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THEORY OF INTERFACIAL STEPWISE
ION/COORDINATION PARTICLE
EXCHANGE AND ITS APPLICATIONS

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China Ocean Press 1985

**INTERACTION OF TRACE METALS AND SUSPENDED
MATTER IN SEAWATER — AN ATTEMPT TO
INVESTIGATE THE REACTION MECHANISMS**

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ABSTRACT

This is the third in a series of papers on the subject of the interaction between metal ions and suspended particulate matter in seawater. In our two previous papers (Chang and Chen, 1984a and b) we described the ion exchange pH range and reaction isotherms for such interaction. We have now extended the study to include the interaction of Cu and Cd in seawater with illite, kaolinite and montmorillonite. Our results show stepwise ion exchange/precipitation isotherms, two steps in the curve for kaolinite and three steps each for the illite and montmorillonite curves. Tracer studies with radioactive ^{24}Na indicate that Cu^{2+} and Cd^{2+} in pure water first replace only the H^+ ion and then also the Na^+ ion on illite and montmorillonite. Cu^{2+} and Cd^{2+} , however, replace Na^+ at all steps for all three clays.

INTRODUCTION

Interactions between divalent trace metal ions and clays have been studied extensively, but few experiments have been performed in a seawater medium, and the reaction mechanisms have not been extensively evaluated. Krauskopf (1956) studied the adsorption percentage of thirteen trace metals (including Cu and Cd) on marine particulate material such as clays, but he did not investigate the reaction isotherms and mechanisms. Chester (1965) studied the adsorption of Zn and Co on illite in seawater and reported Langmuir-Freundlich type reaction isotherms. He found that the reaction isotherm is linear at low metal concentrations. O'Conner and Kester (1975) investigated the pH range and the influence of foreign ions on the adsorption of Cu and Co on illite, but they did not study reaction isotherms. Takematsu (1979) studied the adsorption of divalent metal ions on particles and reported Langmuir-type isotherms. Oakley et al. (1981) studied the distribution of trace metals (including Cu) in marine sediments (including montmorillonite) with similar results as found by Chester. the reaction mechanisms were usually not evaluated in these studies.

Since 1981 we have evaluated the ion exchange pH range and reaction isotherms involving Cu, Pb, Zn, Cd, metal hydroxides, illite, kaolinite, montmorillonite and organic material

based on data generated at the Marine Physical Chemistry Laboratory, Shandong College of Oceanography, People's Republic of China (Sun, 1982; Liu, 1983). These studies have been summarized in our two previous articles (Chang and Chen, 1984a, b). Stepwise ion exchange/precipitation reactions were observed for the systems involving trace metals and metal hydroxides. The interactions between trace metals and clays seemed to be also stepwise, but the evidence was inconclusive. We have since repeated the experiments with different batches of clays. Stepwise ion exchange/precipitation reactions were indeed observed for the systems involving Cu, Cd, illite, kaolinite and montmorillonite. Whether trace metals exchange with exchangeable groups on the surface or in the interlayers of the clay lattices, however, is not clear (Enderfield, 1976; Pytkowicz, 1983). Experiments designed to elucidate the reaction mechanisms of the reactions involving the trace metals, Cu, Cd, and the clays, illite, kaolinite and montmorillonite were performed at Oregon State University, USA; the preliminary results are presented here.

BACKGROUND ON REACTION MECHANISMS

Demumbrum and Jackson (1956) used infrared absorption to study the ion exchange reaction mechanisms of Cu and Zn with clays. They reported that Cu and Zn react with the hydroxyl groups on the clays. Hodgson et al. (1964) suggested that divalent heavy metal ions react with clays according to the following mechanism:



or

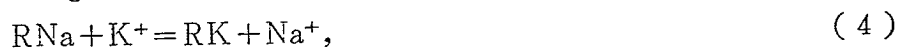


These equations indicate that the metal ions or metal hydroxide ions exchange with H^+ of the hydroxyl group on the clays.

