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CHEMISORPTION OF COPPER ON HYDROXY-ALUMINUM-HECTORITE: AN ELECTRON SPIN RESONANCE STUDY

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Abstract—Copper adsorption on a hydroxy-aluminum-hectorite complex (OH-Al-hectorite) at pH 4.5, 5.7, 7.4, and 7.8 was examined by means of electron spin resonance. The spectra of these samples were compared to those of Cu^{2+}-hectorite and various aluminum hydrous oxides. Copper on the OH-Al-hectorite in aqueous gels occurred as mobile $Cu(H_2O)_6{}^{2+}$ and chemisorbed to discrete sites of the OH-Al interlayer. As pH was increased, the ratio of chemisorbed to mobile Cu^{2+} increased. At pHs above 7 the solubility product of $Cu(OH)_2$ was exceeded, but chemisorbed Cu^{2+} remained as the dominant species. These results contrast with the precipitation of Cu observed on microcrystalline gibbsite above pH 5 and indicate that the interlayer OH-Al retained more Cu^{2+} on discrete sites. The greater adsorption capacity probably resulted in part from a higher specific surface area. Electron spin resonance spectra of Cu^{2+} in air-dried films of the OH-Al-hectorite at pH 4.5 and 7.4 showed Cu^{2+} in square planar symmetry, oriented with the *z*-axis perpendicular to the OH-Al-hectorite a-b plane. At the higher pH, the spectrum resembled that of $Cu(OH)_4{}^{2-}$ on alumina, suggesting a ligand exchange mechanism for Cu^{2+} adsorption on the complex.

Key Words—Adsorption, Aluminum, Copper, Electron spin resonance, Hectorite, Hydroxy-aluminum complex.

INTRODUCTION

Numerous studies attest to the tendency for heavy metals in soils to associate with oxides and hydrous oxides of iron and aluminum (e.g., Kinniburgh *et al.*, 1976). Hydrous oxides have been reported as coatings on clay minerals in soils and sediments, but few studies have examined the adsorption of metals to such coatings. Harsh and Doner (1984) recently showed that Cu^{2+} adsorption to a hydroxy-aluminum-montmorillonite complex was pH-dependent and that the Cu was nonexchangeable. Furthermore, electron spin resonance (ESR) of the adsorbed Cu^{2+} produced a rigid-limit signal similar to that found for Cu^{2+} coprecipitated with or adsorbed on noncrystalline alumina (McBride, 1982a). Because of spin interactions between adsorbed Cu^{2+} and structural Fe^{3+}, resolution of the spectra was poor.

The present paper reports the spin parameters determined by ESR for Cu^{2+} adsorbed on and coprecipitated with an hydroxy-aluminum hectorite complex and avoids the problem of structural Fe^{3+}. Unlike Cu^{2+} adsorbed on Na- or Mg-hectorite (McBride, 1982b), a rigid-limit ESR signal was observed for hydrated samples, indicating Cu^{2+} chemisorption to discrete sites. The chemical environment of the Cu^{2+} was found to depend on pH and the water content of the clay. The spin parameters were comparable to those of Cu^{2+} on other aluminum hydrous oxides and silicates.

MATERIALS AND METHODS

The <2-μm fraction of hectorite from Hector, California (sample SHCa-1, obtained from the Source Clays Repository of The Clay Minerals Society) was separated by gravity sedimentation. It was shaken overnight with 1 N sodium acetate adjusted to pH 5.0 to remove $CaCO_3$. The clay was then washed (washing refers to shaking with the desired solution, centrifuging until clear, and decanting the supernatant solution) five times with 1 N $NaClO_4$ and dialyzed for three days with several changes of deionized, distilled water (DDW). The electrical conductivity of the final dialysate was 3.5×10^{-3} dS/m.

