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ANION INTERACTIONS WITH FRESHLY PREPARED HYDROUS IRON OXIDES[1]

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Abstract—Infrared analysis showed that the bonding habit of oxyanions with freshly precipitated hydrous ferric oxides depends upon the nature of the anion and its hydration level. Monovalent oxyanions adsorb through an electrostatic interaction with the hydrated hydrous oxide surface. All divalent oxyanions, with the exception of tellurate, coordinate directly with surface iron cations. Tellurate, an octahedral anion, apparently penetrates and incorporates in the hydrous oxide structure. The symmetry of the free anion has a significant role in determining the configuration of the resultant complex. For anions of the same charge, those with tetrahedral geometry (in uncoordinated states) show a higher degree of specificity for the surface than the trigonal planer anions. Without exception, each bidentate bridging complex forms by replacement of protonated and unprotonated hydroxyls. With the anion geometry and the charge being equal, the suspension pH determines the adsorption capacity of the hydrous oxide.

Key Words—Anion adsorption, Bidentate bridging, Infrared spectroscopy, Iron oxide.

INTRODUCTION

Knowledge of the bonding sites and coordination habits of oxyanions on hydrous iron oxides can provide insight into the structure of the hydrous surface and can explain reactions that occur at these surfaces. In light of the current interest in the interaction of toxic chemicals with soil constituents and their structural transformations, an investigation of the bonding characteristics of certain anionic species has been undertaken.

The location and bonding structure of oxyanions associated with *freshly precipitated* hydrous iron oxides has not been thoroughly defined. The presence of anions in the hydrous oxide structure was recognized in aging studies, first by Fripiat and Pennequin (1965) and later by Lahann (1976). They observed that in an acid medium the transformation of iron hydroxides to goethite and hematite resulted in a decline in solution pH and a concurrent release of chloride ions. Many studies have not evaluated the influence of the anion on the structure or surface properties of hydrous iron oxides. For example, the presence of surface or structural anions was not investigated by Towe and Bradley (1967) or by Chukhrov *et al.* (1973) in their structural analyses of ferrihydrite. Russell (1979) found evidence of surface hydroxyls in his preparation of ferrihydrite, but overlooked a possible nitrate interaction with surface coordination sites. Hsu and Ragone (1972) and Hsu (1972) studied the aging of hydrolyzed iron(III) solutions without ascertaining the influence of the perchlorate anion on the stability of the initial precipitate or the subsequent transformation processes.

The papers by Parfitt *et al.* (1975) and Parfitt and Smart (1978) represent the only studies of the surface properties of amorphous hydrous iron oxides. They found for crystalline and amorphous iron oxyhydroxides that two surface hydroxyl groups (or surface-coordinated $-OH_2^+$ species) were replaced by phosphate and sulfate anions resulting in a binuclear bridging complex.

The present paper presents evidence that oxyanions adsorb on freshly prepared hydrous iron oxides by a predictable coordination mechanism and that the anions satisfy a high proportion of surface coordination sites. In addition, the bonding habit and adsorption maximum of the anion appears to be related to its charge, geometry, and the suspension pH.

MATERIALS AND METHODS

Hydrous iron oxides were precipitated by the dropwise addition of 1 N $FeCl_3$ to a 1 N NH_4OH solution until the OH/Fe^{3+} ratio equaled 3.0 (pH 6.5). The resultant suspension was thoroughly dialyzed for 24 hr at which time no further chloride was detected in the external solution. A portion of the gel was freeze-dried for use in exchange-isotherm experiments. The remainder was used for infrared spectroscopic (IR) analysis by washing 250 mg of the suspension five times with a 0.1 N solution of the anion of interest followed by 5 washings with deionized water. A portion of the final suspension was dried on a AgCl window at a concentration of approximately 0.5 mg/cm^2. IR spectra were recorded on a Perkin Elmer Model 567 spectrophotometer. A glass cell fitted with Irtran-2 windows was used for recording air-dried and evacuated (10^{-5} torr) spectra.

Exchange isotherms were measured by adding 25 mg of the freeze-dried oxide to 15 ml of a solution contain-

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ing a specific concentration of $NaNO_3$, Na_2SO_4, Na_2SeO_4, Na_2HAsO_4, or $Na_2H_4TeO_6$. All samples were shaken for 24 hr at 25°C ± 1°. A supernatant free of colloidal material was produced by centrifugation and was analyzed for the adsorbate anion, Cl^-, and pH.

