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Cu^{2+}-ADSORPTION CHARACTERISTICS OF ALUMINUM HYDROXIDE AND OXYHYDROXIDES[1]

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Abstract—The nature of Cu^{2+} adsorption by boehmite, gibbsite, and noncrystalline alumina was studied over a range of equilibrium pH (4.5–7.5) and Cu^{2+} concentration (10^{-3}–10^{-8} M) by electron spin resonance (ESR). Available chemisorption sites at pH 4.5 were the most numerous for noncrystalline alumina (~1 mmole/100 g), less for boehmite, and least for gibbsite as indicated by the relative strength of the rigid-limit ESR signal attributed to Cu^{2+} adsorbed at discrete sites. The chemisorption process involved immobilization of Cu^{2+} by displacement of one or more H_2O ligands by hydroxyl or surface oxygen ions, with the formation of at least one Cu–O–Al bond. As the pH was raised from 4.5 to 6.0, essentially all of the solution Cu^{2+} appeared to be adsorbed by the solids. However, the noncrystalline alumina and boehmite chemisorbed much of the total adsorbed Cu^{2+} (10 mmole/100 g), whereas precipitation or nucleation of $Cu(OH)_2$ in the gibbsite system was indicated. Precipitated Cu^{2+} was more readily redissolved by exposure to NH_3 vapor than chemisorbed Cu^{2+}.

Key words—Adsorption, Alumina, Aluminum, Boehmite, Copper, Electron spin resonance, Gibbsite.

INTRODUCTION

The relative importance of oxides and oxyhydroxides of aluminum and iron in the adsorption of Cu^{2+} by clays and soils is difficult to evaluate. Clay-size phyllosilicates probably contain oxide impurities to various extents, with the result that "specific adsorption" of metal ions by clays may arise from metal-oxide interactions (Jenne, 1968). Strong evidence exists that most of the adsorption sites of pure layer silicate clays maintain a "loose" electrostatic bond with ions such as Cu^{2+} (Clementz *et al.*, 1973; McBride *et al.*, 1975; McBride, 1976) unless the pH is raised to a level which induces surface hydrolysis of the metal. The effect of this hydrolysis is to cause Cu^{2+} to become less exchangeable (i.e., specifically absorbed) at higher pH. The strong bonding of Cu^{2+} by organic matter in soils provides an additional adsorption mechanism but there is not general agreement regarding the relative importance of organic and mineral forms of Cu^{2+} in soils (Shuman, 1979).

It is well known that pure Fe and Al oxides and oxyhydroxides are capable of adsorbing Cu^{2+} in a nonexchangeable form (Kinniburg *et al.*, 1976; Forbes *et al.*, 1976). Adsorption by noncrystalline alumina involves a direct Al–O–Cu bond (McBride, 1978). Because truly noncrystalline oxide minerals probably do not exist in soils, the present study was undertaken to compare Cu^{2+} adsorption on noncrystalline alumina, boehmite, and gibbsite. The results should determine whether mechanisms of trace-metal bonding are comparable on different alumina minerals.

MATERIALS AND METHODS

Adsorption of Cu^{2+} on boehmite, gibbsite, and noncrystalline alumina was measured by equilibrating 0.10 g of solid with 20 ml of Cu^{2+} solution in 0.05 M NaCl solution at room temperature. The samples were shaken in capped centrifuge tubes for one day, or for much longer periods of time to assess the importance of slow adsorption reactions. The samples were then centrifuged, and the supernatants were analyzed for Cu^{2+} by atomic absorption spectrophotometry. The amount of adsorbed Cu^{2+} was determined by the measured difference in solution Cu^{2+} concentration before and after reaction with the mineral. In addition, the pH of supernatants was measured and ESR spectra were obtained on the wet unwashed mineral samples using a Varian E-104 (X-band) spectrometer. Selected mineral samples were washed with $CaCl_2$ solution or water, and the ESR spectra were obtained after the washing procedure.

Copper ions were coprecipitated with $Al(OH)_3$ by adding 10^{-4} moles of Cu^{2+} in solution (as $CuCl_2$) to 10^{-2} moles of Al^{3+} in solution (as $Al(NO_3)_3$) and rapidly adding enough NaOH to precipitate the Al^{3+} completely (as $Al(OH)_3$). The product was then dialyzed for one week, and the ESR spectrum of the precipitate was obtained.

The effect of pH on Cu^{2+} adsorption by noncrystalline alumina, boehmite, and gibbsite was determined by placing 0.100 g samples of the solids in centrifuge tubes and adding 20 ml of 5×10^{-4} M Cu^{2+} in 0.05 M NaCl. The pH values of the mixtures were adjusted with NaOH over a range from 5 to 7, and the samples were shaken overnight. After centrifuging, the pH and Cu^{2+} concentrations of the supernatants were determined. However, at higher pH values, Cu^{2+} concentrations

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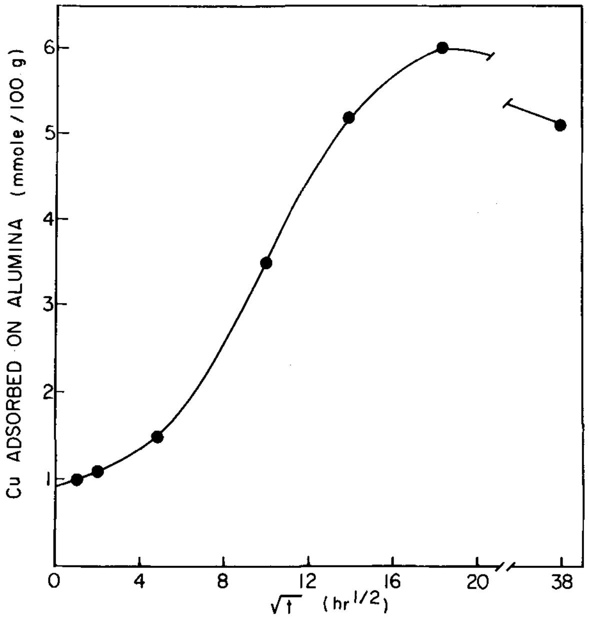


Figure 1. Adsorption of Cu^{2+} by noncrystalline alumina as a function of time.

were generally below the detection limit of flame atomic absorption, and the Cu^{2+} activity was measured with an Orion specific ion electrode. The unwashed, undried minerals were analyzed by ESR at the pH of equilibration.