The procedures used to prepare and characterize a OH-Al-montmorillonite were described in detail by Harsh and Doner (1984). Variations in the preparations of the OH-Al-hectorite are described here. A suspension containing 8 meq of $Al(ClO_4)_3$/g hectorite was titrated to a 2.25 OH/Al ratio with NaOH over 10.5 hr. The initial pH was 2.9 and increased to 4.2 at the end of the titration. Aging for 67 days resulted in a quasiequilibrium condition in which pH, total Al, and monomeric Al in the bulk solution had remained constant for more than 14 days. Washing the clay with 1 N $NaClO_4$ left 5.7 meq of nonexchangeable Al, equivalent to 148 mg of $Al(OH)_3$ precipitated. Details of the X-ray powder diffraction (XRD) analysis were also described by Harsh and Doner (1984).

Table 1. d(001) spacing of OH-Al-hectorite.

Saturating cation	Temperature (°C)	Hydration state	d-spacings d(001) (Å)	d(002) (Å)
K^+	25	air-dried	16.1	
K^+	110	P_2O_5-dried	13.8	4.9
K^+	300	P_2O_5-dried	13.4	4.82
Mg^{2+}	25	air-dried	16.3	
Mg^{2+}	65	ethylene glycol treated	15.6	4.82

Table 2. Cu^{2+} activity and adsorption in OH-Al-hectorite suspensions.[1]

Sample	pH	Cu activity	pCu + 2pOH	% Cu adsorbed
1	4.49	5.14×10^{-4}	22.3	<1%
2	5.68	6.80×10^{-6}	21.8	98.6%
3	7.36	2.43×10^{-6}	18.9	99.0%
4	7.82	1.68×10^{-6}	18.1	99.5%

[1] The suspensions were 0.33% by weight and were equilibrated for 11 days with 5×10^{-4} M $Cu(ClO_4)_2$ at various pHs.

An OH-(Al,Cu)-hectorite was prepared in this manner except that 0.035 meq of Cu^{2+} was added to the 8 meq Al^{3+}/g of clay, and no washing was performed. Copper was coprecipitated with Al^{3+} in a solution containing 0.06 eq $Al(ClO_4)_3$ and 0.002 eq $Cu(ClO_4)_2$ by titrating rapidly with 0.062 eq of NaOH. The precipitate was dialyzed against several changes of DDW for three weeks at ambient temperature (25 ± 3°C) and resulted in a two-phase gel containing blue and white components. The ESR spectrum of the whole precipitate was obtained.

Samples for the ESR experiments were prepared by adding 0.100 g of OH-Al-hectorite in suspension to 0.017 N $NaClO_4$ and 5×10^{-4} M $Cu(ClO_4)_2$ to make a total of ~30 g of suspension in 40-ml, screw-cap centrifuge tubes. The pH was adjusted over the first 24 hr with HCl or NaOH to give a range of values. Samples were shaken occasionally at room temperature for 11 days at which time a constant pH had been obtained. The total mass of suspension and initial [Cu^{2+}] was calculated by summing the $NaClO_4$ and acid or base additions to determine the total mass of solution. Total Cu in centrifuged subsamples was determined by atomic absorption spectrophotometry, and adsorbed Cu^{2+} was calculated by difference. Copper activity was estimated using the Davies equation for activity coefficients and conditional formation constants for $CuOH^+$ and $Cu_2(OH)_2^{2+}$ (Baes and Mesmer, 1976). Unwashed, centrifuged gels were either placed in capillary tubes or prepared as air-dried, self-supporting films. ESR spectra were obtained on a Varian E-104 (X-band) spectrometer.

RESULTS AND DISCUSSION

XRD patterns of oriented samples confirmed that an OH-Al interlayer was formed in the hectorite (Table 1). Air-dried samples saturated with K^+ or Mg^{2+} showed 16.1- and 16.3-Å spacings, respectively, with no evidence of a separate gibbsite phase. The interlayer underwent partial collapse when heated, as evidenced by the reduction of the d(001) spacing to less than 14 Å and the appearance of a 4.8–4.9-Å gibbsite peak. Samples heated to 65°C in a desiccator containing ethylene glycol failed to expand and also produced a 4.82-Å peak even at this low temperature. These results indicate that the OH-Al interlayer in this system was unstable with respect to a separate gibbsite solid phase when the sample was heated and water was removed.

