

## ON THE MECHANISM OF THE ADSORPTION OF TRACE COPPER BY BENTONITE

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**Abstract**—The adsorption of trace quantities of Cu ( $3.89 \times 10^{-6}$  to  $3.00 \times 10^{-4}$  M) by a bentonite clay from calcium acetate solution was studied over the range of pH 4.27–5.87. The data were fitted to an existing adsorption equation and the 'best' values of the adsorption parameters were calculated. The proton, cupric ion and mono (hydroxy) cupric complex were found to be the adsorbed species. The adsorption sites are of two types. It has been postulated that the majority of sites are lattice hydroxyl groups located at crystal defects and edges. The remainder arise from organic matter adsorbed by the clay and are the more important in the adsorption of Cu at very low metal concentration and at pH < 5.4. The implication of the results on the potential use of bentonite clay to remove trace amounts of Cu from mine waste waters is considered briefly.

### INTRODUCTION

STEGER (1973) has recently suggested the use of bentonite clay to reduce the concentration of undesirable trace metals such as Cu and Zn in mine waste water. The effectiveness of this method, however, decreases as the pH of the waste water drops below 5. Therefore, it was thought worthwhile to increase our understanding of the mechanisms of this adsorption process by evaluating quantitatively the effect of pH on the adsorption by bentonite of metals such as Cu.

Although bentonite has exchangeable interlayer cations (Grim, 1953), it can also concurrently adsorb trace quantities of metal; e.g. Cu (Heydemann, 1959). DeMumbrum and Jackson (1956) studied the additional adsorption of Cu by a Ca-montmorillonite and concluded that the increment in exchange capacity is specific to a cation such as Cu and is due to the dissociation of hydroxyl groups in the octahedral aluminate layer. The extent of Cu adsorption found by DeMumbrum and Jackson (1956), however, was 1–2 orders of magnitude higher than that in the present study. It cannot, therefore, be assumed that the proposed mechanism of hydroxyl dissociation is responsible, *in toto*, for the adsorption of Cu at the true trace levels of concentrations used herein.

The adsorption of Cu can occur only at structural hydroxyls which are accessible to the metal bearing solution. Hydroxyls located at edges or crystal defects are easily accessible but comprise only a small fraction of total structural hydroxyls. For the majority, it can be postulated that access is provided through silica net openings. However, since the entrance of the metal into the lattice would require the complete dehydration of the metal, access to all structural hydroxyls must be considered to be highly improbable because of the higher energy requirements in aqueous medium.†

The presence of organic matter could be of importance in the adsorption of trace quantities of Cu by bentonite. Indeed, organic adsorption sites (e.g. phenol or carboxylic acid groups) would also exhibit a pH dependence.

The extent of adsorption of trace Cu increases with an increase in Cu concentration and with a rise in pH, due to the dissociation of the adsorption sites, and/or the formation of  $\text{Cu}(\text{OH})^+$  which, because of its single charge, is adsorbed to a greater extent than is  $\text{Cu}^{2+}$  (Bower and Truog, 1940). This latter observation may also be important for other singly-charged Cu complexes and, in particular, for  $\text{Cu}(\text{Ac})^+$ , the mono (acetato) Cu(II) complex, which is the predominant Cu species in the calcium acetate solution.

To date, few data have been obtained in a systematic fashion to inter-relate quantitatively the effects of both copper concentration and pH on the adsorption by bentonite of trace quantities of copper. The available data have been presented in the form of either the Freundlich (Heydemann, 1959) and/or Langmuir (De

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† Indeed, one referee has pointed out that he has infra-red evidence that the structural hydroxyls are unperturbed in an air-dried Cu-montmorillonite.

and Prasad, 1962) adsorption isotherms. The values of the constants in these isotherms vary with the pH value at which the adsorption of Cu occurs.

For the adsorption of small quantities of radioactive species by zeolites, Boyd *et al.* (1947) derived general equations by formal analogy with the Langmuir adsorption equation. For the adsorption of a cation,  $M_i$ , from a mixture of  $n$  singly-charged cations in solution, the following equation may be written

$$\left(\frac{x}{m}\right)_{M_i} = \frac{sb_i[M_i]}{1 + \sum_{j=1}^n b_j[M_j]} \quad (1)$$

where  $(x/m)_{M_i}$  = amount of  $M_i$  in mg of clay,

$[M_j]$  = concentration (or activity) of cation,  $M_j$ ,

$s$  = constant identified as the total exchange capacity, and

$b_j$  = constant related to the energy of adsorption of  $M_j$ .