Nitrate was determined photometrically by measuring the absorbance at 220 nm with a Varian-Cary 219 UV-VIS spectrophotometer. A turbidimetric method was used to measure sulfate concentration. In this procedure Ba^{2+} precipitated the sulfate; after an appropriate equilibration time, absorbance was measured at 500 nm and compared to a standard curve. Selenate and arsenate concentrations were determined by atomic absorption analyses. Tellurate was measured by polarigraphic methods using a Princeton Applied Research Model 174A Polarograph.

RESULTS AND DISCUSSION

Infrared spectra

The IR spectrum of the air-dried, nitrate-hydrous iron oxide complex closely resembled that predicted for the nitrate anion in its free state (Table 1, Figure 1). The nitrate ion possesses D_{3h} point-group symmetry in the free ionic state which predicts two bands designated as the ν_1 and ν_3 vibrations [the assignments and nomenclature of Nakamoto (1978) are used throughout]. If the symmetry of the ion is lowered by interaction with the hydrous oxide surface, a splitting of the degenerate ν_3 fundamental should occur. The extent of the splitting will then depend on the point-group symmetry of the ion in its bound state (Nakamoto, 1978). Figure 1A shows the slight splitting which was observed for the air-dried Fe oxide-nitrate complex. It is likely that the lowering in symmetry is a result of hydrogen bonding of the nitrate ion with surface OH_2^+ groups. As the gel was dehydrated, a distinct ν_4 vibration appeared corresponding to a change of symmetry from the D_{3h} to the C_{2v} point group (Figure 1). The change in symmetry is envisaged as an anion moving from an ionic environment to direct coordination of one nitrate oxygen to a surface iron cation. This mechanism is confirmed by the similarity in band position with the unidentate nitrate-cobalt(III) complex (Table 1).

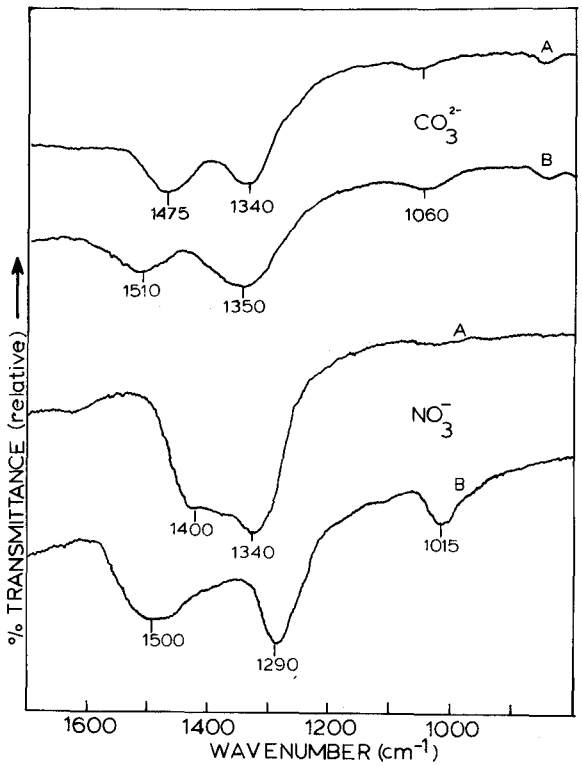


Figure 1. Infrared spectra of nitrate and carbonate adsorbed by hydrous iron oxide: A = air-dried; B = evacuated.

Table 1. Infrared band positions of perchlorate, nitrate, and carbonate anions in selected complexes and in hydrous iron oxides.

Anion-complex	Symmetry	Frequency (cm^{-1}) ν_1	ν_2	ν_3	ν_4	Reference
Free perchlorate ($KClO_4$)	T_d	935		1170–1050		Nakamoto (1978)
Unidentate perchlorate, $Cu(ClO_4)_2 \cdot 2H_2O$	C_{3v}	920		1158–1030		Nakamoto (1978)
Fe oxide-perchlorate (air-dried)		920		1090		This work
Fe oxide perchlorate (evacuated)		920		1160, 1090, 1040		This work
Free nitrate	D_{3h}	1050		1350		Nakamoto (1978)
Unidentate nitrate, $[Co(NH_3)_5NO_3]PtCl_4$	C_{2v}	1012		1481	1269	Ross (1972)
Fe oxide-nitrate (air-dried)		1040		1400	1340	This work
Fe oxide-nitrate (evacuated)		1015		1500	1290	This work
Unidentate carbonate, $[Co(NH_3)_5CO_3]Cl$	C_s	1062	741	1488	1351	Ross (1972)
Fe oxide-carbonate (air-dried)		1060	~700	1475	1340	This work
Fe oxide-carbonate (evacuated)		1060	~700	1510	1350	This work

