Charge reduction and regeneration in K^+, Na^+, Mg^{2+}, Ni^{2+} and Co^{2+}-exchanged Wyoming Bentonite

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Received 19 April 1991; accepted 21 May 1991

Controlled calcination of ion-exchanged Wyoming Bentonite in the presence and absence of ammonia leads to layer charge reductions. Detailed chemical analyses of both unexchangeable and exchangeable species lead to the conclusion that in no case is there migration of the original interlamellar cations into the octahedral region of the layers although, in terms of ionic radius alone, Mg^{2+}, Ni^{2+} and, possibly Co^{2+}, might be expected to do so. The production of unexchangeable Mg, Ni or Co, is identified as resulting from high temperature hydrolysis leading to hydroxide or oxide formation.

Keywords: Montmorillonite; Bentonite, clay; charge reduction/regeneration; cation migration

1. Introduction

It has long been known that interlamellar H^+ or Li^+ cations [1–3] migrate into the sheets of montmorillonites, and related materials, under the influence of heat. Their destination is the octahedral layer where most, frequently all, of the layer charge is generated. This process leads to charge reduction and a concomitant fall in the cation exchange capacity (cec). The general view has been that the migrating ions become trapped in the octahedral vacancies, and this is surely true of H^+. As long ago as 1964 [4] it was suggested, among other possibilities, that, on penetrating to the octahedral layer, Li^+ might interact with layer hydroxyls to yield $-OLi + H^+$. The fact that both Li^+ and Mg^{2+}-exchanged montmorillonites collapse (d_{001} spacing ca. 9.3 Å) on heating above 350 °C, and do not rehydrate although the Mg^{2+}-clay shows acidic properties, and that the ionic radii of Li^+ (0.68 Å) and Mg^{2+} (0.66 Å) are so similar, led to the further suggestion [4] that interlamellar Mg^{2+} was also capable of migration into the sheet and possibly also of interacting there with hydroxyls to yield protons. Only very recently [5] has it been shown that lithium ions do indeed quantitatively lithiate the sheet to release protons.

There are, of course, numerous cations other than Mg^{2+} that are closely comparable in ionic radius with Li^+ e.g. Ni^{2+} (0.69 Å), Co^{2+} (0.72 Å), Zn^{2+} (0.74 Å). Thus, if ionic size alone is determining, thermally induced migration of interlamellar cations into the octahedral layer of the sheet structure may be a more general phenomenon than has been supposed. We describe here a study of the effect of calcination of Mg^{2+}, Ni^{2+} Co^{2+}-exchanged Wyoming Bentonite directed at this proposition.

2. Experimental

Materials: Non-clay impurities in the Wyoming Bentonite (B.D.H. Ltd., Poole, U.K.) were removed by repeated aqueous suspension and centrifugation of the raw material, substantial fractions of the denser and lighter fractions being rejected each time. The cleansed material was then split into fractions to be exchanged, respectively, with Na^+, K^+, Mg^{2+}, Ni^{2+} or Co^{2+}. Each fraction was then taken into suspension in solution (1 M) of the chloride of one of the several metals, then centrifuged and washed free of chloride. This process was twice repeated. Each sample was then dried overnight at 60 °C before grinding, sieving and storing in a closed container.

cec determination: This was carried out 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 which was then back titrated. Repetitive measurements established the results to be accurate to 1 mequiv./100 g. dry clay.

Compositional analysis: Chemically based analysis of Al, Na or K is best performed by flame emission spectroscopy (FES) of appropriate solutions. This technique requires addition to the test solutions of 2000 $\mu g\ cm^{-3}$ of K^+ as ionization suppressor (Na^+ for K^+ analysis) and, since alkali metal perchlorates are insoluble, solids must be taken into solution in HF, a procedure requiring care and patience to achieve a representative solution. Linear calibrations in FES were restricted to the changes; Al (0–10 $\mu g\ cm^{-3}$) and Na/K (0.05–2 $\mu g\ cm^{-3}$) so that considerable and accurate dilution of the test solutions was normally needed. For the determination of Al, it is crucially important to use an optimised N_2O/C_2H_2 flame to achieve a sufficiently high flame temperature to ensure quantitative dissociation of the metal.

