will be much much less here because very small ions are moving. But if it is bound to a mineral colloid as it is shown here then the transport range will be much much larger so it will go to a longer distance or it can bind to the bulk mineral phase which is actually shown here. When the bulk mineral phase is directly the neptunium may be binding or it may be binding at a function at a complex of this mineral colloid.

So, either way, you will find that the neptunium becomes immobilized because it is bound to the bulk mineral phase. The mobile neptunium is which is going as such transported as the ion or it is getting transported as a complex form in the mineral colloid. Now this binding can be by ion exchange where the actinide ion can get exchanged with an ion present in the mineral surface. This is called the ion exchange or it can be by something called a surface complexation. the mechanism of the surface complexation will be discussed in some of the subsequent slides. This surface complexation can take place on the surface of iron, manganese, aluminum, titanium, or silicon oxides which have hydroxide, carbonates, sulfides, or clay. So these types of things can be this surface complexation can take place.

Actinide Mineral Interaction

Interaction between the actinide and the clay/oxide surface
Electrostatic/chemical

For sorption or retention
They should have Opposite charges

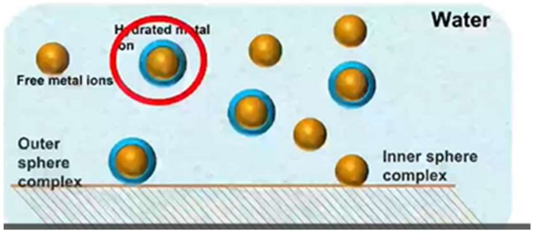
For Release/ Desorption Same charges

Now the actinide mineral interaction so we have this mineral surface as shown here in the schematic it depends on the pH value here in the increasing pH value mineral surface can have a zero charge at the PZC, and if it is lower then the PZC will have a positive charge, and at the higher than the PZC will have a negative charge. This is how the mineral surface will behave as a function of the pH, and there can be an interaction between the actinide, and the clay oxide surface which is electrostatic or it can be a chemical interaction based on that the complexes will be formed. If you have the anionic species then they will be interacting at the lower pH value or the positive species will be binding the mineral surface at the positive part of the mineral surface will be binding the negatively charged complexes or at the higher pH value where you have the mineral surface having a net negative charge it will be binding with the positively charged ions or the complexes. Now for sorption or retention, they should have opposite charges that is the mineral surface, and the binding actinides ions should have the opposite charges, if you want to be released or dissorbed from the mineral surface then you should have the same charged species. In that case, it will be released from the mineral surface.

Mechanism and nature of complexation

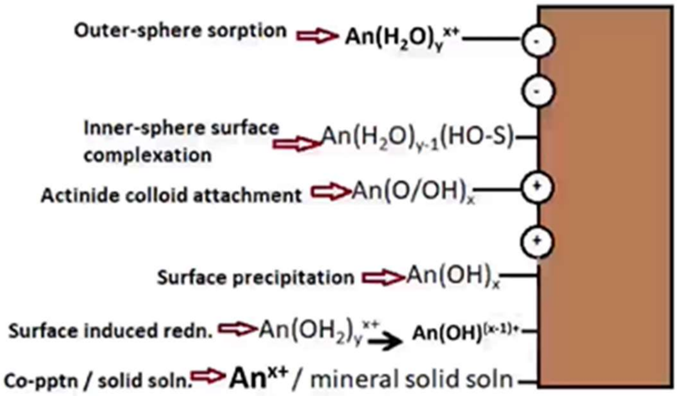
Possible interaction/absorption mechanism
-ion exchange (with interlayer cation in clays)
- Surface complexation (with surface hydroxy groups)

Nature of complex
Inner sphere → partial or no hydration sphere
Outer sphere →
with hydration sphere



Now the mechanism, and the nature of the complex formation as I have already mentioned this is two types of interactions one is ion exchange where the interlayer cation in the clays is getting replaced by the cations, the actinides, and there can be surface complexation with the surface hydroxyl group. So in this case it is binding with the hydroxyl groups present at the mineral surface, and the nature of the complex can be either the inner sphere or the outer sphere. In the case of the inner sphere, there will be either partial or no hydration sphere of this metal ion when it is forming a complex. For example, we have shown here some complex bigger ones in the metal ion, and it is having some water molecules are present.

Now this will be moving when it is going to bind with this clay mineral in that case these water molecules which are there around the metal ion those water molecules are to be removed, and then it will form a complex. In the case of the outer sphere complexation the water molecules need not be removed, and there can be interaction between the water molecule which is binding to the metal ion with that of the clay mineral surface. That is how it is forming an outer sphere complex. In this case, one will very soon the inner sphere complex where all the water molecules are removed from the inner coordination sphere of the metal ion, and that is how it forms a complex with the clay mineral.



In the inner sphere complex, the hydrated metal ions sheds its primary hydration sphere and attach to the mineral surface by largely covalent bond, whereas in outer sphere complexation, the metal ions retains its primary hydration sphere and approach electrostatically to a critical distance .

