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Ionic migration and charge reduction in Ni^{2+}-, Co^{2+}- and Zn^{2+}-exchanged Texas montmorillonite

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Controlled calcination of ion-exchanged Texas montmorillonite leads to layer charge reduction. Detailed chemical analyses of both exchangeable and unexchangeable metal species lead to the conclusion that, in complete contrast to the situation with Wyoming bentonite, Ni^{2+}, Co^{2+} and Zn^{2+} are all capable of migrating from the interlamellar space into the octahedral region of the sheets where they are (i) isomorphously exchanged for Mg^{2+}, and to a proportionately smaller extent, for Fe^{2+}, (ii) trapped in the octahedral vacancies. In addition, they are converted to unexchangeable species on the interlamellar sheet surfaces by high temperature hydrolysis leading to hydroxide or oxide formation. It is suggested that protons within the octahedral region are bound as $-OH_2^+$ rather than simply physically trapped.

Keywords: Montmorillonite; clay; charge reduction; cation migration

1. Introduction

It is well known that H^+ or Li^+ cations can leave the interlamellar region of montmorillonites by migration into and through the TOT sheets under the influence of heat [1–3]. Since the sheet negative charge is thereby reduced, there is a balancing reduction in cation exchange capacity (cec). Migrant H^+ cations have been thought to be trapped in the octahedral vacancies but we have shown recently [4] that Li^+ reacts there with an available –OH group to create –OLi and liberate H^+ which can subsequently be extracted into the interlamellar region by high temperature treatment of the clay with base; thus restoring the cec. We subsequently tested the proposition that ionic radius determined the ability to traverse the sheet by studying the effects of calcination of Mg^{2+}-, Ni^{2+}- and Co^{2+}- exchanged Wyoming bento-

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nite [5] and found that in no case did these cations enter the sheet although unexchangeable species of the metals were formed. These were identified as hydroxide or oxide resulting from high temperature hydrolysis of the hydrated cations.

We now report a similar study on Ni^{2+}-,Co^{2+}- or Zn^{2+}- exchanged Texas montmorillonite since, despite the close similarity of this material with Wyoming bentonite in most respects, the results obtained are very different.

2. Experimental

Materials: Non-clay impurities in the Texas montmorillonite (English China clays) were removed by repeated aqueous suspension and centrifuging of the raw material, substantial amounts of the denser and lighter fractions being rejected each time. The cleansed material was then divided into four portions, the "original" and three others exchanged, respectively, with Ni^{2+}, Co^{2+} or Zn^{2+}. Exchange was effected by taking the clay into suspension in a solution (1 M) of the metal chloride and, after some hours, centrifuging and washing free of chloride, a process twice more repeated. These materials were subsequently dried overnight at 60°C before grinding and sieving (passing 140 mesh ASTM) and storing in a tightly closed container.

cec determination: This was done by the standard method of NH_4^+-exchange followed by steam distillation from NaOH solution in a micro-Kjeldahl system. The entrained NH_3 passed into standard HCl and its amount determined by titration. The values obtained by repetitive experiments were established to be reproducible to ± 1 mequiv./100 g dry clay.

Compositional analysis: This was carried out by atomic absorption spectroscopy (AAS). For analysis of Mg by this method a releasing agent (La^{3+}; 10^4 μg cm^{-3}) must be added and since both metal fluorides are insoluble in HF, the solvent used here to make up all clay sample solutions was 1 : 1 v/v 40% HF/70% $HClO_4$. Linear calibration in AAS for Mg is achieved in the range 0.05–1.00 μg cm^{-3}, for Zn over the range 0.10–2.00 μg cm^{-3} and for Fe, Ni or Co over the wider range, 0–15 μg cm^{-3}. Test solutions were diluted appropriately to bring the analyte into the appropriate range.

In order to ascertain the amounts of the various cations that were either exchangeable or not, samples of each variety of the clay were first subjected to TGA to determine the water content and, thus, the dry weight, and then suspended in known amount in 0.5 M HCl. The supernatant liquid was collected and analysed as described to establish the amount of exchangeable metal now in solution. The residual solids, now H^+-exchanged, were washed to neutrality, dried at 60°C, subjected to TGA analysis and then dissolved in known amount in the acid solvent before analysis as described to provide a value for the amount of unexchangeable metal.

3. Results

The results of the experiments are listed in table 1.

