HIGH SURFACE AREA SOLIDS OBTAINED BY REACTION OF MONTMORILLONITE WITH ZIRCONYL CHLORIDE

S. YAMANAKA[1] AND G. W. BRINDLEY

Mineral Sciences Building, The Pennsylvania State University
University Park, Pennsylvania 16802

Abstract—Exchange reactions of Na-montmorillonite with zirconyl chloride solutions give products with basal spacings near 18 Å which are stable to 500°C and have surface areas of the order of 300–400 m²/g. The Na ions are exchanged with tetrameric hydroxy cations $[Zr_4(OH)_{14} \cdot nH_2O]^{2+}$. The high surface area is attributed to the porosity formed by stable zirconium oxide "pillars" formed by dehydroxylation of the complex cation. The nitrogen adsorption isotherms are of Langmuir type and are consistent with adsorption in interlayer micropores. Reduced-charge montmorillonites, formed by application of the Hofmann-Klemen procedure, give either similar or slightly smaller surface areas.

Key Words—Adsorption, Exchange, Hydroxyzirconium, Montmorillonite, Surface, Zirconium.

INTRODUCTION

The present investigation forms part of a program to study the formation of stable, high surface area solids by developing oxide pillars between the layers of expanding layer silicates. A previous study of hydroxy-aluminum beidellites (Brindley and Sempels, 1977) used hydroxy-aluminum polymeric cations developed in solutions with OH/Al ratios mainly in the range 2.0–2.5. The basal spacing of the prepared clays was near 17 Å and persisted without collapse to about 500°C. Surface areas between 200 and 500 m²/g were obtained depending on whether the initial Na ions were wholly or partially replaced by hydroxy-aluminum ions.

The present study is concerned with the incorporation of hydroxy complexes of zirconium in normal montmorillonite and in reduced charge montmorillonites. Aqueous solutions of zirconyl chloride, $ZrOCl_2$ contain tetrameric hydroxy complexes of the type $[Zr_4(OH)_{16-n}(H_2O)_{n+8}]^{n+}$, the charge per Zr atom being n/4 (Muha and Vaughan, 1960). In a previous study of the fixation of zirconium by acid montmorillonite from solutions of zirconyl chloride, Bittel et al. (1959) reported that about 110–120 milliatoms of zirconium were fixed (exchanged) per 100 g clay with an exchange capacity of about 100 meq/100 g clay, or in other words the charge per Zr atom was slightly less than +1. They considered that the most probable explanation was that the zirconium was fixed "sous forme d'ions très condensés." In the present work a quantitative evaluation of the zirconyl-exchanged montmorillonite is given and the thermal stability and surface area of the resulting products are discussed.

EXPERIMENTAL

Montmorillonite

A Wyoming montmorillonite supplied by the American Colloid Company with the trade name "Volclay"

was used. The same montmorillonite was used in a previous study (Yamanaka and Brindley, 1978) where the chemical analysis and structural formula are given. Na- and Li-saturated samples were prepared by treatment with the respective 1 N chloride solutions, with subsequent washing by centrifugation and dialysis to remove excess chloride.

Reduced charge montmorillonites (RCM) were prepared by the method described by Brindley and Ertem (1971). Li- and Na-montmorillonite were fully dispersed separately in water and the two dispersions were mechanically mixed in various ratios. After centrifugation and drying at 60°C, the mixtures were heated at 200°C for 24 hr. Hofmann and Klemen (1950) showed that when Li-montmorillonite is heated, the Li ions move into octahedral positions and neutralize locally the charges resulting from Mg-for-Al substitutions. The layer charge and the exchange capacity of the clay are thereby reduced.

The cation exchange capacity (CEC) was determined on RCMs as follows: The RCM was dispersed in a mixture of acetone and 1 N sodium acetate solution; it was then saturated with Ca^{2+} ions using 1 N $CaCl_2$. The exchanged amount of Ca^{2+} was determined by atomic absorption after extraction with $MgCl_2$. The CEC determined on the basis of sample weight after drying at 110°C was in the range of 86.2 to 49.0 meq/100 g for different sample preparations.

Preparation of hydroxy-zirconium-montmorillonite

Na-montmorillonite was fully dispersed in water and then an excess 0.1 M $ZrOCl_2 \cdot 8H_2O$ solution was added to the dispersion. After standing for various times with occasional shaking, the dispersed montmorillonite was separated by centrifugation and washed repeatedly with distilled water until chloride ion free. The resulting solid was dried at 60°C.

