Clays and Clay Minerals, Vol. 28, No. 4, 281–284, 1980.

REACTION OF HYDROXY-BISMUTH POLYCATIONS WITH MONTMORILLONITE

SHOJI YAMANAKA, GUNJI YAMASHITA, AND MAKOTO HATTORI

Department of Applied Chemistry, Faculty of Engineering
Hiroshima University, Hiroshima, 730 Japan

Abstract—Interlayer sodium ions of montmorillonite were exchanged with hydroxy-bismuth polycations which were prepared from bismuth perchlorate solutions by the addition of NaOH. Assuming the charge density of the silicate layer to be unchanged, the compositions of the polycations involved in the exchange can be estimated from the amount of bismuth taken up by the montmorillonite and from the ignition loss between 110° and 800°C. The derived compositions are near $[Bi_6(OH)_{16}]^{2+}$ irrespective of the ratio of OH:Bi in the perchlorate solution. The basal spacing of the hydroxy-bismuth montmorillonites is about 16 Å at 110°C, which corresponds to that of hydroxy-chromium montmorillonite having a high surface area of about 250 m^2/g. The surface areas of the hydroxy-bismuth montmorillonites, however, are less than 80 m^2/g.

Key Words—Bismuth, Cation exchange, Hydrolysis, Hydroxy-bismuth, Montmorillonite, Surface area.

INTRODUCTION

The interlayer cations of expanding layer silicates can be exchanged with polymeric hydroxy-metal cations (see, e.g., Rich, 1968; Lahav *et al.*, 1978). Recently studies have been made of the exchange reactions of the polymeric cations of aluminum (Brindley and Sempels, 1977), nickel (Yamanaka and Brindley, 1978), zirconium (Yamanaka and Brindley, 1979), and chromium (Brindley and Yamanaka, 1979). An interesting common feature of these reactions is the much higher basicity of hydroxy cations taken up by the clays than those of the initial hydroxy-metal solutions used. Furthermore, the basal spacings enlarged by interlayering of hydroxy-aluminum and hydroxy-zirconium cations persist to about 500°C without collapse, and the resulting solids have surface areas as high as 300–500 m^2/g.

As a part of a continuing program in this area, the present study concerns the reaction between hydroxy-bismuth polycations and Na-montmorillonite.

EXPERIMENTAL

Preparation of hydroxy-bismuth solution

A small excess of bismuth oxide was dissolved in a known amount of perchloric acid, and the solution was filtered to remove undissolved bismuth oxide. The concentration of bismuth in the solution was analyzed, and the solution was diluted with distilled water to a final concentration of 0.1 M. The ratio of ClO_4:Bi in the solution thus prepared was slightly greater than 3. Excess perchloric acid was titrated with sodium hydroxide. Hydroxy-bismuth solutions with basicities OH/Bi = 0, 0.5, 1.0, 1.5, and 2.0 were prepared by further titrating the above perchlorate solution with 0.1 N NaOH.

Preparation of hydroxy-bismuth montmorillonite

The procedure used to prepare hydroxy-bismuth montmorillonite was similar to those used for hydroxy-zirconium (Yamanaka and Brindley, 1979) and hydroxy-chromium montmorillonites (Brindley and Yamanaka, 1979). Separate 300-mg samples of Na-montmorillonites (a Wyoming montmorillonite supplied by the American Colloid Company as used in previous studies) were dispersed in 20 ml of water, and 60 ml of a hydroxy-bismuth solution was added. After stirring for 1 hr, the montmorillonite was separated and washed repeatedly with distilled water to remove excess electrolyte and dried at 40°C in air.

The change in basal spacing of hydroxy-bismuth montmorillonites on heat treatment to 500°C was followed by X-ray powder diffraction (XRD) examination of thin layers of the clay on glass slides. Surface areas were determined volumetrically by nitrogen adsorption at liquid nitrogen temperature after heating the samples at temperatures ranging from 110° to 500°C. The adsorption isotherm followed Langmuir monolayer adsorption.