4. Discussion

Turning first to the data for the materials dried at 60°C we see that the cec for the X^{2+}-exchanged materials are quantitatively accounted for by the amounts of X^{2+} determined in the exchange solutions. The small amounts of X found in the unexchangeable fractions are similar to those found with Wyoming bentonite and, we believe, reflect the inability of NH_4^+ to achieve 100% competitive exchange of these cations. When these are added to the exchangeable amounts recorded the "true" cec emerges at about 70 mequiv./100 g dry clay, in reasonable accord with the value determined for the original (Ca^{2+}/Na^+) material.

On calcining the original material at 200°C for 18 h the amounts of unexchangeable Mg and Fe remain unchanged and neither metal could be detected in the NH_4^+ exchange solution. The fall in cec from about 73 to 67 units on heating is a common observation, variously attributed to elimination of external exchange sites and/or thermal repair of external defects, of to high temperature hydrolysis of cations to yield protons which then move into the vacancies in the octahedral sublayer.

The results for the X^{2+}-exchanged clays after calcination at 200°C are, however, very different. Considerable amounts of X^{2+} become unexchangeable while readily measurable amounts of Mg^{2+} and a trace of Fe^{2+} are found in the exchange-

Table 1
Compositions of original (Ca^{2+}/Na^+) and ion-exchanged Texas montmorillonite after heating at 60 or 200°C (18 h): interlamellar cation = X; cec in mequiv./100 g dry clay; data for metal in mg atom(ion)/100 g dry clay. (na = not analysed)

	cec	Exchangeable				Unexchangeable			Total		
		X	Mg	Fe	$\sum +$	X	Mg	Fe	X	Mg	Fe
dried (60°C)											
original	72.6	na	–	–	–	na	58.6	9.4	na	58.6	9.4
Ni^{2+}-exchanged	69.0	34.2	–	–	68.2	0.7	58.2	9.9	34.9	58.2	9.9
Co^{2+}-exchanged	69.0	34.4	–	–	68.8	0.6	58.0	10.3	35.0	58.0	10.3
Zn^{2+}-exchanged	68.5	34.0	–	–	68.0	0.9	58.6	10.8	34.9	58.6	10.8
calcined (200°C)											
original	67.3	na	–	–	–	na	58.7	9.5	na	58.7	9.5
Ni^{2+}-exchanged	54.0	16.4	5.7	0.1	44.4	20.2	52.2	9.5	36.6	57.9	9.6
Co^{2+}-exchanged	61.8	24.5	6.0	0.1	61.2	9.8	51.6	10.0	34.3	57.6	10.1
Zn^{2+}-exchanged	60.3	26.1	3.2	0.2	59.0	6.1	54.8	10.2	32.2	58.0	10.4

able fraction in total contrast to the results for Wyoming bentonite. These can only have originated in the octahedral sub-layer and so it is clear that isomorphous exchange by X^{2+} has occurred.

It is pertinent at this point to test the quality of the data. For the eight sets of data presented we find total Mg = 58.2 ± 0.4 and total Fe = 10.0 ± 0.5 while, from the six relevant data sets, total $X^{2+} = 34.7 \pm 1.3$. These results are consistent to well within any reasonable estimate of experimental error. Further, the Mg and Fe results correspond, in units of g atom/formula weight, to Mg = 0.42 and Fe = 0.07. Dr. T. Lovelock and Mr J.R. Jones, working independently in this department, have each established that the stoichiometric formula of the Texas montmorillonite used here is $Si_8[Al_{3.52}Mg_{0.42}Fe^{2+}_{0.07}]O_{20}(OH)_4$. Our present results are, obviously, in complete accord. To the limits of accuracy indicated above, therefore, the analytical data can be interpreted with confidence.