Previous studies suggest that most if not all of the Al should have been precipitated within the interlayer region of the hectorite. First, if the $Al(OH)_3$ had precipitated as a single gibbsite sheet of 4.85-Å thickness, as on montmorillonite (Slaughter and Milne, 1958), the nonextractable Al would have covered less than one-third of the hectorite surface, based on a 782-m^2/g surface area for hectorite (van Olphen and Fripiat, 1979). Second, Turner and Brydon (1965) showed that precipitation of gibbsite outside of the interlayer did not occur over at least an 8-month period until >8 meq of Al^{3+}/g smectite had precipitated or a >2.7 OH/Al mole ratio was used in the titration. Finally, Barnhisel (1977) pointed out that a linear decrease in cation-exchange capacity (CEC) with increasing amount of Al precipitated occurs when ≤190 mg of $Al(OH)_3$ is precipitated per gram of silicate clay. These results would not be expected if a substantial amount of Al had precipitated outside of the interlayer.

Solution activities of Cu^{2+} at various pHs show that the solubility of $Cu(OH)_2$ (pK_{so} = 19.36; Baes and Mesmer, 1976) had been exceeded in samples 3 and 4, whereas samples 1 and 2 were undersaturated with respect to the hydroxide (Table 2). These results were qualitatively similar to those of McBride (1982b) for a Cu^{2+}-saturated hectorite. This pH-dependent adsorption was explained by McBride in terms of Cu^{2+} precipitation. The ESR results presented below, however, do not support that explanation for the Cu-OH-Al-hectorite system.

Figure 1 shows ESR spectra for wet gels in capillary tubes. Both isotropic (G_0 = 2.18–2.19) and rigid-limit spectra ($g_\perp$) were present signifying the presence of $Cu(H_2O)_6^{2+}$ adsorbed on discrete sites on the complex. Because the rigid-limit signal was weak, it was not possible to determine the value of $g_\perp$. Either the weak signal or the possible existence of a range of Cu species on the surface precluded resolution of the $g_\parallel$ line shape and $A_\parallel$ hyperfine splitting, and, thus, did not allow calculation of the maximum rotational tumbling time

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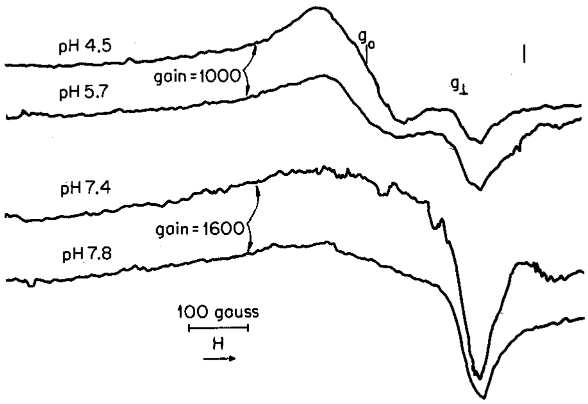

Figure 1. Electronic spin resonance spectra of unwashed OH-Al-hectorite gels equilibrated for 25 days with 5×10^{-4} M $Cu(ClO_4)_2$ (samples 1–4, Table 2). The high-field vertical line in this and following figures denotes the g = 2.0027 field position.

