Clays and Clay Minerals, Vol. 28, No. 4, 311–318, 1980.

ADSORPTION OF CADMIUM AND COBALT ON MONTMORILLONITE AS A FUNCTION OF SOLUTION COMPOSITION[1]

YAIR EGOZY[2]

Chemistry Division, Oak Ridge National Laboratory
Oak Ridge, Tennessee 37830

Abstract—Adsorption of Co^{2+} and Cd^{2+} on Wyoming montmorillonite was studied by the batch equilibration technique, as a function of salt concentration (0.01–4 M NaCl and $NaNO_3$), pH (5.0–6.5), adsorbate concentration (trace–10^{-2} moles/liter), and presence of complexing ions. Comparison was made with the adsorbability of Sr^{2+}, known to follow simple ion-exchange equations. The distribution coefficients for Co and Cd in noncomplexing media varied with salt concentration (from ~500 liters/kg in 0.01 M Na^+ to ~10 liters/kg in 1 M Na^+; pH = 5), but to a lesser extent than that of Sr. Adsorbability varied also with pH (~1 order of magnitude/pH unit), especially at high ionic strength, compared to a negligible pH effect on Sr. The distribution coefficients of Cd and Co decreased with increasing loading on the clay at a very low percentage (0.2%) of the ion-exchange capacity compared to Sr (20%). These data suggest two classes of sites participating in the adsorption of Cd and Co.

The adsorbability of Cd in highly concentrated chloride solution (>1 M) was less than 1 liter/kg, presumably because of the chloride complex formation. This effect increased with increasing pH. The low adsorbability of Cd on montmorillonite from concentrated NaCl solution is promising with respect to its use as a tracer for monitoring flow through formations containing montmorillonite.

Key Words—Adsorption, Cadmium, Cation exchange, Cobalt, Montmorillonite, Strontium.

INTRODUCTION

Adsorption of ions on natural materials and the ion-exchange properties of clay minerals have been subjects of interest for years. Micellar-polymer flooding for enhanced oil recovery, selection of geological media for nuclear waste isolation, and migration of toxic elements from industrial streams to groundwater and their effect on agriculture and public health have increased the degree of interest in this field (see, e.g., Doner, 1978; Farrah and Pickering, 1976, 1977; Ferrell and Price, 1978; Frost and Griffin, 1977; Garcia and Page, 1976; and Levy and Francis, 1976). The equilibria between aqueous solutions and minerals of the host formation greatly influence the performance of surfactants and polymers injected to increase oil production, and tracer ions that are not readily adsorbed by mineral materials have been employed to monitor the movement of groundwater through permeable formations. Such applications are not limited to enhanced oil recovery; problems such as aquifer shifts, salinity migration into inland areas, and utilization of geothermal energy also call for a systematic study of the adsorbability of potential tracer ions on a variety of minerals under controlled conditions. Tracer ions are needed that will be effective in groundwaters having a wide range of salt concentration, from a few meq/liter to brines containing as much as 5 moles/liter. The adsorbability of tracer ions from concentrated salt solutions is of special interest to the nuclear-waste isolation program, as salt deposits are being considered for nuclear waste burial, and water intrusion into such formations will result in concentrated salt solutions.

Anions are preferred to cations as tracers because at normal groundwater pHs most minerals are cation exchangers and the adsorption of anions is much lower than that of cations. In addition to simple anions, ions which form anionic species in the media of interest must also be considered, such as negatively charged metal-hydroxy complexes in basic solutions. For solutions of low pH and high NaCl concentration, chloride complexes may also be considered. For example, Nelson *et al.* (1964) found that the adsorbability of cadmium chloride complexes was much less on organic cation exchangers from HCl than from $HClO_4$ for acid concentrations greater than 0.1 M. The adsorbability of Co, on the other hand, was similar in both solutions, up to acid concentrations of 6 M, mainly because Co does not form chloride complexes. Also, the mobility of Cd in soils was found by Doner (1978) to be greater in sodium chloride solution than in perchlorate solution, which

[1] Research sponsored by the Division of Fossil Fuel Extraction, U.S. Department of Energy under contract W-7405-eng-26 with Union Carbide Corporation.

[2] On leave from Research & Development Authority, Ben-Gurion University, Beer-Sheva, Israel.

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https://doi.org/10.1346/CCMN.1980.0280410 Published online by Cambridge University Press

suggests that anionic cadmium chloride complexes formed in the former solution and were not adsorbed by the minerals of the soil.

