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HYDROXY-NICKEL INTERLAYERING IN MONTMORILLONITE BY TITRATION METHOD

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Abstract—Nickel nitrate solution is potentiometrically titrated (a) with montmorillonite, (b) without montmorillonite, in the nitrate solution. X-ray powder diffraction and chemical analyses are made of the products formed by the clay at various stages of titration. The pH values of the titration curve (a) are lower than those of curve (b) until the brucite-like hydroxy-nickel interlayer is more or less complete. The resulting product then closely resembles a chlorite. The preferential precipitation of hydroxide in the interlayer region is explained in terms of the acidic character of montmorillonite interlayers.

Key Words—Chlorite, Interlayer, Montmorillonite, Nickel, Potentiometric.

INTRODUCTION

Various methods have been reported for preparing hydroxy interlayers in expanding layer silicates. These methods fall into two main groups: (i) a direct cation exchange method, (ii) a titration procedure. In method (i) the mineral, dispersed in water, is reacted with solutions containing hydrolyzed cations; after the exchange reaction, the excess cations are removed by centrifugation and washing. The method is applicable to cations which can be hydrolyzed extensively without precipitation of hydroxides. Examples are $Al(OH)_x$ and $Fe(III)(OH)_x$ in single or polymerized forms. Work prior to 1968 has been reviewed by Rich (1968); later studies include work by Sawhney (1968), Carstea et al. (1970), Herrera and Peech (1970), Brown and Newman (1973), Brindley and Sempels (1977).

In method (ii), cations in an appropriate solution are added to the dispersed clay and the resulting clay + solution is then hydrolyzed by simple addition of alkali in a predetermined amount or by progressive titration. This latter procedure, which is used in the present work, is applicable to cations which can be hydrolyzed only slightly before precipitation occurs. It has been applied particularly in attempts to develop chlorites or chlorite-like phases from montmorillonite by condensing hydroxide sheets between the silicate layers. Caillère and Hénin (1949) were pioneers in this type of study. Slaughter and Milne (1960) and Gupta and Malik (1969) made more detailed studies along similar lines. Attention was directed mainly towards intercalating $Mg(OH)_2$ and $Ni(OH)_2$ sheets between the silicate layers. The precise mechanism of the process has not been established but the general consensus is that the hydroxide is deposited on or sorbed by the silicate surfaces. In the present work, an attempt is made to follow the deposition of nickel hydroxide by potentiometric titration, with chemical and X-ray powder diffraction examination of the products formed at different stages of the process. The results lead us to conclude that the hydroxide-forming reaction takes place primarily *within* the interlayers of the layer silicate where the reaction conditions are different from those in the bulk solution. The results are relevant to the formation of chlorite-like phases and so-called "intergrade" minerals in nature.

EXPERIMENTAL

Montmorillonite

A Wyoming montmorillonite supplied by the American Colloid Company under the name "Volclay" was used. The montmorillonite was dispersed in distilled water and the $<2\ \mu$ fraction was separated by sedimentation. This fraction was saturated with 1 M NaCl and the excess electrolyte was removed by centrifugation and washing and subsequently by dialysis. The cation exchange capacity (CEC) was determined on the Na-montmorillonite dried at 110°C. The clay was saturated with $CaCl_2$ solution and the amount of exchanged Ca^{2+} was determined by atomic absorption spectroscopy after extraction with $MgCl_2$ solution The CEC thus determined, 83.5 meq/100 g, agreed well with the value (82.5) calculated from the Na content which was determined by the total analysis of the Na-montmorillonite.

Potentiometric titration

Separate 300 mg samples of Na-montmorillonite (dried at 60°C) were dispersed in 30 ml of 0.1 M $Ni(NO_3)_2$ carbonate-free solutions, and agitated by ultrasonic vibration. One of these suspensions was titrated potentiometrically with 0.1 N NaOH under vigorous stirring and with N_2 gas flowing at 20°C. The pH value at each stage of the titration was measured by using the Beckman Expandomatic pH meter. The titrated suspension was allowed to stand for one day to attain equilibrium at each stage of titration before the pH measurement. A nickel nitrate solution (0.1 M, 30 ml) was titrated similarly without clay for comparison. The other suspensions containing Na-montmorillonite also were titrated with 0.1 N NaOH but the titration was stopped at a given stage, and the pH values of these suspensions were measured after 10 days standing in

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Table 1. Basal spacings, Å, of products at various stages of titration.