O'Conner and Kester (1975) represented the reaction between the metals Cu and Co and illite in seawater as the exchange of Cu^{2+} (or Co^{2+}) with H^+ on the clay:



Stumm and Morgan (1981) studied the relative affinity of cations with clays and implied that Na^+ on the clays exchanges with cations in solution:



Aston (1978) used the same type of equation. These reactions, however, can not be used to explain the observed stepwise reaction isotherms. We suspected that trace metals perhaps exchange with Na^+ and/or H^+ under different conditions of the medium, and we have decided to clarify the problem by using ^{24}Na as a radiotracer. The experiments that yielded the stepwise ion exchange/precipitation reaction isotherms and mechanisms are described below.

EXPERIMENTAL PROCEDURES

1. Stepwise ion exchange reaction isotherm

The clays used in the experiments are all from China and were purified and sieved by 40–80 mesh sieves before being placed in the seawater medium. They were also equilibrated with 5% Na_2CO_3 to replace K^+ on the particles by Na^+ . The concentrations of Cu and Cd on the clays and in solution after equilibration were analyzed by atomic absorption. The experimental procedures have been described in our previous papers and elsewhere (Liu et al., 1980, 1981; Sun, 1982; Zhang et al., 1982; Liu, 1983; Chang and Chen, 1984a,b) and are not repeated here.

2. Stepwise ion exchange reaction mechanism

(a) Sodium-24 exchange reactions: $^{23}\text{NaNO}_3$ was irradiated to produce $^{24}\text{NaNO}_3$ shortly before the experiment. The $^{24}\text{NaNO}_3$ was then dissolved in distilled water and equilibrated with the clays for three hours. After equilibration, the clays were separated from solution by either filtration or centrifuge, dried at 70°C but not sieved again, and subdivided into 100 μm samples. Each clay sample and 100 ml of Cu or Cd solution of various

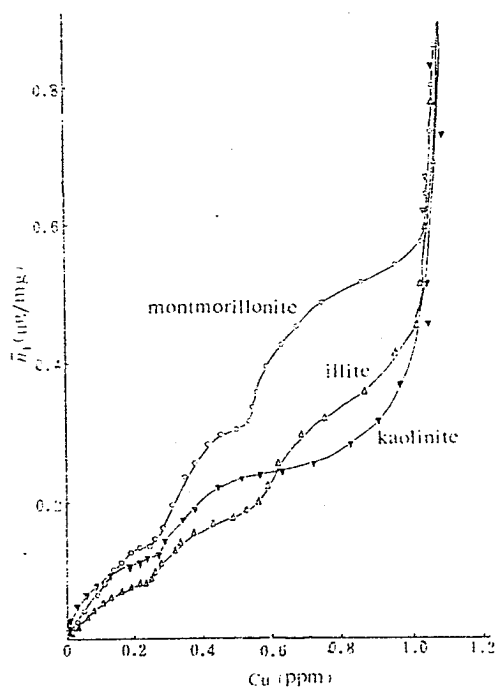


Fig. 1. Isotherms for the interactions between Cu^{2+} and montmorillonite, illite and kaolinite, respectively at $\text{pH}=7.0$. \bar{n}_1 is the amount of Cu exchanged per mg of clay. Cu is the concentration of copper in the solution at equilibrium.