Analysis

The clay sample was dried at 800°C to constant weight, and the weight loss between 110° and 800°C was recorded as $H_2O(+)$. Higher temperatures were not used to avoid the vaporization of bismuth oxide. The dried sample was decomposed and dissolved by hydrofluoric and nitric acids. Bismuth was determined colorimetrically by using thiourea (Asmus, 1954); sodium was determined by flame analysis.

Copyright © 1980, The Clay Minerals Society

https://doi.org/10.1346/CCMN.1980.0280406 Published online by Cambridge University Press

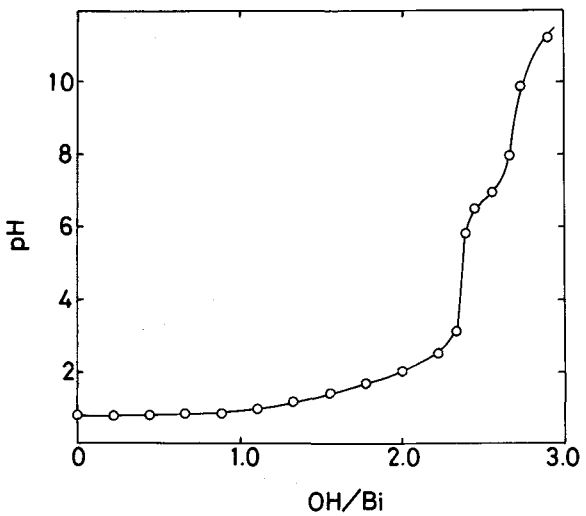


Figure 1. Titration curve for 0.1 M bismuth perchlorate with 0.1 N NaOH.

RESULTS AND DISCUSSION

A titration curve for 0.1 M bismuth perchlorate solution with 0.1 N NaOH is shown in Figure 1. The change in pH was very small until bismuth hydroxide began to precipitate at OH/Bi $\approx$ 2.4 with sudden increase in the pH. The well established species of bismuth cations present in solutions are $Bi(OH)^{2+}$ and $[Bi_6(OH)_{12}]^{6+}$ (Baes and Mesmer, 1976). The latter is predominant, and its concentration increases as the titration proceeds. A shoulder around OH/Bi = 2.4 in the titration curve is attributed to the occurrence of additional polymeric species of Bi^{3+}, such as $[Bi_9(OH)_{20}]^{7+}$ and $[Bi_9(OH)_{21}]^{6+}$.

The XRD patterns of Na-montmorillonite treated with hydroxy-bismuth solutions with 0 to 2.0 basicities resemble each other even after the samples were heated to 500°C. The patterns for the products where OH/Bi = 1.0 are shown in Figure 2. As seen in the figure, the basal spacing of the sample dried at 110°C is about 16 Å and nearly regular with (002), (003), and (005) reflections. After heating the sample at 200°C, the (001) reflection disappeared, and the reflections of higher orders shifted slightly. The (001) broad reflection returned on heating at 500°C to a value of about 9.8 Å, indicating a complete collapse of the clay. The disappearance of the (001) reflection on heating to 200°C can be interpreted in terms of the large X-ray scattering power of Bi atoms. It seems likely that even a slight rearrangement of bismuth atoms due to a partial collapse of the layer on heating causes remarkable reduction in the reflection intensity.

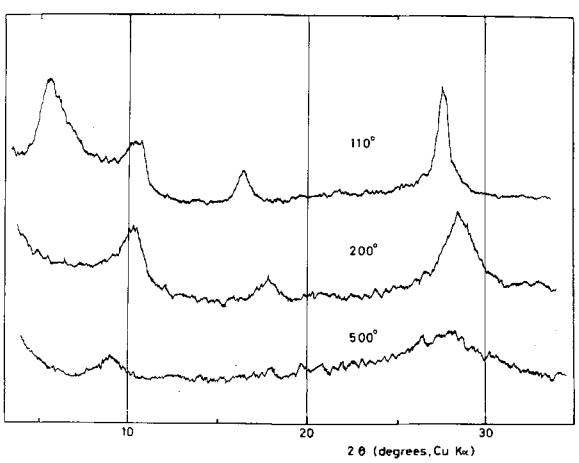


Figure 2. X-ray diffraction patterns (CuKα radiation) for hydroxy-bismuth montmorillonites obtained from the hydroxy solution where OH/Bi = 1.0 after heat treatment at 110°, 200°, and 500°C.