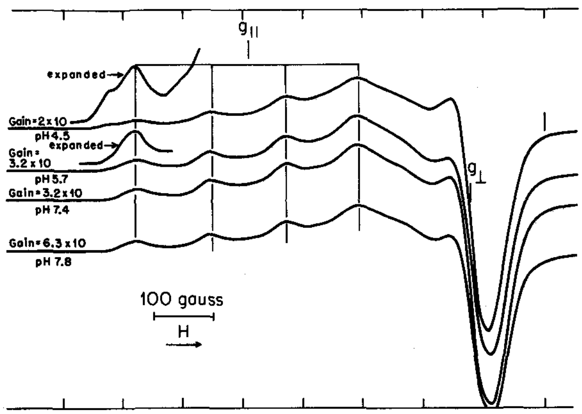

Figure 2. Electronic spin resonance spectra of frozen (113°K) gels of Cu loaded OH-Al-hectorite (samples 1–4, Table 2).

required to give an anisotropic signal. Nevertheless, the position of $g_\perp$ ($g_0 > g_\perp > 2.0023$) is consistent with the presence of a chemisorbed Cu^{2+} species (McBride, 1982a). The hydroxy-aluminum polymers must have provided the chemisorption sites inasmuch as similar rigid-limit spectra were observed for Cu^{2+} adsorbed on hydrous oxides of Al^{3+} (McBride, 1982a). No such signal, however, was produced by Cu^{2+} in layer silicates containing several layers of water molecules (Clementz *et al.,* 1973). Consistent with the adsorption data, the g_0 line decreased in intensity relative to the $g_\perp$ line with increasing pH, indicating that $Cu(H_2O)_6^{2+}$ was removed from solution and possibly from exchange sites through chemisorption on the hydrous oxide. Precipitation of $Cu(OH)_2$ was not a dominant reaction because the rigid-limit signal was maintained at high pH. Precipitation of $Cu(OH)_2$ would have led to significant electron spin-electron spin dipolar line-broadening due to the proximity of Cu atoms in the hydroxide phase (Wertz and Bolton, 1972; McBride, 1982b).

Due to the weak nature of the ESR signal at room temperature, spin parameters had to be obtained for both adsorbed and coprecipitated Cu^{2+} at 113°K (Figure 2). The spin parameters, $g_\perp$, $g_\|$, and $A_\|$, were nearly identical for Cu adsorbed on OH-Al-hectorite, Cu co-

Table 3. Electron spin resonance parameters for Cu^{2+} complexes and adsorbed species.

Sample	$g_\|$	$g_\perp$	$A_\|/hc$ (cm^{-1})	α^2	Reference
Cu in $Al(OH)_3$:gel	2.35	2.07	−0.0138	0.80	This work
OH-Al,Cu-hectorite; gel (113°K)	2.37	2.08	−0.0136	0.82	This work
Cu on OH-Al-hectorite; pH 4.5, 5.7, 7.4, 7.8; gel (113°K)	2.36	2.08	−0.0136	0.81	This work
pH 4.5; air-dried film	2.34	2.07	−0.0165	0.87	This work
pH 7.4; air-dried film	2.30	2.07	−0.0136	0.75	This work
Cu on hectorite: pH 4.8–8.6; air-dried film	2.35	2.07	−0.0163	0.87	McBride (1982b)
Cu on microcrystalline gibbsite; wet film	2.35	2.06	−0.0154	0.84	McBride *et al.* (1984)
Cu on noncrystalline alumina: aged 60 days; gel	2.37	2.08	−0.0138	0.83	McBride (1982a)
$Cu(H_2O)_6^{2+}$ (77°K)	2.39	2.07	−0.0142	0.83	Poupko and Luz (1972)
$Cu(OH)_4^{2-}$ (77°K)	2.16	2.05	−0.0186	0.83	Ottaviani and Martini (1980)
$Cu(OH)_4^{2-}$ on alumina (77°K)	2.34	2.05	−0.0132	0.77	Ottaviani and Martini (1980)

Electron spin resonance spectra obtained at 298°K unless otherwise noted.