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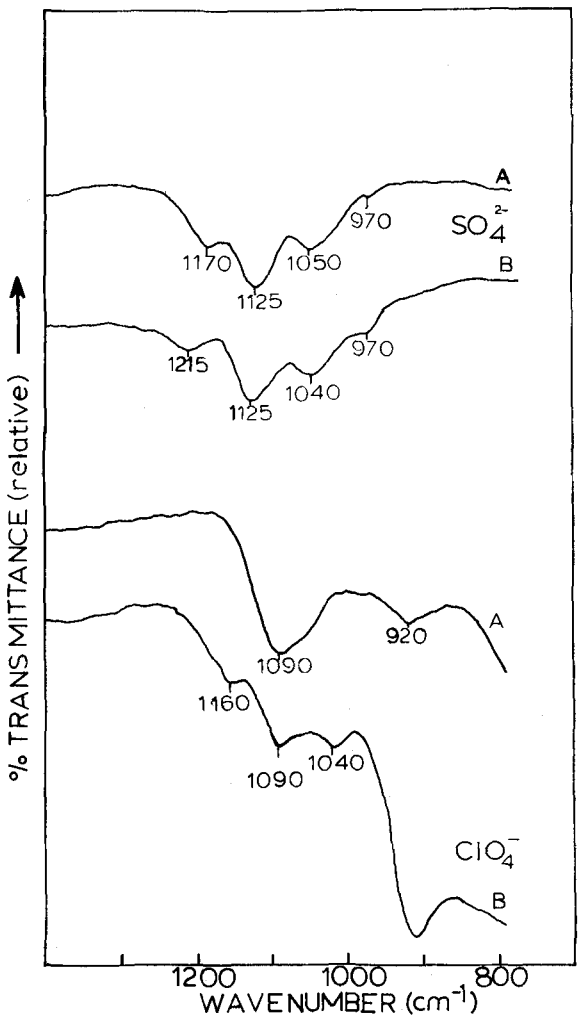


Figure 2. Infrared spectra of perchlorate and sulfate adsorbed by hydrous iron oxide: A = air-dried; B = evacuated.

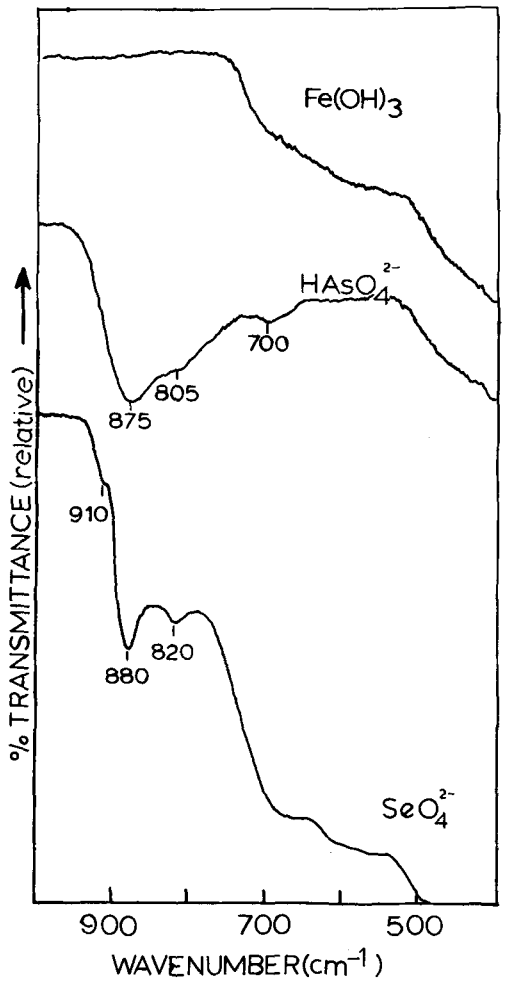


Figure 3. Infrared spectra of adsorbed selenate and arsenate (air dried). Also shown is the infrared spectrum of $Fe(OH)_3$ with chloride as the exchangeable anion.