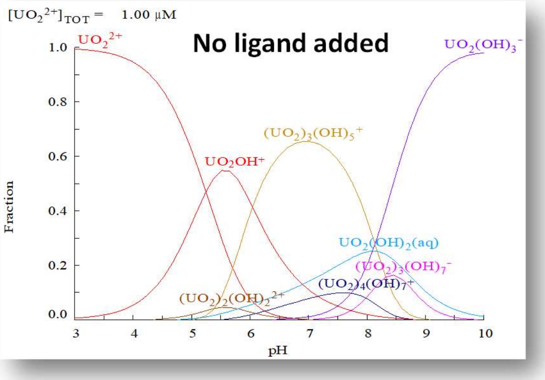
Spectroscopic techniques to identify nature of surface complex

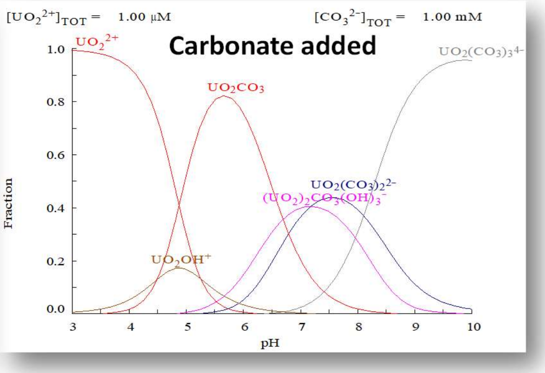
-EXAFS

-TRLFS and others such as Raman, FTIR etc…

If one wants to have the final details of the mechanism then the following can be considered. Now we also have outer sphere surface and inner sphere surface complexations with some of the examples I have shown here. In the case of the outer sphere substance, we have an activated complex of the actinide. Actinide is symbolized as An x plus, and there are a y number of water molecules forming a hydrated or activated complex of the actinide ion. Now this entire thing is coming this entire species is coming very close to the surface, and then it is forming outer sphere sorption. So that is how it interacts with the negatively charged part, and then it binds at the surface, and also there can be inner-sphere surface complexation. In this case, you have this actinide H_2O y the same species as whatever I have mentioned here, and in this case, the same species is now interacting with the surface species which is which is best shown here. Along with that, it is forming some bonding that is how it is the inner sphere surface complexation that can actinide colloid attachment. In this case, you have this colloid means this actinide is binding with the colloids where the colloid can be either intrinsic colloid or pseudo colloid. That can be surface precipitation in this case this actinide ion is interacting with hydroxide, and it is forming a precipitate as you know this hydrolysis it can form species like OH_x species will be formed, and this will form a precipitate, and it will be lying on the surface. There can be surface-induced redox reaction also where this oxidation state can change from X plus to X minus once the reduction is taking place., and there also can be co-precipitation or solid solution formation where you have this actinide ion which interacts with the mineral surface, and it is forming an actinide mineral co-precipitation of the solid solution formation. So these are the different types of interactions that the actinides are forming with the clay mineral at the mineral surface as I have already mentioned it can form sorption, it can form surface complexation, it can have precipitation, it can have co-precipitation, but there can be also a reduction in the surface. Now this can be monitored by spectroscopy techniques, those are the EXAFS or the TRLFS, and also other techniques such as Raman as well as Fourier transform infra-red spectroscopy.

EXAMPLE: % Uptake of U(VI) by goethite and kaolinite.





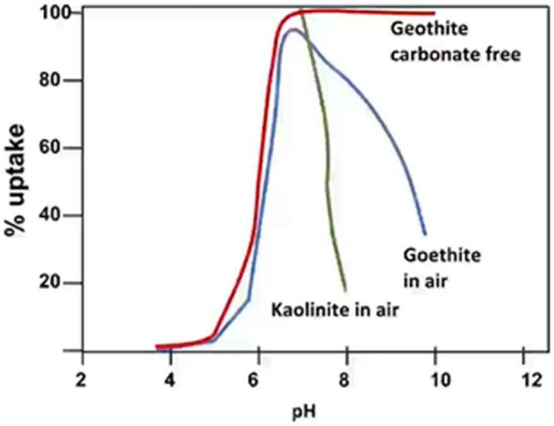
Before going to results, let us look at the speciation of U(VI) in aquatic media. U(VI) forms only +ve species up to pH ~7.3 in absence of any ligand whereas the formation of –ve uranylcarbonato species is preferred at pH ~7 in presence of CO_3^{2-}.

Now we'll take some examples, UO_2^{2+} uptake we would like to study by goethite and kaolinite. So in this case what we do is? first, we should try to understand the speciation diagram of that of the uranyl ion, now as I have already mentioned with the actinide chemistry course this uranyl ion also forms very strong complexes with carbonate as well as oxygen with the hydroxides. So in the case where you do not have any carbonate present in the system, you have the species uranyl ion at the very low pH values, which actually goes on decreasing, and as you form the monohydroxo species, and subsequently you have the dihydroxo species also, and like that you will have different polymeric species also are formed. This is how the speciation of uranyl ion with increasing pH values shows. But if you have the carbonate present in the aquatic system, then you have these carbonate complexes formed so at the low pH value you have the uranyl species as already mentioned, and you also have the carbonate species formed at around pH 5.5 or so. So you have this uranyl carbonate species which at a higher concentration of the OH^- at higher pH values you get the uranyl carbonate species which has more number of carbonates attached or you also can have the polymeric in this case you have the dimeric species where you have the hydroxo as well as carbonate complexes are formed with the two moieties of uranyl ion. So now let us see whether we have the studies carried out at different pH values containing carbonate as well as without the carbonate.

EXAMPLE: % Uptake of U(VI) by goethite and kaolinite.

At pH ~7: Both Goethite and kaolinite have +ve charge before pH 7 and –ve charge after pH 7.

Let use see the results for Goethite_CO$_2$ free (red line). Since both surface charge and the uranyl species are +ve at pH<3, there is no sorption, as we move to higher pH surface become partially –ve and we see increase in the uranyl sorption, after pH 7 the surface is fully –ve and uranyl species in +ve so ~100% uptake of U(VI). Whereas in the other two cases , Goethite and kaolinite in air, after pH 7, surface is still –ve but uranyl forms –ve carbonato species, hence there is repulsion between the two and uranyl uptake decreases.