In the Cu^{2+}-adsorption experiments described above, the availability of the adsorbed Cu^{2+} to ligand-displacement reactions was tested by exposing the minerals to NH_3 vapor (from concentrated NH_4OH) overnight. Changes in the ESR spectrum after this treatment were used to indicate the degree of Cu^{2+}-NH_3 bond formation.

Surface areas of the alumina minerals as determined by B.E.T. isotherm analysis of N_2 adsorption data were 111 m^2/g for noncrystalline alumina, 143 m^2/g for boehmite, and 5.9 m^2/g for gibbsite. Noncrystalline alumina was prepared by rapid addition of NaOH to an $AlCl_3$ solution followed by washing and freeze drying without aging, whereas boehmite was prepared by aging $Al(NO_3)_3$ solutions at 180°C for 12 hr. A surface area of 143 m^2/g was determined on a sample of boehmite which was somewhat more crystalline than that used for the adsorption experiments. Therefore, the value of 143 m^2/g may be a somewhat low estimate of the surface area. The prepared boehmites were characterized by X-ray powder diffraction and infrared spectroscopy. The gibbsite sample was obtained from the Aluminum Company of America.

RESULTS AND DISCUSSION

Cu^{2+} adsorption on noncrystalline alumina

The initial adsorption of ~1.0 mmole Cu^{2+}/100 g on noncrystalline alumina was quite rapid (Figure 1). This was followed by a slow adsorption over two weeks, producing a maximum adsorption of 6.0 mmole/100 g. During this period the solution pH remained in the range 4.9–5.1. However, after 60 days the pH dropped to 4.4, and the total adsorbed Cu^{2+} decreased to 5.1 mmole/100 g (Figure 1). Evidently, aging of the alumina gel released protons which in turn caused a partial desorption of Cu^{2+}.

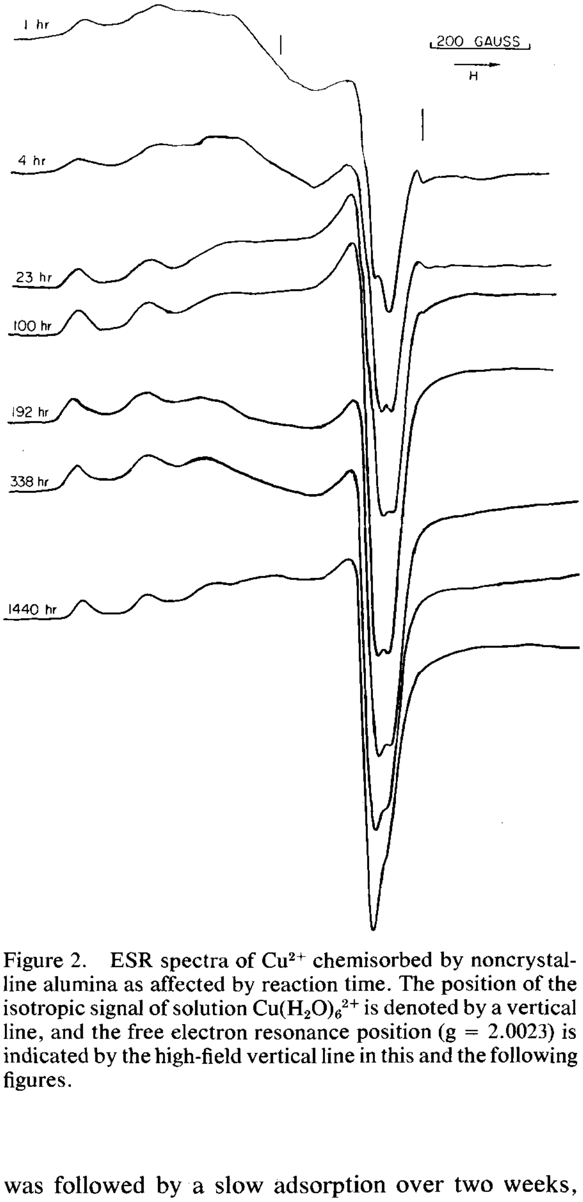


Figure 2. ESR spectra of Cu^{2+} chemisorbed by noncrystalline alumina as affected by reaction time. The position of the isotropic signal of solution $Cu(H_2O)_6{}^{2+}$ is denoted by a vertical line, and the free electron resonance position (g = 2.0023) is indicated by the high-field vertical line in this and the following figures.

The ESR spectrum of Cu^{2+} adsorbed on the alumina became more intense with longer equilibration times because of the slow adsorption process, and showed changes in the measured hyperfine splitting (A) and g-values (Figure 2). Close inspection of the spectrum of Cu^{2+} initially adsorbed (Figure 2, 1-hr reaction time) revealed a rigid-limit spectrum as well as an isotropic resonance characteristic of free $Cu(H_2O)_6{}^{2+}$ (indicated by the vertical line in Figure 2). The latter resonance

