Inorganica Chimica Acta, *73* (1983) 41–44

Transition Metal Ion (Cu^{2+}, Mn^{2+}, VO^{2+})–Montmorillonite Interactions

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Received December 27, 1982

Calcium montmorillonite removes significant quantities of copper(II) from aqueous solutions by both ion exchange (mainly with Ca^{2+}) and surface adsorption of the copper(II) salt. The ratio of exchanged to adsorbed copper(II) shows a strong anion dependence. Removal of copper(II) is effectively eliminated by the addition of a large excess of sodium chloride, but e.s.r. data give evidence for the adsorption of a new cuprate(II) species.

Work with vanadyl(IV) and manganese(II) solutions indicates that a slow hydrolysis of the exchanged ion, to a simple hydroxospecies, occurs on prolonged exposure of montmorillonite to aqueous solutions of the metal ions.

Introduction

It is well known that the uptake of heavy metal ions by clay minerals can be a function of many factors including solution pH [1], the concentration of the metal [2] and the nature of any ligands present [2, 3]. Minimal uptake of metal ions occurs when they are present as anionic complexes [4]. There is good reason to believe that clay minerals present in the geological strata containing a waste disposal site have some cleansing effect on heavy metal containing leachate which runs off from the site [5]. Thus the clays fulfil an important role in protecting ground water sources from contamination. We have been concerned to obtain more information on the clay–metal interactions which may be involved and have selected particularly copper(II), manganese(II) and the vanadyl cation (VO^{2+}) for study, since these species permit investigation by e.s.r. spectroscopy.

Montmorillonite (see experimental section) is a naturally occurring layer aluminosilicate whose structure is similar to that of pyrophillite except that there is isomorphous replacement of aluminium(III) by magnesium(II) or iron(II) in the octahedral sheet, and aluminium(III) for silicon(IV) in the tetrahedral sheet. The resulting negative charge is balanced by exchangeable cations positioned between the aluminosilicate layers and the large internal surface area (*ca.* 800 m^2/g) thus becomes available for the adsorption of a variety of molecules [6].

Studies of transition metal ions on montmorillonite using e.s.r. spectroscopy are not unknown [7], however since the mineral is present in rocks at disposal sites we wished to model the interaction between our probe transition metal ions and the clay under conditions which approached those within the disposal site. We were interested particularly in the permanence of the immobilisation of the ion within the leachate. These considerations dictated experimental design and we report in this paper such data as appear to us to be new.

Experimental

Montmorillonite* used in this work was obtained from Berk Limited. Electron spin resonance data were obtained with a JEOL PE-1X instrument operating in the X band; g-factors were measured using a manganese(II) standard (line 4, $g = 1.981$; separation of lines 3 and 4 = 86.9 Hz). X-ray powder diffraction data were obtained using Co Kα radiation ($\lambda = 1.79$ Å) with iron filters. Visible spectra were obtained with a Unicam SP8-100 spectrophotometer.

Copper was determined by titration with standard EDTA [8] using a 0.5% solution of alizarin complexone in dilute ammonium acetate buffered to pH 4.3 as indicator. Measurement of solutions pH were made with a direct reading E.I.L. model 23A pH meter via a glass electrode and calomel reference.

Two sets of experiments were carried out. The first set was with copper(II) and was designed to

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*SiO_2, 52.2; Al_2O_3, 12.8; Fe_2O_3, 10.2; TiO_2, 0.6; MgO, 2.5; CaO, 2.2; K_2O, 0.4; Na_2O, 0.1; H_2O (<105 °C), 12.3; H_2O (>105 °C), 6.6; cation exchange capacity 80–85 mequiv. per 100 g.

TABLE I. Data for 0.1 *M* Copper(II) Solutions in Contact with Montmorillonite over Seven Days. Labile copper(II) is that which is released on further treatment with distilled water.

Copper(II) Salt	Initial pH (solution)	Δ (pH) (7 days)	Total Copper(II) Removed[a]	Exchanged Copper(II)[a]	Labile Copper(II)[a]
$CuCl_2$	4.2	−0.4	6.98	5.39	1.59
$CuSO_4$	5.0	−0.5	8.12	3.87	4.25
$Cu(NO_3)_2$	4.4	−0.4	7.61	6.07	1.54
$Cu(ClO_4)_2$	2.5	+0.6	7.36	6.02	1.34

[a] mg copper(II) g^{-1} clay.

investigate the removal of copper(II) ions from aqueous solution over periods up to seven days; also to determine to what extent the nature and concentration of the anion might influence this removal. The second set was carried out with copper(II), manganese(II) and salts of VO^{2+} (vanadyl(IV)). The object was to glean information on the nature of the exchanged ion within the clay environment.