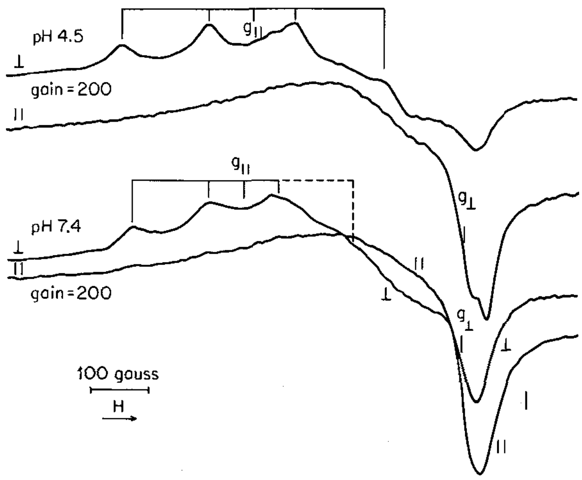

Figure 3. Electronic spin resonance spectra of oriented air-dried films of samples 2 (pH 4.5) and 4 (pH 7.4). Samples were oriented perpendicular (⊥) and parallel (∥) to the magnetic field.

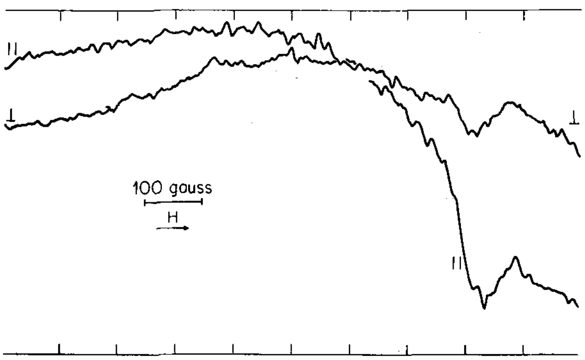

Figure 4. Electronic spin resonance spectrum of Cu coprecipitated with OH-Al-hectorite on an air-dried film oriented perpendicular (⊥) and parallel (∥) to the magnetic field.

precipitated with $Al(OH)_3$, Cu coprecipitated with Al on hectorite [OH-(Al,Cu)-hectorite], and Cu on noncrystalline alumina (Table 3). This similarity indicates that Cu^{2+} occupied similar sites regardless of whether Cu^{2+} was added before or after precipitation of $Al_x(OH)_y^{3x-y}$. Although the spin parameters in the frozen samples did not appear to depend on pH, expansion of the hyperfine splitting of the pH 4.5 sample showed a second, rigid-limit spectrum, evident as a shoulder on the low-field line shape (Figure 2). This shoulder was undoubtedly due to $Cu(H_2O)_6^{2+}$ or $Cu(H_2O)_4^{2+}$, because mobile $Cu(H_2O)_6^{2+}$ was present in the unfrozen sample. This shoulder did not occur in the pH 5.7 sample where most of the Cu^{2+} had been chemisorbed.

Permanent charge sites were relatively unavailable to Cu^{2+} at pH 4.5 because <0.2 mmole of Cu^{2+} was adsorbed per 100 g of complex. Competition for exchange sites by Al^{3+} and its hydrolysis products presumably inhibited electrostatic attraction of Cu^{2+}. Although more permanent charge sites may have become available with increasing pH as Al was neutralized by OH^-, the ESR spectra indicate that rigidly bound Cu^{2+} increased relative to mobile Cu^{2+} as pH increased. Harsh and Doner (1984) found that Cu^{2+} adsorption by Na-OH-Al-montmorillonite did not displace Na^+ from exchange sites. These results indicate that the Al-OH sites constituted the preferred sites for Cu^{2+} adsorption.

McBride *et al.* (1984) found that copper adsorbed on microcrystalline gibbsite tended to polymerize and precipitate, probably as $Cu(OH)_2$, at [Cu] = 5×10^{-4} M and pH > 5. This reaction was not evident in the present system because polymerization of $Cu(OH)_2$ would have led to significant line broadening in the ESR spectrum as a result of Cu^{2+} electron spin-electron spin dipolar interaction. The absence of polymerization on OH-Al-hectorite is attributed to the high adsorption capacity of the interlayer $Al(OH)_3$ relative to the microcrystalline gibbsite. In the OH-Al-hectorite system, 14 mmole Cu^{2+}/g complex (120 mmole/g $Al(OH)_3$) was adsorbed at pH 5.7 compared to a maximum adsorption (before the onset of polymerization/precipitation) of <0.5 mmole Cu^{2+}/100 g microcrystalline gibbsite.