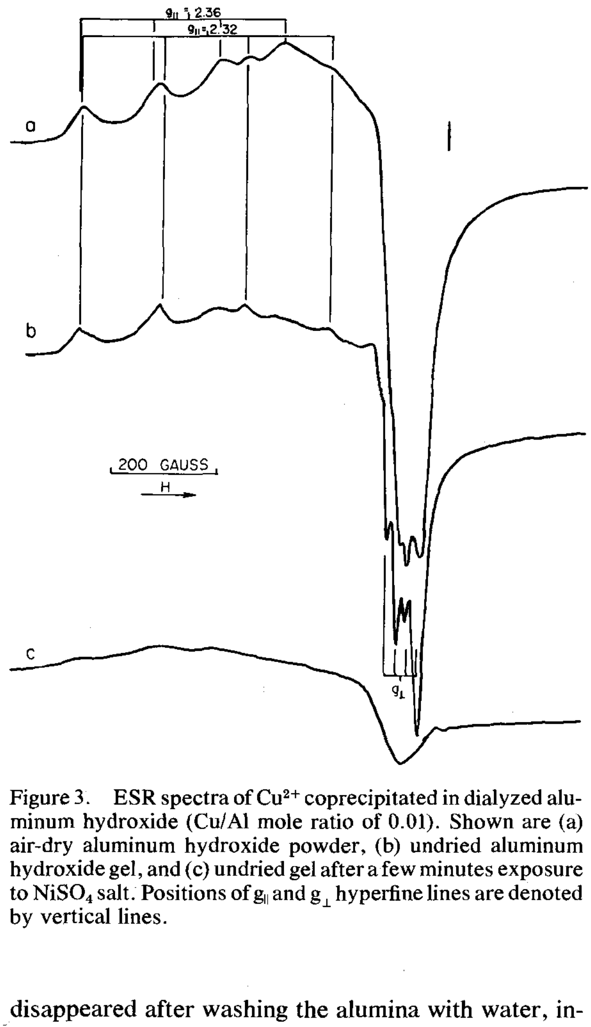


Figure 3. ESR spectra of Cu^{2+} coprecipitated in dialyzed aluminum hydroxide (Cu/Al mole ratio of 0.01). Shown are (a) air-dry aluminum hydroxide powder, (b) undried aluminum hydroxide gel, and (c) undried gel after a few minutes exposure to $NiSO_4$ salt. Positions of $g_{\parallel}$ and $g_{\perp}$ hyperfine lines are denoted by vertical lines.

disappeared after washing the alumina with water, indicating that this signal arose from nonadsorbed Cu^{2+} in the aqueous phase. The ESR parameters of the rigid-limit Cu^{2+} were estimated to be $g_{\parallel} = 2.32$, $g_{\perp} = 2.07$, and $A_{\parallel} = 155$ gauss ($0.0168\ cm^{-1}$), $A_{\perp} = 17.7$ gauss ($0.0017\ cm^{-1}$). Resolution of the hyperfine components of $g_{\perp}$ is not commonly achieved because of the small value of $A_{\perp}$, although this level of spectral detail has been observed in dry Mg^{2+}-smectites with small amounts of Cu^{2+} occupying exchange sites (McBride *et al.*, 1975) and also in strongly dehydrated zeolites with only a fraction of the exchange sites occupied (Nicula *et al.*, 1965). Evidently the adsorbed Cu^{2+} ions are well dispersed on the alumina surface; otherwise dipolar broadening effects would prevent observation of the $g_{\perp}$ hyperfine components. An adsorption level of 1 mmole/100 g on noncrystalline alumina with a surface area of 111 m^2/g should result in an *average* Cu^{2+}–Cu^{2+} separation distance on the surface of about 43 Å. Even at the highest adsorption level of 6 mmole/100 g, the average separation was 18 Å, still large enough to prevent significant Cu^{2+}–Cu^{2+} dipolar interaction.

After longer reaction times, the isotropic resonance of free Cu^{2+} disappeared as a result of increased adsorption, and a second rigid-limit spectrum progressively increased in intensity. This is most readily seen as a change in shape of the $g_{\perp}$ signal (Figure 2). The parameters of this second signal after 60 days of reaction were $g_{\parallel} = 2.37$, $g_{\perp} = 2.08$, and $A_{\parallel} = 125$ gauss ($0.0138\ cm^{-1}$). No estimate of $A_{\perp}$ could be made, possibly because of a decrease in the magnitude of $A_{\perp}$ which prevented resolution of individual hyperfine lines.

The data suggest that two separate mechanisms are involved in Cu^{2+} adsorption on noncrystalline alumina. The first is characterized by a rapid adsorption process and a relatively low adsorption level (~1 mmole Cu^{2+}/100 g) and produces an ESR signal with a low $g_{\parallel}$ value and high $A_{\parallel}$ value. The second adsorption process occurs over several weeks; it results in a greater amount of adsorbed Cu^{2+} (~5 mmole/100 g) and produces an ESR signal with a high $g_{\parallel}$ and low $A_{\parallel}$ value. Since "specific" Cu^{2+} adsorption on the hydroxide surface involves the displacement of H_2O ligands on Cu^{2+} by OH^- or oxygen anions, shifts in the ESR g and A parameters probably reflect changes in the number of surface groups bonded to Cu^{2+}. The $Cu(H_2O)_6^{2+}$ ion has $g_{\parallel} = 2.40$ and $A_{\parallel} = 0.0128\ cm^{-1}$ (Lewis *et al.*, 1966), whereas the planar $Cu(OH)_4^{2-}$ complex has $g_{\parallel} = 2.26$ and $A_{\parallel} = 0.0186\ cm^{-1}$ (Ottaviani and Martini, 1980). Evidently, increased coordination of Cu^{2+} to OH^- at equatorial ligand positions causes a decrease in $g_{\parallel}$ and an increase in $A_{\parallel}$. By comparison, coprecipitated Cu^{2+} in aged aluminum hydroxide produces a rigid-limit ESR spectrum that can be resolved into two sets of resonances with parameters similar to those of adsorbed Cu^{2+} ($g_{\parallel} = 2.31$–2.32 and $A_{\parallel} = 156$ gauss ($0.0169\ cm^{-1}$), $g_{\parallel} = 2.36$ and $A_{\parallel} = 130$ gauss ($0.0143\ cm^{-1}$)) as shown in Figure 3a. A comparison of these ESR parameters with those of $Cu(H_2O)_6^{2+}$ and $Cu(OH)_4^{2-}$ suggests that the chemisorbed and coprecipitated Cu^{2+} exists in two ligand environments. The spectrum with low $g_{\parallel}$ and high $A_{\parallel}$ may result from Cu^{2+} coordinated to several surface oxygen or hydroxyl ions, while that with high $g_{\parallel}$ and low $A_{\parallel}$ may have a more limited association with the surface. Estimates of degree of covalency of the Cu–O σ bonds from these two sets of ESR parameters produce values of $\alpha^2 = 0.83$–0.85, where α^2 is a function of bond covalency (Kivelson and Neiman, 1961). Similarly, the parameters for $Cu(H_2O)_6^{2+}$ and $Cu(OH)_4^{2-}$ in aqueous solutions are in the same range, indicating that the Cu–O bonds of chemisorbed Cu^{2+} are fairly ionic and similar in degree of covalency to the Cu–O bonds of $Cu(H_2O)_6^{2+}$ and $Cu(OH)_4^{2-}$. Spectral data (unpublished) obtained for vanadyl (VO^{2+}) adsorbed on noncrystalline alumina and coprecipitated in $Al(OH)_3$ generally agree with those obtained for Cu^{2+}, indicating metal–OH or metal–O–Al bonding of the rigidly bound metal with little difference observed between the ligand fields of chemisorbed and coprecipitated metal.