Series (i)

(Experiments were carried out in triplicate). Montmorillonite portions (10 g) were placed in a set of seven stoppered polyethene bottles and covered with a standard solution of copper(II) sulphate (100 cm^3, 0.1 *M*). The bottles were then shaken for periods of one to seven days after which the clay was filtered and the solution content of copper(II) determined as above. A similar experiment was run in parallel to enable the pH of the solution to be monitored day by day.

The filtered clay specimens were air dried and carefully returned to a fresh set of polyethene bottles, covered with distilled water (100 cm^3) and shaken for 24 h. Copper(II) released to the solution was determined by EDTA titration.

The experiments were then repeated replacing copper(II) sulphate with copper(II) chloride, copper(II) nitrate, and copper(II) perchlorate (in each case 100 cm^3 of the 0.1 *M* solution). Finally, eleven samples of montmorillonite (10 g) were treated, in stoppered polyethene bottles, with solutions of copper(II) chloride (100 cm^3, 0.1 *M*) which were 0.1–5 *M* in sodium chloride. Specimens were shaken for 24 h, the clay was filtered and air dried then treated with distilled water (100 cm^3) as above. The copper content of both the initial filtrate and of the solution obtained from distilled water treatment of clay was determined. The presence of 1 *M* NaCl reduced the copper(II) exchanged from ~7 mg g^{-1} clay to ~2 mg g^{-1} clay. At 4 *M* NaCl no analytically detectable exchange occurred although even at 5 *M* NaCl small quantities of sorbed copper(II) were detectable by e.s.r. spectroscopy (see later).

TABLE II. E.s.r. Data for Vanadyl(IV) and Manganese(II) Ion Exchanged onto Montmorillonite.

Salt (Aqueous – 0.1 *M*)	Contact time – 1 week[a]		Contact time – 1 month[a]	
	g_{iso}	⟨A⟩[b]	g_{iso}	⟨A⟩[b]
$(VO)SO_4$	1.96	106	1.92	124
$(VO)Cl_2$	1.96	106	1.94	126
$MnSO_4$	2.00	92	1.98	87
$MnCl_2$	2.00	92	1.98	82

[a] For washed clay equilibrated with laboratory atmosphere. [b] Hz.

Table I gives data for the averaged uptake of copper(II) over days 2 to 7 of the experiment (no significant change was seen after 24 h) and divides this quantity into that portion which is ion exchanged and that which is surface adsorbed. The variation of pH over the period of the experiment is expressed as Δ(pH) and is related to the initial pH.

Series (ii)

The second series of experiments involved, in addition to copper(II) salts; the chlorides and sulphate of manganese(II) and vanadyl(IV). The experimental design was as above but the specimens were left for periods in excess of one month with occasional agitation rather than continuous shaking. E.s.r. spectra were monitored for the clay after (a) air drying and (b) treating with distilled water (100 cm^3) and shaking over 24 h, then air drying. E.s.r. spectra were also monitored for the clay specimens (before and after washing) for series I. Table II collects relevant e.s.r. data.

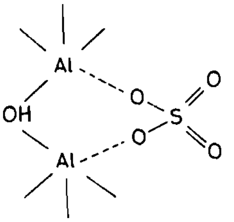
X-ray powder diffraction data were obtained for montmorillonite and copper(II) montmorillonite. Both specimens were equilibrated in the same laboratory environment. The basal spacing d(001) was, in both cases, 13.6 Å. This could imply that mainly calcium(II) ions are released and examinations of copper(II) solutions in contact with montmorillonite using atomic absorption spectroscopy showed that exchangeable ions were released in the order:

$Ca^{2+} > Mg^{2+} > Na^{+} > K^{+}$

Results and Discussion

The experiments described in series (i) (experimental section) were designed to model, in an admittedly idealised fashion, possible metal ion–clay interactions at disposal sites. Thus the seven days contact of solutions with clay may model a slow percolation of metal containing leachate, and the subsequent treatment with distilled water models subsequent exposure of the clay minerals to more dilute leachate or to increased water flow due to natural precipitation. The implications of the results in the practical context have been discussed elsewhere [9].