The carbonate anion in its free state also belongs to the D_{3h} point group. However, unlike the nitrate-iron oxide complex, considerable splitting of the ν_3 occurred for adsorbed carbonate in both the air-dried and evacuated states (Table 1, Figure 1). Unequivocally this anion coordinates as a unidentate ligand even under hydrated conditions. As further evidence of unidentate bonding the bands observed here correspond well with the unidentate carbonate complex of Co(III) reported in Table 1. Apparently the anion's divalent charge is chiefly responsible for its strong interaction with the hydrous oxide surface. The presence of bicarbonate was ruled out because IR bands characteristic of HCO_3^- near 1640, 1400, and 1230 cm^{-1} (Grigor'ev *et al.*, 1972) were absent.

Perchlorate, sulfate, selenate, and arsenate anions belong to the T_d point group in the free ion state. In this form the ν_3 and ν_4 fundamental bands are infrared active. Should the symmetry decrease upon coordination, a splitting of the ν_3 would occur. For a unidentate complex (C_{3v} symmetry) two bands appear, and for a bidentate complex (C_{2v} symmetry) three bands are present. The distinction between a bidentate chelate and a bidentate bridging complex can be made by comparison with known complexes.

The hydrous iron oxide-perchlorate complex revealed only one band when air dry indicating a strictly electrostatic interaction under these conditions (Table 1, Figure 2). Three bands appeared in the spectrum of the evacuated oxide, corresponding to anions in both a free state and as a unidentate complex (Figure 2). The two bonding habits might be expected to exist concurrently for a weakly coordinating ligand.

The IR spectrum indicated a stronger form of interaction for the divalent sulfate anion. The appearance

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of the ν_1 fundamental and the splitting of the ν_3 into three bands clearly demonstrates the coordination of the sulfate anion to the iron cation (Table 2, Figure 2). A bidentate bridging complex is suggested by a comparison of these bands with those given for the Co(III) bidentate bridging compound (Table 2). A bidentate bridging complex was suggested by Parfitt and Smart (1978) for sulfate adsorbed on amorphous iron oxyhydroxide in the presence of protons.

Similar results were found for selenate and arsenate. Three bands attributable to the ν_3 fundamentals were found under air-dried and evacuated conditions (Figure 3, Table 2). The correspondence between IR data from this experiment and data for the selenate-CO(III) bidentate bridging complex confirms the bridging configuration. Unfortunately no references are available for an arsenate bidentate bridging compound with which to compare IR data from this study. The assignment of bonding structure for arsenate is based on the results for sulfate and selenate and those reported for phosphate (Parfitt *et al.*, 1975). Because of these similarities in ionic shape, structure, and IR spectra, a bidentate bridging bonding habit is proposed for arsenate.

Adsorption isotherms

Additional evidence for the location and adsorption mechanism of oxyanions was provided by exchange experiments. The anion-exchange capacity for electrostatically bound anions on a freshly precipitated hydrous iron oxide at pH 5.0 was determined to be 0.86 meq/g oxide. Assuming the chloride ion does not coordinate directly to the surface iron cation, this value represents an average population of protonated surface hydroxyls. Therefore, the adsorption of anions above this amount involves mechanisms other than replacement of chloride ions.

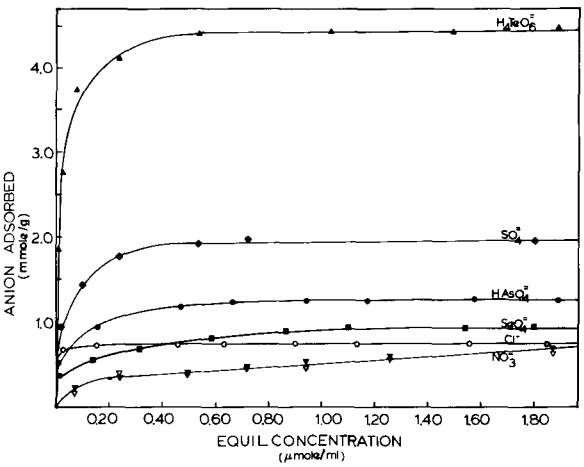


Figure 4. Adsorption isotherms for selected anions on freshly precipitated hydrous iron oxides at 25°C. The chloride-release curves are designated by open circles for sulfate, arsenate, selenate, and tellurate, and open triangles for nitrate.