The exchange adsorption of two cations of unequal charge,  $M_1^{r+}$  and  $M_2^{p+}$ , is governed by the equation

$$\left(\frac{x}{m}\right)_{M_1^{r+}} = \frac{sb_1[M_1^{r+}]^r}{1 + b_1[M_1^{r+}]^r + b_2[M_2^{p+}]^p} \quad (2)$$

Because of the complexity of the mechanism of the adsorption of trace amounts of Cu by bentonite, it was felt that the application of the modified forms of the Boyd equation to the Cu adsorption data would be the most convenient (and effective) approach to obtain a better comprehension of the mechanism.

## EXPERIMENTAL

The bentonite clay was obtained from Fisher Scientific Company. X-ray diffraction analysis of the sample indicated the presence of a trace of feldspar. The  $<2 \mu\text{m}$  fraction of the bentonite was obtained by gravity sedimentation, treated three times with 0.5 N calcium acetate and washed three times with de-ionized water. The removal of traces of calcium acetate is not necessary. The treated fraction was then dried at  $60^\circ\text{C}$  for 48 hr and the aggregated bentonite ground to  $-60$  mesh. X-ray diffraction analysis showed no feldspar to be present. The clay was found to contain 0.07 per cent C by the combustion method. This carbon was assumed to be organic matter. Hereafter, the terms 'bentonite' and 'clay' will refer to this  $<2 \mu\text{m}$  fraction.

\* It must be noted that  $\text{Cu}(\text{Ac})^+$  and  $\text{Cu}(\text{Ac})_2$  are probably partially hydrated but this has been omitted for simplicity.

A stock suspension of bentonite was prepared by diluting 10.00 g of clay to 2 l. with de-ionized water. This material was stored, with occasional agitation, for 30 days in order to allow the 'coarse'  $-60$  mesh aggregates to be broken down by the water.

The adsorption of Cu was studied as follows. A 25.00 ml aliquot of the stock suspension of clay, a 25.00 ml aliquot of a stock solution of calcium acetate and a 5.00 ml aliquot of a solution of suitable Cu and  $\text{HNO}_3$  concentrations were shaken together for 18 hr. In this manner, the analytical Cu concentration,  $T_{\text{Cu}}$ , and the pH of the mixtures were varied from  $3.89 \times 10^{-6}$  to  $3.00 \times 10^{-4}$  M and from 4.27 to 5.89 respectively. The concentration of calcium acetate was  $2.72 \times 10^{-2}$  M in all experiments. The clay was allowed to settle for 15 min and the clear supernatant liquid was then centrifuged to remove the last vestiges of clay. By this procedure, any effect of heating caused by centrifugation on the equilibrium was eliminated. The residual Cu concentration and pH of the supernatant liquid were determined as below.

For those experiments in which  $T_{\text{Cu}} > 1.53 \times 10^{-5}$  M, the residual Cu concentration was determined by atomic-absorption. For those samples in which  $T_{\text{Cu}} \leq 1.53 \times 10^{-5}$  M, the bathocuproine method of Penner and Inman (1963) was used.

The pH of the supernatant liquid was measured with an Orion Model 801 pH-meter and Corning 476022 glass electrode.

The results of the adsorption experiments are given in Table 1.  $T_{\text{Cu}}$  is, of course, given in moles/l. CuZ, the amount of Cu adsorbed by the clay, is given in equivalents/2.27 g clay. The unit of 2.27 g clay was chosen because this is the weight of clay in 1 l. of mixture (i.e. clay suspension, plus calcium acetate solution and copper solution). This unit is very convenient in the calculations which follow. Each experimental result in Table 1 is the average of a minimum of three determinations.

All calculations were performed with the help of a CDC 6400 computer using programs written in this laboratory.

For two samples in which maximum adsorption of Cu was observed, the supernatant liquid was analyzed for Cr, Fe, Co, Ni and Zn but none was detected in either trial. It is apparent, therefore, that the adsorption of Cu does not occur by exchange with other trace metals previously adsorbed on the clay.

## CALCULATIONS

### Concentration of Cu species

In acetate solution, Cu is present as  $\text{Cu}(\text{H}_2\text{O})_n^{2+}$ ,  $n = 4$  or  $6$ ,  $\text{Cu}(\text{Ac})^+$  and  $\text{Cu}(\text{Ac})_2^*$  where Ac repre-

Table 1. Copper adsorption data: (amount of copper adsorbed at indicated pH)