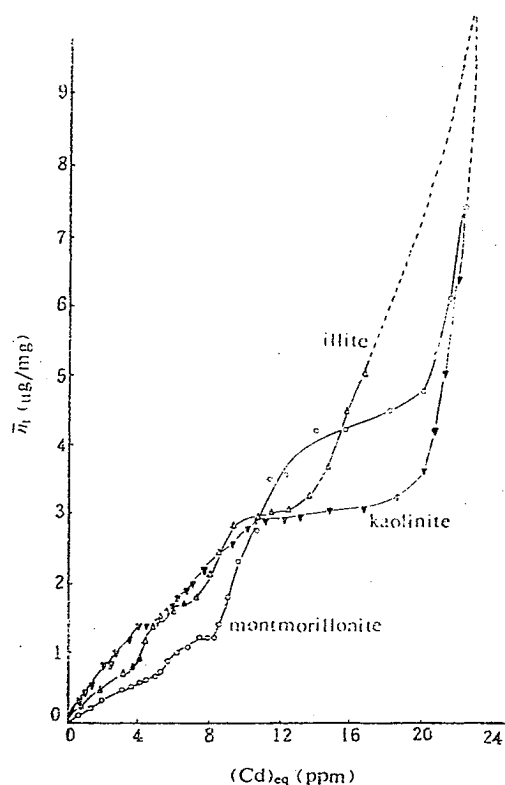


Fig. 2. Isotherms for the interactions between Cd^{2+} and montmorillonite, illite and kaolinite, respectively at $\text{pH}=9.0$. \bar{n}_1 is the amount of Cd exchanged per mg of clay. Cd is the concentration of cadmium in the solution at equilibrium.

concentrations (Puratronic, 99.999% purity) were put into a 250 ml Erlenmeyer flask without pH adjustment, shaken for two hours at 25°C and filtered. The ^{24}Na activities in the filtrate and clay were determined separately. The Cu and Cd impurities in all our solutions were less than 1 ppb and were ignored. The slight possibility of clay dissolution (Kittrick, 1979) was also ignored.

(b) Experiments involving irradiation of clays: The experimental procedure and clays used were the same as used above except the clays were irradiated to produce ^{24}Na prior to the experiments in pure water. The ^{24}Na activities in the filtrate and clay were determined after ion exchange.

(c) Experiments involving analysis of Na: The experimental procedure and clays used were the same as used above except the filtrate and clay were analyzed for Na by neutron activation after ion exchange in pure water.

RESULTS AND DISCUSSION

1. Stepwise ion exchange reaction isotherm

Figs. 1 and 2 show the isotherms for the interactions of Cu^{2+} and Cd^{2+} , respectively, with illite, kaolinite and montmorillonite in seawater. The results indicate that Cu^{2+} and Cd^{2+} undergo a two-step ion exchange reaction with kaolinite but a three-step reaction with illite and montmorillonite. We suspect that first, the hydroxyl groups on the edges of the kaolinite lattice interact with the metals; the hydroxyl groups on the sides or in the interlayers interact with metals only after the edge sites have been saturated with metals. The result is a two-step isotherm. The three steps for illite and montmorillonite may be caused by the exchange of foreign cations (such as Na^+) in the clay interlayers with Cu^{2+} and Cd^{2+} as well, forming the extra step. Kaolinite, on the other hand, does not have sufficient concentrations of foreign cations in the interlayers to form the extra step.

Figs. 1 and 2 do not provide information as to which step corresponds to hydroxyl groups exchange and which to foreign cations exchange. The tracer study discussed below was an attempt to provide some clues.

2. Tracer studies:

(1) *Mobility of Na^+ in the clays*

We have determined the amount of Na and K in the clays by neutron activation analysis. Na and K are found to constitute 4.25% and 1.25%, respectively of illite, 0.183% and 0.122%, respectively of kaolinite, and 3.29% and 0.31%, respectively, of montmorillonite. Filtration blank studies indicate that usually less than 1% of all clays pass through the filter paper, yet approximately 30% of Na^+ in the clays pass through the

filter. This result seems to indicate that approximately 29% of the Na^+ on the clays that we used is adsorbed physically but readily re-dissolve in water.

The addition of several drops of dilute NH_4OH solution increases the blank value dramatically to as much as 90% of the Na^+ originally in the clay. This result further indicates that the Na^+ ions on the clays are quite mobile and are readily exchangeable (Sayles and Mangelsdorf, 1977).