Other studies have shown that the adsorption of Co on montmorillonite is pH dependent in the pH range 5–6 (Maes *et al.*, 1975; Maes and Cremers, 1975; Peigneur *et al.*, 1975), a phenomenon that was interpreted in terms of structural hydroxyl groups of the clay or hydroxy-aluminum compounds. The total ionic strength of solutions used in these studies was 0.01 M, and the Co concentration on the clay was 2.7×10^{-4} moles/kg of dry clay. Hodgson (1960) found that the adsorption of Co on Ca-montmorillonite in 0.1 M $CaCl_2$ solution is also pH dependent and proposed that two adsorption processes are responsible, one requiring 1–2 days to reach a maximum, and a second, much slower, non-exchangeable process. Farrah and Pickering (1977) reported only a slight pH dependence for the adsorption of Cd on montmorillonite in water to which no other electrolyte has been added, while Frost and Griffin (1977) noted a significant difference in the adsorption of Cd from landfill leachate as compared with that from pure sodium nitrate solution. Garcia-Miragaya and Page (1976) found that one hour was sufficient to obtain equilibrium for the adsorption of Cd from sodium salt solutions at pHs between 6.5 and 7. They also found that the adsorption from NaCl solution was lower than that from $NaClO_4$ solution, at salt concentrations greater than 0.01 M.

From these studies, it is clear that several factors influence the adsorbability of ions on clays, including salt concentration, pH, and degree of loading on the adsorber. This paper reports the results of a study of the adsorption of Cd^{2+}, Co^{2+}, and Sr^{2+} on montmorillonite from solutions of a wide range of salt concentrations and at pHs from 5.0 to 6.5. The adsorption of Sr on montmorillonite (see Shiao *et al.*, 1978, and the references contained therein) can be explained in terms of simple ion-exchange mechanisms and therefore serves as a reference to which the adsorbability of Cd and Co can be compared. Cd and Co are transition metals that differ in their ability to form chloride anionic complexes. Montmorillonite is of particular interest because its relatively high ion-exchange capacity implies a contribution to overall adsorption behavior disproportionate to its weight fraction in geological media.

VARIABLES

The three variables listed above were considered as follows.

Salt concentration

The ion-exchange equilibrium between ions A^{a+} and B^{b+} in the solution and the clay phases may be expressed as:

$$bA^{a+} + aB^{b+}{}_{clay} = bA^{a+}{}_{clay} + aB^{b+} \qquad (1)$$

The equilibrium constant may be expressed as

$$K_{AB} = \frac{(A)^b{}_{clay}(B)^a}{(A)^b(B)^a{}_{clay}}\Gamma_{AB} = D_A{}^b\frac{(B)^a}{(B)^a{}_{clay}}\Gamma_{AB} \qquad (2)$$

where Γ_{AB} is the activity coefficient quotient (see, e.g., Shiao *et al.*, 1978) and D_A is the distribution coefficient of ion A between the clay and the solution, defined as the concentration of A in the solid phase (moles/kg dry solid) divided by its concentration in the solution (moles/liter).

When only traces of A are present, that is, when its concentration in the solid phase is much smaller than the capacity of the clay, when Γ_{AB} is constant, and when electrolyte invasion is negligible, it follows from Eq. (2) that:

$$d \log D_A/d \log(B) = -a/b \qquad (3)$$

i.e., the plot of log D_A vs. log (B) will be linear with the slope of $-a/b$.

pH

pH has several effects on the distribution coefficient. At different acidities, the species present in the solution may be different. The concentration of hydroxy complexes (mentioned above) is a function of the pH. The pH may have an effect on the solid phase too; for example, the capacity of oxides, and selectivity of ions towards oxides is known to be pH dependent (Kraus *et al.*, 1960). Precipitation may also occur, especially in the high pH range. Precipitation of hydroxides and carbonates that are formed above pH of 8 may be misinterpreted as large distribution coefficients, especially if the batch-equilibration method is used. The pH in this investigation was limited to less than 7 so that no precipitation would occur.

Degree of loading on the adsorber

The distribution coefficient depends on the degree of loading (i.e., the adsorbate concentration in the solid phase), and is less when the loading is greater. For many adsorbers, such as organic ion exchangers, the distribution coefficient is constant for a wide range of concentration of the adsorbate and decreases only when the loading is greater than 10% of capacity. For other adsorbers the range of constant D as a function of loading (the linear isotherm range) may be smaller. In any case, the degree of loading is important when comparing distribution coefficients between systems of different salt concentration, different pH, etc. The comparison should be made at the same loading for all samples. Since it is difficult to adjust loading in the non-linear isotherm range in the batch-equilibration method, it is convenient to make the comparisons in the low loading range where the adsorption isotherm is linear

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and the distribution coefficient does not depend on loading.

