# A STUDY OF THE ADSORPTION OF Ni(II) AND Cu(II) BY CLAY MINERALS

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**Abstract**—The adsorption of Ni(II) and Cu(II) on to the clay minerals kaolinite, chlorite, and illite has been investigated. The quantity of Ni(II) at pH 6 and Cu(II) at pH 5 adsorbed has been found to vary in the manner chlorite > illite > kaolinite. Examination of the mode of bonding of the metal ions to the clay minerals using X-ray photoelectron spectroscopy (XPS) has been carried out. Comparison of the binding energies for metal ions in octahedral sites in selected minerals (reference minerals) and in simple nickel and copper containing compounds with values for Ni(II) and Cu(II) adsorbed on chlorite indicate that nickel(II) is probably bound as the aquo ion while copper(II) may be adsorbed as $Cu(OH)^+$.

## INTRODUCTION

The interaction of selected metal ions, particularly Ni(II) and Cu(II), with clay minerals has been investigated in recent years (Swartzen-Allen and Matijevic, 1974.) Most recently, Farrah and Pickering (1976a,b) have studied the adsorption of copper on kaolinite, illite and montmorillonite as a function of pH and as a function of added complexing ligands. The principal conclusion of the study was that copper is sorbed through coordination to adsorbed hydroxyl ions at the edges of the clay and by sorption at negative sites on the mineral faces. It was suggested that, in alkaline medium, the clay acts as a nucleation center for the formation of copper hydroxy species.

O'Connor and Kester (1975) investigated the adsorption of copper on illite as a function of pH, solid phase concentration and composition of solution. From the data obtained, the sorption process is represented as a surface process in which $Cu^{2+}$ is exchanged for the hydrogen ion chemically bound to the mineral surface.

ESR studies of the nature of adsorbed copper in various minerals have been published by McBride (1976a,b), Clementz *et al.* (1973, 1974) and McBride *et al.* (1975). The results indicate that at values of low relative humidity the copper ion is present as the planat tetra-aquo complex. The copper ion exists as the hexa-aquo species under conditions of the normal partial pressure for water.

Studies of the nature of nickel ions adsorbed on clay minerals and other solid substrates have been less numerous. The electronic absorption spectra of nickel(II) adsorbed on silica gel under various conditions of humidity and solution composition have been studied by Hathaway and Lewis (1969). It is reported

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that nickel(II) exists on the surface in a chemical form similar to that found in solutions. Variation in humidity and ligand markedly affect the absorption spectrum which is due to an alteration in the coordination number and structure of the adsorbed nickel complex. Other investigators have reported thermodynamic parameters for adsorption of nickel and other ions on silica (Dugger *et al.*, 1964). Additional studies of the quantitative aspects of Ni(II) adsorption are reviewed by Swartzen-Allena and Matijevic (1974).

Studies of the chemical nature of metal ions in minerals using XPS have been successful in identifying the oxidation state of iron in lunar materials (Huntress and Wilson, 1972). Measurements of the binding energies of aluminum in a variety of materials have revealed that binding energies are affected by stoichiometric changes in composition (Lindsay *et al.*, 1973), but are not affected by alterations in coordination geometry (Anderson and Swartz, 1974). XPS studies of metal ions adsorbed on mineral surfaces have been valuable in describing the chemical nature of cobalt on metal oxides (Tewari and Lee, 1975) of iron on clay minerals (Koppelman and Dillard, 1975) and heavy metals on montmorillonite (Counts *et al.*, 1973). The of XPS in studying the mechanism of adsorption of phosphates and silicates on gibbsite has been reported (Alvarez *et al.*, 1976).

In an effort to provide evidence for the chemical nature of the adsorbed metal ions, it was the objective of this study to examine untreated chlorite and chlorite after sorption of nickel(II) and copper(II) using X-ray photoelectron spectroscopy (XPS). From a comparison of the measured binding energies of sorbed metal ions with standard metal-containing compounds and minerals, it was anticipated that a better description of the chemical nature of the adsorbed metal ion would emerge. The results of a study of a study of the interaction of Ni(II) and Cu(II)

with chlorite, illite and kaolinite at pH values below those necessary to form metal hydroxides are presented.

## EXPERIMENTAL

The experimental procedures have been described previously and will be reviewed here briefly (Koppelman and Dillard, 1975).