Table 1. Chemical analyses of interlayer compositions of hydroxy-bismuth montmorillonites.

	OH/Bi ratios of initial solutions				
	0	0.5	1.0	1.5	2.0
Compositions (wt. %) on 110°C dry basis					
Bi	24.2	24.5	25.6	26.8	27.2
Na	0.78	0.63	0.30	0.40	0.16
$H_2O(+)$	5.8	5.8	5.3	5.4	5.3
Interlayer compositions per formula unit containing $O_{10}(OH)_2$					
Bi	0.59	0.61	0.64	0.68	0.70
Na	0.17	0.14	0.08	0.10	0.04
OH	1.29	1.37	1.08	1.22	1.20
O	0.17	0.14	0.30	0.30	0.31
[(OH) + 2(O)]/Bi	2.76	2.71	2.63	2.68	2.60

The results of elemental analyses for bismuth and sodium are summarized in Table 1, together with weight loss (H_2O+) data for heating from 110° to 800°C. Half of the interlayer sodium ions were exchanged with hydroxy bismuth cations in the bismuth perchlorate solution even without the addition of NaOH. The remaining interlayer sodium ions were gradually exchanged as the basicity of the bismuth solutions increased. The interlayer compositions were calculated on the basis of $O_{10}(OH)_2$ anion composition on the following assumptions:

1. The composition of the silicate layer, $[(Si_{3.93}Al_{0.07})(Al_{1.55}Fe_{0.20}Mg_{0.25})O_{10}(OH)_2]^{-0.32}$, is unchanged during the exchange reaction.
2. The interlayer hydroxy-bismuth cations which balance the negative layer charge have a composition of $[Bi_x(OH)_yO_z]^{+0.32}$.
3. Ignition loss $H_2O(+)$ comes from the escape of y(OH) from the hydroxy-bismuth cations and of $O_{10}(OH)_2$ from the silicate layer.

The calculated compositions in the table suggest that

https://doi.org/10.1346/CCMN.1980.0280406 Published online by Cambridge University Press

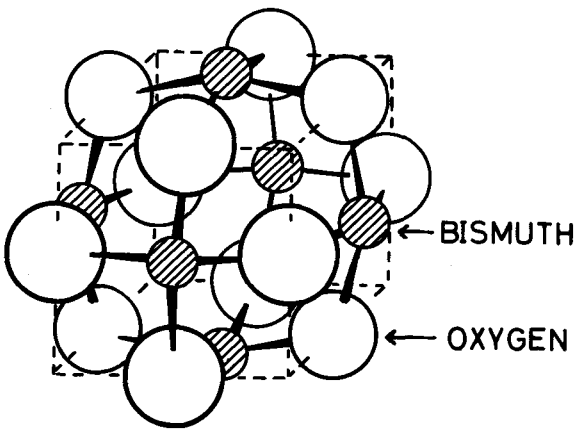


Figure 3. Structural model of hydroxy-bismuth cation $[Bi_6(OH)_{12}]^{6+}$ from Levy *et al.* (1959).

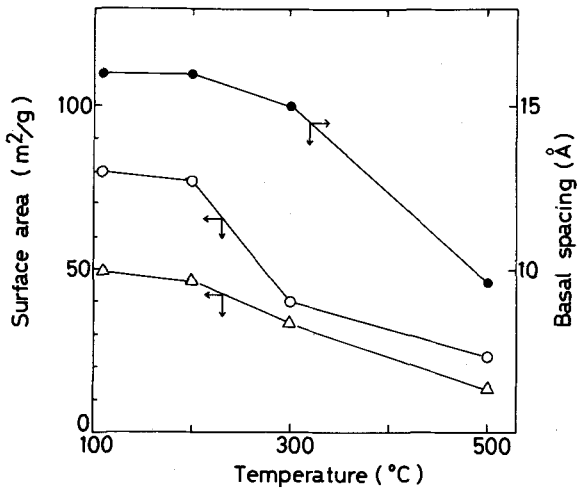


Figure 4. Surface areas and basal spacings of hydroxy-bismuth montmorillonites obtained from the hydroxy solutions vs. treated temperature; ○, OH/Bi = 0 and △, OH/Bi = 2.0.