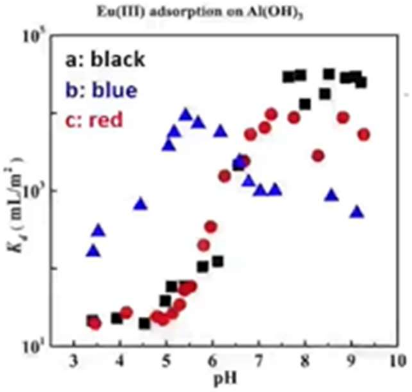
Now in the example, we come here for this uranyl ion uptake by goethite as well as kaolinite. At pH 7 we have both goethite and kaolinite have positive charge which is determined from their PZC value. So before pH 7, and negative charge can be after pH 7.

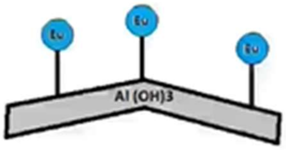
So now we will see mark here at the pH 7 is the value we mark here. We will see before pH 7, and after pH 7. Now carbonate-free goethite if you take that is the red line which are the experimental values. If you see that there will initially there will be no sorption of uranyl ion but subsequently with increasing pH values then there will be uptake of this uranyl ion because of the hydroxy species, and it will increase, and it will go up even after pH 7 you get nearly 100 percent uptake of the uranyl ion. Now you go to a goethite where the carbon dioxide is there shown by the blue line in the figure.

In that case initially of course we have this uptake there, but beyond pH 7 because of the carbonate complexation, it is forming now the negatively charged species so it starts dropping. it is not forming a complex in that case because after the PZC values there will be repulsive interactions. So it is not forming any complex. Now if you have the kaolinite in the air that case also similar behavior is observed goethite initially you have uptake starting from a pH 4 value, and it goes up to pH 7, and then there is a relatively more steep decrease in the uptake of uranyl that means uranyl is coming out of kaolinite phase.

Effect of Humic Acid (HA) onto sorption of trivalent lanthanides

The sorption of Eu(III) on three systems **a)** $Al(OH)_3$ suspension, **b)** $Al(OH)_3$ suspension with dissolved HA, **c)** suspension of $Al(OH)_3$-HA hybrid

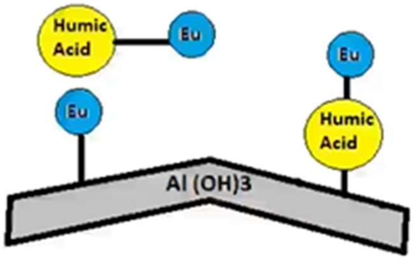


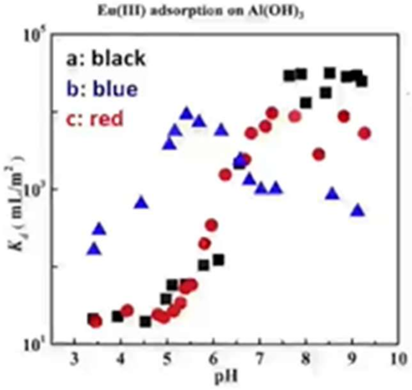


System (a): A typical adsorption profile of polyvalent metal cation and could be interpreted by surface complexation reactions between the species of Eu(III) in aqueous phase and the hydroxyl groups on surfaces of the adsorbent.

So now what we see the this is a very simplistic case in this case we had only carbonate present but in actual conditions groundwater conditions you have the humic acid also present in the aquatic system that is the humic acid will be present, and it will form complexes with the trivalent lanthanides or actinide ions here. The convenience we have taken the trivalent lanthanides which are bearings more or less similar way as that of the trivalent actinides so we have taken the europium as the case study, and we are trying to see how it is sorption is there onto the alumina surface or whatever is aluminum hydroxide surface how this uptake on this europium 3 ion is there.

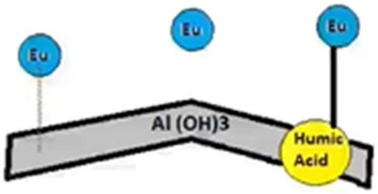
So we have three case studies number one is just the aluminum hydroxide suspension we have, and we try to study the europium sorption on to that, and for case b we have the aluminum hydroxide suspension with the dissolved humic acid, and case c where you have the suspension of aluminum hydroxide, and humic acid hybrid. So both humic acid in the suspension, as well as aluminum hydroxide, are also in there in the suspension case of c. Now we come to the first case where you have only aluminum hydroxide suspension as shown in this figure this europium 3 will be forming a complex with aluminum hydroxide at the pH value which is greater than the PZC value. Now these are the black points that are different in this case a. You see here that initially this uptake is not there or the sorption is not there but beyond pH 5 there is a slow increase in this uptake, and then you find this some sort of a saturation is reaching beyond around pH 7.5 or so it is because of the complexation of europium 3 ion with the deprotonated aluminum hydroxide which is there beyond pH 7.5. So this is what is our case a.

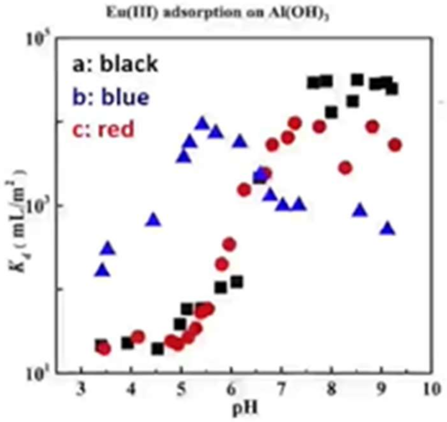




System (b): The enhanced adsorption at low pH could be interpreted by HA adsorption which modified electrostatic property of the adsorbent and favours Eu(III) adsorption because additional sites for Eu(III) were provided by adsorbed HA molecules. At high pH, HA adsorption on surfaces is not there but favoured its complexation with Eu(III) in aqueous phase thereby decreasing its sorption onto the $Al(OH)_3$ surface.