On an OH-Al-montmorillonite, Harsh and Doner (1984) showed that Cu adsorption on the nonexchangeable $Al_x(OH)_y^{3x-y}$ also exceeded that on the microcrystalline gibbsite examined by McBride *et al.* (1984) by nearly two orders of magnitude. Unpublished transmission electron micrographs obtained in the present authors' laboratory of freeze-fracture replicas of the OH-Al-montmorillonite surface show that the interlayer material exists as islands, ~150 Å in diameter. Precipitation on hectorite should have produced $Al(OH)_3$ particles similar in size to those on the montmorillonite because of the similar charge properties of these two smectites. The edge-to-face surface area ratio should be much greater for the $Al(OH)_3$ on hectorite than for the microcrystalline gibbsite, which has a particle diameter of ~2000 Å (McBride *et al.*, 1984). The large edge-to-face ratio accounts, at least in part, for the high adsorption capacity of $Al(OH)_3$ on hectorite, because the edge sites, i.e., $-OH$ and $-OH_2$ groups bound to only one Al atom, are the most reactive adsorption sites (Parfitt *et al.*, 1977). The relationship between particle size and Cu^{2+} adsorption on gibbsite is demonstrated by the fact the rigid-limit signal for chemisorbed Cu^{2+} was not observed on coarse gibbsite with an edge-to-face site ratio much less than that of microcrystalline gibbsite (McBride, 1982a).

Reactive surface sites should also have been more numerous if the crystallinity had been reduced and/or the negative surface charge had been increased relative to pure gibbsite. Coprecipitation of Si with Al or Si adsorption on gibbsite have been shown to lower the point of zero charge of the hydrous oxide (Tschapek *et al.*, 1974; Perrott, 1977; Pyman *et al.*, 1979; Jepson *et al.*, 1976). Substitution of Li^+ or Mg^{2+} into the hydrous oxide structure might also have increased its negative surface charge or reduced its crystallinity. McBride (1978) showed that Cu^{2+} retention by noncrystalline alumina increased with increasing Mg^{2+} in the coprecipitate and attributed this phenomonon to a higher surface area of the Mg-richer material. Keller and Stevens (1983) recently reported the presence of Li^+ in aluminous chlorites. Inasmuch as Mg^{2+}, Li^+, and Si are released from hectorite under acidic conditions (Barshad and Foscolos, 1970; Tiller, 1968), they were probably introduced into our system during preparation of the OH-Al-hectorite. Thus, their possible effect on the sorptive properties of the complex must be considered.

Electron spin resonance spectra of air-dried films of the pH 4.5 samples showed that the Cu^{2+} complex was oriented with its *z*-axis perpendicular to the a-b plane of the OH-Al-hectorite (Figure 3). Copper coprecipitated with OH-Al-hectorite (Figure 4) gave a weak spectrum due to low Cu^{2+} concentration in the precipitate, but had the same orientation, reaffirming that its site occupancy was similar in both materials. Although the complexity of the spectra of the pH 4.5, air-dried sample suggests that Cu^{2+} existed in more than one environment, elongated axial symmetry $g_\parallel > g_\perp$ was clearly evident. Spin parameters for Cu^{2+} in the pH 4.5 sample were nearly identical to those for Cu^{2+}-hectorite (Clementz *et al.*, 1973; McBride, 1982b) which is consistent with a chemical environment in which Cu^{2+} is coordinated to H_2O or Al-OH in the *xy* plane and to silicate oxygens along the *z*-axis.

