

Arsenic adsorption mechanism on clay minerals and its dependence on temperature

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Abstract—In the present study, the As(V) removal efficiency of different clay minerals was investigated as a function of solution pH, time, As(V) concentration, and temperature. Arsenic mobility was also investigated by determining the As(V) released from the loaded samples by leaching with various aqueous solutions. The kinetics of adsorption was observed to be fast and reached equilibrium within 3 h. As(V) adsorption on studied clays was pH dependent and maximum adsorption was achieved at pH 5.0. The maximum adsorption capacity was calculated by fitting the Langmuir equation to the adsorption isotherms and found to be 0.86, 0.64, and 0.52 mg As(V)/g of kaolinite, montmorillonite, and illite, respectively. The negative effect of temperature on As(V) adsorption showed the interactions to be exothermic. Based on the results, it was found that among the studied clay minerals, kaolinite was the best As(V) adsorbent and montmorillonite had strong retention capacity. The electrokinetic behavior of kaolinite and montmorillonite was modified in the presence of As(V), indicating that adsorption involves inner sphere surface complexation and strong specific ion adsorption.

Key words: Adsorption, Leaching, Arsenic, Clay, Langmuir Isotherm, Isoelectric Point

INTRODUCTION

The chronic toxic effects on human health of excessive intake of arsenic have been extensively studied, and well documented in the literature [1]. It is usually accepted that an arsenic concentration in the range 0.01-0.05 mg/L is the maximum human tolerance level, and different countries have established different standards for the same [2]. Many methods have been proposed and developed for arsenic removal from water, but adsorption is the widely used method for arsenic mitigation. Different adsorbents have been tried for arsenic removal [2], and there is a wide variation in their effectiveness, as well as cost. The latter becomes an important factor in determining the treatment technique in several developing countries like Bangladesh and India. The use of natural materials offers an advantage of abundance and cost. In addition, such materials are ideal for one-time use requiring no regeneration. This is an important convenience, especially in areas which are remote, have no regeneration facility, or for communities where drinking water is usually handled by women and children who are not trained enough to handle regeneration. Among the natural materials, use of minerals and ores containing oxides and hydroxides has been successfully used for arsenic mitigation [3,4].

Among the advantages of clay are its excellent capacity to exchange cations and anions, which stem from their high surface area and their tendency to adsorb water in the interlayer sites [5]. Also, these are exchanged with some exchangeable ions present on the clay surface. Structurally, clay is made up of common layer of silicates with different combinations of two simple structural units,

namely, silicon tetrahedron and aluminum or magnesium octahedron. In clay minerals some of the common exchangeable cations are Ca^{2+} , Mg^{2+} , Fe^{2+} , K^+ and Na^+ , while the common anions are SO_4^{2-} , Cl^- , PO_4^{3-} and NO_3^- . Generally, the surface of clay is negatively charged. Therefore, the information on its capacity to adsorb different cations from a variety of systems is widely available [6]. Unfortunately, little information is available about arsenic adsorption on clay; since, octahedrally coordinated aluminum is a major constituent of clay, strong surface complexes with arsenic are also expected [7]. Arsenic can also be strongly adsorbed to electropositive hydroxides such as Fe, Al and Ca which often coat clay particles [8]. Fewer documents are available about the effect of temperature on arsenic adsorption, since temperature might play an important role in controlling the distribution of arsenic in the environment. The use of clay for removing arsenic offers an opportunity to use a material commonly available in Eastern India and Bangladesh, where arsenic occurs in ground water.

Limited information on adsorption of arsenic using different clays suggests that the pH influences the distribution of arsenic species present in solution and activates the anion adsorption sites on clay minerals, thus affecting adsorption. Griffin and Shimp [9] in a study of As(V) adsorption by kaolinite and montmorillonite found maximum adsorption of As(V) occurs at pH 5.0. The mechanism of adsorption has been ascribed to inner sphere complexation (specific adsorption). According to another study, at low pH, hydroxyl groups exposed on the periphery of metal oxides, clay minerals and amorphous silicate minerals are protonated and acquire a positive charge. These protonated (activated) sites are then available for the interaction and adsorption of the arsenical anions present in solution [10].