Sample No.	Heat treatment 100°C	300°C	500°C	H_2O vapor	Eth. Gly vapor
1	10.3	9.7	9.6	15.9	17.0
2	11.0b	10.3b	10.3	18.0	16.8
3	13.0	vvb	11.3	15.5	16.4
4	14.8	vvb	12.0	14.9	14.8
5	14.8	15.0b	12.1	14.8	14.8
6	14.8	14.8b	12.1	14.8	14.8
7	14.8	14.8b	12.1	14.8	14.8

Sample numbers 1-7, see Figure 1.

Heat treatment, 20 hr at each temperature.

H_2O vapor, ∿ 100% R.H. at 20°C, 20 hr.

Eth. Gly. vapor, ethylene glycol vapor at ∿ 40°C, 6 days.

b, broad basal reflections; v, very

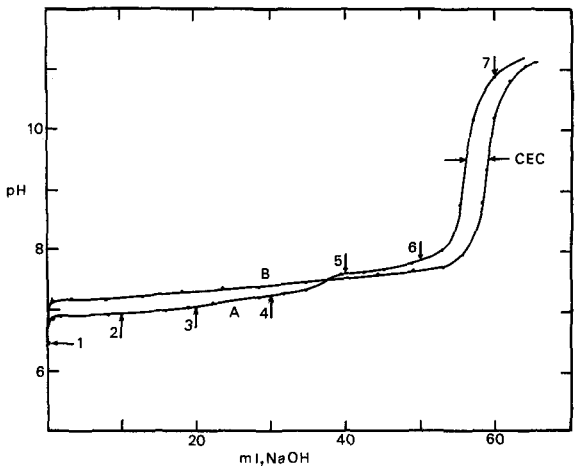


Fig. 1. Titration of nickel nitrate solution (30 ml, 0.1 M solution) by 0.1 N NaOH solution. (A) In the presence of Na-montmorillonite (300 mg); (B) Without clay.

N_2 gas. These values were almost the same as those determined after equilibration for one day at the corresponding stages of titration. After the pH measurements at the different stages of titration, the dispersed montmorillonites were separated and washed repeatedly with distilled water to remove electrolyte. The resulting samples were used for atomic absorption analysis and X-ray diffractometer study.

RESULTS

Titration curves

Two titration curves, A and B, obtained respectively with and without the presence of clay are shown in Figure 1. Curve B, without clay present, rises sharply with the first addition of NaOH. Precipitation of $Ni(OH)_2$ begins immediately. The amount of NaOH required to complete the titration is almost quantitative and the endpoint appears at a molar ratio OH/Ni = 1.97. Titration curve A, with clay present, consists of two stages. In the first stage, the pH values are smaller than those of the corresponding points of curve B. In the second stage, curve A rises above curve B and the amount of NaOH required to complete the titration is less than that without clay. The difference in the amounts of NaOH between the two end points is 91 meq/100 g of clay. This amount is almost equal to the cation exchange capacity of the clay because this amount of nickel should be retained in the ionic form if nickel ions completely replace the sodium ions of the clay.

X-ray powder diffraction data

Seven different titration points are designated in Figure 1 by the numbers 1–7. Basal spacings of the montmorillonites obtained under these conditions were measured after heating at 100°, 300°, and 500°C, each for periods of about 20 hr, after saturation with water and with ethylene glycol vapors. The results are listed in Table 1.

Sample 1, see Figure 1, is the product obtained after addition of the nickel nitrate solution to the clay suspension and prior to addition of NaOH. The product is Ni-montmorillonite and the chemical analysis is given later. The basal spacings after heat treatment, exposure to water vapor (20°C, ~100% RH, 24 hr), and exposure to ethylene glycol vapor (40°C, 6 days) are typical for a divalent ion montmorillonite.