EXPERIMENTAL

A Na-montmorillonite (The Clay Minerals Society Source Clay SWy-a) from Crook County, Wyoming was used for this study. Radioactive tracers were used for the adsorbability measurements. Cd^{115} was made by neutron bombardment in the High Flux Isotope Reactor at Oak Ridge National Laboratory. Co^{57} and Sr^{85} were purchased from New England Nuclear Corporation (Boston, Massachusetts). A NaI well-type scintillation counter was used to count the γ emission of the radioisotopes. When counting the Cd^{115}, energy discrimination was used to eliminate counts of the indium daughter.

Part of the clay was purified following Jackson's procedure (Jackson, 1956) which involved removing insoluble carbonates by using 1 M acetate buffer (pH 5), removing organic matter by using 30% hydrogen peroxide, and removing iron not incorporated in the clay structure with sodium citrate and sodium dithionite. Finally, the clay was converted to the sodium form by contacting it with 1 M NaCl solutions several times. The excess sodium salt was washed out with 60% methanol-water mixtures, and the clay was dried at 60°C and ground in a jar mill. The <325 mesh-size fraction was collected for the following experiments. For a few experiments, the clay was only partially purified; the steps concerning removal of organic matter and iron were eliminated. The difference in the pretreatment of the clay samples had some effect on the observed adsorbabilities but not on the general behavior of the system.

Distribution coefficients were determined using a conventional batch-equilibration technique in which a known amount of clay (20–800 mg) was contacted with a known volume of solution (3–10 ml) and shaken at room temperature. The samples were centrifuged in a du Pont Sorvall R-C Refrigerated Super Speed centrifuge at 5000–10,000 rpm for 15 min.

When a clay sample is contacted with the salt solution, it may change the solution's pH. To obtain the desired condition, the clay was prewashed three times with a solution of the supporting electrolyte and the pH adjusted if necessary. Only then, a solution of the tracer in the same supporting electrolyte was added to the clay. A final pH measurement of the supernatant was taken after equilibration.

RESULTS

Equilibration time

To determine the time needed for equilibration, the adsorbability on montmorillonite of Co from solutions of various concentrations of sodium nitrate was studied as a function of time. In this experiment the aliquots used for analyses were recombined with the original solutions, and the experiment was continued. As shown in Figure 1, the time needed to obtain the equilibrium value was within experimental error, less than 1.5 hr at the low sodium concentration and about 20 hr at the highest sodium concentration. The adsorbability rate for Cd from sodium nitrate was found to be identical to that of Co. A minimum period of 24 hr was, therefore, chosen for all equilibrations.

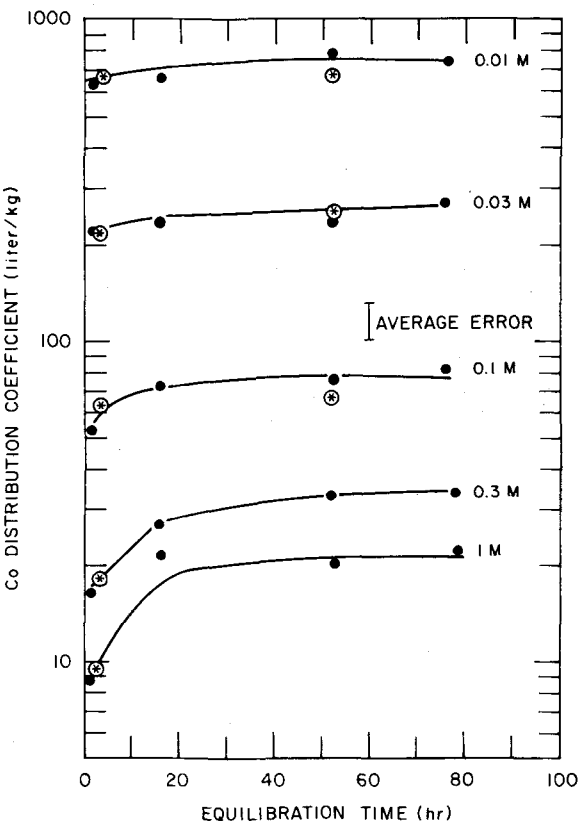


Figure 1. Measured distribution coefficients of Co on montmorillonite from different concentrations of $NaNO_3$ as a function of equilibration time. Acetate concentration: 0.01 M. ⊛ = Points measured after removing most of the activity from the solution (see text).