Highly reduced charge montmorillonite did not swell in water and did not react with a $ZrOCl_2 \cdot 8H_2O$ solution. These clays were dispersed in a mixture of acetone and

---

119

Table 1. Chemical analyses of Na-montmorillonite and hydroxy-Zr-montmorillonites.

	Na-mont.	1 hr treatment	16 hr treatment
SiO_2	60.6	47.1	45.7
Al_2O_3	21.2	16.3	15.9
Fe_2O_3	4.10	2.85	2.73
MgO	2.59	1.89	1.83
Na_2O	2.54	0.11	0.14
ZrO_2	n.d.	13.8	13.9
$H_2O(+)$	6.04	7.74	7.39
$H_2O(-)$	2.81	11.63	13.33
Cl	n.d.	0.00	0.00
Total	99.88%	101.42%	100.92%
Si	3.93	3.95	3.95
Al^{IV}	0.07	0.05	0.05
Al^{VI}	1.55	1.56	1.57
Fe	0.20	0.18	0.18
Mg	0.25	0.24	0.24
Na	0.32	0.02	0.02
Interlayer hydroxy material			
Zr	—	0.56	0.58
OH	—	1.94	2.02
H_2O	0.31	0.22	0.11
Effective charge per Zr atom[1]	—	0.53$_5$	0.51$_7$

$H_2O(-)$: ignition loss below 110°C.
$H_2O(+)$: ignition loss from 110° to 1000°C.
In all cases, the anions in the layer structure are $O_{10}(OH)_2$.
[1] This charge = [layer charge, 0.32 − no. of Na ions]/ no. of Zr atoms.

water (300 mg of RCM in 10 ml of acetone + 10 ml of water), and then 30 ml of 0.1 M $ZrOCl_2 \cdot 8H_2O$ was added to the dispersion. The products were washed and dried in the manner described.

Surface area determinations

Surface areas of samples heated at various temperatures up to 600°C for 20 hr were determined by using a Quantasorb Surface Area Analyzer of Quantachrom Corporation. Samples were degassed at 200°C for 2 hr by flowing dry N_2 gas before measurement.

Elemental analysis

Elemental analysis of the hydroxy-Zr-montmorillonites was carried out by atomic absorption spectroscopy employing $LiBO_2$ fusion (Medlin et al., 1969). Chlorine was determined indirectly by atomic absorption method after precipitation as AgCl by adding a known excess of silver nitrate. The concentration of unreacted silver was determined after separation of the AgCl (Westerlund-Helmerson, 1966). Zirconium was determined colorimetrically by using xylenol orange (Jeffery, 1975).

RESULTS

Chemical analysis

The analytical data for the Na-montmorillonite treated with 0.1 M $ZrOCl_2$ solution for 1 and 16 hr are given

in Table 1, together with the data for the initial Na-montmorillonite. The formula of the initial montmorillonite is evaluated on the basis of an anion composition $O_{10}(OH)_2$ or a total cation valence of +22. The formulae of the hydroxy-Zr-montmorillonites are obtained by assuming that the layer charge remains unchanged.

The data indicate that essentially all the sodium ions were exchanged with hydroxy-zirconium cations and that the exchange reaction was completed within 1 hr. The apparent charge for an exchange zirconium atom is close to 0.5. This low charge indicates that zirconium is taken up by montmorillonite in the form of polynuclear cations; in the general formula given previously, $n \simeq 2$.

Fixation of zirconium

The CEC of the hydroxy-Zr-montmorillonite was measured by a method similar to that used to determine the CEC of RCM. The observed value was 33 meq/100 g, which is about one-third of the value for the initial Na-montmorillonite. No zirconium was detected in the $CaCl_2$ solution used for the CEC measurement, and only a slight change in basal spacing was observed after the measurement. The observed CEC is considerably larger than can be attributed to edge effects. Since no zirconium is removed by the exchange reaction, it seems most likely that protons associated with the hydroxy-zirconium are involved.

It is noteworthy that there is a true fixation of the zirconium by the montmorillonite. Bittel et al. (1959) described as fixation the amount of zirconium taken up from the zirconyl solution. Here we use the term in the sense that the zirconium is not exchangeable.