For the Co^{2+}-exchanged clay, 9.8 mg ion/100 g dry clay become unexchangeable following calcination. This is counterbalanced by 6.1 units of Mg^{2+} and Fe^{2+} moving into the interlamellar region and so becoming exchangeable. Thus, 3.7 units of Co^{2+} are unaccounted for. Clearly, in order to effect isomorphous substitution of Mg or Fe in the octahedral sub-layer, the Co^{2+} must penetrate to the vacancies in that region. If we initially assume that the unaccounted 3.7 units of Co^{2+} are, in fact, trapped there, this should reduce the layer charge and lead to a corresponding fall of 7.4 units of cec. We would then expect a cec of 61.6 mequiv./100 g dry clay, exactly as found. Similarly, 6.1 mg ion/100 g dry clay of Zn^{2+} become unexchangeable and are counterbalanced by the emergence of 3.4 units of exchangeable Mg^{2+} and Fe^{2+}. Thus, 2.7 units of Zn are unaccounted for. Assuming these ions also to be trapped in the octahedral vacancies, we would anticipate a fall in cec from 69.5 to 63.1 mequiv./100 g dry clay. We find 60.3. At first sight these figures seem in close enough accord given the quoted accuracy of cec measurements. However, we note that the total measured exchangeable cation content of the calcined Zn^{2+}- exchanged clay would provide a cec of 59.0, essentially the value found, but that the total Zn (exchangeable and unexchangeable) is at the lower edge of the quoted analytical accuracy, being 2.7 mg ion/100 g dry clay short. Since the calculated and actual cec agree, the error must lie in the value quoted for the unexchangeable Zn^{2+}. Adding this quantity back to the 6.1 g ion/100 g dry clay quoted gives 8.8 units which, in turn, yields a calculated cec of 60.9, in agreement with the experimental value. We therefore conclude that the amended value for unexchangeable Zn rather than the quoted value is correct. These calculations establish that the material balances and the cec's are totally consistent and that, therefore, there are no undetermined protons in the exchange solutions. We recognise, however, that they do not prove that Co^{2+} or Zn^{2+} are the trapped species since if, as with Wyoming bentonite, they are hydrolysed on heating to hydroxide/oxide in the interlamellar region and, *all the protons generated* migrate into the sheets, the charge balance calculations would be unaffected. However, the occurrence of isomorphous exchange suggests otherwise.

The effect of calcination on the Ni^{2+}-exchanged clay is significantly different. Again, we have clear evidence of isomorphous exchange of Mg^{2+} and Fe^{2+} but now 20.2 mg ion/100 g dry clay of Ni are found to be non-exchangeable although the amounts of exchangeable $Mg^{2+}$and Fe^{2+} appearing in the interlamellar space are the same as those found with the Co^{2+}-exchanged clay. Furthermore, the cec reduces only to 54.0 mequiv./100 g dry clay rather than the 40 units of cec that would result if all unexchangeable Ni existed as trapped Ni^{2+} since only 5.7 mg ion/100 g dry clay are isomorphously exchanged. Thus, only about half the residual 14.4 mg ion/100 g dry clay of unexchangeable Ni could be located as Ni^{2+} in the octahedral vacancies. The shortfall in cec that this represents can only be attributed to the existence of undetected cations in the interlamellar region. These can only be H^+.

We have recently shown [5] that when Li^+ penetrates the structure under the influence of heat, the octahedral sub-layer reaction $-OH + Li^+ \rightarrow -OLi + H^+$ occurs. It was long ago speculated [1–3] that the corresponding process $-OH + X^{2+} \rightarrow -OX^+ + H^+$ might occur with divalent cations of ionic radius small enough to allow transport through the sheet. If we postulate that the residual (unbalanced) 14.4 mg ion/100 g dry clay of unexchangeable Ni is actually present as $-ONi^+$ *and* that the balancing protons all *leave* the sheet for the interlamellar region the calculable cec is 54.5 mequiv./100 g dry clay, exactly as found. This possibility receives some support from the FTIR spectra wherein the intensity of the 3650 cm^{-1} absorption, characteristic of the O–H stretch of lattice hydroxyls, is reduced on calcination of the Ni^{2+}-exchanged clay. Indeed, the spectrum is virtually identical with that of the lithiated clay. However, while no intensity change at 3650 cm^{-1} is seen with the calcined Zn^{2+}-exchanged clay, some occurs with the Co^{2+}- exchanged clay for which it has not proved necessary to invoke a proton generating step in the octahedral sub-layer. The evidence is thus inconclusive.

We know, from proton titration studies for example, that hydrated multi-valent cations are hydrolysed in the interlamellar region, undergoing reactions such as, for example,

$$Ni^{2+} \cdot xH_2O \rightarrow [Ni(OH)]^+ \cdot (x-1)H_2O + H^+,$$
$$[Ni(OH)]^+ + (x-1)H_2O \rightarrow Ni(OH)_2 + (x-2)H_2O + H^+$$

with, possibly, subsequent thermal dehydration to oxide. We have shown also [5] that, with Ni^{2+}- or Co^{2+}-exchanged Wyoming bentonite, this is what occurs and that there is no significant migration of the metal cation into the sheet. The evidence on this score is so strong that it cannot be discounted.

In summary, it is indisputable that with Texas montmorillonite, in the conditions described, Ni^{2+} (0.69 Å), Co^{2+} (0.72 Å) and Zn^{2+} (0.74 Å) all can enter the octahedral sub-layer and there isomorphously substitute for Mg^{2+}, and trivially, Fe^{2+}. In each case, the amount of unexchangeable metal produced exceeds that involved in the substitution. Since isomorphous exchange occurs and the analytically determined concentrations of exchangeable X^{2+}, Mg^{2+} and Fe^{2+} for the calcined Co^{2+} and Zn^{2+} clays balance closely the measured cec's, the excess of unexchangeable ions would seem to be present as X^{2+} trapped in the octahedral vacancies.