### Minerals

The kaolinite used in both the adsorption and XPS studies was a Georgia kaolinite, obtained from the Georgia Kaolin Company through the courtesy of Dr. Wayne Bundy. This batch of kaolinite has been designated Hydrite-R by Georgia Kaolin. The kaolinite, reported by the supplier to have a mean particle size of 0.77 $\mu$m with >90% of the particles being smaller than 3 $\mu$m, was used as received. The $N_2$ BET surface area was 12 $m^2$/g and the cation exchange capacity was 7 mequiv./100 g.

The illite was a Fithian, Illinois illite (API standard No. 35) and was obtained from the Illinois Geological Survey. The sample particle size was reduced to less than 10 $\mu$m by grinding. The $N_2$ BET surface area was 49 $m^2$/g and the cation exchange capacity was 20 mequiv./100 g.

The chlorite used for both the adsorption and XPS studies was from Ishpeming, MI, and was obtained from Wards Natural Science Establishment. The sample particle size was reduced to less than 10 $\mu$m by grinding. The $N_2$ BET surface was 14 $m^2$/g and the cation exchange capacity was 16 mequiv./100 g.

The sample of lizardite from New Caledonia was provided by Dr. G. W. Brindley, College of Earth and Mineral Sciences, Pennsylvania State University [Sample No. 10 (National Museum, Madrid, J. L. Martin-Vivaldi)]. Pimelite was provided by Dr. J. White, Division of Mineralogy, Smithsonian Institution, U.S. National Museum (Sample No. B18020, obtained from Kosemitz near Frankenstein, Silesia, Poland). The dioptase mineral was supplied by Dr. J. R. Craig, Department of Geological Sciences, VPI & SU (Sample No. G268, Tsumeb, Africa).

### Solution measurements

Metal ion solutions of 100 ppm were prepared from the metal nitrate salts; $Ni(NO_3)_2 \cdot 6H_2O$ (Fischer, certified) and $Cu(NO_3)_2 \cdot 6H_2O$ (Fischer, certified). Sample solutions were prepared in deionized double distilled water (Barnstead still). The pH of the test solutions was adjusted to the desired value by dropwise addition of dilute NaOH (0.5%) or HCl (0.1 N).

Samples of the clays (5 g) were placed in 1-l. vessels containing a Teflon vacuum stopcock and side-addition arm. The side arm was sealed with a rubber septum and evacuated to below $10^{-4}$ torr. The vessel was then filled with argon to a pressure of 850 torr. The appropriate volume of the argon-saturated solution was added, the system purged with argon to remove any trapped air, and the system repressurized to 850 torr with argon. Samples were placed in a constant temperature bath maintained at $25° \pm 0.5°C$. Stirring was achieved daily for 30-min periods employing submersible Teflon coated magnetic stirring plates. Aliquots were removed, using a 30 $cm^3$ syringe equipped with a 11 in. needle, by piercing the septum seal. A vessel argon pressure of 850 torr was maintained throughout the experiment. The total contact time of the adsorbent with the test solution was 7 days. Upon completion of this reaction time, the solutions were separated from the solids by centrifuging the suspensions at 10,000 rev/min in polycarbonate centrifuge tubes for 30 min at 5°C in a Lourdes centrifuge. Using Stoke's Law it was determined that this centrifugation method would collect all particles >0.1 $\mu$m.

The metal ion concentration in the aliquots was determined by atomic absorption spectroscopy using a Perkin–Elmer Model 503 spectrophotometer. A multielement hollow cathode (Fischer Scientific) lamp was used in the atomic absorption measurements. pH measurement and dissolved silica determinations were carried out as described previously (Koppelman and Dillard, 1975).

### XPS spectra

The principle of X-ray photoelectron spectroscopy (XPS) is based on measuring the kinetic energy of electrons ejected from a sample upon bombardment of the sample by monochromatic X-rays. From this experimental measurement, the binding energy of the electron can be evaluated from the expression

$$hv = BE + KE + \phi,$$

where $hv$ is the energy of the monochromatic photon beam (soft X-ray), BE is the binding energy of the electronic state of some element of interest, KE is the measured kinetic energy of the ejected electron, $\phi$ is the work function—an instrumental correction factor used to calibrate the energy scale (correction for charging, etc.).

XPS spectra were measured using a AEI ES-100 photoelectron spectrometer according to procedures given earlier (Koppelman and Dillard, 1975). It is important to recognize that XPS is essentially a surface technique. Although the X-ray beam penetrates into the bulk of the sample, the *effective* sampling depth is determined by the escape depth of the photo ejected electrons. The effective depth is probably <50 Å for these clays.

In this study, $hv$ is fixed at 1486.6 eV by using an aluminum X-ray target. Kinetic energy is measured using a hemispherical electrostatic analyzer. Since all minerals examined in this work are non-conductors, it was necessary to correct the measured core electron binding energies for charging.