Reversibility of the adsorption reaction

A second set of samples, identical to that described above, was prepared. The only difference was that about 80% of the equilibration solution was replaced by fresh Co-free $NaNO_3$ solution at 1.5 hr from the beginning of the experiment, and the adsorbability was determined after additional 1.5 hr. The solution was replaced again at 16 hr from the beginning of the experiment, and the adsorbability was determined at 52 hr. The measured distribution coefficients at 3 and 52 hr are marked by ⊛ in Figure 1. As the values obtained fell close to the values of the adsorption test (solid circles in Figure 1), it is concluded that the adsorption is

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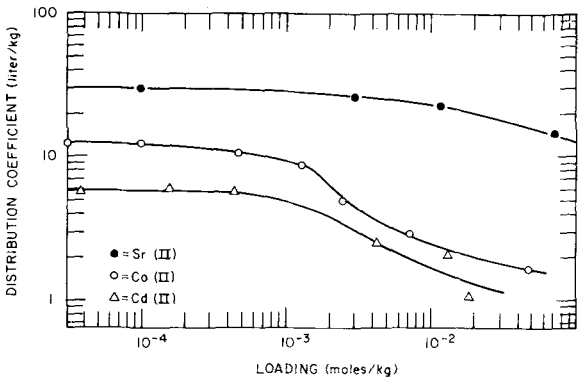


Figure 2. Distribution coefficients as a function of loading on montmorillonite from 0.1 M NaCl–0.1 M NaAc adjusted to pH 5.

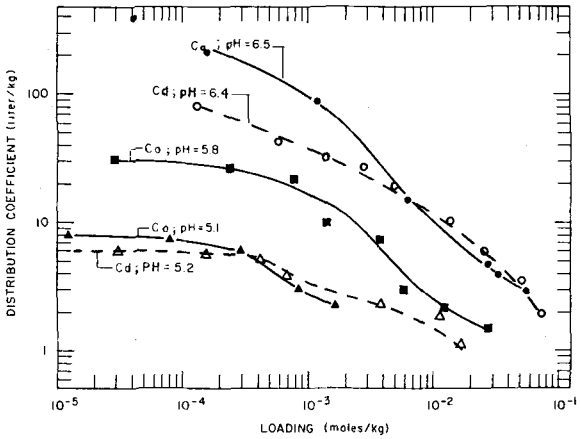


Figure 3. pH effect on loading isotherms of Co on montmorillonite from 1 M NaCl–0.1 M NaAc, and Cd from 0.1 M NaCl–0.1 M NaAc.

reversible at least in the range of time used. If the adsorption was not reversible, D_{Co} values should have been higher than those obtained when the Co was moving from the solution to the solid.

Loading effect on distribution coefficient

Figure 2 shows plots of the distribution coefficients of Sr, Co, and Cd as a function of their concentration in the clay (loading on the clay). The results for Sr were taken from Shiao *et al.* (1978). This plot shows that the distribution coefficient of Sr at pH 5 is constant for loading values as high as 10^{-2} moles/kg. Similar results were obtained by the present author for Sr at pH 6.5.

The distribution coefficients of Cd and Co are constant only as high as loadings of 10^{-3} moles/kg and decrease at higher loadings. At pH 6.5 the distribution coefficients of Co and Cd (Figure 3) decline at loadings above 10^{-4} moles/kg. It can be seen that the change in the distribution coefficient as a function of pH was larger in the low loading range than in the high loading range.

To stay in the linear isotherm range in which the distribution coefficient is independent of the loading, all adsorption measurements (other than loading isotherms) were carried out with adsorbate concentration in the range of 10^{-6}–10^{-7} M.

Buffering by acetate

It was found convenient to add a buffer to the solutions under study in order to obtain and maintain a constant pH for any set of experiments. The addition of up to 0.1 M acetate buffer to the solution of strontium had no effect on the distribution coefficient (Shiao *et al.*, 1978). The adsorbabilities of Co and Cd from 0.1 M Na solution as a function of acetate concentration are given in Figure 4. The distribution coefficients decreased with increasing acetate concentrations for both ions. This observation suggests formation of Co and Cd complexes with acetate, whose adsorbability is lower than that of the free ions. The decline of D with increase of acetate concentration was stronger for Cd than for Co. This observation is in agreement with the known stability constants for the acetate complexes (Smith and Martell, 1976). The expected change of observed D with change in acetate concentration for different assumptions for the distribution coefficient ratio θ of the complexed and free ions are given in Figure 4 as solid lines. These calculations are based on stability constants of 15.8 and 6.5 for Cd and Co, respectively.