The observation that much of the metal initially removed from solution is labile is, in one sense, trivial. However it is not without practical consequences [9]. More interesting in the chemical sense is the marked anion dependence of the ratio of exchanged to labile copper, with copper(II) sulphate giving particularly anomalous results. The solution pH changed slightly over the seven days exposure to the clay but neither sufficiently, nor in the correct direction to induce significant hydrolysis of the aquated copper(II) ions. It may be that the sulphate anion, in addition to the extra negative charge, has a stereochemical affinity with the positive edge of the clay crystals as illustrated in the following formula [10]:



The effect of phosphate(V) on the adsorption of copper(II) is similar [11] and may well have a similar explanation. Otherwise the anion effect is as would be expected from a consideration of charge, size (solvation) and Lewis basicity.

Both analysis and monitoring of the clay by e.s.r. spectroscopy showed that equilibrium with the solution was reached after 24 h, at least as far as exchange was concerned. There is some evidence however that the amount of a particular metal salt adsorbed onto the clay surface may continue to increase if the contact between clay and solution extends over many months [5].

One set of experiments was carried out with the deliberate addition of sodium chloride. Not surprisingly exchange was eliminated at high chloride concentrations – probably by swamping the exchange of copper(II) by the large excess of sodium(I). However even when analysis could detect the removal of no copper(II), e.s.r. spectroscopy revealed that very small quantities had been adsorbed. This material was seen when the NaCl concentration was 5 *M*, but was labile in distilled water. The spectrum was well resolved and showed $g_\perp$ (2.20) and $g_\parallel$ (2.00) with $A_\parallel$ = 80 Hz. The low g factor may be consistent with a d_{z^2} ground state for the adsorbed species [12] which in turn implies a trigonal bipyramidal stereochemistry. $[CuCl_5]^{3-}$ is an unproven possibility.

The e.s.r. spectrum of the montmorillonite used contains broad features due to the iron(III) content, including an absorption at g = 2.00 which overlaps with the broad absorptions arising from copper(II). Thus, whilst the e.s.r. data for copper parallel the analytical data and show that the initial exchange is complete in 24 h, it becomes difficult to detect anisotropy in the signal unless, as above, definite resolution of hyperfine structure on the parallel component occurs. We therefore carried out some experiments with vanadyl(IV) and manganese(II) where the 99.76% natural abundance of ^{51}V (I = 7/2) and the 100% abundance of ^{55}Mn (I = 5/2) ensure confident identification of spectral components.

The e.s.r. data for both VO^{2+} and Mn^{2+} after one week of contact between clay and metal ion solution give values of g and ⟨A⟩ which are close to those expected for the aquo-complexes. Furthermore the isotropic spectra indicate that the ions are freely tumbling. This is consistent with previous work involving Mn^{2+} and montmorillonite [13]. Unlike our recent experience with kaolinite [14], no evidence is found for differing exchange sites.

When the clay is allowed to remain in contact with the metal ion solution for excess of one month, the colour of the clay, in the case of the vanadyl solution, is finally green. A better resolved e.s.r. spectrum is obtained and small changes in both g and ⟨A⟩ are seen (Table II). The electronic absorption spectrum of the supernatant vanadyl(IV) solution remains unchanged during the period of contact with the clay, hence it is likely that the exchanged species has undergone chemical changes.

Some related studies have been carried out with VO^{2+} on hectorite [15] where a solution environment is noted for doping at a 50% level, but when the doping level is only 5% an anisotropic spectrum of an immobilised vanadium(IV) species is seen. McBride [15] has suggested this form to be $[VO(OH)_2(H_2$-

$O)_3]$. Our data indicate that the new species on montmorillonite is freely tumbling and the identical data for sulphate and chloride solutions eliminate the need to consider that sulphato- or chloro-complexes have been formed. We suggest that the species present is $[VO(OH)(H_2O)_4]^+$ since this would reasonably be an intermediate to McBride's $[VO(OH)_2(H_2O)_3]$.

Not surprisingly little visual change in the clay is noted on prolonged exposure to manganese(II) solutions. In this case also, however, the e.s.r. data indicate that chemical change has occurred since small changes in both g and ⟨A⟩ are noted (Table II). The new species freely tumbles and, following the logic of the above paragraph, may be $[Mn(OH)(H_2O)_5]^+$.

It would appear that the slow hydrolysis of metal ions exchanged onto clays is now a well established phenomenon.

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