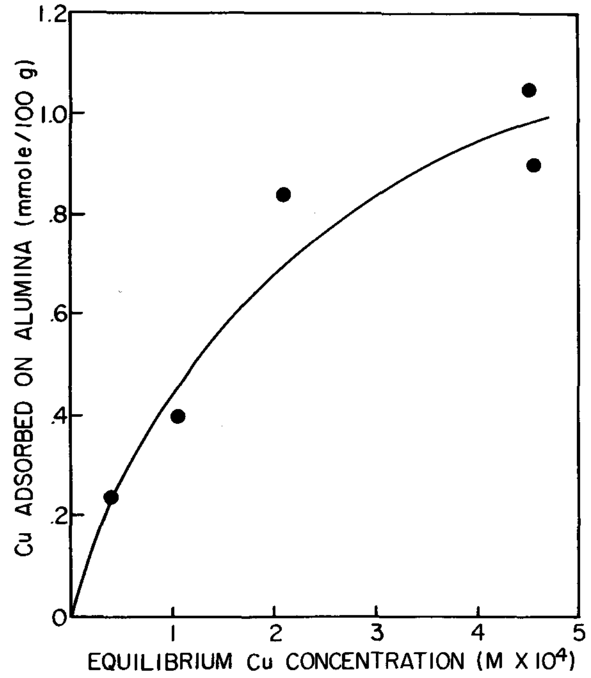


Figure 4. Adsorption isotherm of Cu^{2+} on noncrystalline alumina after 90 min of reaction time at a pH of 4.5–4.6.

The predominant ESR spectrum of Cu^{2+} coprecipitated in the undried alumina (Figure 3b) had $g_{\parallel} = 2.32$, $g_{\perp} = 2.05$, $A_{\parallel} = 156$ gauss ($0.0169\ cm^{-1}$), and $A_{\perp} = 21.3$ gauss ($0.0020\ cm^{-1}$), but air-drying or freezing (at liquid N_2 temperature) tended to increase the relative intensity of the $g_{\parallel} = 2.36$ signal. Much of the Cu^{2+} substituted in this alumina was probably at or near the particle surfaces, because rapid treatment with dithionite or Ni^{2+} salt eliminated most of the Cu^{2+} ESR signal, leaving a broad, weak spectrum (Figure 3c). Dithionite chemically reduces Cu^{2+} to nonparamagnetic species, whereas Ni^{2+} ions broaden ESR signals beyond detection by magnetic dipolar interactions if they are able to diffuse near the paramagnetic species. In addition, exposure to NH_3 vapor for one day shifted much of the Cu^{2+} spectrum toward lower g values, indicating the availability of the coprecipitated Cu^{2+} to ligand displacement. The fact that divalent metal substitution increases the surface area of Al and Fe oxides precipitated from solution (McBride, 1978; Nalovic *et al.*, 1975) suggests that these ionic impurities preferentially occupy positions at or near the oxide surfaces to avoid internal charge imbalances.

The ESR parameters of Cu^{2+} initially chemisorbed on hydrated alumina are very similar to those of Cu^{2+} in type X and Y zeolites dehydrated at 400°C (Nicula *et al.*, 1965; Conesa and Soria, 1978). Dehydration of zeolites at successively higher temperatures produced a reduction in the values of $g_{\perp}$ and $g_{\parallel}$ while increasing $A_{\parallel}$ and allowing the hyperfine lines of $g_{\perp}$ to be resolved. Temperatures of 200°C and higher caused the partial removal of inner-sphere hydration water from $Cu(H_2O)_6{}^{2+}$ and permitted the remaining hydration water to hydrolyze. Thus, dehydration of Type Y zeolite at temperatures above 100°C converted one type of spectrum ($g_{\parallel} = 2.38$, $g_{\perp} = 2.09$, $A_{\parallel} = 0.0133\ cm^{-1}$) into another ($g_{\parallel} = 2.33$, $g_{\perp} = 2.07$, $A_{\parallel} = 0.0166\ cm^{-1}$, $A_{\perp} = 0.0017\ cm^{-1}$), a result consistent with the thermally induced hydrolysis of $Cu(H_2O)_6{}^{2+}$ to form hydroxy-Cu^{2+}.

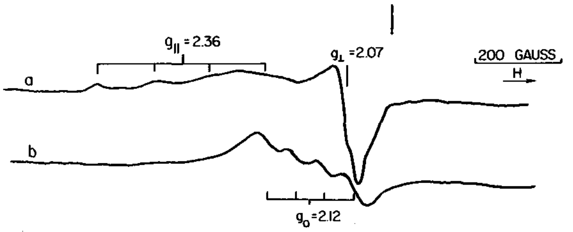


Figure 5. ESR spectrum of chemisorbed Cu^{2+} on boehmite at low pH after 48 hr of reaction time (a), and the spectrum of the same sample after one day of exposure to NH_3 (b).