the interlayer hydroxy-bismuth cations are partly dehydroxylated on heating even at 110°C, thus the basicity of the hydroxy cations is given by [(OH) + 2(O)]/Bi in the table. As pointed out as a common feature of the exchange reactions of clay with hydroxy-metal cations, the basicity of interlayer hydroxy-bismuth cations is much larger than that of the hydroxy solution. Moreover, the basicity was almost constant regardless the basicity of the initial solution. This result suggests that a single hydroxy-bismuth cationic species was involved in the exchange reactions. This contrasts with hydroxy-chromium and hydroxy-aluminum montmorillonites where OH/metal ratios of interlayer cations vary with basicities of the hydroxy-metal solutions (Veith, 1978).

Since the principal hydroxy-bismuth cations in solutions are in the form $[Bi_6(OH)_{12}]^{6+}$, it is reasonable to assume that the interlayer hydroxy species are also Bi_6 species. The interlayer compositions given in Table 1 indicate that the hydroxy species on Bi_6 basis is close to $[Bi_6(OH)_{16}]^{2+}$ which will be partly dehydroxylated on drying at 110°C.

The structure of $[Bi_6(OH)_{12}]^{6+}$ was determined by an XRD study of bismuth solutions (Levy *et al.*, 1959). As shown in Figure 3, bismuth atoms are in octahedral arrangement with four hydroxy groups per bismuth, with the oxygen atoms at the centers of octahedral edges. The bismuth–bismuth distance between opposite apices of the octahedron is 5.23 Å. In the interlayer $[Bi_6(OH)_{16}]^{2+}$ ions, four additional hydroxyl groups seem to attach to bismuth atoms. The expanded spacing of the montmorillonite is compatible with the interlayering of the monolayer of hydroxy-bismuth polycations.

Surface areas of the bismuth-hydroxy montmorillonites heated to 500°C are shown in Figure 4. Although there is a parallel relation between the surface area and the basal spacing, surface areas are all less than 80 m²/g, which is much smaller than the 250 m²/g for hydroxy-chromium montmorillonite having a similar spacing of 16 Å at 200°C (Brindley and Yamanaka, 1979). Evidently the basal spacing of hydroxy-metal complexes is not the only factor which determines surface areas. A possible explanation is that most of the pores in the hydroxy-bismuth montmorillonite are isolated for some reason, so that nitrogen penetration does not occur. Information on the orientation and distribution of the hydroxy-metal cations in the interlayer spaces is needed for further discussion.

ACKNOWLEDGMENT

This study was supported in part by a grant-in-aid for a special research project from the Ministry of Education of Japan.

REFERENCES

Asmus, A. (1954) Photometrische Wismutbestimmung in Blei–Zinnlegierungen: *Z. Anal. Chem.* **142,** 255–266.

Baes, C. F., Jr. and Mesmer, R. E. (1976) *The Hydrolysis of Cations:* John Wiley, New York, 375–383.

Brindley, G. W. and Sempels, R. E. (1977) Preparation and properties of some hydroxy-aluminum beidellites: *Clay Miner.* **12,** 229–237.

Brindley, G. W. and Yamanaka, S. (1979) A study of hydroxy-chromium montmorillonites and the form of the hydroxy-chromium polymers: *Amer. Mineral.* **64,** 830–835.

Lahav, N., Shani, U., and Shabtai, J. (1978) Cross-linked smectites. I. Synthesis and properties of hydroxy-aluminum montmorillonite: *Clays & Clay Minerals* **26,** 107–115.