The present work examines some of the Indian clays for their possible use as adsorbing agents for arsenic. It is within this context

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that adsorption and mobility of As(V), using three different clays, were investigated. Arsenic mobility was investigated in detail by determining the As(V) released from the loaded samples by leaching with various aqueous solutions. The effect of temperature on adsorption was studied by running adsorption experiments at 40, 55 and 70 °C. To better understand the adsorption mechanism, results of these runs were also used to determine different thermodynamic constants.

MATERIALS AND METHODS

1. Clay Sample Characterization

In this study three different clays, i.e., Kaolinite, Montmorillonite and Illite, collected from the eastern part of India were used. The clay samples were ground and sieved, and the fraction containing $-75\ \mu\text{m}$ was used in this study without any further pre-treatment. The surface area of the sample was determined by BET method using five-point surface N_2 (Micromeritics, Model- TRISTAR, V 5.02, USA). Silica content was determined by weight loss after treatment with hydrofluoric acid. Total iron was determined by titration with potassium permanganate. Density was measured by a PRECISA analytical balance fitted with density measurement kit (Model XT 202A, Switzerland). Other metal analysis was carried out by ICP-AES (Jobin Yvon, JY-38) after acid digestion.

2. Adsorption Capacity

1,000 mg/L As(V) stock solution was prepared from $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$ salt, which was subsequently used to prepare experimental solutions of specified concentrations. Adsorption studies were carried out in 250 mL glass conical flasks. The solid/liquid ratio used in this study was 1 : 10 (10 g of adsorbent in 100 mL arsenic solution). Control adsorption experiments showed that: (I) maximum As(V) adsorption occurred at pH 5.0 for all the adsorbents, and (II) in presence of adsorbent, the supernatant As(V) concentrations became constant within 3 h of contact time, which was taken to mean that equilibrium had been reached within this period. So, all adsorption experiments were carried out at pH 5.0 and 3 h contact time. The pH adjustment was done by using HCl or NaOH before the addition of adsorbent. Arsenic concentration in solution varied from 10 to 200 mg/L. All experiments were carried out at room temperature (25 ± 1) °C unless otherwise mentioned. After the arsenic bearing solution of required strength and the clay samples were introduced, the flasks were capped tightly and immersed into the temperature controlled water bath and then shaken for required time at the rate of 150 ± 10 cycles/min with a mechanical shaker (Julabo-SW-20C). After the required time, the suspension was centrifuged and filtered through a $0.2\ \mu\text{m}$ membrane filter paper. The arsenic concentration in aqueous solutions was determined by using ICP-AES.

3. Leaching Test

The As(V) loaded solids were washed with deionised water, and dried at room temperature and used for leaching study. The concentration of As(V) in the solid was determined by the acid digestion of the residue followed by analyzing arsenic in the solution. For each leaching experiment, 5 g of dried As-loaded solids was added to 100 mL (solid/liquid ratio 1 : 20) of the extractant of appropriate concentration. The pH of the leaching solution was maintained at 5.0 ± 0.1 . The leaching reagents were deionised water

(DW), 0.1 M oxalate and 0.1 M citrate. The suspension was shaken for 18 h followed by filtration and arsenic analysis as described above.

4. TCLP Test

The extraction fluid consisted of a buffered acetic acid solution at pH 4.93, prepared by adding 64.3 mL of 1N NaOH and 5.7 mL of glacial acetic acid to water, and diluting to a final volume of 1 L. Other leaching procedures were same as mentioned earlier. A solid is classified as non-toxic for arsenic levels in the filtrate below 5 mg/L; otherwise, the solid is classified as toxic [11].

5. Iso-electric Point (IEP)

Electrophoretic mobility (EM) was carried out by using a zeta master instrument (Malvern with a rectangular quartz cell) at room temperature. 25 mg clay samples were washed twice with 10 mL of 1 M NaClO_4 followed by three washings with 10 mL of 10 mM NaClO_4 . 100 mL of the suspension solution (1 mM NaClO_4) was adjusted from pH 3 to 9, adding either 1.0 M HClO_4 or 1.0 M NaOH, giving a concentration of approximately 0.25 g/L. The suspension was dispersed for 10 min with an ultrasonic probe and then shaken overnight on a shaker. The pH of the final supernatant was measured before the EM measurement was made. The optical unit contained a 2 mW Helium Neon Laser. Triplicate EM was measured by using a 30 count time, 150 mV voltage and 5 mA current. Plotting the EM versus pH, the IEP corresponds to the pH value where electrophoretic mobility is zero.