The initial rapid chemisorption of Cu^{2+} on noncrystalline alumina depended upon the equilibrium Cu^{2+} concentration, and approached an apparent maximum at ~1.0 mmole/100 g (Figure 4). The available sites for this adsorption mechanism were evidently quite limited at the low pH (4.5) used to obtain this isotherm.

Cu^{2+} adsorption on boehmite and gibbsite

The adsorption of Cu^{2+} on boehmite at low pH (4.5) was much less (<0.5 mmole/100 g) than on noncrystalline alumina, with no significant reduction in the Cu^{2+} concentration of 20 ml of 5×10^{-4} M $CuCl_2$ after reaction with 0.100 g of boehmite for a week. This low level of adsorption occurred despite the high surface area of the boehmite. However, a small amount of adsorption was detected by ESR, as shown by the appearance of a rigid-limit spectrum in the wet, unwashed boehmite with $g_{\parallel} = 2.36–2.37$, $g_{\perp} = 2.07$, and $A_{\parallel} = 125–130$ gauss (Figure 5a). This signal was apparent after 1.5 hr of reaction, but did not appear to increase in intensity after one day of equilibration. No change in g or A parameters occurred over 8 days of equilibration, a result unlike that for the noncrystalline alumina. The higher g values and lower hyperfine splitting of Cu^{2+} on boehmite, when compared with the initially adsorbed Cu^{2+} on alumina, suggests less Cu^{2+} bonding to surface groups on boehmite than on alumina. Exposure of the boehmite sample to NH_3 vapor caused the rigid-limit signal of adsorbed Cu^{2+} to be converted to a four-line isotropic signal with $A_0 = 66$ gauss, $g_0 = 2.12$ (Figure 5b). The g-value, indicative of $Cu(NH_3)_4{}^{2+}$ (Nicula *et al.*, 1965), and the isotropic nature of the signal are evidence that NH_3 readily removed Cu^{2+} from

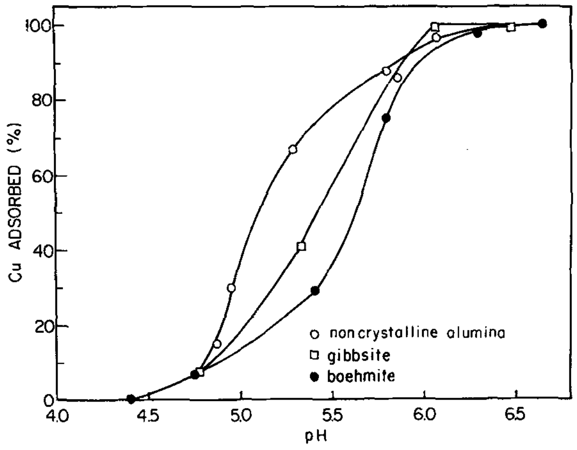


Figure 6. Effect of pH on Cu^{2+} adsorption by noncrystalline alumina, boehmite, and gibbsite.

adsorption sites on the boehmite surface, causing the ion to rotate freely in solution.

The gibbsite sample adsorbed measurable Cu^{2+} (~0.7 mmole/100 g) with no pH adjustment, probably due to the somewhat higher pH (~4.8) attained in the gibbsite system when no acid or base was added. However, no well-defined ESR signal could be observed for this adsorbed Cu^{2+}. Despite this lack of signal, exposure of the gibbsite to NH_3 vapor produced the isotropic $Cu(NH_3)_4^{2+}$ spectrum, proving that Cu^{2+} "adsorbed" by the gibbsite was readily desorbed by ligand-displacement reactions.

Effect of pH on Cu^{2+} adsorption

All three alumina materials demonstrated Cu^{2+} adsorption that was highly dependent on equilibrium pH (Figure 6). The pH-pCu equilibrium data (Figure 7) demonstrate that the Cu-alumina systems were not oversaturated with respect to the solubility of CuO or $Cu(OH)_2$. The noncrystalline alumina became more undersaturated with increasing time. The boehmite and gibbsite systems were often very little different in Cu^{2+} solubility at a given pH than comparable aqueous solutions without minerals added. It is likely that neither boehmite nor gibbsite possessed enough chemisorption sites to control the solubility of Cu^{2+} in the concentration range used in this study. It is not certain from these solubility data, however, if the boehmite and gibbsite surfaces provided nucleation sites for adsorption of hydroxy-Cu or if Cu^{2+} precipitated as a separate hydroxide phase.

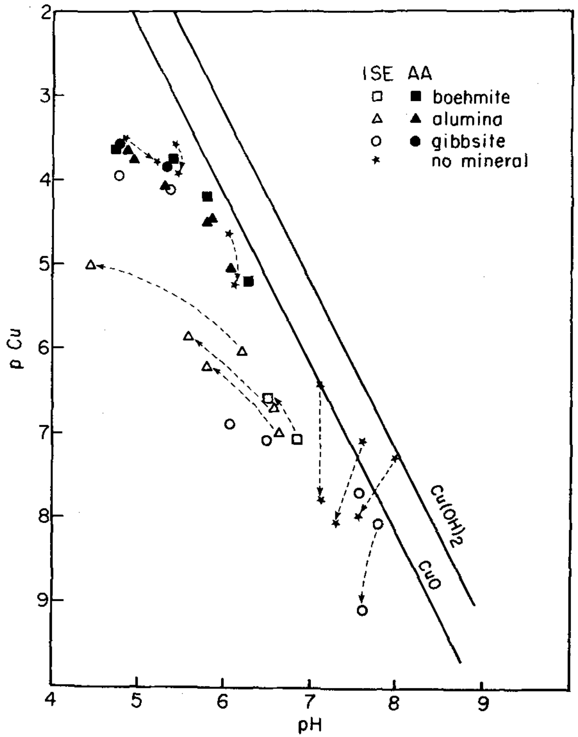


Figure 7. Solubility diagram for Cu^{2+} after one day in aqueous solution (star) noncrystalline alumina (triangle), boehmite (square), and gibbsite (circle) systems. Open symbols represent Cu^{2+} activity measurements made by ion selective electrode while closed symbols represent activities determined from atomic absorption (concentrations corrected to activities by the Debye-Huckel equation). Arrows mark the shift of solubility data after four weeks equilibration time for the Cu^{2+} mineral systems and after three weeks for aqueous Cu^{2+} with no mineral present. Solubility lines are drawn from the known solubility products of $Cu(OH)_2$ and CuO (Baes and Mesmer, 1976).