$T_{Cu}$ ( $10^{-5}$ M)	CuZ ( $10^{-5}$ equiv./2.27 g clay)				
	5.87	5.62	5.40	5.11	4.27
0.389			0.356	0.353	0.283
0.630	0.597	0.595	0.562	0.534	0.409
1.23	1.08	0.996	0.885	0.852	0.708
1.53	1.19	1.11	1.01	0.949	0.732
3.62	1.58	1.32	1.17	1.09	
7.23	2.13	1.83	1.67	1.43	
10.8	2.38	2.06	1.84	1.62	
15.1	2.60	2.28	2.00	1.73	
30.0	2.98	2.60	2.28	1.84	

sents acetate. The concentration of  $Cu(OH)_2$  is negligible in this system at  $pH < 6$  and the formation of Cu-acetate dimers need not be considered at the low Cu concentrations used. The concentration of all complexes can be calculated as follows

$$[Cu(OH)] = k_{OH}^{Cu}[Cu][OH] \quad (3)$$

$$[Cu(Ac)] = k_{Ac}^{Cu}[Cu][Ac] \quad (4)$$

$$[Cu(Ac)_2] = \beta_{2,Ac}^{Cu}[Cu][Ac]^2 \quad (5)$$

$$[Ca(OH)] = k_{OH}^{Ca}[Ca][OH] \quad (6)$$

$$[Ca(Ac)] = k_{Ac}^{Ca}[Ca][Ac] \quad (7)$$

$$[HAc] = k_{Ac}^H[H][Ac] \quad (8)$$

The charges of the species have been omitted for clarity. The values of the formation constants are available in the literature (Martell and Sillen, 1964). The value of  $[OH]$  is, of course, calculated by

$$[OH] = k_w/[H] \quad (9)$$

where a value of  $10^{-14}$  is assumed for  $k_w$ . The values of  $[Cu]$ ,  $[Ca]$  and  $[Ac]$  are calculated as below.

$$T_{Cu} = [Cu] + [Cu(OH)] + [Cu(Ac)] + [Cu(Ac)_2] + CuZ \quad (10)$$

$$T_{Ca} = [Ca] + [Ca(OH)] + [Ca(Ac)] \quad (11)$$

$$T_{Ac} = [Ac] + [HAc] + [Ca(Ac)] + [Cu(Ac)] + 2[Cu(Ac)_2] \quad (12)$$

where  $T_{Cu}$ ,  $T_{Ca}$  and  $T_{Ac}$  are the analytical concentrations of Cu, Ca and acetate respectively. For calcium acetate,  $T_{Ac} = 2T_{Ca}$ . It is assumed that the amounts of adsorbed  $Ac^-$  and  $Cu(Ac)^+$  are negligible compared to the other terms on the right-hand side of equation (12). At  $T_{Ac} = 5.44 \times 10^{-2}$  M, the maximum

value of adsorbed  $Ac^-$  is  $2 \times 10^{-6}$  equiv./2.27 g clay (Bingham *et al.*, 1965). Furthermore, even if it is assumed that all of the Cu adsorbed by the clay is in the  $Cu(Ac)^+$  form, the omission of these two terms in equation (12) results in a maximum error of 1 per cent and greatly simplifies further calculations.

Equations (3–12) can be combined to give

$$[Cu] = \frac{T_{Cu} - CuZ}{1 + k_{OH}^{Cu}[OH] + k_{Ac}^{Cu}[Ac] + \beta_{2,Ac}^{Cu}[Ac]^2} \quad (13)$$

$$[Ca] = \frac{T_{Ca}}{1 + k_{OH}^{Ca}[OH] + k_{Ac}^{Ca}[Ac]} \quad (14)$$

$$[Ac] = \frac{T_{Ac} - 2(T_{Cu} - [Cu]) - CuZ - [Cu(OH)]}{1 + k_{Ac}^H[H] + k_{Ac}^{Ca}[Ca] - k_{Ac}^{Cu}[Cu]} \quad (15)$$

The values of  $[Cu]^*$ ,  $[Ca]$  and  $[Ac]$  for each data point are obtained by an iterative procedure. A value of  $[Ac] = 0.8 T_{Ac}$  is arbitrarily chosen and the corresponding values of  $[Cu]$  and  $[Ca]$  are calculated using equations (13 and 14). Then, using these values of  $[Cu]$  and  $[Ca]$ , a new value of  $[Ac]$  is calculated using equation (15). This procedure is repeated until there is no further significant change in  $[Cu]$ ,  $[Ca]$  and  $[Ac]$ , which usually requires four iterations.

It was found that, for the range of  $T_{Cu}$  studied, the concentration of each Cu species is nearly a constant fraction of the concentration of residual Cu,  $Cu_r$ . The values for each Cu species are given in Table 2.

There may be some question concerning the use of the pH of the bulk solution phase in the equilibrium calculations because, in fact, the acidity of the clay surface is greater (and, therefore, the pH is lower) than that of the bulk solution (Bailey and White, 1970). This difference in acidity is very important in the adsorption of basic compounds. For acidic compounds, (e.g. acetic acid), however, it is the pH of the bulk solution (Frissel, 1961) that determines when positive adsorption occurs.

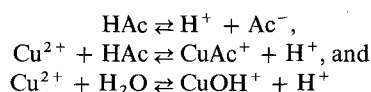
\* Again, the degree of hydration of the Cu ion has been omitted for simplicity.