(2) *Reactions involving exchanged ^{24}Na*

The amounts of ^{24}Na (dps, disintegrations per second) exchanged into the solutions (circles) and left on the clays (crosses) for two sets of experiments are plotted vs the equilibrium Cu^{2+} concentrations in Figs. 3a and 3b. These two sets of experiments were

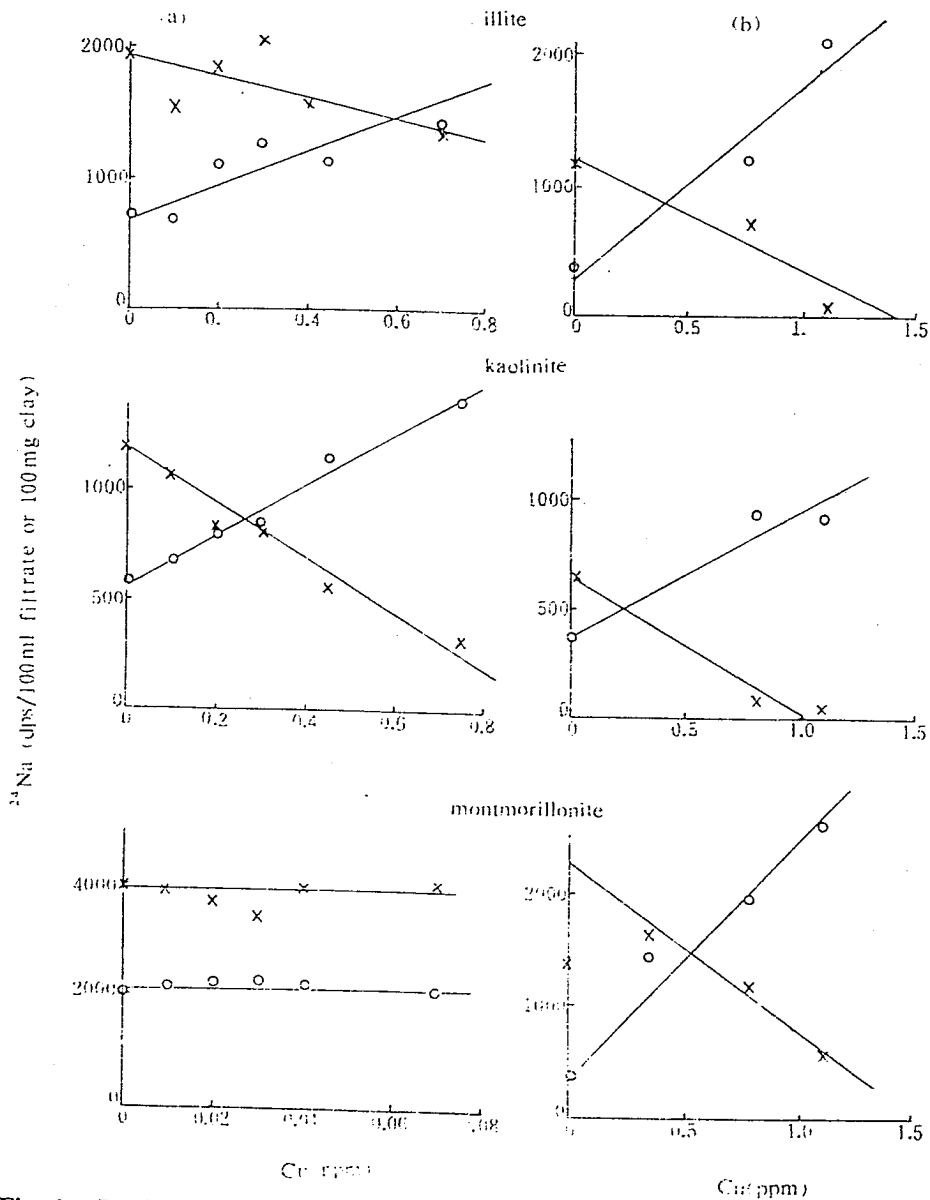


Fig. 3. Radioactivities of ^{24}Na in filtrate (O) and in the clays (X) vs the Cu equilibrium concentrations in the filtrate. Data in (a) and (b) are from two independent sets of experiments based on reactions involving exchanged ^{24}Na . No NH_4OH was added.

performed with different ^{24}Na activities. No pH adjustment was made in the experiments but in order to compare the results the equilibrium Cu^{2+} concentrations were adjusted to the same pH background (pH=7.0) based on the ion exchange percentage vs pH relationships (Chang and Chen, 1984a).