The ESR spectra of Cu^{2+} adsorbed in the boehmite system increased in intensity as the pH was raised (Figure 8a), although the signal intensity did not increase as rapidly as the adsorption level. The existence of the rigid-limit spectrum at adsorption levels as high as 10 mmole/100 g indicates that individual Cu^{2+} ions were adsorbed at discrete surface sites as the pH was raised; however, small amounts of precipitated $Cu(OH)_2$ would not have been detected by ESR because of the very broad signal produced by Cu-Cu interaction in $Cu(OH)_2$. The increase in adsorption from 0.7 mmole/100 g at $pH = 4.75$ to 10 mmole/100 g at $pH = 6.64$ had little *qualitative* effect on the observed rigid-limit spectrum (Figure 8a).

In contrast to boehmite, gibbsite showed only slight evidence of rigid-limit Cu^{2+} at low pH and no increase in signal intensity with increasing pH and increasing Cu^{2+} adsorption (Figure 8b). Evidently, the "adsorbed Cu^{2+}" in this system did not occupy discrete sites on gibbsite surfaces, but was nucleated or precipitated so that Cu-Cu dipolar interactions prevented observation of an ESR signal. There is no evidence from this study to prove that the gibbsite surfaces had any effect on Cu^{2+} solubility as the pH was raised.

The intensity of the rigid-limit Cu^{2+} signal increased

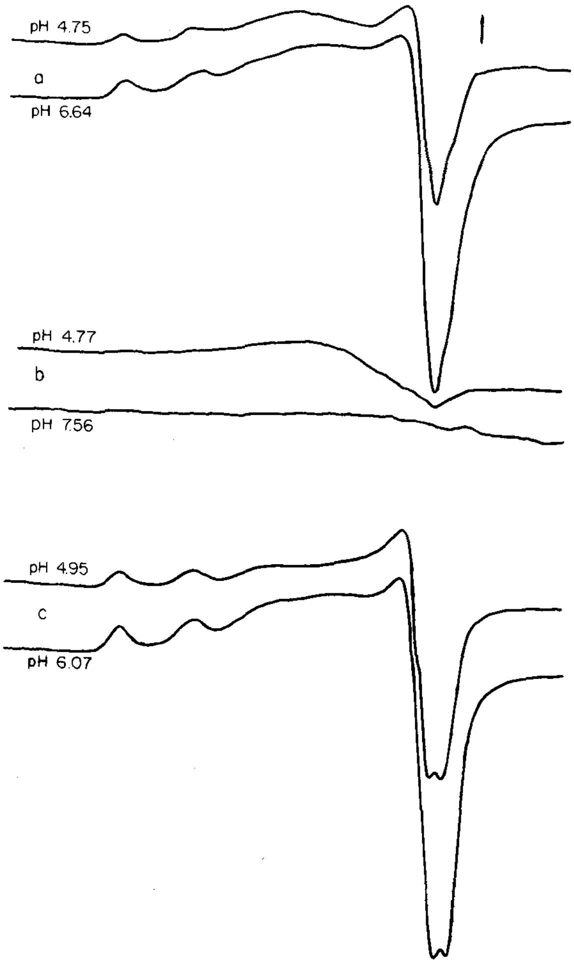


Figure 8. ESR spectra of alumina minerals as affected by pH: (a) boehmite at pH = 4.75 and 6.64 with 0.7 and 10.0 mmole Cu^{2+} adsorbed per 100 g, respectively; (b) gibbsite at pH = 4.77 and 7.56 with 0.7 and 9.9 mmole Cu^{2+} adsorbed per 100 g, respectively; (c) noncrystalline alumina at pH = 4.95 and 6.07 with 3.0 and 9.6 mmole Cu^{2+} adsorbed per 100 g, respectively.

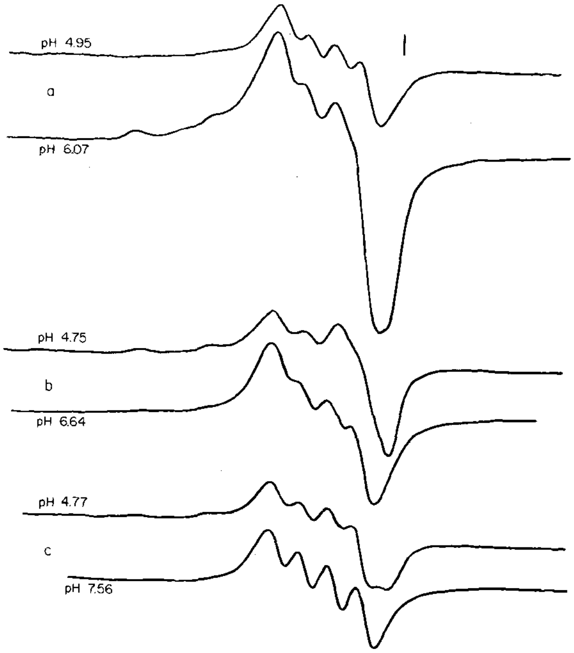


Figure 9. ESR spectra of alumina minerals after exposure to NH_3 vapor for one day: (a) noncrystalline alumina at pH = 4.95 (3.0 mmole Cu^{2+}/100 g) and 6.07 (9.6 mmole Cu^{2+}/100 g); (b) boehmite at pH = 4.75 (0.7 mmole Cu^{2+}/100 g) and 6.64 (10.0 mmole Cu^{2+}/100 g); and (c) gibbsite at pH = 4.77 (0.7 mmole Cu^{2+}/100 g) and 7.56 (9.9 mmole Cu^{2+}/100 g). The pH and Cu^{2+} adsorption values represent the equilibrium conditions before addition of NH_3.