Table 2. Concentration of Cu species in solution: (expressed as a percentage of total Cu)

pH	Cu(H <sub>2</sub> O) <sup>2+</sup>	Concentration of Cu species (%)		
		Cu(OH) <sup>+</sup>	Cu(Ac) <sup>+</sup>	Cu(Ac) <sub>2</sub>
5.87	21.69 (0.06)*	3.60 (0.01)	67.96 (0.04)	6.74 (0.03)
5.62	22.80 (0.07)	2.126 (0.003)	68.55 (0.05)	6.52 (0.03)
5.40	24.10 (0.08)	1.356 (0.004)	68.40 (0.05)	6.14 (0.03)
5.11	26.82 (0.08)	0.774 (0.003)	67.10 (0.06)	5.31 (0.03)
4.27	45.01 (0.01)	0.192 (0.002)	52.85 (0.03)	1.96 (0.01)

\* Numbers in brackets represent the deviation from mean for all Cu concentrations.

The formation of Cu complex species is, of course, dependent on the pH of the bulk solution; e.g.



It is reasonable to assume that the adsorption of such species would also be determined by the pH of the bulk solution.

#### Adsorption parameters

Two assumptions must be made in order to modify the Boyd equations for the adsorption of copper by bentonite. First, only the adsorption of protons and charged Cu complexes need be considered. Calcium species do not adsorb at the exchange sites under consideration (DeMumbrum and Jackson, 1956). Second, adsorbed acetate either does not affect the adsorption of Cu or, if it does, the effect remains constant over the pH range studied. This latter alternative is quite reasonable since the extent of acetate adsorption is constant over the pH range 2–6 (Bingham *et al.*, 1965). A constant influence on the adsorption of Cu by adsorbed acetate becomes a systematic error in the data and will be reflected in the value of  $s$ , the total exchange capacity.

By combining equations (1 and 2) and modifying the component terms to represent all active species, the equation describing the adsorption of Cu<sup>2+</sup> is:

$$\left(\frac{x}{m}\right)_{\text{Cu}^{2+}} = \frac{sb_1[\text{Cu}]}{1 + f(b, \text{Cu}, \text{H})} \quad (16)$$

where  $f(b, \text{Cu}, \text{H}) = b_1[\text{Cu}] + b_2[\text{Cu(OH)}]^2 + b_3[\text{Cu(Ac)}]^2 + b_4[\text{H}]^2$ . For singly charged Cu complex species (e.g., Cu(OH)<sup>+</sup>) the equation becomes

$$\left(\frac{x}{m}\right)_{\text{Cu(OH)}^+} = \frac{sb_2[\text{Cu(OH)}]^2}{1 + f(b, \text{Cu}, \text{H})} \quad (17)$$

The experimental quantity, CuZ, gives no information concerning the nature of adsorbed copper. CuZ is,

in fact,  $[(\text{Cu}^{2+})\text{Z} + \text{Cu(OH)}\text{Z} + \text{Cu(Ac)}\text{Z}]$ . The equation, therefore, most pertinent to the quantity, CuZ, is

$$\text{CuZ} = \frac{s(b_1[\text{Cu}] + b_2[\text{Cu(OH)}]^2 + b_3[\text{Cu(Ac)}]^2)}{1 + f(b, \text{Cu}, \text{H})} \quad (18)$$

It must be noted that, in fact, there may be more than one type of site. The adsorption of Cu can occur at structural hydroxyls, the two types of which have been already mentioned. The participation of organic matter cannot be ruled out. It is to be expected that the values of the parameters,  $s$  and  $b_i$ , would differ for each type of site. A more appropriate equation describing the adsorption of Cu is

$$\text{CuZ} = \sum_{j=1}^n \frac{s_j(b_{j,1}[\text{Cu}] + b_{j,2}[\text{Cu(OH)}]^2 + b_{j,3}[\text{Cu(Ac)}]^2)}{1 + f_j(b, \text{Cu}, \text{H})} \quad (19)$$

where  $n$  = number of types of sites.

A double weighting of the data was necessary to give satisfactory results in the calculation of the adsorption parameters. First, the reliability of Cu<sub>s</sub>, the residual total Cu concentration, is not the same for all data points. Cu<sub>s</sub> is the average of at least three determinations and, thus, the reliability of Cu<sub>s</sub> is determined by the precision of the mean.

The use of calibration curves in the methods employed to measure Cu<sub>s</sub> in this study, however, can impose errors that have the effect on lowering the attainable precision. For those values of Cu<sub>s</sub> determined by atomic adsorption, a precision of  $\pm 3 \times 10^{-7}$  M for  $T_{\text{Cu}} \leq 1.08 \times 10^{-4}$  M was estimated. For  $T_{\text{Cu}} = 1.51 \times 10^{-4}$  M and  $3.00 \times 10^{-4}$  M, the precision was estimated to be  $\pm 6 \times 10^{-7}$  M and  $\pm 9 \times 10^{-7}$  M respectively, because either sample dilution or scale compression of the instrument was necessary to determine Cu<sub>s</sub>. For those values of Cu<sub>s</sub> determined by the bathocuproine method, the precision was estimated to be  $\pm 8 \times 10^{-8}$  M.