From Figure 4, it is clear that for both Cd and Co, the change of the adsorbability that might be caused by adding up to 0.02 M NaAc is small. Therefore, acetate

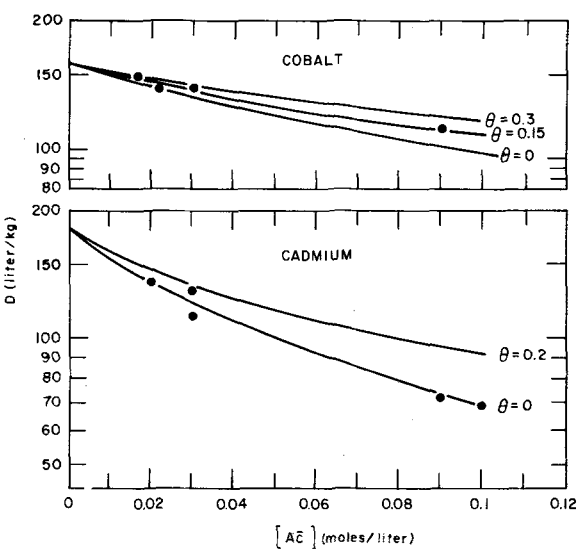


Figure 4. Effect of acetate on the distribution coefficients of Cd and Co on montmorillonite from 0.1 M Na^+ at pH 5.6. θ is the ratio of the adsorbability of the complexed to the free metal ions (see text).

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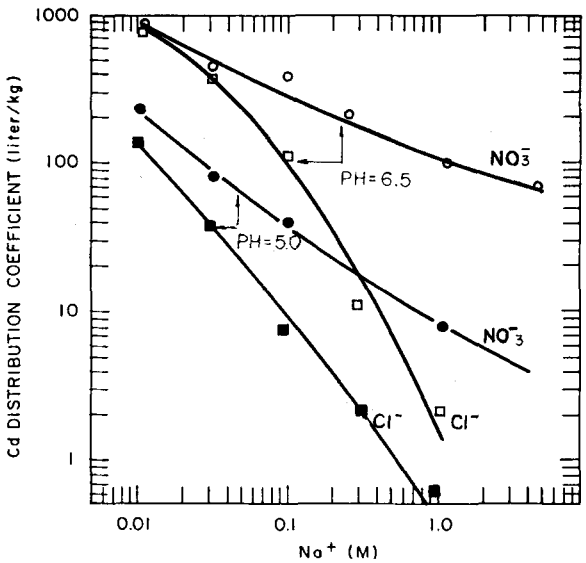


Figure 5. Distribution coefficients of Cd on montmorillonite from solutions of NaCl and $NaNO_3$ as a function of salt concentration for pH of 5.0 to 6.5. Acetate concentration: 0.01 M.

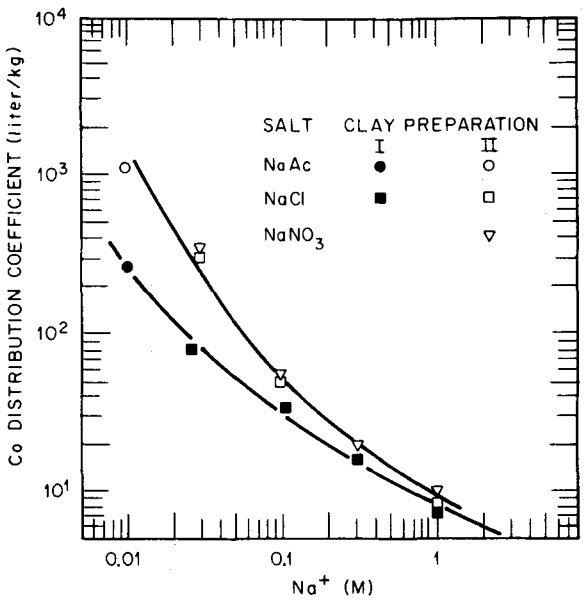


Figure 6. Co distribution coefficients as a function of salt concentration for nitrate and chloride salts and two clay preparations. Solutions were buffered with 0.01 M NaAc to pH = 5.0. The 0.01-M solution contained only NaAc.

concentration was generally limited to 0.01 M NaAc (with the exception of the experiments described in Figures 2–3).

Adsorption from nitrate vs. chloride solutions

The adsorbability of Cd from sodium chloride and sodium nitrate solutions, as a function of salt concentration at pH 5, is given in Figure 5. The adsorbability of Cd from chloride solutions was found to be lower than from nitrate solution, and the difference increased as the salt concentration increased. These observations are consistent with the effect expected for chloride complexing of the Cd on its adsorbability on the clay. The higher the chloride concentration was, the lower the average charge of the Cd (Kraus and Nelson, 1959), and the lower its adsorbability. This phenomenon is similar to that found for the acetate complexes of Cd and Co.

Similar measurements were carried out for Co. As expected, the chloride and nitrate curves are almost identical for a given clay preparation (Figure 6). A displacement of the distribution coefficient at a given salt concentration was observed for different clay preparations. The reason for this difference is not fully understood. All comparisons of adsorbabilities for different adsorbates, pH, etc., were carried out on samples from the same preparation.