Sample 4 and subsequent samples retain a basal spacing of 14.8 Å up to 300°C, but collapse to 12.1 Å at 500°C. They exhibit no swelling in water, water vapor, or ethylene glycol. The products behave in the manner of chlorites. The basal spacings are nearly regular and the recorded values are based mainly on 002, 003, and 004 reflections. The 001 reflection is weak but increases in intensity at 500°C in the normal manner of chlorites. The temperature stability is less than that of most well-developed chlorites, but the lower temperature of collapse to a 12.1 Å spacing for the fine-grained material is not unusual. These results agree with those of the earlier investigations. In particular, the basal spacing of 14.8 Å, which is greater than the range of spacings 14.2–14.4 Å for most chlorites, confirms the earlier results.

Samples obtained at points 6 and 7 on the titration curve showed the presence of NiO after heating at 500°C. Evidently these samples contain more nickel than is accommodated in the interlayer sheets. When these samples were washed with 0.05 N HCl for 10 min prior to heating, no NiO was detected by X-ray powder diffraction. The results indicate that nickel is precipi-

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Table 2. Chemical analyses and formulae of initial Na-montmorillonite and products 1–7 (see Figure 1).

	Na-M	1	2	3	4	5	6	7
SiO_2	60.6	55.9	49.6	45.0	40.3	37.3	34.6	33.0
Al_2O_3	21.2	19.4	17.5	15.7	13.9	12.9	12.1	11.3
Fe_2O_3	4.10	3.78	3.28	2.79	2.57	2.57	2.09	2.11
MgO	2.59	2.30	2.01	1.82	1.68	1.55	1.46	1.41
CaO	0.00	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Na_2O	2.54	0.00	0.00	0.00	0.00	0.00	0.00	0.00
NiO	n.d.	3.5	12.4	19.2	25.3	30.3	34.2	36.3
H_2O+	6.04	6.66	8.38	9.99	12.15	13.12	13.30	13.79
H_2O-	2.81	9.52	6.71	4.65	3.54	2.67	2.58	3.03
Total	99.88	101.06	99.88	99.15	99.44	100.41	100.33	100.94
Si	3.93	3.94	3.93	3.95	3.95	3.94	3.94	3.95
Al^{IV}	0.07	0.06	0.07	0.05	0.05	0.06	0.06	0.05
Al^{VI}	1.55	1.55	1.56	1.57	1.56	1.54	1.56	1.55
Fe	0.20	0.20	0.20	0.19	0.19	0.20	0.18	0.19
Mg	0.25	0.24	0.24	0.24	0.24	0.24	0.25	0.25
Na	0.32	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Ni	-	0.20	0.79	1.35	1.99	2.57	3.13*	3.50*
OH	-	0.08	1.26	2.38	3.66	4.82	5.94*	6.68*
H_2O	0.31	0.52	0.58	0.74	1.14	1.24	1.09	1.17
OH + H_2O	0.31	0.60	1.84	3.12	4.80	6.06	*	*

* includes externally precipitated $Ni(OH)_2$

tated preferentially between the silicate layers up to or slightly beyond point 5 on the titration curve. Beyond this point, the interlayer becomes saturated with nickel and the excess is precipitated as $Ni(OH)_2$ which forms NiO on heating at 500°C.

CHEMICAL ANALYSES OF PRODUCTS AND STRUCTURAL FORMULAE

Analytical data obtained by atomic absorption analysis for the initial Na-montmorillonite and for the samples labelled 1–7 on the titration curve are given in Table 2. The formula for the original Na-montmorillonite, derived on the basis of the anion composition $O_{10}(OH)_2$, indicates that the silicate layer charge is −0.32 per formula unit. The formulae for the samples 1–7 were evaluated assuming that the layer charges were maintained during the titration, and that the interlayer material has a composition of the form $[Ni_x(OH)_y \cdot mH_2O]^{+0.32}$. Even at point 1 on the titration curve, prior to addition of NaOH, a small proportion of OH ions appears to be taken up with the nickel ions. From point 2 to point 5, increasing amounts of Ni and (OH) are taken into the interlayer almost up to the limit which would be expected for a complete hydroxide interlayer as in chlorites. The limiting composition would be $[Ni_3(OH)_{5.68}0.32 H_2O]^{+0.32}$ with a charge of +0.32 to balance the negative layer charge.