To account for charging of the clay samples in the evaluation of the spectrometer work function, the binding energy of the Si $2p_{1/2,3/2}$ core level was used

Table 1. Adsorption data Ni(II) and Cu(II) on chlorite, illite and kaolinite

| Clay | Metal ion | Adsorbed [mole M(II)/g clay] ($\times 10$) | pH(initial) | pH(final) (7 days) |
|------|-----------|--------|-------------|---------------------|
| Chlorite | Ni(II) | 6.13 | 6.00 | 6.69 |
| Illite | Ni(II) | 4.09 | 6.00 | 6.25 |
| Kaolinite | Ni(II) | 0.681 | 6.00 | 5.08 |
| Chlorite | Cu(II) | 9.44 | 5.00 | 4.63 |
| Illite | Cu(II) | 2.52 | 5.00 | 4.75 |
| Kaolinite | Cu(II) | 1.26 | 5.00 | 4.86 |

as an internal standard. The absolute binding energy of the silicon level was measured in two separate experiments. In one measurement, a thin gold film was vapor deposited on to the sample surface and the binding energy of the Au $4f_{7/2}$ (BE = 83.4 eV) level used to calibrate the energy scale for the Si $2p_{1/2,3/2}$ level. In another determination, a thin film of background spectrometer carbon was allowed to build up on the sample, and the C $1s_{1/2}$ (BE = 284.6 eV) level used in the calibration of the binding energy scale. The Si $2p_{1/2,3/2}$ binding energy determined by the two methods agreed to within the experimental precision ($\pm 0.1$ eV). By using the silicon in the clay as the reference standard, alterations in the measured binding energy due to charging were minimized.

Clay minerals samples were ground in an agate mortar and pestle before placing them on the probe. The samples were prepared by dusting samples on to double stick cellophane tape or by evaporating an acetone dispersion of the sample on to a gold plated probe. The vacuum inside the instrument during the measurements was about $10^{-7}$ torr.

Table 2. Binding energies for nickel and copper

| Compound | Binding energy ($\pm 0.1$ eV) $2p_{3/2}$ level | Ref. |
|----------|-------------------------------------------------|------|
| Ni(II) adsorbed (chlorite) | 856.6 | a |
| Ni(OH)$_2$ | 856.0 | a |
| NiO | 854.4 | b |
| | 854.0 | c |
| | 853.4 | d |
| Ni$_2$O$_3$ | 855.7 | c |
| Pimelite | 857.0 | a |
| Lizardite | 857.0 | a |
| Cu(II) adsorbed (chlorite) | 935.5 | a |
| Cu(OH)$_2$ | 934.4 | a |
| CuO | 933.2 | d |
| Cu$_2$O | 933.2 | d |
| Dioptase | 935.1 | a |

(a) This work.
(b) Matienzo et al. (1973).
(c) Kim and Davis (1972/73).
(d) McIntyre and Cook (1975).

## RESULTS AND DISCUSSION

The data for the adsorption of Ni(II) and Cu(II) ions are summarized in Table 1 for the three clays. The solutions of nickel were begun at pH 6 and the copper solutions started at pH 5 for the adsorption experiments on chlorite, illite and kaolinite. These initial pH values were selected to enhance the number of negative adsorption sites on the clay and to obtain the metal ions predominantly as aquated ions. At these initial pH values Ni(II) and Cu(II) ions are present as the aquo complexes [Ni(II), 100%; Cu(II), 99.8%]. It was observed that the pH increased for Ni(II) adsorption on chlorite and illite, and decreased for Ni(II) adsorption on kaolinite and for Cu(II) adsorption on all three clays. Although the pH of the solutions changed, the values did not exceed those necessary for precipitation of the metal hydroxide in the bulk solution. The adsorption of Ni(II) and Cu(II) varies in the same manner for each metal ion on the three clays. The amount of metal ion adsorbed varied in the manner chlorite > illite > kaolinite.

The XPS spectra for chlorite samples on which nickel(II) and copper(II) had been adsorbed were measured. Chlorite was selected as the mineral for this initial study since chlorite adsorbed the greatest quantity of the metal ion. The binding energies were also measured for inorganic materials and for aluminosilicate minerals that contained nickel(II) and copper(II) in octahedral coordination sites. The binding energy results for these measurements are summarized in Table 2. The binding energy values are presented for the core $2p_{3/2}$ levels of nickel and copper. The error limit +0.1 eV represents the precision of the measurement. The accuracy is probably $\pm 0.2$ eV and is determined by the known accuracy of the standard used to calibrate the spectra.