Fe, Mg, Ni and Co, on the other hand, are more readily determined by atomic absorption spectroscopy (AAS). Mg analysis requires addition of a releasing agent (La^{3+}; 10^4 $\mu g\ cm^{-3}$) and since both fluorides are insoluble, the solvent of choice is 1:1 v/v 40% HF/70% $HClO_4$. Although not strictly necessary for Fe, Ni or Co determination, this solvent was again preferred. Linear calibration in AAS for Mg extended over the range, 0.05–1.00 $\mu g\ cm^{-3}$, but for Fe/Ni/Co, over the wider range 0–15 μg cm^{-3}. Requisite dilution of the original test solutions thus differed considerably.

Charge reduction / regeneration: Controlled calcination (temperature and/or time) allows production of a family of clays of cec ranging from the value for the parent material down to virtually zero [5,6]. Regeneration of charge can be achieved be exposure of the charge-reduced material to strong base. The reduction-regeneration procedure can, in fact, be carried out in one step [5] by calcining the clay in the presence of NH_3. The samples of K^+, Na^+, Mg^{2+} and Ni^{2+}-exchanged clays used here were, in turn, sealed in an autoclave under high pressure of ammonia gas (50 atm. at 300 ° C) and heated at 300 ° C for eight hours. On cooling and venting of ammonia the material was repeatedly washed to pH7. Followed drying at 60 ° C, each was tested for residual NH_3. None was found. Finally, each batch was exchanged several times with Al^{3+} solution as described earlier to remove the original exchangeable cations. For one set of experiments reported, involving Ni^{2+} and Co^{2+}-exchanged clays, the ammonia was omitted while also the composition of the exchange solution following Al^{3+}-exchange as well as a structural composition was determined.

3. Results

Samples of the "cleansed" material used here, exchanged with six different cations, yielded an average cec of 78.5 ± 2.0 mequiv./100 g dry clay after drying overnight at 60 ° C. Repetitive chemical analysis of the Al, Mg and Fe contents of this material yielded the average values (g.atom/formula weight): Al, 3.41; Mg, 0.35; Fe, 0.31 (sum = 4.07). The layer charge of 0.58(-)/formula weight, corresponding to the cec, means that 0.51 resides in the octahedral layer and this, in turn, means that $Fe^{2+} = Fe^{3+}$. Thus, the stoichiometric formula of this bentonite is $(Si_{7.93}Al_{0.07})[Al_{3.34}Mg_{0.35}Fe^{2+}_{0.155}Fe^{3+}_{0.155}]O_{20}(OH)_4$.

Table 1 lists the results of compositional analyses of the exchanged species.

Table 2 lists comparable data for the Ni^{2+} and Co^{2+}-exchanged bentonite calcined in air at 200 ° C for 18 hr. in the absence of NH_3. In the experiments, concentrations of exchangeable ions in solution were determined following Al^{3+}-exchange; as before, structural analysis was performed on the Al^{3+}-exchanged materials.

4. Discussion

Before proceeding to detailed evaluation of the results several general points are worth making. First, from both tables we see that, with the exception of the calcined Mg^{2+}-exchanged clay (table 1), the data for unexchangeable Mg and Fe are constant, irrespective of exchanged ion or treatment. The anomaly of table 1

Table 1

Structural composition of original (dried at 60 ° C) and Al^{3+}-exchanged calcined (8 hr. in NH_3 at 300 ° C) and charge regenerated Wyoming Bentonite. Original interlamellar cation is indicated. Cec in mequiv./100 g dry clay; other data represent unexchangeable metal in g.atom/formula weight.