Since we cannot say exactly at what point on the titration curve free $Ni(OH)_2$ is first formed but only that it must occur between the points 5 and 6, therefore we can claim only that the interlayer nickel ions must exceed 2.57 per formula unit and probably approach close to the ideal value of 3.0. We observe also that the combined OH + H_2O in the interlayer approaches closely to 6.0. It is understandable that as the interlayer approaches a full complement of nickel ions, the final filling of the interlayers may take place slowly, i.e., a kinetic factor may be involved.

DISCUSSION

The X-ray and chemical data support the conclusion that nickel hydroxide is precipitated preferentially between the silicate layers until an almost complete brucite-like sheet is developed. The final stage of the reaction may be kinetically controlled. The difference between the two titration curves in Figure 1 suggests a possible mechanism of the reaction. The important fact is that the medium remains more acid, (lower pH), when clay is present in the titrating system.

The immediate reaction between Na-montmorillonite and the nickel nitrate solution is the conversion of the clay to Ni-montmorillonite; the completeness of this reaction is shown by the chemical analysis of product no. 1.

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It is known that water of hydration associated with interlayer cations is polarized and tends to be dissociated to a greater extent than in normal solutions (see Ducros and Dupont, 1962; Mortland et al., 1963; Touillaux et al., 1968; Yamanaka et al., 1974). This process can be represented as follows:

$$Ni^{2+} \leftarrow \underset{\displaystyle H}{\overset{\displaystyle |}{OH}} \rightleftharpoons [Ni(OH)]^{+} + H^{+} \qquad (1)$$

The dissociated protons may be ion-exchanged or neutralized and further Ni ions taken up by the clay as the titration proceeds. The reaction then proceeds as follows:

$$\underset{\text{(interlayer)}}{[Ni_x(OH)_y mH_2O]^{+0.32}} + \underset{\text{(sol.)}}{Ni^{2+}} + 2\,H_2O \rightarrow$$

$$\underset{\text{(interlayer)}}{[Ni_{x+1}(OH)_{y+2} \cdot mH_2O]^{+0.32}} + 2\,H^{+} \qquad (2)$$

The fully developed brucite-like interlayer may have the composition $[Ni_3(OH)_{5.68}(H_2O)_{0.32}]^{+0.32}$.

The successful development of the titration curves shown in Figure 1 requires that NaOH be added slowly and with vigorous stirring in order to avoid local increases of pH which would carry curve A above curve B prior to completion of the reaction. However, if this should happen locally and some $Ni(OH)_2$ be precipitated prior to completion of the internal reaction, the acidity of the system as a whole may be sufficient to redissolve this premature $Ni(OH)_2$ and reestablish true equilibrium. Avoidance of local concentrations of NaOH, however, is difficult to ensure and therefore sufficient time to maintain equilibrium at each stage of titration is very important. The exact cross-over point of curves A and B is rather uncertain. Therefore the fact that sample 5, after the cross-over point, contains only 2.57 nickel ions as compared with 3.0 for a full layer, is not altogether surprising. It is satisfactory that sample 6 clearly shows externally precipitated $Ni(OH)_2$.

In the present study and in all previous work, the enlarged basal spacing of the product, about 14.8 Å, as compared with 14.2–14.4 Å for true chlorites has been observed. Both Slaughter and Milne (1960) and Gupta and Malik (1969) attributed the result to "the necessity of accommodating the original exchange cations of the montmorillonite used." This suggestion is certainly not valid in the present work. It seems more likely that the presence of water molecules causes the slightly increased basal spacing.

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Резюме- Раствор азотнокислого никеля был потенциометрически титрован /а/ с монтмориллонитом и /в/ без монтмориллонита в раствор нитрата.Полученные из глины продукты были исследованы в порошке методом дифракции рентгеновских лучей и химическими анализами.Значения pH кривой титрования /а/ меньше,чем кривой /в/,пока более или менее не завершится формирование бруситоподобного прослоя гидроокиси никеля.После этого полученный продукт близко напоминает хлорит.Преимущественное осаждение гидроокиси между слоями объясняется кислотной средой,существующей на поверхностях слоев монтмориллонита.

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