RESULTS AND DISCUSSION

1. Characterization of the Clay Samples

The physico-chemical properties of the clay samples are presented in Table 1. As expected, the major constituent of all the clay samples was SiO_2 followed by Al_2O_3 . Kaolinite contained high concentration of Al_2O_3 compared to other two clays; whereas, the surface area of montmorillonite was $58\ \text{m}^2/\text{g}$, maximum among the three clay minerals.

2. Adsorption Capacity

To be considered as a good adsorbent a material is expected to combine a high arsenic adsorption capacity with a small arsenic release in further contact with aqueous phases. Initial experiments showed that the adsorption of As(V) was found to be concentration dependent for the studied clay adsorbents. So, the distribution

Table 1. Physico/chemical composition of different clay minerals

Constituents (wt%)	Illite	Kaolinite	Montmorillonite
SiO_2	53.6	43.8	49.8
Al_2O_3	15.9	36	20.0
K_2O	7.2	0.9	1.4
Na_2O	0.6	1.58	2.5
MgO	2.87	0.7	2.8
CaO	1.35	0.6	5.3
Fe_2O_3	1.7	2.5	4.8
Loss on ignition (1,100 °C)	16.8	13.9	13.4
Surface area (m^2/g)	28	33	58
Porosity (cc/g)	0.32	0.31	0.26
Density (g/cm^3)	2.29	2.61	2.47

of As(V) between the two phases can be expressed in terms of adsorption isotherm. The experimental data obtained were applied to linear forms of Langmuir (Eq. (1)) and Freundlich (Eq. (2)) isotherms.

$$C_e/q_e = 1/(bQ) + C_e/Q \quad (1)$$

where, C_e (mmol/L) is the equilibrium concentration of adsorbate in the solution, Q denotes the number of moles of solute adsorbed per unit weight of adsorbent in forming a monolayer on the adsorbent surface, b is the Langmuir constant related to binding energy.

$$\ln q_e = \ln K + 1/n \ln C_e \quad (2)$$

where, q_e is quantity of As(V) adsorbed at equilibrium (mmol/g), K is a constant which is a measure of sorption capacity and $1/n$ is a measure of adsorption density. Table 2 summarizes the results of the adsorption isotherm parameters. The results indicate that the Langmuir isotherm model (Correlation Coefficient (r^2)=0.95-0.98) can describe the isotherm better than the Freundlich isotherm model (r^2 =0.84-0.88), which is mostly applicable to non-specific adsorption on heterogeneous solid surfaces. As shown in Table 2, the Langmuir isotherm for As(V) was characterized by a strong adsorption bond energy as indicated by the constant "b", typical characteristics of a monolayer adsorption. This was further supported by a low Q value, which signifies the adsorption process to be monolayer.

Fig. 1 shows a plot of C_e/q_e versus C_e for three types of clays. From the slope of best fit, the maximum loading capacity (Q) for the clay adsorbents were determined and found to be 0.86, 0.64 and 0.52 mg As(V)/g of kaolinite, montmorillonite, and illite, respectively. This shows that kaolinite is the better adsorbent compared to other two clays, as can be explained by the chemical composition of the different clay materials. The mixed composition of iron and aluminum is more in kaolinite compared to the other two clays. This

Table 2. Langmuir and Freundlich isotherm constants for the clay adsorbents (adsorbent=40 g/L, pH=5.0, contact time=3 h)

Adsorbent	Langmuir constants			Freundlich constants		
	Q	b	r^2	n	K	r^2
Illite	0.007	25.66	0.97	1.78	0.015	0.87
Kaolinite	0.012	31.22	0.98	1.49	0.037	0.88
Montmorillonite	0.009	18	0.95	1.71	0.045	0.84