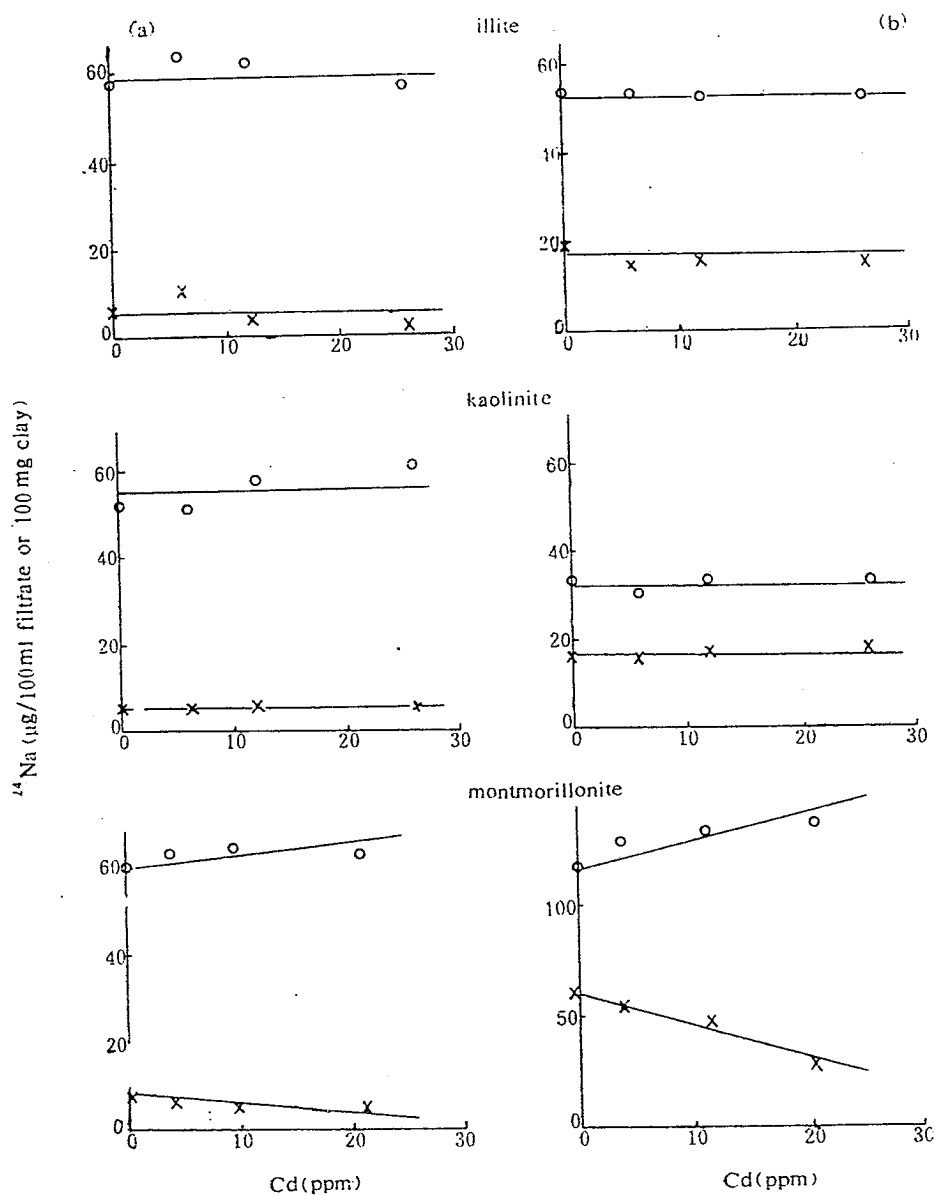


Fig. 4: Radioactivities of ^{24}Na in filtrate (O) and in the clays (X) vs the Cd equilibrium concentrations in the filtrate. NH_4OH was added. Data in (a) are from experiments based on reactions involving exchanged ^{24}Na . Data in (b) are from experiments in which the clays are irradiated to produce ^{24}Na directly.