Now coming to case b here we have the humic acid in the solution phase as shown in this case of the figure you have the humic acid also in the solution phase that is our now it is forming a complex it can form a complex in the two ways first europium humic acids complex is formed, and that whole complex is present in the solution phase then europium without forming a complex with the humic acid the chance is very very less but some fraction of the europium 3 is not forming a complex with the humic acid, and that particular fraction of the europium 3 plus ion is binding to the aluminum hydroxide surface. The third case is that europium 3 is forming a complex with the humic acid, and the humic acid is binding to the aluminum hydroxide. So in this case in the last two cases that is the europium 3 which is binding to aluminum hydroxide or europium 3 humic acid complex which is binding to the aluminum hydroxide in this case europium 3 is getting immobilized on the alumina surface on the other hand the europium 3 humic acid surface it is actually mobile it is present in the solution phase, and it is mobile.

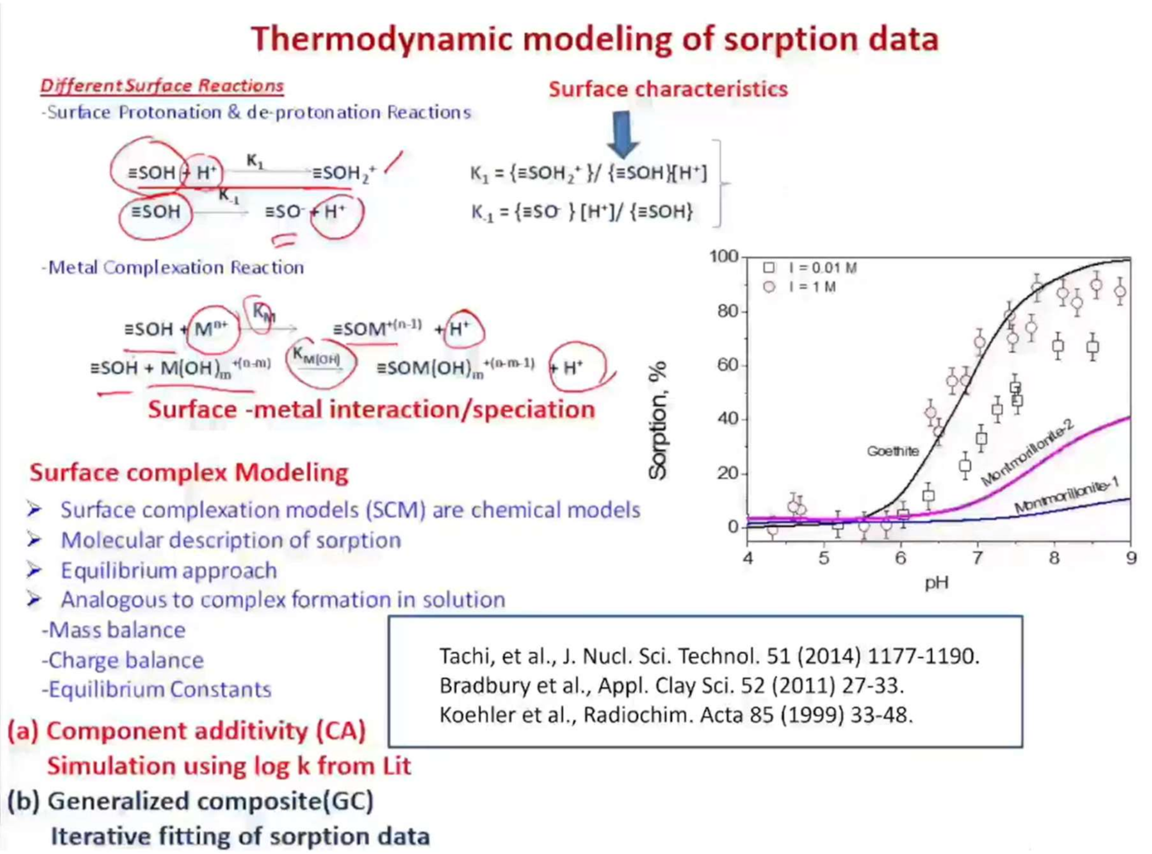




System (c): It is interesting that the adsorption of Eu(III) on $Al(OH)_3$ in the presence of fixed HA was quite different from that in the presence of dissolved HA of the same amount. The adsorption edges of Eu(III) in the presence of fixed HA were coincided with those in the absence of HA (Fig. (a), (b) and (c)). The "missing" effect of fixed HA must relate to the coordination state of its functional groups.

The fixed HA in the hybrid samples did not introduce enough new adsorption sites to the adsorbents. So, fixed HA did not increase Eu(III) adsorption at low pH and did not decrease Eu(III) adsorption either. As a result, the adsorption edges in the presence of fixed HA at two different amounts were on the same line as that in the absence of HA.

Now in the case of case C, we have this aluminum, and humic acid both are fixed which means the humic acid is now interacting with the aluminum surface, and it is a part of the alumina, and in this case, europium 3 is forming a complex directly with alumina as shown here all the or it is binding to the humic acid which is in turn is already fixed with the alumina surface. This case is represented by the profile given by the red balls as the data points.