Adsorption as a function of sodium concentration at constant pH

Figure 7 summarizes the adsorption of Co, Cd, and Sr as a function of sodium concentration at pH = 5 for noncomplexing media (chloride for Sr, taken from Shiao *et al.*, 1978, and nitrate for Co and for Cd). The log D–log(Na) function for Sr is linear, and its slope is −1.6, in comparison with −2 expected for an ideal divalent/monovalent ion exchange. The log D–log(Na) functions for Co and Cd were similar. The curves are

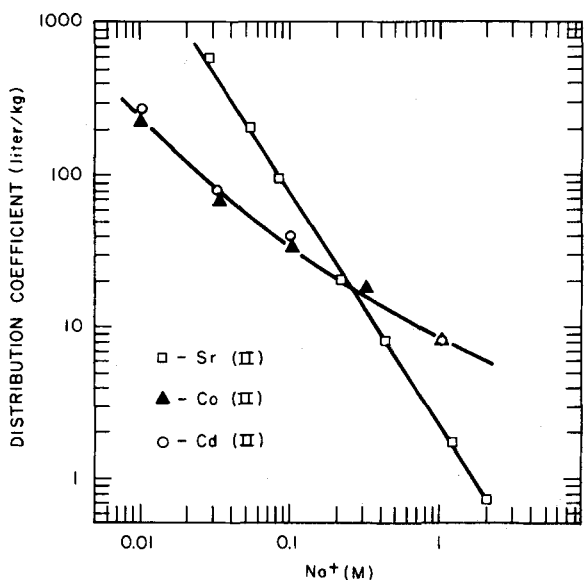


Figure 7. Comparison of distribution coefficients of Sr, Co, and Cd on montmorillonite from noncomplexing salt solutions as a function of salt concentration. Salts used: NaCl for Sr and Co; $NaNO_3$ for Cd. Acetate concentration: 0.01 M.

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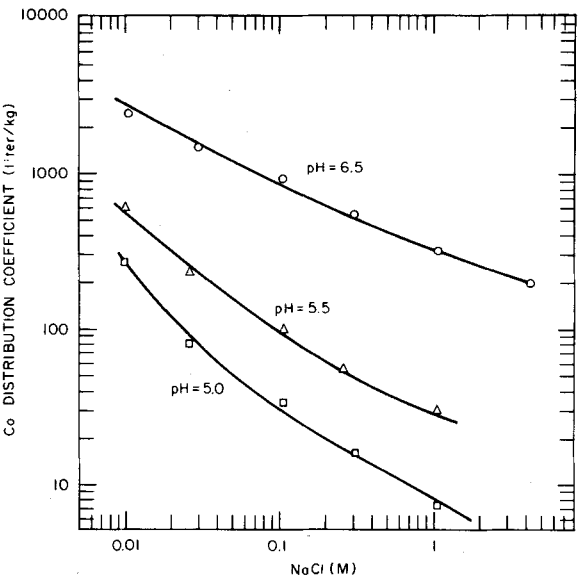


Figure 8. Distribution coefficients of Co on montmorillonite from NaCl solution containing 0.01 M NaAc as a function of salt concentration for pH of 5 to 6.5.

not linear, and the slopes are much less than −2 expected from Eq. (3) indicating that more is involved than the simple ion-exchange equilibrium described by Eq. (1).

Adsorbability as a function of pH

Figures 5 and 8 show the distribution coefficients of Co and Cd in NaCl solutions, and of Cd in $NaNO_3$ solutions of different pH values. All distribution coefficients are higher at the higher pH. For Cd in nitrate solution and Co in chloride solution, where the cations are not complexed, adsorbability increases with pH; this increase is higher at the higher sodium concentrations. For Cd in chloride solutions, the increase of adsorbability with pH is, within experimental error, practically independent of sodium concentration. The distribution coefficient of Cd at high salt concentration at a given pH is more than 10 times lower in chloride than in nitrate solutions. This difference increases with pH.

DISCUSSION

Several differences in the adsorption behavior of Cd and Co in comparison with Sr were noted:

(1) Distribution coefficients for Co and Cd decrease rapidly at loadings that are a very small fraction of the capacity of the clay, whereas the Sr distribution coefficient is constant up to loadings that are higher by at least 1 order of magnitude than the capacity for Co and Cd.
(2) Distribution coefficients for Co and Cd are highly pH dependent, especially at low loading and high salt concentration, whereas the Sr distribution coefficient is almost pH independent.
(3) The log D–log(Na) functions for the adsorption of Co and Cd are curved and have slopes that are much less than those that might be predicted from simple ion-exchange equations. The slopes decrease as pH increases. For strontium adsorption, the log D–log(Na) function is linear with a slope close to the expected value of −2.