The reported binding energies (Table 2) for similar compounds are in good agreement with those measured by others when account is taken of the difference in the standard binding energy values used to calibrate the spectra. The features of the spectra for Ni(II) (Figure 1) and for Cu(II) (Figure 2) adsorbed on chlorite reveal information on the chemical nature of the adsorbed metal ion. Each spectrum is characterized by an intense narrow main peak and a diffuse peak at higher binding energies. These dif-
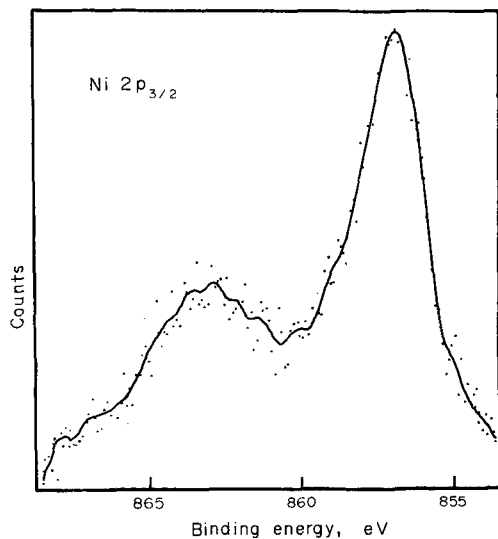
Figure 1. Ni $2p_{3/2}$ XPS spectrum of Ni(II) adsorbed on chlorite.

fuse peaks are due to satellite structure which is commonly noted for paramagnetic ions. An additional feature is noted in the copper spectrum. The shoulder at lower binding energy on the main copper $2p_{3/2}$ photopeak is due to photoreduction of the adsorbed Cu(II). This phenomenon has been observed in other copper(II) systems, (Frost *et al.*, 1972; Rosencwaig *et al.*, 1971; Wallbank *et al.*, 1973) and has been studied in sufficient detail to permit an explanation of the copper photopeak shape. The main peak and the associated satellite peak are due to copper(II). The intensity of the main peak and the associated satellite are reduced essentially to zero if the XPS measurements are carried out for a time greater than about 6 hr. After this time the shoulder peak at lower bind-
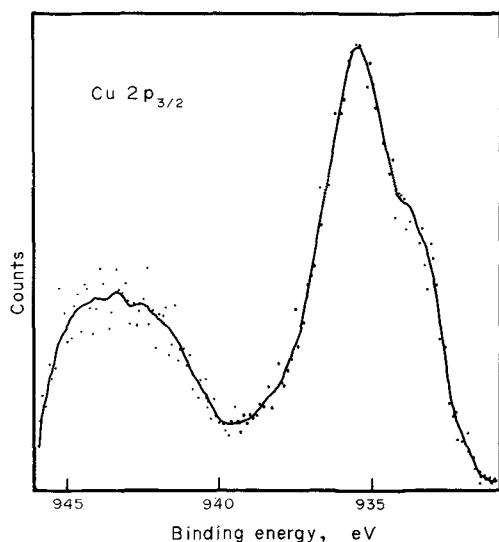


Figure 2. Cu $2p_{3/2}$ XPS spectrum of Cu(II) adsorbed on chlorite.

ing energy (Figure 2) grows to be the only peak in the spectrum and the satellite disappears. The resulting spectrum with no satellite structure and the measured binding energy are both characteristic of copper(I). For Cu(II) adsorption, the spectra measured in this study were all obtained in less than 3 hr, to minimize complications in interpretation of the spectra due to photoreduction. The spectrum in Figure 2 was obtained in less than 2 hr.