At pH 3.5 nitrate showed a nearly 1:1 exchange with Cl^-, whereas complete chloride displacement occurred only at a very high nitrate equilibrium concentration (Figure 4). These results fully suggest an electrostatic interaction and therefore confirm the bonding habit proposed by IR analysis.

The divalent sulfate anion demonstrated a very high affinity for the oxide surface and attained a plateau value of nearly 2.0 mmole/g. In addition, the equilibrium pH (6.2) was significantly higher than that of the 0.1 M sulfate solution (5.8) or the hydrous oxide itself (4.0). An adsorption mechanism consistent with these results must involve the direct replacement of hydroxyl (OH^-) and protonated hydroxyl (OH_2) groups. In this respect,

Table 2. Infrared band positions of sulfate, selenate, and arsenate anions in selected complexes and in hydrous ion oxides.

Anion-complex	Symmetry	Frequency (cm^{-1}) ν_1	Frequency (cm^{-1}) ν_3	Reference
Free sulfate	T_d		1104	Nakamoto (1978)
Bridging bidentate sulfate				
$(NH_3)_4Co(NH_3)(SO_4)Co(NH_3)_4$	C_{2v}	995	1170, 1105, 1050	Nakamoto (1978)
Fe oxide-sulfate (air-dried)		970	1170, 1125, 1050	This work
Fe oxide-sulfate (evacuated)		970	1215, 1125, 1040	This work
Free selenate	T_d		870	Weighardt and Eckert (1971)
Bridging bidentate selenate				
$[Co_2(SeO_4)_2OH(NH_3)_6]^+$	C_{2v}	801	908, 872, 822	Weighardt and Eckert (1971)
Fe oxide-selenate (air-dried)			910, 880, 820	This work
Fe oxide-selenate (evacuated)			915, 880, 815	This work
Free arsenate	T_d		800	Beech and Lincoln (1971)
Unidentate arsenate				
$Co(NH_3)_4AsO_4 \cdot 5H_2O$	C_{3v}	800	851, 817	Beech and Lincoln (1971)
Bidentate chelate arsenate				
$Co(NH_3)_4AsO_4$	C_{2v}	768	872, 859, 740	Beech and Lincoln (1971)
Fe oxide-arsenate (air-dried)			875, 805, 700	This work
Fe oxide-arsenate (evacuated)			875, 802, 700	This work

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the hydrous iron oxides used in this study apparently behave in a manner similar to hydrous alumina (Rajan, 1978). In that study sulfate adsorption also resulted in a release of OH^- from the surface. The fact that the isotherm reached a plateau with no further adsorption at high equilibrium concentrations indicates that anion penetration into the oxide structure did not occur. The supposition of monolayer surface coverage is substantiated by comparison of surface areas calculated from the sulfate adsorption data (250 m^2/g, assuming 19.7 $Å^2$/ion) and water adsorption isotherms (295 m^2/g).

Selenate and arsenate also demonstrated adsorption isotherms indicative of a high specificity for the hydrated surface. Hydroxyl release with adsorption was also detected for these anions because the equilibrium pH (6.9 and 8.2, respectively) was higher than their respective solution pH values (6.5 and 8.0). The pronounced difference in adsorption maxima among the divalent anions is attributable, in part, to the differences in equilibrium pH. This trend is expected for an amphoteric solid, in which an increase in solution pH toward the point of zero charge of the hydroxide, 8.1 (Parks, 1965), produces a decrease in the number of anion adsorption sites.

The octahedral tellurate anion showed an adsorption maximum nearly twice that of sulfate (Figure 4) and an equilibrium pH (11.0) far above the point of zero charge of the hydrous oxide. An adsorption value of 4.0 mmole/g cannot be explained simply by surface coverage. It appears that the anion either penetrates and incorporates into the oxide structure through structural rearrangement that produces a new ferric tellurate complex. Unfortunately the bonding habit of this anion cannot be elucidated from IR spectra of the complex because the Te-O fundamentals are obscured by the Fe-O vibrations of the gel.