Thermodynamic modeling of sorption data

Different Surface Reactions

-Surface Protonation & de-protonation Reactions

$\equiv SOH + H^+ \xrightarrow{K_1} \equiv SOH_2^+$

$\equiv SOH \xrightarrow{K_{-1}} \equiv SO^- + H^+$

Surface characteristics

$K_1 = \{\equiv SOH_2^+\}/\{\equiv SOH\}[H^+]$

$K_{-1} = \{\equiv SO^-\}[H^+]/\{\equiv SOH\}$

-Metal Complexation Reaction

$\equiv SOH + M^{n+} \xrightarrow{K_M} \equiv SOM^{+(n-1)} + H^+$

$\equiv SOH + M(OH)_m^{+(n-m)} \xrightarrow{K_{M(OH)}} \equiv SOM(OH)_m^{+(n-m-1)} + H^+$

Surface -metal interaction/speciation

Surface complex Modeling

- Surface complexation models (SCM) are chemical models
- Molecular description of sorption
- Equilibrium approach
- Analogous to complex formation in solution

-Mass balance
-Charge balance
-Equilibrium Constants

(a) Component additivity (CA)
Simulation using log k from Lit

(b) Generalized composite(GC)
Iterative fitting of sorption data

Tachi, et al., J. Nucl. Sci. Technol. 51 (2014) 1177-1190.
Bradbury et al., Appl. Clay Sci. 52 (2011) 27-33.
Koehler et al., Radiochim. Acta 85 (1999) 33-48.

Now we also come to the thermodynamic modeling of the data that I was mentioning it is something called surface complexation modeling. So here we have the different surface reactions. For simplicity, surface hydroxides are represented as SOH. So in the case of the silicates we have this type of functional group is there at the surface of the siloxyl groups which have triple bond SOH. Now this can take up a proton, and give this type of group where it forms a cationic surface site or it can also release a proton, giving an anionic surface site. That means the silica is behaving either way it can have a cationic site also it can have an anionic site, and these metal complexation reactions can be either with the cationic site also it can use the anionic sites depending on the nature of the complex the metal ion has formed. The complexation reaction also can be directly binding to the SOH functional group which is present in the silica surface where you have this Mn plus metal ion which is binding to the SOH again where this sort of a replacement reaction this hydrogen ion is coming out of the silica surface, and the similar way you also can have the hydroxy complex of the hydrolyzed species also interacting with the SOH surface, and there also you have one hydrogen ion is coming out.

So now this is how the surface complexation is taking place in the silica surface. Now when we have different types of clay minerals present in the aquatic system they will form similar types of complexes, and the surface complexation model, or SCM, is actually a chemical model but it takes into account this complexation which takes part in the metal ion or this case the actinide ion with different clay minerals. It takes care of this molecular description of the sorption. It also has an equilibrium approach, and it is analogous to the complex formation in the solution but it has to take care of the mass balance, charge balance, and then the equilibrium constants. So how to go about it? We have the equilibrium constants, the K values as mentioned in the above reaction in the metal ion is Km, or the KmOH values are already reported for a particular clay mineral or a particular metal ion in the literature.

So we can try to have our experiments done, and after getting the experimental data we can try to fit into the different types of complexation the clay minerals, and then from that we can get an idea what is the mechanism of this complex formation or the substance of the clay mineral. I have given one case study here in the right-hand side figure where the neptunium sorption and two different clay minerals have been done. In this case, we have taken bentonite clay, and this uptake has been seen at two different ionic strength conditions that are 0.01 molar as well as 1 molar condition given by the black, and the red data points., and this modeling has been reported in the literature.

This blue line is that of the montmorillonite which has been reported by Tachi et al., and this purple one is again the uptake value of neptunium which you can calculate from the equilibrium constants which is reported by Bradbury, and Bains. This is for montmorillonite and this black line which is given here is reported by Koehler et al., and this is for goethite. Now goethite plays a more important role in case of the bentonite clay whatever has been taken in this particular study.

, and as you can see in this fitting curve whatever is obtained considering the goethite which matches very well with the experimental data points suggesting that goethite is probably playing a more important role in the case of the option of this neptunium ion in this bentonite clay. This is how the surface complexation model, usually this is helping., two approaches in this surface complexation model is the component additivity or the CA model which I have already discussed where you have the different type of clay mineral, and you take the log K value from the literature, and then you try to do it, give the weightage to those fraction of the clay mineral, and try to generate, model the data, and match with the experimental data., and the second approach is the generalized composite or the GC where you have the sorption data, and you keep on doing the iterative fitting, and that is how you can find out what is the composition, what are the mechanism of the absorption of the actinides onto the clay mineral.