In the pH 7.5 sample, the stereochemistry of the complex was the same as in the above samples as shown by its orientation behavior (Figure 4). A reduction in both the $g_\parallel$ and $A_\parallel$ spin parameters, however, indicates that the chemical environment was changed. The spin parameters for Cu^{2+} in this system are very similar to those reported by Ottaviani and Martini (1980) for $Cu(OH)_4^-$ adsorbed on alumina (Table 3). The molecular orbital coefficient, α^2, calculated with the Kivelson and Neiman (1961) theory from the $g_\perp$, $g_\parallel$, and $A_\parallel$ parameters (Table 3), is also similar to that calculated by Ottaviani and Martini for $Cu(OH)_4^-$ on alumina. The small value of α^2 for these two systems relative to the other Cu^{2+} complexes in Table 3 implies that the σ plane bonding in the former complexes possesses more covalent character. (The α^2 coefficient ranges from 0.5 for completely covalent bonds to 1.0 for completely ionic bonds.) Covalency could have been increased either by direct bonding to Al-OH groups or deprotonation of H_2O coordinated to Cu^{2+}. Because $Cu(OH)_4^-$ in solution has the same α^2 coefficient as $Cu(H_2O)_6^{2+}$, direct bonding of Cu to Al-OH groups by ligand exchange is a more probable mechanism. This behavior was not observed in microcrystalline gibbsite (McBride *et al.*, 1984) because Cu^{2+} polymerization occurred above pH 5.

CONCLUSIONS

Copper adsorption on OH-Al-hectorite differs from that on hectorite in two respects. First, it is highly pH dependent, and, second, it is chemisorbed to discrete sites. Thus, the principal adsorption sites of the clay complex must be on the $Al_x(OH)_4^{3x-y}$ polymers. The adsorption also differs from that on microcrystalline gibbsite in that much more Cu^{2+} exists at discrete sites as monomeric Cu^{2+}. The OH-Al phase on hectorite has a far greater adsorption capacity, probably as a result of greater surface area and possibly due to differences in surface characteristics. Air-dried films of the clay complex gave ESR spectra that suggest a square planar Cu^{2+} complex oriented with its *z*-axis perpendicular to the hectorite sheets. At pH 4.5 most of the Cu^{2+} was present as $Cu(H_2O)_4^{2+}$. At pH 7.4 the spectrum resembles that of $Cu(OH)_4^{2-}$ on alumina, suggesting deprotonation of the $Cu(H_2O)_4^{2+}$ complex and/or complexation with the hydroxide surface.

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Резюме—Адсорбция меди комплексом гидрокси-алюминий-гекторит (OH-Al-гекторит) при pH равным 4,5, 7,4, и 7,8 исследовалась при помощи електронного спинового резонанса. Спектры этих образцов сравнивались со спектрами Cu^{2+}-гекторита и различных водных окисей алюминия. Медь на OH-Al-гекторите в водных гелях залегала в виде $Cu(H_2O)_6^{2+}$ и хемисорбировалась на дискретных местах слоя OH-Al. При увеличении pH, отношение хемисорбированных ионов к подвижным ионом Cu^{2+} также увеличивалось. При значениях pH выше 7, величина произведения растворимости $Cu(OH)_2$ превышалась, но хемисорбированный Cu^{2+} оставался главным видом. Эти результаты сопоставлялись с осаждением Cu, наблюдаемому на микрокристаллическом гиббсите при pH выше 5, и указывали на то, что слой OH-Al удерживал большое количество Cu^{2+} на дискретных местах. Большая адсорбционная способность была, вероятно, частично результатом большой удельной площади поверхности. Спектры электронного спинового резонанса Cu^{2+} в осушенных на воздухе фильмах OH-Al-гекторита при pH равных 4,5 и 7,4 указывали на квадратную плоскую симметрию Cu^{2+} с осей *z* по направлению нормальному к плоскости a-b OH-Al-гекторита. При высших pH, спектр был похожий на $Cu(OH)_4^{2-}$ на глиноземе, указывая на лигандовый механизм обмена для адсорбции Cu^{2+} комплексом. [E.G.]