To take into account the reliability of the data, a weighting factor was calculated by

$$w_r = \left[ 1 - \left( \frac{\text{Precision}}{\text{Cu}_s} \right) \right]^2 \quad (20)$$

Since there is approximately a thousand-fold change in  $\text{Cu}_s$  but only a ten-fold change in the precision of the data, equation (20) in effect gives a greater weighting to data at high  $T_{\text{Cu}}$ ; i.e. high  $\text{CuZ}$ .

The second weighting of the data is a consequence of the variation in the sensitivity of  $\text{CuZ}$  to changes in  $\text{Cu}_s$ . As  $T_{\text{Cu}}$  increases,  $\text{CuZ}$  also increases but in a non-linear way. The result is that  $\text{CuZ}$  becomes more and more insensitive to changes in  $T_{\text{Cu}}$  and, therefore, less and less useful in the selection of the most satisfactory mathematical model. The preferential use of  $\text{CuZ}$  data at low  $T_{\text{Cu}}$  is required. This was done by weighting the data according to

$$w_s = 1 - \frac{\text{Cu}_s}{T_{\text{Cu}}} \quad (21)$$

The total weight given to each data point, therefore, is

$$w = w_r \cdot w_s \quad (22)$$

It must be stated that several other forms of  $w_r$  and  $w_s$  were used in initial calculations. The expressions given above, however, were found to be the most effective in the solution for the adsorption parameters in equation (19).

Since both  $s_j$  and  $b_{j,k}$  are calculated in like manner, they can be represented by  $Q_l$ , where  $l = 1, 5 \text{ N}$ , and the right-hand side of equation (19) can be represented by  $F(Q_1, Q_2, \dots, Q_{5\text{N}}, \text{Cu}, \text{H})$  or simply  $F$  for simplicity in expressions used below. Taylor series expansion of equation (19) about  $Q_l^0$ , the estimated values of  $Q_l$ , gives

$$\text{CuZ} - F_1^0 - \sum_{i=1}^{5\text{N}} \left( \frac{\partial F_i}{\partial Q_i} \right) \delta Q_i = 0 + \text{residual} \quad (23)$$

for each data point. Herein,  $F_1^0 = F_i(Q_1^0, Q_2^0, \dots, Q_{5\text{N}}^0, \text{Cu}, \text{H})$  and  $\delta Q_i$  represents the shift in value to be applied to  $Q_i^0$ . The partial derivatives are evaluated numerically (Draper and Smith, 1966) by

$$\left( \frac{\partial F_i}{\partial Q_i} \right) \delta Q_i = F_i(Q_1^0, Q_2^0, \dots, Q_i^0 + \delta Q_i, \dots, Q_{5\text{N}}^0, \text{Cu}, \text{H}) - F_i^0 \quad (24)$$

For any set of values of  $Q_i^0$  and  $\delta Q_i$ , the sum of the squared residuals for  $n$  data point is

$$U = \sum_{i=1}^n w_i \left[ \text{CuZ}_i - F_i^0 - \sum_{i=1}^{5\text{N}} \left( \frac{\partial F_i}{\partial Q_i} \right) \delta Q_i \right]^2 \quad (25)$$

where  $w_i$  is the weight to be assigned to each data point. Those values of  $\delta Q_i$  which minimize  $U$  must be determined. The 'best' values for the adsorption parameters,  $Q_l$ , will then be given by  $Q_l^0 + \delta Q_l$ .

The mode of calculation of the 'best' values of  $Q_l$  is closely related to an existing relaxation technique (Watkins and Jones, 1961). Estimates of all  $Q_l$  (i.e.  $Q_l^0$ ) were made. A shift,  $\delta Q_1$ , was applied to  $Q_1^0$  until  $U$  was minimized. Herein, all  $\delta Q_l, l = 2, 5 \text{ N}$ , were set at zero. The newly calculated value of  $Q_1$  (i.e.  $Q_1^0 + \delta Q_1$ ) was retained in subsequent calculations. A shift,  $\delta Q_2$ , was applied to  $Q_2^0$  and  $U$  was again minimized. The new value for  $Q_2$  (i.e.  $Q_2^0 + \delta Q_2$ ) was retained. Herein, all  $\delta Q_l, l = 2, 5 \text{ N}$  were set at zero. This procedure was reiterated until a new and "better" value was obtained for each  $Q_l$ . Using these new values of  $Q_l$  as estimates, the scheme of calculation was repeated until a set of values of  $Q_l$  was found that did indeed minimize  $U$ . This method generates a hyperplane defined by  $Q_l^0$  and  $\delta Q_l, l = 1, 5 \text{ N}$ , and  $U$ . Since the generation of the hyperplane depends on  $Q_l^0$ , it is possible that 'best' values of  $Q_l$  of questionable reliability can be obtained at times. This behavior has also been detected in more rigorous methods for solving mathematical models that are non-linear in the desired constants (Rosotti *et al.*, 1971). It is important, therefore, that 'best' values of  $Q_l$  be calculated using several values of  $Q_l^0$ . The true 'best' values of  $Q_l$  are those for which the hyperplanes are co-incident to give a minimal value of  $U$ .