In the case of the calcined Ni^{2+}-exchanged clay, however, the evidence demands that hydrolysis leading to hydroxide/oxide formation with liberation of H^+ also occurs. The foregoing logic demands that we assume that some of the unexchangeable Ni is trapped in the octahedral vacancies as Ni^{2+}. Since the amounts of isomorphously exchanged Mg^{2+} and Fe^{2+} are so similar for the Ni^{2+} and Co^{2+} clays, as a reasonable assumption we will take the amounts that are trapped also to be the same. Then, to produce a balance between analysis and cec for the Ni^{2+}-clay we would need to have the unexchangeable Ni disposed as 5.8/4.0/10.4 (isomorphous/vacancy/oxide–hydroxide). To achieve the experimental cec of 54 units, 15 mg ion/100 g dry clay of H^+ would have to enter the sheet, leaving 14 units in the interlamellar space. Then, however, the sum of exchangeable ions and protons corresponds to a cec of 59 units. As in the case of the Zn^{2+}-clay earlier, we now point out that the total Ni determined in the calcined product was on the edge of error, 2 mg ion/100 g dry clay too much being found. Since the analysis of the unexchangeable fraction is significantly more difficult we place this error there. Then the Ni disposition becomes 5.8/4.0/8.4 which with 7 units of H^+ entering the lattice and 10 units remaining in the interlamellar space gives us the required cec of 54 units. We believe that the error is real and that the amended value (18.2 mg ion/100 g dry clay) of unexchangeable Ni is correct. Given this, any distribution of unexchangeable Ni between vacancy occupation and hydroxide/oxide formation will lead to concordance of the data.

The foregoing proposals, whilst reconciling the data, present us with three new problems.

It is no surprise that we are not required to propose hydrolysis of the Zn^{2+}-clay but it is anomalous that, whereas the effect is considerable for Ni^{2+} it is apparently zero, or thereabouts for Co^{2+}. In our corresponding study of calcined Wyoming bentonite, hydroxide/oxide formation in the Ni^{2+}-clay was very considerable, but only about twice as much as observed with the Co^{2+}-clay. The present results offer us no prospect of resolving this anomaly. Insofar as the Ni^+-clay is concerned high temperature reduction in hydrogen supports the general interpretation since, following such treatment, the material now shows considerable activity as a reducing catalyst for alkenes and dienes due, we infer, to production of Ni^0, as well as activity characteristic of a protonic catalyst. This work is in course of preparation for publication.

In rejecting one possible explanation of the lack of balance between the analytical and cec data we emphasised that all known evidence is that sheet penetration from the interlamellar region, rather than the reverse, occurs where H^+ is available. Indeed, thermal treatment of proton exchanged clay can produce material wherein the cec is reduced from, say 80 units, to 8 of less and this cannot be thermally reversed. Yet, our explanation explicitly assumes that isomorphously substituted Mg^{2+} and Fe^{2+} is totally transferred to the interlamellar region. The explanation we offer is that H^+ does not exist as a bare proton when it occupies an octahedral vacancy. Instead, it interacts with available hydroxyl (–X–OH) to form XOH_2^+ (cf. H_3O^+). The associated bond energy then presents a substantial barrier to dissociation and will maintain a high concentration of (nominally) H^+ against the concentration gradient.

Finally, why is it that lattice penetration and isomorphous substitution occur with Texas montmorillonite but not with Wyoming bentonite? These clays share closely similar physical properties and differ chemically only in the facts that there is (i) a small amount of Al in the tetrahedral layer of the bentonite and (ii) the octahedral layer compositions are: bentonite $[Al_{3.34}Mg_{0.35}Fe^{2+}_{0.155}Ge^{3+}_{0.155}]$ and Texas $[Al_{3.51}Mg_{0.42}Fe^{2+}_{0.07}]$. It may be that the small amount of Al in the tetrahedral layer of the bentonite denies access to ions other than H^+ or Li^+, but this seems unlikely. The far more significant feature is the very considerable difference in Mg/Fe ratio and, of course, the presence of Fe^{3+} in the bentonite. From table 1 it is clear that Fe^{2+} is only isomorphously replaced in the Texas clay with great difficulty (the proportion of replacement it accounts for is about a factor of ten less than its compositional proportion with respect to Mg^{2+}). We thus favour the view that the absence of isomorphous exchange with the bentonite stems from the very high Fe content.

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