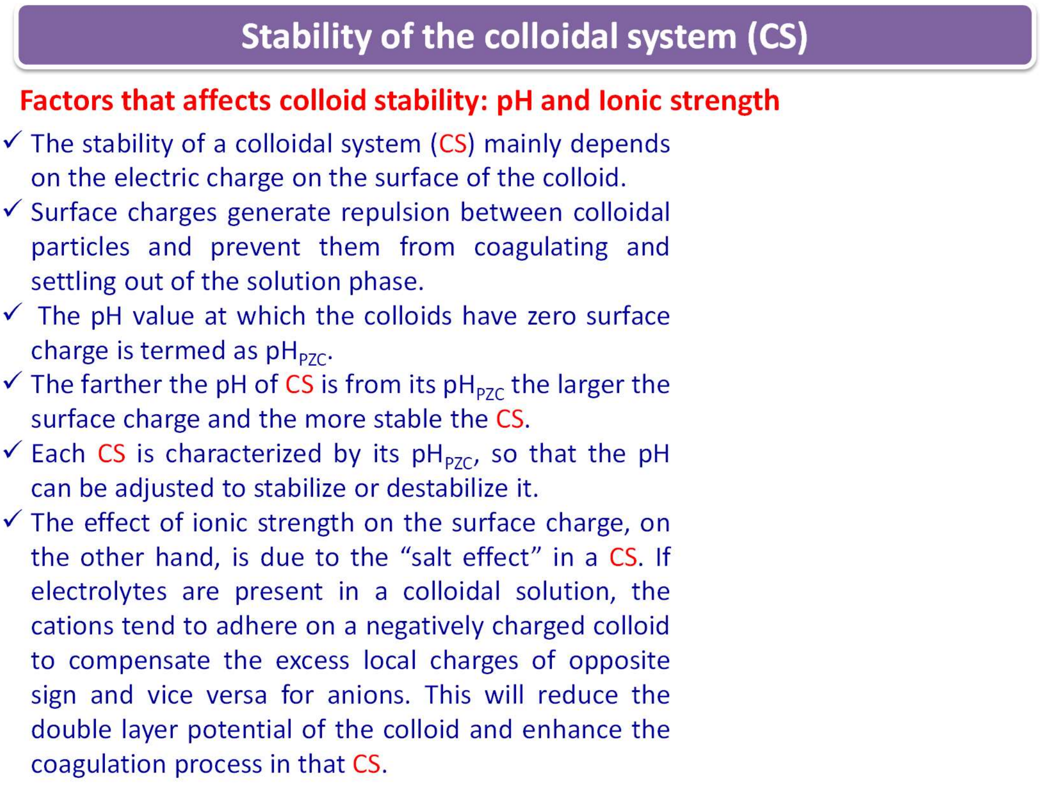
Colloidal transport of actinides

Two types of actinide colloids have been identified in groundwater

1. Intrinsic or real colloids, as those composed primarily of an actinide and formed by condensation of actinide molecules or ions by a hydrolytic or precipitation process. The chemical properties of intrinsic colloids are expected to be similar to their original compounds in macroamounts. Intrinsic colloids are also called “real”, “pure”, “eigen”, “primary”, and “true” colloids. intrinsic colloids are mostly generated by the products of actinide hydrolysis through oxo and/or hydroxyl bridge formation;.

2. Pseudocolloids, are the products of actinide elements (colloids or ions) adsorbed onto groundwater colloids due to their affinity to these colloids or hydrophobic properties of the dispersing medium. The chemical properties of pseudocolloids are expected to be similar to the groundwater colloids to which they are attached. Other terms such as “associative” or “fremd may be used for pseudocolloids as well.

Now the colloidal transport of the actinides, two types of actinite colloids are identified in the groundwater. As already we know actinides when you go to very high pH values undergo hydrolysis, and they also form polymers under the existing conditions. So in those cases, you get more than one number of actinite ions that come together, and they form colloids. That is called the intrinsic colloid or the real colloid, some people call it also eigen or primary colloid, even true colloid. So these are basically the actinite hydrolysis products that are through the Oxo or hydroxy bridge formation. There is another one called a pseudo colloid, where the colloid is formed by another metal ion, and in that case the actinite is absorbed onto the colloids formed by the second metal ion, and that can be some other metal ion like the transition element metal ion which is forming a colloid under the groundwater condition or the experimental conditions, and there the actinide is getting sorbed onto the colloid of the other metal ion, and this is called an associative or pseudo colloid.



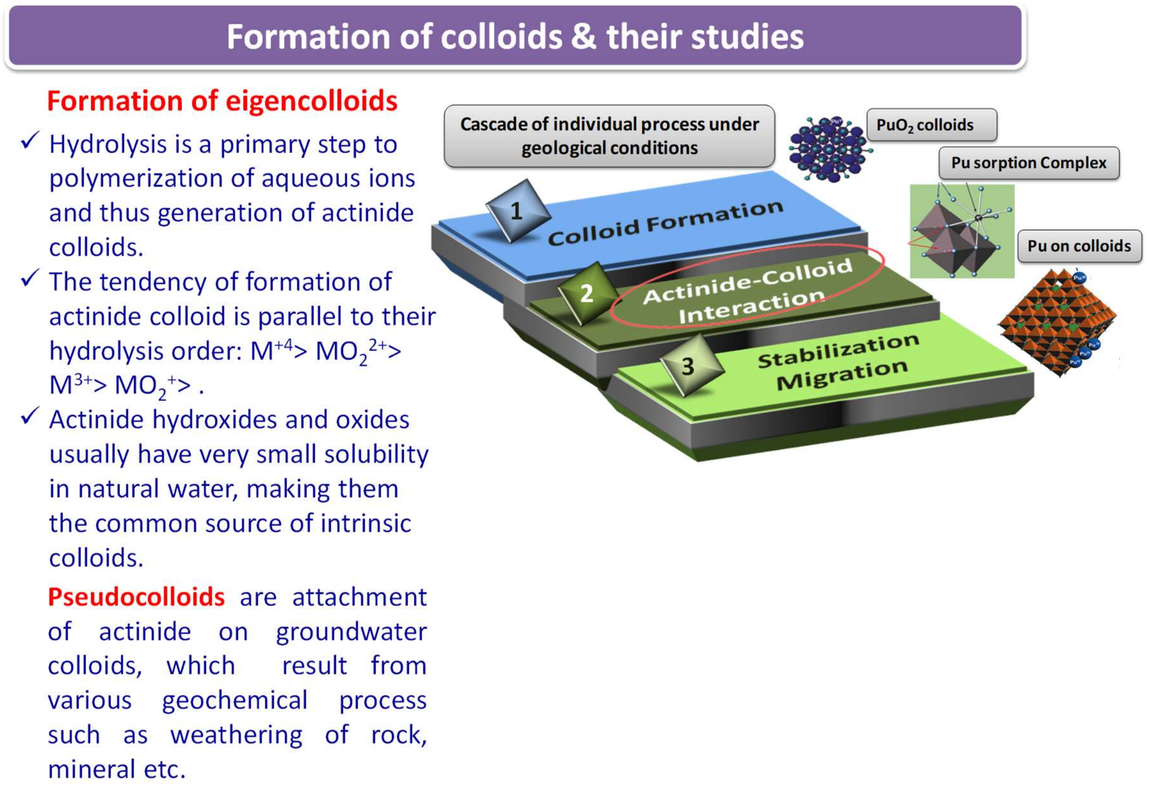
Stability of the colloidal system (CS)