The nature of the adsorption isotherm suggests that adsorption takes place either on two compounds or on two sites, i.e., the clay and an impurity, or two types of sites on the clay itself. Peigneur *et al.* (1975) and Maes and Cremers (1975) studied the adsorption of Co on montmorillonite from a 0.01 M NaCl solution and attributed the change of adsorbability with pH to the change in the relative contribution of adsorption at "broken bonds" and edges of particles, compared to the contribution of the cation-exchange capacity (simple ion exchange) to the total adsorbability. The pH effect found by Maes and Cremers (1975) is smaller than reported here, but the NaCl concentration is also lower. If Maes and Cremers' explanation is valid for the higher sodium concentration range studied here, the adsorbability of the Co (and Cd) on sites sensitive to pH must also be independent of the concentration of sodium chloride in the solution. If this is the case, the contribution of pH-sensitive sites to overall adsorption would be more significant at high sodium ion concentrations, where the amount of adsorption predicted by ion-exchange equations would be relatively low. In addition, it is necessary that the pH sensitivity for the adsorption of Co and Cd be similar, and higher than that for the adsorption of Sr, as shown in this study.

Recently, Kinniburgh *et al.* (1975, 1976) showed that the adsorbability of trace quantities of Co, Cd, Sr, and other cations on hydrous oxide gels of iron and aluminum is high even from 1.0 M $NaNO_3$. The reported Co and Cd isotherms are almost identical for aluminum and iron oxides. The adsorbability of Co and Cd is highly pH dependent between pH 5 and 7 (the same pH range that was studied here for the clay), while for Sr the sensitive pH range is between 7 and 9. Moreover, the change in the adsorbability per pH unit is much higher for Co and Cd than for Sr.

In view of these observations, it seems to be reasonable to assume that the montmorillonite in the present study adsorbed Co and Cd on two classes of sites: on one, cation-exchange behavior is followed, and on the other the adsorption behavior is similar to that on hydrous oxide gels of aluminum and iron. The latter sites correspond to the edges and "broken bonds" of the montmorillonite, in the terminology of Maes and Cremers (1975). This is also in agreement with the kinetic observations presented in Figure 1 and with the assumption that the adsorption on the second type of sites

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is slower than that on the interlayer cation-exchange sites.

Cd in chloride solution, where the average charge of its complexes is considerably less than +2, may be less adsorbed by the hydrous oxides in the pH range of interest, and therefore, the pH effects described for the noncomplexed Cd are much larger. As a result, adsorbability of Cd at high chloride concentration is low even for pH of 6.5. As far as soils or sediments containing large proportions of montmorillonite are concerned, cadmium seems to have promise as a tracer at high chloride concentration in the pH range studied.

SUMMARY

The adsorbability of Cd onto Wyoming montmorillonite is much lower from chloride solutions than nitrate solutions when the total salt concentration is greater than 0.01 M. Also, the increase in the Cd distribution coefficient on montmorillonite with increasing pH in the range 5–6.5 is lower in chloride solution than in nitrate solution. Cadmium seems promising as a tracer for monitoring movements of solutions of moderate to high chloride concentration.

In noncomplexing media, the adsorbability of Cd and Co increases with pH, especially at high (~1 M) sodium concentration. Cd and Co distribution coefficients decrease with increasing salt concentration; however, much less sharply than the Sr distribution coefficient, especially at higher pH value.

The distribution coefficients of Cd and Co decrease with increasing loading on the clay. This decrease is significant at loadings as low as 10^{-3} moles/kg. The distribution coefficients of Sr, on the other hand, are essentially constant up to 0.02 moles/kg loading, and decrease approximately as predicted by ideal ion-exchange behavior.

ACKNOWLEDGMENTS

Many hours of discussion with J. S. Johnson, K. A. Kraus, and R. E. Meyer are gratefully acknowledged. Appreciation is expressed also to B. H. Ketelle for his help with the radioisotopes.

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(Received 14 June 1979; accepted 5 December 1979)

https://doi.org/10.1346/CCMN.1980.0280410 Published online by Cambridge University Press