Figs. 3a and 3b show similar results, both with high blank values in the solutions as explained before. At low concentrations (Fig. 3a) below the equilibrium Cu^{2+} concentration of 0.1 ppm, ^{24}Na on illite and montmorillonite does not seem to be replaced by Cu^{2+} . Since Fig. 1 indicates that Cu^{2+} is ion exchanged onto these clays, the result in Fig. 3a suggests that Cu^{2+} replaces H^+ but not Na^+ at low concentrations. The precision of our single-tracer

experiment, however, is insufficient to allow us to say this for certain. In contrast, it does appear that Cu^{2+} replaces $^{24}\text{Na}^+$ on kaolinite at 0.1 ppm Cu^{2+} (Fig. 3a), based on both filtrate and clay analyses.

At Cu equilibrium concentrations higher than 0.1 ppm (Figs. 3a and 3b) the amount of $^{24}\text{Na}^+$ in the filtrates increases in the same amount as it decreases on the clays. This phenomenon indicates that more and more Na^+ is continuously ion exchanged with Cu^{2+} at higher concentrations, in agreement with the results shown in Fig. 1. Although the data presented in Figs. 3a and 3b are insufficient in quantity and quality to show steps, they do indicate that Cu^{2+} replaces Na at all steps at the corresponding Cu^{2+} concentrations observed in Fig. 1.

Fig. 4a shows the $^{24}\text{Na}^+$ activity vs the Cd equilibrium concentrations. Since the Cd^{2+} ion exchange has high efficiency at high pH range (Chang & Chen, 1984a), we added NH_4OH to bring the pH to approximately 8.8, but in doing so we increased the $^{24}\text{Na}^+$ blank values drastically. The precision of the data becomes insufficient for us to detect the small number of $^{24}\text{Na}^+$ replaced by Cd^{2+} in illite and kaolinite. There is a small signal in montmorillonite, indicating that $^{24}\text{Na}^+$ is replaced by Cd^{2+} so that the Na^+ concentration in the filtrate increases as the Na^+ concentration decreases in the clay.

(3) *Experiments involving irradiation of clays*

Instead of irradiating $^{23}\text{NaNO}_3$ to produce $^{24}\text{Na}^+$ followed by the equilibration of $^{24}\text{Na}^+$ with clays, we irradiated the clays directly before the experiment to generate $^{24}\text{Na}^+$ on the clays at an NH_4OH adjusted pH of 8.7. The $^{24}\text{Na}^+$ activities in the filtrates and clays were measured after the ion exchange. The results for the interaction between Cd^{2+} and the three clays are shown in Fig. 4b. High Na^+ blank values are again present because NH_4^+ replaced Na^+ on the clays. Not enough Na^+ is left in illite and kaolinite to be exchanged by Cd^{2+} . Cadmium ion, however, seems to replace Na^+ on montmorillonite because $^{24}\text{Na}^+$ activities increased in the filtrate as the activities decreased in the clay.

By comparing the montmorillonite result in Figs. 2, 4a, 4b at the same Cd equilibrium concentrations we are tempted to say that Cd^{2+} exchanges with Na^+ at all three steps found on Fig. 2.

(4) *Experiments involving the analysis of Na^+*

In this set of experiments involving Cu^{2+} we did not generate $^{24}\text{Na}^+$ but instead measured $^{23}\text{Na}^+$ in the filtrates and clays by neutron activation after the experiment. The results are shown in Fig. 5. The Cu^{2+} equilibrium concentrations were adjusted to the same pH (7.0) based on the ion exchange percentage and pH range relationships (Chang and Chen, 1984a). The results are similar to those presented in Figs. 3a and 3b. Not all sodium in kaolinite, however, seem to be readily exchangeable in this experiment.