Factors that affects colloid stability: pH and Ionic strength

- ✓ The stability of a colloidal system (CS) mainly depends on the electric charge on the surface of the colloid.
- ✓ Surface charges generate repulsion between colloidal particles and prevent them from coagulating and settling out of the solution phase.
- ✓ The pH value at which the colloids have zero surface charge is termed as pH_{PZC}.
- ✓ The farther the pH of CS is from its pH_{PZC} the larger the surface charge and the more stable the CS.
- ✓ Each CS is characterized by its pH_{PZC}, so that the pH can be adjusted to stabilize or destabilize it.
- ✓ The effect of ionic strength on the surface charge, on the other hand, is due to the “salt effect” in a CS. If electrolytes are present in a colloidal solution, the cations tend to adhere on a negatively charged colloid to compensate the excess local charges of opposite sign and vice versa for anions. This will reduce the double layer potential of the colloid and enhance the coagulation process in that CS.

Now what are the factors that determine the stability of the colloidal system? The factors of this colloidal system mainly depend on the electric charge on the surface of the colloid. Naturally, depending on the charge, if the charge is too much the colloid will break., and because of the repulsion between the colloidal particles, it will prevent them from coagulating and settling out of the solution phase. Also, your factor which determines the pH value at which the colloids have the zero surface charge, that is the pHpzc.

Then the farther the pH of the colloidal system from the PZC the larger the surface charge, and the more stable the colloidal system., and each colloidal system is characterized by its pH pzc so that the pH can be adjusted to stabilize or destabilize it. Also, the important factor is the salt effect or the ionic strength on the surface charge. So depending on that if the electrolyte is present in a colloidal solution the cations tend to adhere to a negative charge colloid to compensate excess local charge of the opposite sign, and vice versa for the anions. This will reduce the double-layer potential of the colloid, and enhance the coagulation process in that colloidal system.



Formation of colloids & their studies

Formation of eigencolloids

- ✓ Hydrolysis is a primary step to polymerization of aqueous ions and thus generation of actinide colloids.
- ✓ The tendency of formation of actinide colloid is parallel to their hydrolysis order: $M^{+4} > MO_2^{2+} > M^{3+} > MO_2^{+} >$.
- ✓ Actinide hydroxides and oxides usually have very small solubility in natural water, making them the common source of intrinsic colloids.

Pseudocolloids are attachment of actinide on groundwater colloids, which result from various geochemical process such as weathering of rock, mineral etc.

Now formation of the colloids, and their studies, they already mentioned this formation of the eigen colloids. This is the eigen colloid, the true colloid, or the intrinsic colloid. In this case, hydrolysis is the primary step which is leading to the polymerization, and thus generation of the actinide colloids., and the tendency of this formation of the actinide colloid of course depends on the charge, the ionic potential of the actinides that is the tetravalent. actinide ion has a higher chance of forming an intrinsic colloid, and also the actinide hydroxide and oxides usually have a very small solubility to the natural water making them the common source of the intrinsic colloid. In the case of the pseudo colloids, their attachment of the actinides on the groundwater colloids which are already present in the groundwater system results from various geochemical processes, and it can also from the weathering of the rocks, and minerals you have some colloids that are present in the groundwater system which will be basically the platform where these actinides will be getting sorbed, and for subsequently they will be migrating in the groundwater system.

Formation of colloidal & their studies

Methods for the Study of Actinide Colloids: The properties that are of interest from the environmental point of view are colloidal size distribution, charge on colloids (or PZC), actinide uptake by colloids etc.

Centrifigation, Ultracentrifugation, Filtration and Ultrafiltration are used to separate the colloids from their dispersing media and to obtain the relative particle size distribution of colloids.

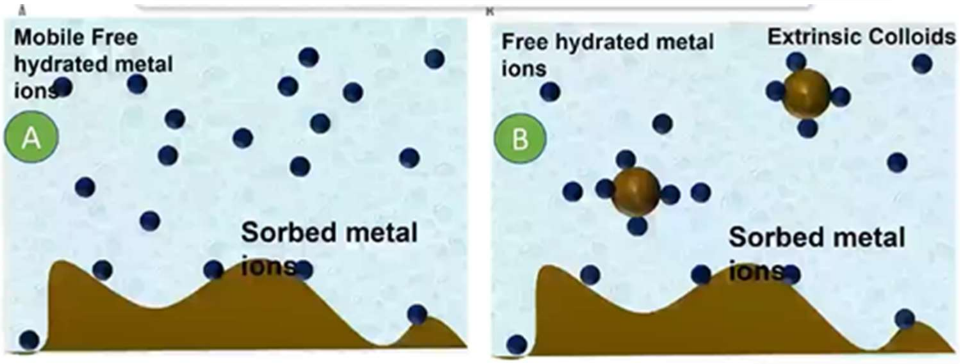
Electrophoresis or Zeta potential measurements *(to determine* colloidal charge)*,* **Spectroscoopy** *(*provides information at micro or molecular levels for characterization of colloids*),* **Ion Exchange and Adsorption** (used to study the adsorption behavior of actinide colloids on the exchanger).

Particle size of colloids were determined using autocorrelation photon spectroscopy which is a laser based light-scattering techniques (DLS, dynamic light scattering). Scanning electron microscopy, energy dispersive X-ray spectroscopy and transmission electron microscopy can be used to obtain insight into **the mechanisms of formation and sorption behavior of colloids.**

Now the formation of the colloids, and their studies, the methods for the study of actinide colloids, the properties that are of interest from the environmental point of view, and the colloid size distribution can be done by studies like our DLS or so. Also, this charge on the colloid can be found by the PZC, and the actinide uptake by the colloids can be done by the normal uptake studies. By ultracentrifugation, filtration, or ultrafiltration this can be done to separate the colloids from the dispersed media.