Резюме—С помощью метода дозированного равновесия изучалась адсорбция Co^{2+} и Cd^{2+} монтмориллонитом из Вайоминга, как функция контцентрации соли (0,01–4 M NaCl и $NaNO_3$), pH (5,0–6,5), концентрации адсорбата (след = 10^{-2} мол/литр) и присутствия составляющих ионов. Было проведено сравнение с поглощаемостью Sr^{2+}, которая, как известно, описывается простым уравнением ионного обмена. Коэффициенты распределения для Co и Cd в некомплексной среде изменялись с изменением концентрации соли (от ~500 литров/кг в 0,01 M Na^+ до ~10 литров/кг в 1 M Na^+; pH = 5), но в меньшей степени, чем коэффициент для Sr. Поглощаемость также изменялась с изменением pH (~1 порядок величины/единица pH), особенно при высокой ионной силе, по сравнению с незначительным влиянием pH на Sr. Коэффициенты распределения Cd и Co уменьшались с повышением нагрузки на глину при очень низком проценте (0,2%) ионной обменной способности по сравнению с Sr (20%). Эти данные указывают на существование двух классов мест участвующих в адсорбции Cd и Co. Поглощаемость Cd в сильно концентрированном хлоридном растворе (>1 M) была меньше, чем 1 литр/кг, предположительно из-за формирования хлоридного комплекса. Этот эффект возрастал с увеличением pH. Низкая поглощаемость Cd монтмориллонитом из концентрированного раствора NaCl является обещающей в отношении его использования в качестве индикатора для наблюдения за потоком через формации, содержащие монтмориллонит. [N.R.]

Resümee—Die Adsorption von Co^{2+} und Cd^{2+} an Montmorillonit von Wyoming wurde mittels der batch equilibration-Methode untersucht in Abhängigkeit von der Salzkonzentration (0,01–4 M NaCl und $NaNO_3$), dem pH (5,0–6,5), der Konzentration des zu adsorbierenden Ions (Spuren–10^{-2} Mol/Liter) und der Anwesenheit von komplexbildenden Ionen. Ein Vergleich wurde gezogen mit der Adsorbierbarkeit von Sr^{2+}, die bekanntlich einfachen Ionenaustauschgleichungen folgt. Die Verteilungskoeffizienten von Co und Cd in nicht-komplexbildenden Medien variierten mit der Salzkonzentration (von ~500 Liter/kg in 0,01 M Na^+ bis ~10 Liter/kg in 1 M Na^+; pH = 5), aber in einem geringeren Ausmaß als der Verteilungskoeffizient von Sr. Die Adsorbierbarkeit variierte auch mit dem pH (~1 Größenordnung/pH-Einheit), vor allem bei hoher Ionenstärke, verglichen mit dem zu vernachlässigenden Effekt des pH im Fall von Sr. Die Verteilungskoeffizienten von Cd und Co nehmen mit zunehmender Beladung des Tons nur um einen sehr kleinen Prozentsatz (0,2%) der Ionenaustauschkapazität ab, verglichen mit Sr (20%). Diese Ergebnisse deuten darauf hin, daß es zwei Arten von Positionen gibt, die an der Adsorption von Cd und Co beteiligt sind.

Die Adsorbierbarkeit von Cd in hochkonzentrierten Chloridlösungen (>1 M) war weniger als 1 Liter/kg, wahrscheinlich wegen der Bildung von Chloridkomplexen. Dieser Effekt vergrößert sich mit zunehmendem pH. Die geringe Adsorbierbarkeit von Cd an Montmorillonit aus konzentrierten NaCl-Lösungen ist vielversprechend im Hinblick auf ihre Verwendbarkeit als Tracer für den Durchfluß durch Montmorillonithältige Formationen. [U.W.]

Résumé—L'adsorption de Co^{2+} et de Cd^{2+} sur de la montmorillonite du Wyoming a été étudiée par une technique d'équilibration de l'entièreté de l'échantillon en fonction de la concentration de sel (0,01–4 M NaCl et $NaNO_3$), du pH (5,0–6,5), de la concentration d'adsorbat (trace–10^{-2} moles/litre), et de la présence d'ions complexants. Une comparaison a été faite avec l'adsorbabilité du Sr^{2+} qui suit les équations simples d'échange d'ions. La distribution de coefficients pour le Co et le Cd dans un milieu non complexant a varié avec la concentration de sel (de ~500 litres/kg dans 0,01 M Na^+ à ~10 litre/kg dans 1 M Na^+; pH = 5), mais dans une moindre mesure que Sr. L'adsorbabilité a aussi varié avec le pH (~1 ordre de grandeur/unité de pH), spécialementen haute force ionique, comparé à l'effet négligeable du pH sur le Sr. Les coefficients de distribution de Cd et de Co ont décru avec un accroissement de la charge sur l'argile à un très bas pourcentage (0,2%) de la capacité d'échange d'ions, comparé à Sr (20%). Ces données suggèrent 2 classes de sites participant à l'adsorption de Cd et de Co.

L'adsorbabilité de Cd dans une solution de chlorure très concentrée (>1 M) était moins d'un litre/kg, sans doute à cause de la formation du complexe chlorure. Cet effet a augmenté avec l'accroissement de pH. La basse adsorbilité de Cd sur la montmorillonite à partir d'une solution concentrée de NaCl est promettante en fonction de son emploi comme traceur pour contrôler un flux à travers les formations contenant de la montmorillonite. [D.J.]

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