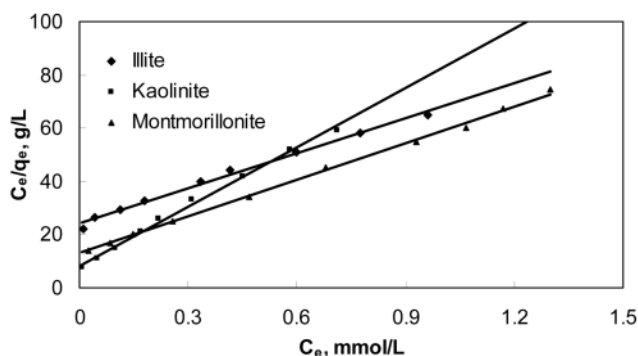


Fig. 1. Langmuir plot for As(V) adsorption on different clays (adsorbent 40 g/L, pH=5.0).

is supposed to be the contributing factor for better loading capacity of kaolinite, as it is well known that Al(III) and Fe(III) are good adsorbents of As(V). On the other hand, the role of quartz is supposed to be limited in the adsorption process, because of their weak affinity towards As(V) [12]. This behavior being confirmed in this study by experiments with clay samples treated with hot HCl to remove the iron and aluminum oxides. High surface area and porosity of kaolinite also supports the view.

3. Effect of Temperature on As(V) Adsorption

The effect of temperature on As(V) adsorption by the clay adsorbents was monitored at four temperatures of 25, 40, 55, and 70 °C (pH 5.0, adsorbent 40 g/L, time 3 h). An increase in the temperature resulted in a decrease in the amount of As(V) adsorbed for all the clay adsorbents, which showed the interactions to be exothermic. A typical example for kaolinite is presented in Fig. 2. At high temperature, the adsorbate-adsorbent complex becomes unstable; as a result, As(V) ions escape from the solid phase to the bulk solution. It is also likely that the instability of the complex may be accompanied by damage to the adsorption sites in the clays decreasing As(V) adsorption at higher temperature.

The thermodynamic adsorption parameters ΔH , ΔS and ΔG (Table 3) are computed from the plots of $\ln K_d$ versus $1/T$ (linear correlation coefficient, $R=0.97$ -0.99) by using the relation

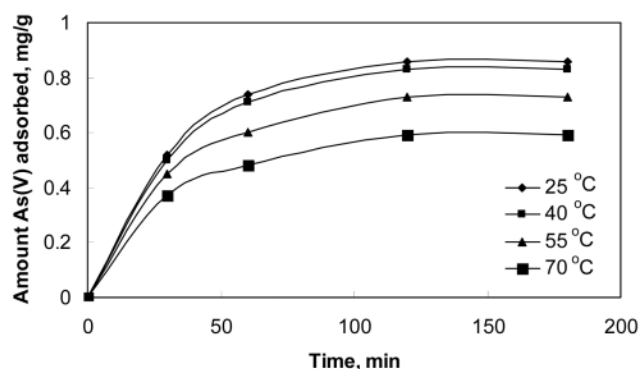


Fig. 2. Effect of temperature on the As(V) adsorption by kaolinite.

Table 3. Thermodynamic data for adsorption of As(V) on clays (adsorbent 40 g/L, pH=5.0, time=180 min)

Minerals	Temperature, °K	$-\Delta H$, kJ/mol	$-\Delta S$, kJ ⁻¹ /mol	ΔG , kJ/mole
Kaolinite	298	59.52	0.219	5.62
	313			8.90
	328			12.18
	343			15.46
Illite	298	51.24	0.177	1.65
	313			4.31
	328			6.98
	343			9.64
Montmorillonite	298	73.90	0.204	-13.16
	313			-10.11
	328			-7.05
	343			-3.99

$$\ln K_d = \Delta S/R - \Delta H/RT \quad (3)$$

where, K_d known as the distribution coefficient of the adsorbate; T the absolute temperature ($^{\circ}\text{K}$), and $R=8.314 \times 10^{-3} \text{ kJ K}^{-1}/\text{mol}$. The plot of $\ln K_d$ versus $1/T$ was linear with the slope and the intercept giving values of ΔH and ΔS . The free energy of specific adsorption ' ΔG ' was calculated from the Gibbs relation, $\Delta G = \Delta H - T\Delta S$ at constant temperature. All these relations are valid when the enthalpy change remains constant in the range of temperature considered.