### RESULTS AND DISCUSSION

The 'best' values of the adsorption parameters are summarized in Table 3. The mathematical model which describes the adsorption of trace amounts of copper most satisfactorily, therefore, is

$$\text{CuZ} = \frac{s_1 b_{1,1} [\text{Cu}]}{1 + b_{1,1} [\text{Cu}] + b_{1,4} [\text{H}]^2} + \frac{s_2 \{ b_{2,1} [\text{Cu}] + b_{2,2} [(\text{Cu}(\text{OH}))^2] \}}{1 + b_{2,1} [\text{Cu}] + b_{2,2} [\text{Cu}(\text{OH})]^2 + b_{2,4} [\text{H}]^2} \quad (26)$$

The calculated values of  $\text{CuZ}$  are plotted against the experimental values in Fig. 1. The observed relationship is a straight line of:

$$\begin{aligned} \text{slope} &= 0.999 \\ \sigma^2 \text{ slope} &= 0.024 \\ \text{intercept} &= 0.003 \\ \sigma^2 (\text{intercept}) &= 0.039 \\ r (\text{correlation coefficient}) &= 0.981 \end{aligned}$$

It must be pointed out that  $b_{j,i}$  are conditional constants since the concentration and not the activity of

Table 3. Value of adsorption parameters

$Q_i$	Value of $Q_i$	Log $Q_i$
$s_1$	$3.71 \times 10^{-5*}$	-4.431
$s_2$	$9.84 \times 10^{-6*}$	-5.007
$s_j, j \geq 3$	0.0	
$b_{1,1}$	$2.87 \times 10^{4\dagger}$	4.458
$b_{1,2}$	0.0	
$b_{1,3}$	0.0	
$b_{1,4}$	$6.52 \times 10^{10\dagger}$	10.814
$b_{2,1}$	$4.80 \times 10^{6\dagger}$	6.681
$b_{2,2}$	$1.03 \times 10^{14\dagger}$	14.013
$b_{2,3}$	0.0	
$b_{2,4}$	$1.87 \times 10^9\dagger$	9.271

\* equiv/2.27 g clay.

† l/equiv

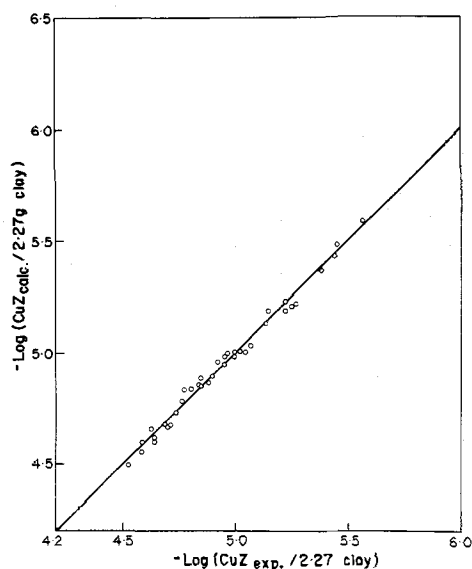
‡ (l/equiv)<sup>2</sup>.

Fig. 1. Plot of values of  $-\text{Log CuZ}_{\text{calc.}}$  calculated using 'best' values of the adsorption parameters against  $-\text{Log CuZ}_{\text{exp.}}$ , the experimentally determined values.

the adsorbable species was used in calculations. The values of these constants, shown in Table 3, therefore are valid only for the experimental conditions used in this study. Nevertheless, the values of  $b_{j,i}$  are very useful for a clarification of the mechanism of the adsorption of Cu.

One surprising feature of the results is that  $\text{Cu}(\text{Ac})^+$  is not adsorbed, at least to a detectable extent, by the clay. Acetate, therefore, acts essentially as a complexing agent to reduce the concentration of adsorbable Cu species, such that the saturation of the clay by Cu

occurs at a higher pH than in the absence of acetate. This permits the study of the effect of a change in pH on the adsorption of Cu where  $[\text{H}^+]$  and the concentration of adsorbable Cu species are similar, even for low values of  $T_{\text{Cu}}$ . Experimental data for regions where a change in pH causes a comparable change in  $[\text{Cu}^{2+}]$  or  $[\text{Cu}(\text{OH})^+]$  are very useful in defining the correct mathematical model and in the calculation of the adsorption parameters therein.