Levy, H. A., Danford, M. D., and Agron, P. A. (1959) X-ray diffraction study of bismuth polymer in aqueous perchlorate solution: *J. Chem. Phys.* **31,** 1458–1461.

Rich, C. I. (1968) Hydroxy interlayers in expansible layer silicates: *Clays & Clay Minerals* **16,** 15–30.

Veith, J. A. (1978) Selectivity and adsorption capacity of

https://doi.org/10.1346/CCMN.1980.0280406 Published online by Cambridge University Press

smectite and vermiculite for aluminum of varying basicity: *Clays & Clay Minerals* **26,** 45–50.

Yamanaka, S. and Brindley, G. W. (1978) Hydroxy-nickel interlayering in montmorillonite by titration method: *Clays & Clay Minerals* **26,** 21–24.

Yamanaka, S. and Brindley, G. W. (1979) High surface area solids obtained by reaction of montmorillonite with zirconyl chloride: *Clays & Clay Minerals* **27,** 119–124.

(Received 5 December 1979; accepted 1 February 1980)

Резюме—Межслойные натриевые ионы монтмориллонита были заменены поликатионами оксивисмута, которые приготовлялись из растворов висмутового перхлората добавлением NaOH. Предполагая, что плотность зарядов силикатного слоя не должна изменяться, состав поликатионов, вовлеченных в обмен, можно определить по количеству висмута принятого монтмориллонитом и из потерь прокаливания при температурах от 110° до 800°C. Полученные составы близки $[Bi_6(OH)_{16}]^{2+}$ независимо от отношения OH:Bi в перхлоратовых растворах. Основной промежуток оксивисмутовых монтмориллонитов равен примерно 16 Å при 110°C, который соответствует промежутку оксихромового монтмориллонита, имеющего большую поверхностную площадь, примерно 250 м²/г. Поверзностные площади висмутовых монтмориллонитов, однако, меньше 80 м²/г. [N.R.]

Resümee—Zwischenschichtnatrium von Montmorillonit wurde gegen Hydroxy-Wismut-Polykationen ausgetauscht, die durch die Zugabe von NaOH aus Wismutperchloratlösungen hergestellt wurden. Unter der Annahme einer unveränderten Ladungsdichte der Silikatlagen kann man die Zusammensetzung der am Austausch beteiligten Polykationen aus der Wismutmenge, die durch den Montmorillonit aufgenommen wird, und aus dem Glühverlust zwischen 110° und 800°C abschätzen. Die abgeleiteten Zusammensetzungen sind etwa $[Bi_6(OH)_{16}]^{2+}$, unabhängig vom OH:Bi-Verhältnis in der Perchloratlösung. Der Basisabstand der Hydroxy-Wismut-Montmorillonite beträgt bei 110°C etwa 16 Å. Dies entspricht dem von Hydroxy-Chrom-Montmorillonit, der eine große Oberfläche von etwa 250 m²/g hat. Die Oberflächen der Hydroxy-Wismut-Montmorillonite sind dagegen unter 80 m²/g. [U.W.]

Résumé—Des ions de sodium interfeuillets de montmorillonite ont été échangés avec des polycations hydroxy-bismuth qui avaient été préparés à partir de solutions de perchlorate par addition de NaOH. Si l'on suppose que la densité de charge de la couche silicée demeure inchangée, les compositions des polycations concernés par l'échange peuvent être estimées par la quantité de bismuth prise par la montmorillonite et par la perte à l'ignition entre 110° et 800°C. Les compositions derivées sont près de $[Bi_6(OH)_{16}]^{2+}$ de manière irrespective de la proportion de OH:Bi dans la solution de perchlorate. L'espacement basal des montmorillonites hydroxy-bismuth est à peu près 16 Å à 110°C, ce qui correspond à celui de la montmorillonite hydroxy-chromium ayant une aire de surface élevée d'approximativement 250 m²/g. Les aires de surface des montmorillonites hydroxy-bismuth sont cependant moins que 80 m²/g. [D.J.]

https://doi.org/10.1346/CCMN.1980.0280406 Published online by Cambridge University Press