The mean adsorption enthalpy, ΔH , was calculated to be -59.52 , -51.24 and -73.90 kJ/mol for kaolinite, illite, and montmorillonite, respectively. The exothermic enthalpy was highest for montmorillonite with a clear indication that although the adsorption of As(V) might be more in case of kaolinite, the As(V) ions are held more strongly by montmorillonite compared to other two clays. Spontaneity of the adsorption process of As(V) on clays is demonstrated by the increase in Gibbs free energy with increase in temperature in the present work. This is in conformity with the exothermic nature of the adsorption process as an increased supply of heat energy would lead to enhanced desorption. In the Indian sub-continent the ground water temperature remains around $\sim 40^{\circ}\text{C}$ throughout the year. So, clay can be applied to removing arsenic from water based on temperature considerations.

4. Leaching Study

The mobility of arsenic and consequent migration to the environment has received relatively little attention compared to determination of adsorption capacity and mechanism. In the present study, the mobility of As(V) loaded with different clays was tested by using different leaching reagents. Following their specific affinities discussed before, the loaded solids employed in this investigation presented arsenic contents varying from 0.52 to 0.86 mg/g . In the case of the TCLP tests pH was buffered at 4.93 with the acetate solution. For the others, pH (un-buffered) varied within 5 ± 0.1 units. Table 4 indicates the average amount of arsenic leached, in duplicate tests. The results showed that kaolinite was very active clay constituent regarding both As(V) adsorption and mobility. In two kaolinite cases

Table 4. Effect of different leaching reagents on arsenic mobility from As(V) -loaded clays

	As(V) in loaded samples (mg/g)	Leaching solutions	Leached As(V), mg/L	Leached As(V), %
Kaolinite	0.86	0.1 M Oxalate	6.6	15
	0.86	0.1 M Citrate	9.8	22.8
	0.86	TCLP	2.2	5.1
	0.86	DW	0.3	0.70
Illite	0.52	0.1 M Oxalate	4.3	16.5
	0.52	0.1 M Citrate	5.1	19.6
	0.52	TCLP	2.0	7.7
	0.52	DW	0.3	1.15
Montmorillonite	0.64	0.1 M Oxalate	4.8	15
	0.64	0.1 M Citrate	3.5	10.9
	0.64	TCLP	1.3	4.1
	0.64	DW	0.3	0.9

(6.6 mg/L in oxalate extraction and 9.8 mg/L in case of citrate extraction) the leached solution exceeded the TCLP specification of 5 mg/L As(V) . For montmorillonite loaded with As(V) the maximum arsenic leached was 15% of the total arsenic adsorbed; whereas, maximum 22.8% arsenic was leached in case of kaolinite. From this point of view, arsenic may be considered more weakly bound on kaolinite surface, in comparison to montmorillonite. This is in agreement with our earlier conclusion that As(V) ions are held more strongly by montmorillonite compared to other two clays due to its higher exothermic enthalpy. In case of DW, negligible amount of As(V) was leached into the solution. That showed the relative potential hazards of arsenic loaded materials when mismanaged in the presence of determined organic leachants. These results are in agreement with a similar study reporting arsenic mobility from natural samples [13].

5. Iso-electric Point (IEP) Study

The nature of the adsorption bond as well as the characteristics of the aqueous phase in contact with the loaded solid determine desorption of an adsorbent from a given substance, thus affecting mobility. Physical or non-specific (outer sphere) adsorption describes