The value of  $b_{1,2}$  indicates that the adsorption of  $\text{Cu}(\text{OH})^+$  need not be considered at  $s_1$ . Therefore, either  $\text{Cu}(\text{OH})^+$  is indeed not adsorbed or the adsorption could not be detected for the range in pH and  $T_{\text{Cu}}$  used in this study. The latter possibility would be a consequence of the relatively small values of  $\text{Cu}(\text{OH})^+$  and a value of  $b_{1,2}$  sufficiently low such that

$$b_{1,2}[\text{Cu}(\text{OH})^+]^2 \ll b_{1,1}[\text{Cu}]. \quad (27)$$

If this were the case, it can be calculated that  $\log b_{1,2}$  must be less than 7.25.

An insight into the nature of  $s_1$  and  $s_2$  can be obtained by consideration of the relative values of  $b_{j,1}$ . The parameters,  $b_{j,1}$ ,  $b_{j,2}^{1/2}$  and  $b_{j,4}^{1/2}$ , are related to the free energy of adsorption of the cations,  $\text{Cu}^{2+}$ ,  $\text{Cu}(\text{OH})^+$  and  $\text{H}^+$ , respectively (Boyd *et al.*, 1947). If, however,  $s_j$  is a dissociable OH group, the adsorption of the cations leads to a true chemical complex. The parameters,  $b_{j,1}$ ,  $b_{j,2}^{1/2}$  and  $b_{j,4}^{1/2}$ , therefore, are, in effect, formation (or stability) constants. The value of these constants is determined to a large extent by the strength of the bond between the cation and the O-donor atom.

It is reasonable to assume that both  $s_1$  and  $s_2$  are OH groups, either the hydroxyls of the aluminate layer or carboxylic and phenolic groups of organic matter. The value of  $b_{1,4}^{1/2}$  and  $b_{2,4}^{1/2}$  is a measure of the basicity of O<sub>2</sub> atoms. Since  $b_{1,4}^{1/2} > b_{2,4}^{1/2}$ , the oxygen atoms of  $s_1$  are more basic than those of  $s_2$ . The relationship between donor atoms basicity and complex stability (Martell and Calvin, 1952) requires that  $b_{1,1} > b_{2,1}$  and  $b_{1,2}^{1/2} > b_{2,2}^{1/2}$ . This relationship is not observed. It can be concluded, therefore, that the difference in the nature of  $s_1$  and  $s_2$  cannot be attributed to basicity alone. In view of the available alternatives, it would seem most realistic to conclude that one of  $s_1$  and  $s_2$  be assigned to the edge and crystal defect hydroxyls of the octahedral aluminate layer and the other to organic matter adsorbed on the clay particles.

It has been concluded from the following evidence that  $s_2$  represents the adsorbed organic matter. First, fulvic acid adsorbed by montmorillonite has an apparent  $\text{pK}_a$  of 4.5 (Schnitzer and Khan, 1972). It is highly



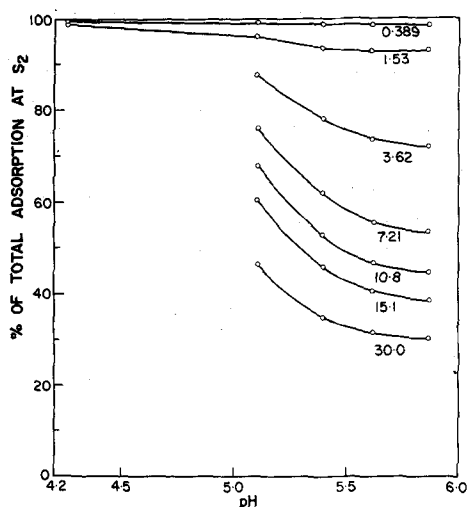


Fig. 2. Relationship of the extent of adsorption of copper at site  $s_2$  as a percentage of total adsorption and the pH of the solution. The numbers are the values of  $T_{Cu}$  ( $10^{-5}$  M) for each plot.

probable that the pK of the same functional groups in other organic matter will be very close to 4.5 also. The value of pK of  $s_2$ , given by  $1/2 \log b_{2,4}$ , is 4.64 whereas that of  $s_1$  is 5.41. The greater affinity for Cu of  $s_2$  compared to  $s_1$  can be rationalized in terms of chelate rather than complex formation. Chelation is the predominant reaction in Cu-organic matter systems (Schnitzer and Khan, 1972). Chelate formation between Cu and lattice hydroxyls must be highly improbable because of structural restrictions. Third, the magnitudes of  $s_1$  and  $s_2$  suggest that  $s_2$  is organic in nature. It can be calculated (using the weight of clay per l. of suspension, carbon content and the magnitudes of  $s_1$  and  $s_2$ ) that, at saturation, the C:Cu ratio is  $\sim 4:1$  at  $s_1$  and  $\sim 16:1$  at  $s_2$ . The ratio of  $s_1$  would seem unrealistic in comparison to known Cu-organic matter systems (Schnitzer and Khan, 1972).