Resümee—Die Kupferadsorption an einen Hydroxy-Al-Hektoritkomplex (OH-Al-Hektorit) wurde bei pH 4,5, 5,7, 7,4, und 7,8 mittels Elektronenspinresonanz untersucht. Die Spektren dieser Proben wurden mit denen von Cu^{2+}-Hektorit und verschiedenen wasserhaltigen Al-Oxiden verglichen. Das Kupfer trat an dem OH-Al-Hektorit in wässrigen Gelen als mobiles $Cu(H_2O)_6^{2+}$ auf und chemisorbierte an bestimmten Plätzen der OH-Al-Zwischenschicht. Wenn der pH zunahm, dann nahm das Verhältnis des chemisorbierten zum mobilen Cu^{2+} zu. Bei pH-Werten über 7 wurde das Löslichkeitsprodukt von $Cu(OH)_2$ überschritten, doch das chemisorbierte Cu^{2+} überwog weiterhin. Diese Ergebnisse stehen im Gegensatz mit der Ausfällung von Cu, die an mikrokristallinem Gibbsit über pH 5 beobachtet wurde, und deuten darauf hin, daß die OH-Al-Zwischenschicht mehr Cu^{2+} an bestimmten Stellen zurückhielt. Die größere Adsorptionskapazität resultierte wahrscheinlich zum Teil aus einer größeren spezifischen Oberfläche. Elektronenspinresonanzspektren von Cu^{2+} in Luft-getrockneten Schichten von OH-Al-Hektorit bei pH 4,5 und 7,5 zeigten, daß Cu^{2+} in einer quadratischen planaren Symmetrie auftritt und mit der z-Achse senkrecht zu der a-b-Ebene des OH-Al-Hektorit orientiert ist. Bei höheren pH-Werten ähnelt das Spektrum dem von $Cu(OH)_4^{2-}$ an Aluminiumoxid, was auf einen Ligandenaustauschmechanismus für die Cu^{2+}-Adsorption an den Komplex hindeutet. [U.W.]

Résumé—On a examiné au moyen de la résonnance à spin d'électrons l'adsorption de cuivre sur un complexe hectorite-hydroxy-aluminium (OH-Al-hectorite) aux pH 4,5, 5,7, 7,4, et 7,8. Les spectres de ces échantillons ont été comparés à ceux de l'hectorite Cu^{2+} et d'oxides aluminium hydrés variés. Le cuivre sur l'hectorite OH-Al dans des gels aqueux se trouve sous forme de $Cu(H_2O)_6{}^{2+}$ mobile et a chémisorbé à des sites discrets de l'intercouche OH-Al. Au fur et à mesure de l'augmentation du pH, la proportion de Cu^{2+} chémisorbé a augmenté par rapport au Cu^{2+} mobile. Aux pH au dessus de 7, le produit de solubilité de $Cu(OH)_2$ a été excédé, mais Cu^{2+} chémisorbé est resté l'espèce dominante. Ces résultats contrastent avec la précipitation de Cu observé sur la gibbsite microcristalline au dessus du pH 5, et indiquent que l'intercouche OH-Al a retenu plus de Cu^{2+} sur des sites discrets. La capacité d'adsorption plus grande était en partie le résultat d'une aire de surface spécifique plus élevée. Les spectres de spin à résonnance d'électrons de Cu^{2+} dans des films d'hectorite OH-Al sechés à l'air aux pH 4,5 et 7,4 a montre Cu^{2+} en symmétrie plane carrée, orienté avec l'axe-*z* perpendiculaire au plan a-b de l'hectorite OH-Al. Au pH plus élevé, le spectre ressemblait à celui de $Cu(OH)_4{}^{2-}$ sur l'alumine, suggérant un mécanisme d'échange de ligand pour l'adsorption de Cu^{2+} sur le complexe. [D.J.]