The satellite peak for nickel and the measured binding energy are both characteristic of a paramagnetic nickel(II) ion in an octahedral environment. This conclusion is supported by the data of Matienzo *et al.* (1973), who found that binding energies in the region of 856–857 eV are characteristic of octahedral Ni(II). The binding energy for adsorbed Ni(II) (Table 2) also compares favorably with that measured for 856.9 eV the hexa-aquo Ni(II) ion as the sulfate (Matienzo *et al.*, 1973). The measured Ni(II) $2p_{3/2}$ binding energy is also similar to the value (856.9 eV) reported for $Ni(NO_3)_2 \cdot 6H_2O$ that had been dried over $H_2SO_4$ for 5 days (Tolman *et al.*, 1973). It appears, therefore, that the XPS data support the notion that the Ni(II) ion is adsorbed as an aquated species, perhaps as the hexa-aquo ion. A comparison of the measured binding energy for Ni(II) in the minerals pimelite and lizardite (857.0 eV) with that for adsorbed Ni(II) (856.6 eV) reveals that the binding energy for nickel is lower than that for Ni(II) in an octahedral environment in the mineral. It is significant that the binding energy for Ni(II) in the hexa-aquo ion and in the minerals are equal, within experimental error. This result appears reasonable since the nickel is present in an octahedral environment in the hexa-aquo ion and in the mineral. On the other hand, it is noteworthy that the binding energy for adsorbed Ni(II) is less than that in the mineral. This lowering of the binding energy indicates that adsorbed nickel is in a more electron-rich environment compared to the mineral. A possible explanation of this effect is that the negative surface potential on the mineral provides an electron-rich environment and a portion of the negative charge is donated to the adsorbed aquo nickel ion. The lowering of the binding energy is about 0.4 eV for the Ni(II) ion. This lowering is less than that noted previously (Koppelman and Dillard, 1975) for the adsorption of Fe(III) and Cr(III) on chlorite, illite and kaolinite. The smaller difference observed for Ni(II) is consistent with the fact that the negative surface potential would be expected to reduce more effectively the charge on trivalent ions compared to divalent ions.

It is also important to note that the binding energy for adsorbed nickel(II) is not equal to that for $Ni(OH)_2$ or NiO. If nickel were adsorbed as the hydroxide or as the oxide, then the binding energy would be expected to be equivalent to that for $Ni(OH)_2$ or for NiO. Recent data by Tewari and Lee (1975) for adsorption of cobalt on metal oxides and by Koppelman *et al.* (1976) for the adsorption of

chromium and cobalt on clay minerals indicate that binding energies for metal hydroxides adsorbed on metal oxides or on clay mineral substrates are equal to the binding energy for the neat metal hydroxide or metal oxide. This data indicates that XPS binding energy data may be used as an aid in identifying the chemical nature of materials adsorbed on substrates.

Examination of the XPS binding energy data for copper adsorbed on chlorite reveals that the situation is unlike that for nickel. The measured binding energies for the neat copper oxides and hydroxide are in agreement with the values published by other workers when differences in the binding energy values for standards are taken into account. The significant result of the binding energy measurements is that the binding energy for adsorbed copper ion is *greater* than that for copper in the reference mineral, dioptase. This is in contrast to the observed *lowering* of the binding energy for adsorbed metal ions compared to a reference mineral (Koppelman and Dillard, 1975). A comparison of the binding energy values of adsorbed Cu(II) with those for $Cu_2O$, CuO, and $Cu(OH)_2$ indicate that the adsorbed copper is not a copper(I) oxide, nor is it cupric oxide or hydroxide. The presence of copper(I) can be eliminated in another way since the satellite structure exhibited in Figure 2 is not characteristic of copper(I). This increase in the binding energy of adsorbed Cu(II) relative to Cu(II) in dioptase and to the Cu(II) oxide and hydroxide indicates that the electron density at the adsorbed site is of lower magnitude. A possible reason for this could be that the copper species adsorbed is $Cu(OH)^+$; not the aquo ion. Substitution of an $OH^-$ group for coordinated water would remove electron density from copper leading to a higher copper $2p_{3/2}$ binding energy. It should be noted that the final pH of the Cu(II) chlorite solution was lower than the initial pH value. This change could result from replacement of coordinated water $OH^-$ which would decrease the final solution pH.

The results reported here provide support for the recent suggestions (Farrah and Pickering, 1976a,b) regarding the chemical nature of adsorbed Cu(II). Polynuclear hydroxy-bridged copper(II) species are believed to be the predominant adsorbed species on kaolinite, illite and montmorillonite. The binding energies for Cu(II) adsorbed on these minerals have not been reported in this study, but based on a comparison of the binding energies for Fe(III) and Cr(III) on kaolinite, illite and chlorite (Koppelman and Dillard, 1975), it is likely that the binding energies for a particular adsorbed metal ion will be similar on different clay minerals. Although it was not possible to measure the binding energies for neat polymeric copper hydroxy species, it is clear from the XPS data that copper is not adsorbed as CuO or as $Cu(OH)_2$.

## CONCLUSIONS

Core binding energy values for nickel(II) and copper(II) adsorbed on chlorite have been measured.

Comparison of these data with binding energies measured for nickel- and copper-containing compounds and reference minerals indicates that nickel is probably adsorbed as the aquo ion while copper may be adsorbed as $Cu(OH)^+$.

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