SUMMARY

This study has shown that IR spectroscopy is a valuable tool in assessing the bonding habit of different oxyanions with hydrous ferric oxides in a hydrated or evacuated state. Monovalent oxyanions were adsorbed primarily via electrostatic interactions with the hydrated surface although other secondary interactions were observed. Direct coordination to two surface iron cations was proposed for all divalent oxyanions except tellurate which appeared to penetrate and incorporate into the hydrous oxide structure.

With charge being equal, the symmetry of the free anion determined the configuration of the resultant complex. Tetrahedral divalent oxyanions used in this study developed bidentate bridging structures, whereas trigonal planer anions showed monodentate coordination. Adsorption capacity was found to be dependent on free anion geometry, with tetrahedral ions showing a higher degree of specificity than trigonal planer anions. With anion geometry and charge being equal, the suspension pH determined adsorption capacity.

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Резюме—Инфракрасный анализ показал, что свойство, связывающее анионы кислорода со свежо осажденными водными окисями железа, зависит от типа аниона и его уровня гидратации. Моновалентные анионы кислорода адсорбируются путем электростатических взаимодействий с гидратированной поверхностью водной окиси. Все двухвалентные анионы кислорода, исключая теллурат, координируют непосредственно с поверхностными катионами железа. Теллурат, октаэдрический анион, вероятно, проникает и включается в структуру водной окиси. Симметрия свободного аниона играет особую родь в определении концентрации получаемого комплекса. В случае анионов одинакового заряда анионы с тетраэдрической геометрией (в нескоординированных состояниях) показывают бодьшую степень особенности по отношению к поверхности, чем тригональные плоскостные анионы. Каждый "двухзубный" связывающий комплекс, без исключения, формируется подстановкой протонных и непротонных гидроокисей. В случае равных геометрии анионов и их заряда, величина pH суспензии определяет адсорбционную способность водной окиси. [E.C.]

Resümee—Infrarotuntersuchungen zeigten, daß die Bindungsart von Oxyanionen mit frisch hergestellten wasserhaltigen Eisenoxiden von der Art des Anions und seinem Hydratationszustand abhängt. Einwärtige Oxyanionen werden durch eine elektrostatische Wechselwirkung an die hydratisierte Oberfläche des wasserhaltigen Oxides gebunden. Alle zweiwertigen Oxyanionen—mit Ausnahme des Tellurats—werden direkt an die Eisenkationen der Oberfläche gebunden. Tellurat, ein oktaedrisches Anion, dringt offensichtlich ein und wird in die Struktur des wasserhaltigen Oxides eingebaut. Die Symmetrie des freien Anions spielt eine wichtige Rolle, da sie die Konfiguration des entstehenden Komplexes mitbestimmt. Bei Anionen der gleichen Ladung zeigen die mit tetraedrischer Symmetrie (im ungebundenen Zustand) ein größeres Maß an Spezifität für die Oberfläche als trigonale planare Anionen. Ohne Ausnahme bildet sich jeder zweizähnig verbrückte Komplex durch Ersatz von protonierten und nichtprotonierten Hydroxylionen. Bei gleicher Anionengeometrie und gleicher Ladung bestimmt der pH der Suspension die Adsorptionskapazität des wasserhaltigen Oxides. [U.W.]

Résumé—L'analyse infrarouge a montré que le mode de liaison d'oxyanions avec des oxides hydrés ferriques fraîchement précipités dépend de la nature de l'anion et de son niveau d'hydration. Les oxyanions monovalents adsorbent par une interaction électrostatique avec la surface de l'oxide hydré hydraté. Tous les oxyanions divalents, excepté la tellurate, coordonnent directement avec les cations fer de surface. La tellurate, un anion octaèdral, pénètre et incorpore apparemment dans la structure de l'oxide hydré. La symmétrie de l'anion libre a un rôle significatif dans la détermination du complexe résultant. Pour des anions de même charge, ceux ayant une géométrie tétraèdrale (dans des états non-coordonnés) montrent un degré de spécificité plus élevé pour la surface que les anions trigonaux plus planes. Sans exception, chaque complexe bidentate reliant se forme par remplacement d'hydroxyles protonatés et non-protonatés. La géométrie et la charge de l'anion étant égales, le pH de la suspension détermine la capacité d'adsorption de l'oxide hydré. [D.J.]

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