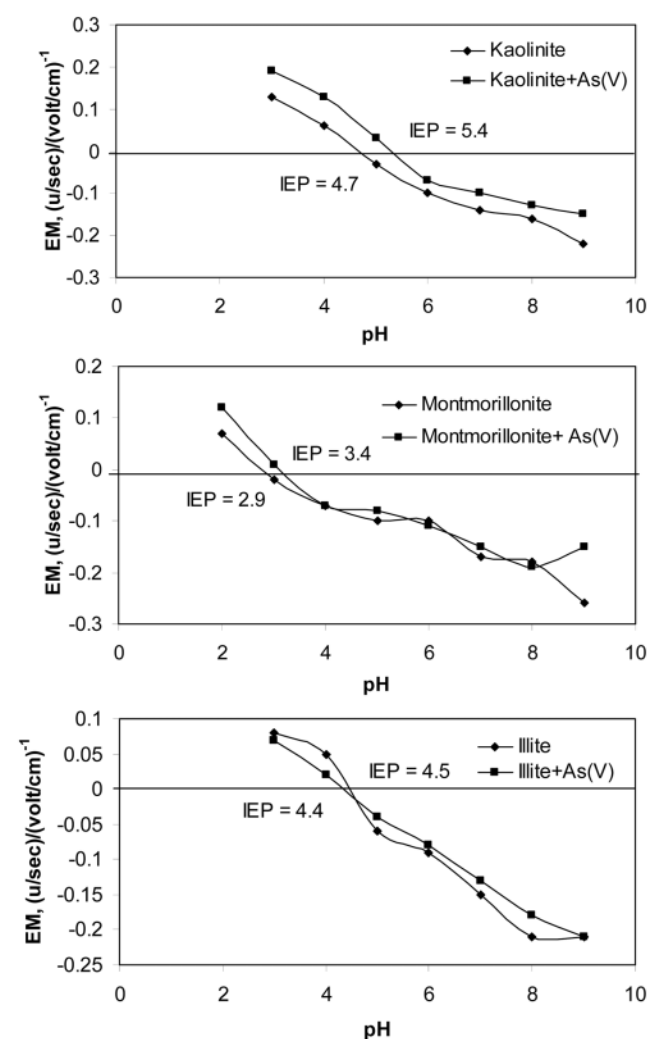


Fig. 3. Electrophoretic mobility as a function of pH, for kaolinite, montmorillonite and illite in the presence and absence of As(V) .

rapid, reversible reactions and relatively weak bonds. Specific adsorption involves bonding energies in the range of those taking place in chemical reactions and therefore accounts for stronger, less reversible adsorption processes. Specific adsorption (Inner-sphere complexation) may cause shifts in the IEP. Electrophoretic mobility (EM) measurements are useful to indirectly identify inner- and outer-sphere complexes [14]. The EM of the different arsenic-loaded and unloaded clays is shown in Fig. 3, describing the sign and the magnitude of the electrokinetic potential as a function of pH.

The IEP values for the unloaded kaolinite, montmorillonite and illite were 4.7, 2.9, and 4.4, respectively. These values were in agreement with those reported in the literature [15]. The slight difference could be due to the nature and content of impurities, origin of sample and method of pretreatment. The electrokinetic behavior of both the kaolinite and montmorillonite was modified in the presence of As(V); whereas, differences between the IEP for illite and illite loaded with As(V) was within the experimental error and therefore cannot be differentiated. For the kaolinite loaded with As(V), the IEP shifted from 4.7 to 5.4. A less significant shifting was observed for the montmorillonite loaded with As(V), with IEP shifting from 2.9 to 3.4. The shift in IEP indicated that adsorption involves inner sphere surface complexation and strong specific ion adsorption [15]. Arsenate ions were not adsorbed as simple counter-ions on the diffuse layer, as it should be if adsorption were dominated by electrostatic attraction. Some mechanisms other than the electrostatic attraction were also operative.

POTENTIAL APPLICATION OF CLAY

As a part of a study on the adsorption of As(V) on natural minerals, the authors and their colleagues have observed that several samples of iron ore and bauxite can adsorb As(V) upto 2 mg/g from solutions containing 10 mg/L As(V). However, the minerals have a problem of permeability, when the particle size is reduced, making them unsuitable for percolation adsorption in a column. This necessitates the use of a binder. Perhaps clay can be used as a binder, where its adsorption property will have an added advantage over other binders.

CONCLUSIONS

The natural clay minerals such as kaolinite, montmorillonite, and illite collected from the eastern part of India can effectively remove arsenic. The general conclusions drawn from the present study are listed below:

1. As(V) adsorption on studied clays were pH dependent and maximum adsorption was achieved at pH 5.0.
2. The maximum adsorption capacity (Q) was calculated by fitting

Langmuir equation to the adsorption isotherms and found to be 0.86, 0.64 and 0.52 mg As(V)/g of kaolinite, montmorillonite and illite, respectively.

3. An increase in adsorption temperature resulted in a decrease in the amount of As(V) adsorbed, which showed the interactions to be exothermic.

4. The results of leaching study showed that kaolinite was very active clay constituent regarding both As(V) adsorption and mobility.

5. From the electrophoretic mobility measurements the adsorption mechanism was assumed to be inner sphere surface complexation and strong specific ion adsorption.

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