Electrophoresis or zeta potential can be done to determine the colloidal charge and adsorption studies can be done in a normal way by adding a radiotracer into the solution phase and then to find out how much the radiotracer is going onto the colloids or the exchanger or in this case the clay mineral, and that is how the adsorption studies can be found out. The particle size of colloids is determined using DLS or the dynamic light scattering method. Also scanning electron microscopy, energy dispersive x-ray spectroscopy, or transmission electron microscopy.

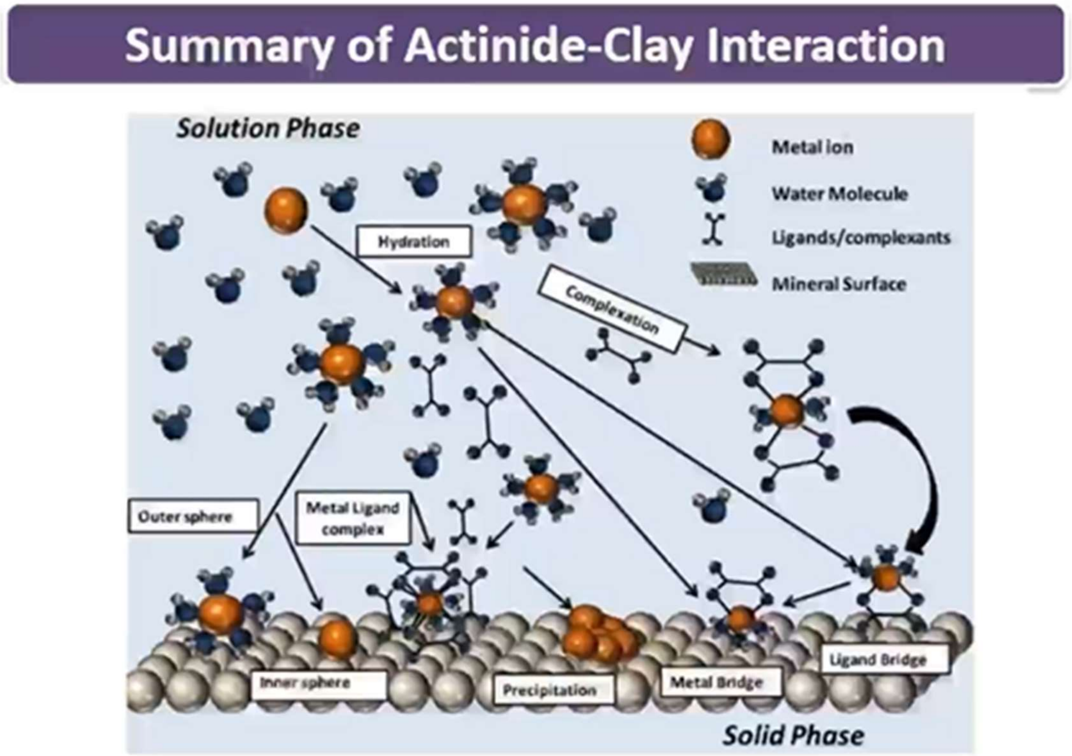
Colloids and the Transport of Radionuclides



A: Contaminant transport in a two-phase system.
Contaminants dissolved in water are mobile and contaminants sorbed to the host rock are immobile.

B: Contaminant transport in a three-phase system.
Contaminants that are sorbed to the host rock can also attach to the mobile colloid and migrate with groundwater.

These are the techniques that can be used to get the size., and as mentioned here you can find that these sorb contaminants, this is the phase is the water phase is there, and this is the sediment phase which is shown here. You see that this rock or the sediment phase is shown here. Now these are the contaminants, the dissolved contaminants which are the actinides. So, they are normally they are mobile on the water surface, but they can get sorbed also onto this rock mineral surface, rock surface which is an immobile surface. This is how they can get immobilized onto the sediment or the rock. They can also form intrinsic colloids or they can form a complex with the pseudo colloid, and then they will be in the mobile in the water surface, and they can mobile get moving in this way, and that is how this actinide can get transported. So, this is how a two-phase method is shown, and this is the contaminant transport in a three-phase system where the main transportation is done either by intrinsic colloid formation or absorption onto a pseudo colloid.



Summary of Actinide-Clay Interaction

Now to summarize, actinide clay interaction you have this solid like here you have iron oxide or iron hydroxide which is present here. Taken for example, it is true for any other oxide, rock, or clay materials, which can have the radionuclide which is having the water molecules here which is coming here, and it is binding to the iron oxide. This is called sorption, and desorption can be there where you have the radionuclide that is forming a complex. It can have a complexation with the ligand which is how it forms a complex that is coming out of the sorbed clay mineral. These are desorption that is determined by the pH value, and the complexation constants.

Once it is forming it can also have the dissolution then it will come again to the aquatic medium. There can be co-precipitation, and there can be dissolution which is how this complex also in the presence of a ligand, there can be dissolution from the clay mineral which is how this becomes mobile, and finally, it comes to the colloidal surface. This is a colloidal surface is given. So this is basically it is a pseudo colloid where you have the radionuclide forming 1, 2, 3, and 4 of them coming together, and forming a complex block of species that can facilitate the transport of actinides. This is the pseudo colloid where you have another metal, and it is forming the colloid, and the radionuclide is binding with this, and this is how it is embedded onto the pseudo colloid.

So this is how the colloidal system is migrating in the groundwater system which is the reason for this actinide migration behavior in the environment. So we have completed the actinide chemistry, and the actinides in the environment. The next two lectures will be on the transactinide. Thank you.