The relationship between the percent of total Cu adsorbed due to  $s_2$  and pH is shown in Fig. 2 for several values of  $T_{Cu}$ . It is evident that the more important site in the adsorption of trace quantities of copper at  $pH < 5.40$  and low values of  $T_{Cu}$  is  $s_2$ . Even at  $T_{Cu} = 1.50 \times 10^{-5}$  M (0.972 ppm  $Cu^{2+}$ ), adsorption of the metal occurs predominantly at  $s_2$  over the pH range studied herein. This value of  $T_{Cu}$  is, in general, much larger than that found in mine waste waters. It is immediately apparent that the effectiveness of bentonite for adsorption of copper from mine water is dependent on the magnitude of  $s_2$ . Therefore, if  $s_2$  does represent organic matter adsorbed by the clay, it is suggested that bentonite as heavily loaded with

organic matter as possible be used to adsorb trace quantities of Cu and other undesirable metals such as  $Zn^{2+}$  and  $Pb^{2+}$  from mine waste waters.

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**Résumé**—L'adsorption de traces de cuivre ( $3,89 \times 10^{-6}$  à  $3,00 \times 10^{-4}$  M) par une bentonite, à partir de solutions d'acétate de calcium a été étudiée dans un domaine de pH allant de 4,27 à 5,87. Les données ont été ajustées à une équation d'adsorption déjà connue et les "meilleures" valeurs des paramètres de l'adsorption ont été calculées. Le proton, l'ion cuivrique et le complexe mono (hydroxy) cuprique ont été reconnus comme étant les espèces adsorbées. Les sites d'adsorption sont de deux types. On a fait l'hypothèse que la plus grande partie des sites est constituée par les groupes hydroxyle du réseau localisés au niveau des défauts cristallins et sur les bords. Le reste de ces sites provient de la matière organique adsorbée par l'argile; c'est la partie la plus importante dans l'adsorption du cuivre aux très basses concentrations en métal et à pH < 5,4. Les conséquences de ces résultats sur l'utilisation possible de la bentonite pour extraire les traces de cuivre présentes dans les eaux résiduelles des mines sont considérées rapidement.

**Kurzreferat**—Die Adsorption von Spuren Mengen von Kupfer ( $3,89 \times 10^{-6}$  bis  $3,00 \times 10^{-4}$  M) durch einen Bentonitton aus Calciumacetatlösung wurde in einem Bereich von pH 4,27–5,87 untersucht. Die Ergebnisse werden mit einer bestehenden Adsorptionsgleichung verglichen und die "besten" Werte für die Adsorptionsparameter berechnet. Das Proton, das zweiwertige Kupferion und ein Monohydroxokupfer-II-Komplex werden als adsorbierte Ionensorten gefunden. Die Adsorptionsplätze sind von zweierlei Art. Es wurde festgestellt, daß die Mehrheit der Plätze Gitterhydroxylgruppen sind, die an Kristalldefekten und -seitenflächen vorliegen. Die übrigen stammen von organischer Substanz, die durch den Ton adsorbiert wurde, und stellen bei sehr geringen Metallkonzentrationen und pH < 5,4 die wichtigeren Plätze für die Kupferadsorption dar. Die Bedeutung der Ergebnisse für eine mögliche Nutzung von Bentonitton zur Entfernung von Spuren Mengen von Kupfer aus Mineralwässern wird kurz erörtert.

**Резюме** — Изучалась адсорбция ничтожного количества меди ( $3,89 \times 10^{-6}$  до  $3,00 \times 10^{-4}$  M) раствором уксуснокислого кальция бентонита по диапазону pH 4,27–5,87. Данные сравнивались с существующими уравнениями адсорбции и высчитывались «лучшие» значения параметров адсорбции. Нашли, что протон, ион, содержащий двухвалентную медь и комплекс монооксида меди являлись адсорбированными веществами. Места адсорбции имеются двух типов. Построили аксиому, что большинство мест являются групповыми оксисоединениями решетки, находящимися на дефектах кристаллов и на их гранях. Остальные образуются из органического вещества адсорбируемого глиной и играют более важную роль в процессе адсорбции меди при очень невысокой концентрации металла и при pH < 5,4. В связи с результатами рассматривается потенциальная возможность использования бентонитной глины для удаления следов меди из сточных вод рудников.