in the noncrystalline alumina system as the pH was increased, as a result of greater Cu^{2+} adsorption (Figure 8c). Like boehmite, the alumina provided separate surface sites for adsorption of Cu^{2+} ions as the pH increased. The nature of these sites did not appear to change with pH and adsorption level, because the $A_{\parallel}$ value remained at about 140 gauss, and the $g_{\parallel}$ and $g_{\perp}$ values were about 2.34 and 2.06, respectively. Drying the noncrystalline gels at 100°C affected the spectrum, shifting $g_{\parallel}$ to lower values and eliminating evidence of hyperfine splitting in the $g_{\perp}$ component.

NH_3 ligand displacement reactions of adsorbed Cu^{2+}

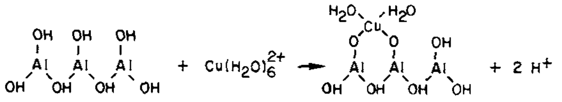
The exposure of moist alumina materials to NH_3 vapor following Cu^{2+} adsorption permitted the "availability" of adsorbed Cu^{2+} to be assessed. Chemisorbed Cu^{2+}, with one or more bonds to surface Al-O groups, would be expected to resist $Cu-NH_3$ bond formation, while physically adsorbed (surface-nucleated) or precipitated $Cu(OH)_2$ might be solubilized by NH_3 by the formation of $Cu(NH_3)_4{}^{2+}$ complexes. Generally, exposure of the Cu^{2+}-alumina systems to NH_3 caused the isotropic $Cu(NH_3)_4{}^{2+}$ spectrum (see Figure 5b) to appear. However, the noncrystalline alumina, with the largest quantity of chemisorbed Cu^{2+}, retained a portion of the Cu^{2+} in a bound form. Evidence for this surface-bound Cu^{2+} is apparent as a rigid-limit spectrum with low $g_{\parallel}$ and $g_{\perp}$ values, attributed to adsorbed Cu^{2+} with partial H_2O ligand displacement by NH_3. This bound form of Cu^{2+} was most evident on the alumina material that had adsorbed the greatest amount of Cu^{2+} (at high pH), as shown in Figure 9a. Like the noncrystalline alumina, NH_3-treated boehmite also retained some Cu^{2+} in a bound form with partial NH_3-ligand displacement, although the $Cu(NH_3)_4{}^{2+}$ spectrum dominated in boehmite that had adsorbed large amounts of Cu^{2+} at higher pH (Figure 9b). It is likely that very little of the 10.0 mmole/100 g of Cu^{2+} adsorbed on boehmite at high pH actually formed direct Cu–O–Al bonds; therefore, most of this Cu^{2+} was readily desorbed as

$Cu(NH_3)_4^{2+}$. It is not surprising, then, that the NH_3 caused Cu^{2+} to readily desorb from gibbsite as shown by the predominance of the isotropic 4-line $Cu(NH_3)_4^{2+}$ spectrum (Figure 9c), because the structure of gibbsite is expected to have few Al-OH groups available to chemisorb Cu^{2+}.

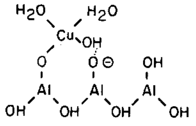
The NH_3-displacement results are consistent with a model of Cu^{2+} chemisorption which assumes reaction at surface OH-groups which are coordinated to only one Al ion. Parfitt (1978) has noted that Al-OH groups on the (001) face of gibbsite are nonreactive toward chemisorption of anions, while edge Al-OH groups are reactive. The gibbsite sample used in the anion-adsorption study had about 6 mmole/100 g of edge Al-OH groups and a surface area of 45 m²/g (Parfitt *et al.*, 1977). Because the gibbsite used in the present study had a much lower surface area, the quantity of edge Al-OH groups was much less than 6 mmole/100 g. Therefore, if Cu^{2+} chemisorption occurred only at the singly coordinated OH^- groups of edges, most of the 10 mmole/100 g of Cu^{2+} that was "adsorbed" on the gibbsite at high pH could not have been bonded by Al–O–Cu linkages. The ease of Cu^{2+} dissolution by NH_3, the weakness of the rigid-limit ESR spectrum of adsorbed Cu^{2+} and the pH-pCu solubility data all support the hypothesis that most of the Cu^{2+} was precipitated or nucleated as $Cu(OH)_2$ on gibbsite surfaces at high pH. Because the ideal boehmite surface has OH^- ions coordinated to one, two, and three Al ions (Parfitt, 1978), whereas the poorly organized surface of noncrystalline alumina is probably dominated by singly coordinated OH^-, these materials should chemisorb more Cu^{2+} than gibbsite. Thus, the quantity of reactive surface-OH^- ions per unit weight of mineral seems to determine the level of chemisorption (noncrystalline alumina > boehmite > gibbsite).