	Original cation				
	K^+	Na^+	Mg^{2+}	Ni^{2+}	Co^{2+}
Original (dried 60 ° C) material					
Mg	0.35	0.35	0.35	0.35	0.35
Fe	0.31	0.31	0.31	0.31	0.31
cec	72.4	78.5	79.4	79.4	79.2
Calcined (300 ° C in NH_3) material					
Mg	0.35	0.35	0.48	0.37	
Fe	0.31	0.31	0.31	0.31	
Ni	–	–	–	0.23	
K	0.035	–	–	–	
Na	–	0.003	–	–	
cec	66.8	67.6	67.1	66.2	

is the low value of the cec of the K^+-exchanged clay. However, we note that the calcined material has a small amount of unexchangeable residual K^+. In fact, this amount, added to the cec brings that figure up to 77 mequiv./100 g. dry clay, in close accord with the other values cited. In table 2 we see that even drying at only 60 ° C leads to unexchangeable Ni^{2+} or Co^{2+} being formed. The amounts are very small (0.005 and 0.003 g.atom per formula weight) and it is noticeable that they are closely similar to the amounts of exchangeable Mg^{2+} and Fe^{2+} found for the calcined material. It is well known [7,8] that K^+ ions become unexchangeable in clay minerals on account of their entry into the Stern layer [7] at the sheet surface following partial dehydration. It would be tempting

Table 2

Composition of original (dried 60 ° C) and Al^{3+}-exchanged calcined (18 hr. in air at 200 ° C) Wyoming Bentonite. $X = Ni^{2+}$ or Co^{2+}; cec in mequiv./100 g dry clay; data for metal in mgram atom (ion)/100 g dry clay.

	cec	Exchangeable			Unexchangeable		
		X	Mg	Fe	X	Mg	Fe
Original (dried 60 ° C) material							
Ni^{2+}-exchanged	79.3	39.8	–	–	0.7	49.4	42.2
Co^{2+}-exchanged	79.2	40.1	–	–	0.4	49.2	42.0
Calcined (200 ° C) material							
Ni^{2+}-exchanged	58.7	21.1	0.6	0.2	20.0	49.5	42.4
Co^{2+}-exchanged	58.0	29.8	0.4	0.3	9.9	49.1	42.2

(50 mgram atom/100 g = 0.36 g.atom (formula weight).

to offer the same account in the case of Ni^{2+} and Co^{2+} here. However, these are small, strongly hydrated cations and there is some indication in the results of isomorphous exchange for Mg^{2+} or Fe^{2+}. There is no doubt that these ions cannot migrate into or our of the clay sheet at 60 °C, even Li^+ transport in montmorillonite is trivially slow below 150 °C [5]. We thus suggest that the unexchangeable Ni^{2+} or Co^{2+} ions are trapped at edges, dislocations etc. and that, on calcination, isomorphous exchange to create exchangeable Mg^{2+} or Fe^{2+}, occurs at these essentially external, locations.

Turning now to the main features of the results it is clear that, on higher temperature calcination, substantial amounts of unexchangeable Mg, Ni or Co are generated and cec's are reduced in both sets of experiments. Having disposed of the possibility that internal cation migration leads to isomorphous substitution in the octahedral layer, three further possibilities based upon the proposition of migration of the original interlamellar cations into the octahedral layer may be listed:

(a) that the ions reside in the octahedral vacancies and cause balancing charge reduction;

(b) that they interact with sheet hydroxyls via

$$M^{2+} + 2(\text{-OH}) \rightarrow \text{-O-M-O-} + 2H^+$$

and (c) that the interaction with sheet hydroxyls is

$$M^{2+} + \text{-OH} \rightarrow \text{-O-}M^+ + H^+.$$

Consider first the data of table 2 for Co^{2+}-exchanged bentonite. The charge corresponding to the unexchangeable Co exactly balances the charge reduction on calcination. Thus, mechanism (a) may be operative but so too, if we accept that *no protons leave the sheet* for the interlamellar region, may (b) or (c). The corresponding data for Ni^{2+}-exchanged bentonite are in decided contrast. The charge corresponding to the unexchangeable Ni corresponds to twice the observed charge reduction. Thus, neither (a) nor (b), alone or together, can account for the facts. Although (c) allows a more or less quantitative charge balance in this case, this requires that we now accept that essentially *all protons leave the sheet*. There is no obvious reason why this should occur in the absence of base. These results clearly cannot be accommodated by a single explanation.