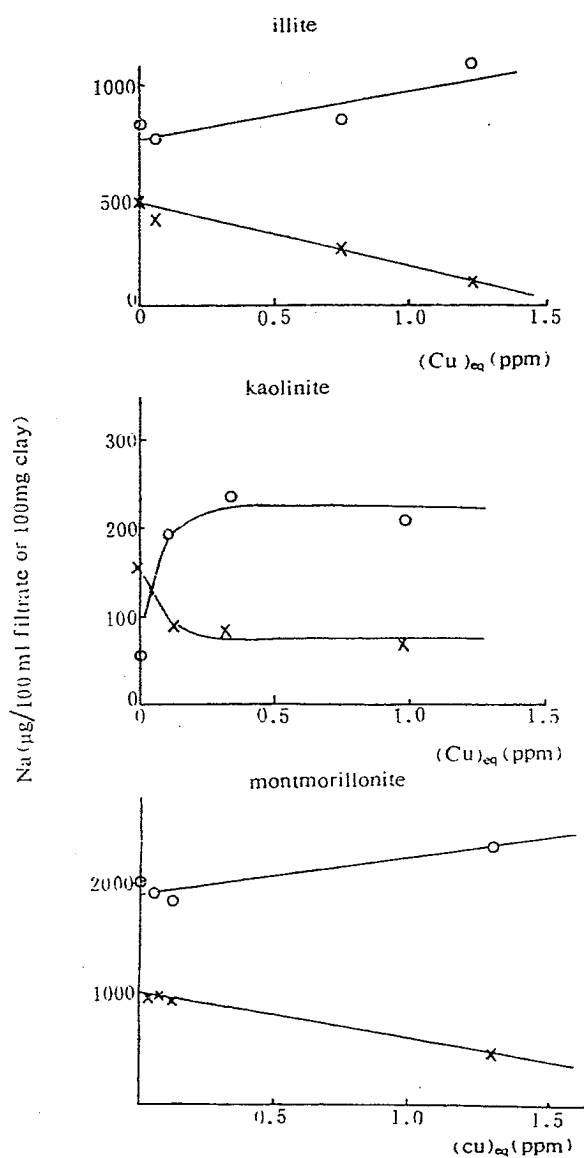


Fig. 5. Na concentrations in filtrate (○) and in the clays (×) vs the equilibrium Cu concentrations in the filtrates. No NH_4OH was added.

CONCLUSION

We have found stepwise ion exchange/precipitation isotherms for the interactions of the metal ions Cu^{2+} , Cd^{2+} , with the clays illite, kaolinite and montmorillonite in seawater—two steps for kaolinite and three steps for illite and montmorillonite. Radiotracer (^{24}Na) studies in pure water indicate that H^+ on illite and montmorillonite may be the first ion replaced by Cu^{2+} and Cd^{2+} . The copper and cadmium ions, however, exchange with Na^+ at all steps for all three clays; the foreign cations in the clay interlayers, therefore, are not responsible for the formation of a step for the stepwise isotherms as we had originally suspected.

The single-tracer experiment performed here does not have the precision to pin-point the exact reaction mechanism. We feel multi-tracer experiments simultaneously measuring Na^+ , K^+ , H^+ , and trace metals are needed in order to understand more profoundly the complicated stepwise ion exchange mechanisms.

This work would not be possible without the generous financial support of the U. S. Department of Energy, speedy and thorough logistical support of the Radiation Center, Oregon State University, and timely advice of C. H. Wang and J. Dymond. C. P. Chang acknowledges partial support from the National Science Foundation of the Academia Sinica (PRC) and the Shandong College of Oceanography. C. T. Chen, during the writing of this paper, was supported by the Office of Naval Research, The Department of Energy and National Science Foundation. We thank C. H. Wang, A. Johnson, M. Conrady, G. H. Keller, R. Collier, C. L. Wei and E. T. Drake for assistance.

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