SUMMARY

Investigations of adsorbed Cu^{2+} on aluminum hydroxide and oxyhydroxide indicate that Cu^{2+} is rapidly immobilized by chemisorption at Al-OH sites with the probable insertion of several OH^- or surface oxygen ions into coordination positions of the hydrated Cu^{2+} ion. At low pH, this mechanism accounts for about 1 mmole/100 g of Cu^{2+} adsorption on noncrystalline alumina, considerably less than this amount on boehmite, and almost none on gibbsite. The active bonding sites are probably surface hydroxyls coordinated to single Al ions, because these sites are numerous in noncrystalline alumina, less prevalent in boehmite, and present only at edges in gibbsite. Chemisorption may involve the formation of a surface complex with adjacent oxygen atoms as shown below:



with the release of two H^+ ions for each Cu^{2+} ion adsorbed, a result consistent with published data on proton release (Forbes *et al.*, 1976). Bonding to a single surface oxygen may also occur, as recently suggested by Ottaviani and Martini (1980), with hydrogen bonding holding the Cu^{2+} in a rigid arrangement:



As the pH is raised, "adsorption" of Cu^{2+} increases in all alumina systems, but part of this increase in boehmite and almost all of the increase in gibbsite is a result of precipitation or surface nucleation of $Cu(OH)_2$ as shown by solubility data, the lack of an observable ESR signal, and the ease of dissolution of the Cu^{2+} by NH_3. However, both boehmite and noncrystalline alumina gave evidence of greater amounts of chemisorbed Cu^{2+} with increasing pH (as high as 10 mmole/100 g for noncrystalline alumina). Unlike precipitated forms of Cu^{2+}, chemisorbed Cu^{2+} ions were bound at discrete sites on the surfaces.

Reaction time was an important factor for noncrystalline alumina, with adsorption at low pH increasing over a period of several weeks. However, this slow process involved a separate bonding mechanism in which the Cu^{2+} may have been coordinated to fewer hydroxyl or surface oxygen ions.

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Резюме—Природа адсорбции Cu^{2+} бемитом, гиббситом, и некристаллическим глиноземом исследовалась в пределах равновесия pH (4,5–7,5) и концентрации Cu^{2+} (10^{-3}–10^{-8} м) посредством электронного спинового резонанса (ЭСР). Места доступной хемосорбции при pH 4,5 были наиболее многочисленные для некристаллических глиноземов (1 ммоль/100 г), менее для бемита и менее всего для гиббсита, как это показала относительная сила жесткого предела сигнала ЭСР, относящегося к Cu^{2+}, адсорбированному в дискретных местах. Процесс хемосорбции включает иммобилизацию Cu^{2+} посредством замещения одного или более лигандов H_2O гидроксилом либо поверхностными ионами кислорода с образованием по крайней мере одной связи Cu–O–Al. Когда pH увеличивалось от 4,5 до 6,0, по существу все Cu^{2+} раствора были, по-видимому, адсорбированы твердыми телами. Однако, некристаллический глинозем и бемит хемосорбировали большую часть целого количества адсорбированного Cu^{2+} (10 ммоль/100 г), тогда как в системе гиббсита происходило осаждение и зародышеобразование $Cu(OH)_2$. Осажденные Cu^{2+} более легко растворялись повторно при доступе пара NH_3, чем хемосорбированные Cu^{2+}. [E.C.]

Resümee—Es wurde die Art und Weise der Cu^{2+}-Adsorption durch Boehmit, Gibbsit, und nichtkristallisiertem Aluminiumoxid im pH-Gleichgewichtsbereich (4,5–7,5) und bei Cu^{2+}-Kontzentrationen von 10^{-3} bis 10^{-8} M durch Elektronenspinresonanz (ESR) untersucht. Die meisten verfügbaren Chemisorptionsstellen bei pH 4,5 waren bei nichtkristallisiertem Aluminiumoxid (1 mMol/100 g), weniger bei Boehmit und am wenigsten bei Gibbsit vorhanden. Dies ging aus der relativen Stärke des ESR-Signals hervor, das von der Menge des gebundenen Kupfers abhängt und von an bestimmten Stellen adsorbiertem Cu^{2+} herrührte. Der Chemisorptionsprozeß umfaßte eine Immobilisierung des Cu^{2+} durch den Ersatz von einem oder mehr H_2O-Liganden durch Hydroxyl- oder Oberflächensauerstoffionen und die Bildung von mindestens einer Cu–O–Al-Bindung. Wenn der pH-Wert von 4,5 auf 6,0 angehoben wurde, schien im wesentlichen alles Cu^{2+} der Lösung durch die Festsubstanzen adsorbiert worden zu sein. Das nichtkristallisierte Aluminiumoxid und der Boehmit chemisorbierten jedoch viel mehr vom gesamten adsorbierten Cu^{2+} (10 mMol/100 g), während im Gibbsit-System eine Ausfällung oder Nukleation von $Cu(OH)_2$ angezeigt wurde. Ausgefälltes Cu^{2+} wurde durch NH_3-Dampf leichter wieder aufgelöst als chemisorbiertes Cu^{2+}. [U.W.]

Résumé—On a étudié par résonance de spin d'électrons (ESR) la nature de l'adsorption de Cu^{2+} par la boéhmite, la gibbsite et l'alumine noncristalline sur une étendue de pH d'équilibre (4,5–7,5) et de concentration de Cu^{2+} (10^{-3}–10^{-8}). Les sites disponibles pour la chemisorption au pH 4,5 étaient les plus nombreux pour l'alumine noncristalline (1,0 mmole/g), moins pour la boéhmite, et le moins pour la gibbsite comme indiqué par la force relative du signal ESR de limite-rigide attribuée au Cu^{2+} adsorbé à des sites discrets. Le procédé de chemisorption impliquait l'immobilisation de Cu^{2+} par déplacement d'un ou de plusieurs ligands H_2O par des ions hydroxyles ou des ions oxygènes de surface, avec la formation d'au moins un lien Cu–O–Al. A fur et à mesure que le pH était élevé de 4,5 à 6,0, toute la solution Cu^{2+} semblait essentiellement être adsorbée par les solides. L'alumine noncristalline et la boéhmite, cependant, ont chemisorbé une grande partie du Cu^{2+} total adsorbé (10 mmole/100 g), tandis qu'une précipitation ou une nucléation du $Cu(OH)_2$ dans le système gibbsite était indiquée. Exposé à une vapeur NH_3, le Cu^{2+} précipité était plus facilement redissout que le Cu^{2+} chemisorbé. [D.J.]