Turning now to the data of table 1 which refer to charge regenerated materials we see that, since regeneration involves proton extraction from the sheet by base, mechanism (a) can confidently be ruled out since it produces no protons and so would demand cec's of ca. 17 (Ni^{2+}) and 42 (Mg^{2+}), each well below the observed values. Mechanism (c) can now, similarly, be discounted since, even with total proton regeneration, the cec's would only be ca. 40 (Ni^{2+}) and 60 (Mg^{2+}). In this case, however, mechanism (b), could provide an explanation. If all protons formed were regenerated, obviously no fall in cec would be observed but, if only some fraction (Mg^{2+}, 66%; Ni^{2+}, 80%) were extracted, the observed cec's would result. But there is no obvious reason for this difference while, as argued earlier, the 200 ° C unregenerated calcination data are clearly incompatible with (b) and, finally, and improbably, (b) requires two hydroxyls to be located in the same vacancy. It can thus also be discounted, a view that receives confirmation from the observation that while the IR spectrum of Li^+-charge reduction of the bentonite, when –OLi is formed, leads to marked change in the intensity of the 3650 cm^{-1} absorption characteristic of the stretching vibrations of structural hydroxyls, no change is observed when Ni^{2+}-bentonite is calcined even though much unexchangeable Ni results [9].

The foregoing leaves no doubt, on the basis of the present evidence, that Mg^{2+}, Ni^{2+} and Co^{2+} do not leave the interlamellar region to enter the octahedral region of the sheet structure on calcination in the conditions used here. The explanation thus lies in events in the interlamellar region.

We see in table 2 that the cec of the original materials are essentially exactly accounted for by the measured exchangeable Ni^{2+} or Co^{2+}. Thus, no other exchangeable ion is present in significant amount. Following calcination at 200 ° C, however, while the cec of the Co^{2+}-clay is closely compatible with the amount of exchangeable Co^{2+}, this is certainly not true of the Ni^{2+}-clay where the total of exchangeable metals leaves 25% (15 mequiv/100 g) of the cec unaccounted for. The results for the 300 ° C calcined (regenerated) clays are even more emphatic since the amounts of residual exchangeable Ni^{2+} and Mg^{2+}, provide shortfalls of cec of 19 and 5 units, respectively. The only possible exchangeable ion that can be present to make up the cec is H^+. Thus, following calcination, in the Ni^{2+}-clay, there are interlamellar protons. The same is probably true to a lesser extent of the Mg^{2+}-clay, which would account for its acidity [4].

Another feature of the results is that the cec's of the four regenerated clays listed in table 1 are identical. This result alone would imply no loss of interlamellar Mg^{2+}, Ni^{2+} or Co^{2+}, to the interior of the sheets since there can surely be none of K^+ or Na^+. The value of 67 mequiv./100 g corresponds, in fact, to that found on calcination of these clays at 150 ° C, and is also the value found for the Cr^{3+}, and Li^+-exchanged varieties so treated. This remarkable uniformity strongly suggests that the cec reduction on calcination is a result of some common structural reorganisation that is independent of the identity of the interlamellar cation. The extent of change is ca. 12.5% of the initial value, a figure well within the range commonly ascribed to the "external" contribution to cec. One manifestation of this external effect, it has been suggested [10] is the often considerable differences in cec observed for a given montmorillonite with different exchanged ions, another is the observation [11] that unwashed materials yield the same cec whatever the exchanged ion but following washing, differences ensue. The explanation offered [12] is that cations held at edges and dislocations are readily hydrolysed but to different extents from cation to cation. The results presented here at consistent with the foregoing observations.

However, it should be noted that the 10 unit drop in cec corresponds to a loss of 0.07 units of sheet charge, precisely the value attributed here to the charge deficit of the readily accessible tetrahedral layer. The results for the Na^+-exchanged material conflict with this alternative explanation, however, since unexchangeable Na^+ was present only in trivial amount although the cec was as for the others.

The only reasonable explanation of the generation of unexchangeable metal that remains is that, on calcination, some hydrolysis of the hydrated ion in the interlamellar region occurs to generate hydroxide or oxide with liberation of protons, viz.

$$M^{2+} + 2H_2O \rightarrow M(OH)_2 + 2H^+$$

$$M^{2+} + H_2O \rightarrow MO + 2H^+.$$

When calcined in air, a proportion of these protons migrate into the octahedral layer and cause charge reduction. When calcined in regeneration conditions, however, they are held in the interlamella region to maintain the cec at the true "internal" value.

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