Basal spacings and dehydration-dehydroxylation data

The Na-montmorillonite treated with 0.1 M $ZrOCl_2 \cdot 8H_2O$ solution showed abnormally large basal spacings. After standing at room temperature in air of about 50% relative humidity, the hydroxy-Zr-montmorillonite gave a basal spacing of 18.8 Å, and in water swelled readily to a spacing of 24.5 Å. The basal spacings, d(001), and the corresponding surface areas, S, after heating for periods of 20 hr at various temperatures up to 600°C are shown in Figure 1. The spacing measurements are based on the first diffraction peak. The higher orders were very weak and broad for the heated samples and the individual spacings were probably variable.

Figure 2 shows the percentage weight loss of the sample after 12 hr heating at each temperature. The whole dehydration-dehydroxylation process of the hydroxy-Zr-montmorillonite can be divided into three stages:

Room temperature–110°C: Dehydration of water molecules loosely absorbed in the interlayer spaces and on external surfaces (16.4% weight loss).
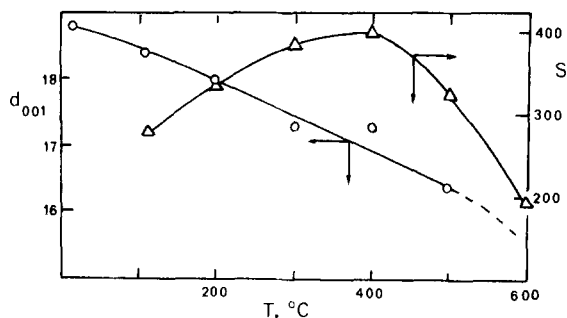
Figure 1.   Basal spacings, d(001), in Å and surface areas, S, in m²/g, of zirconium montmorillonites heated 20 hr at temperatures T, °C.

110°–480°C: Dehydration of water molecules strongly associated with hydroxy-zirconium cations and dehydroxylation of hydroxy-zirconium (4.2% weight loss).

480–850°C: Decomposition of the silicate structure (3.6% weight loss) with a loss of one water molecule per formula unit by dehydroxylation.

The number of water molecules per formula unit evolved in the 110°–480°C stage was calculated by comparing the weight loss in this stage with that in the final stage. The loss in the second stage corresponds to 1.17 water molecules per formula unit. Since 0.58 atom of zirconium is absorbed per formula unit, the dehydration-dehydroxylation reaction in the second step can be formulated as follows, using the average composition of the two analyses in Table 1:

$$[Zr_{0.57}(OH)_{1.98}(H_2O)_{0.17}]^{+0.30} \rightarrow [Zr_{0.57}O_{0.99}]^{+0.30} + 1.16H_2O.$$
interlayer/formula unit
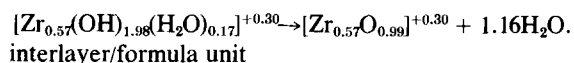
Essentially there is complete agreement between the total analyses shown in Table 1 and the weight loss data of Figure 2. It is seen that the composition of the interlayer material after dehydroxylation is close to ZrO_2, but not exactly because of the necessity of maintaining an interlayer charge of +0.30/formula unit.

Nitrogen sorption and surface area data

Nitrogen sorption data for the heated complexes in the relative pressure range 0.08–0.32 were plotted according to the two adsorption isotherms:

Type I: Langmuir isotherm

$$\frac{P/P_0}{V} = \frac{1}{kV_m} + \frac{P/P_0}{V_m} \qquad (1)$$

Type II: Brunauer, Emmett, and Teller (BET) isotherm

$$\frac{1}{V(P_0/P - 1)} = \frac{1}{CV_m} + \frac{P/P_0}{V_m} \qquad (2)$$

where P/P_0 is the relative vapor pressure, V the volume of gas adsorbed, V_m the volume of gas required for monolayer adsorption, and C and k are constants.

These equations assume respectively (1) monolayer adsorption, and (2) multilayer adsoption on open surfaces. The former adsorption occurs when the pore dimensions approach the dimensions of the sorbate molecules. In such pores, multilayer adsorption is physically impossible.

Figure 3 shows representative plots of nitrogen adsorption based on equations (1) and (2) for the hydroxy-Zr-montmorillonite heated at 300°C for 20 hr. The Langmuir equation gives the linear plot. All of the hydroxy-Zr-montmorillonites heated at the temperatures shown in Figure 1 give Type I adsorption. The areas
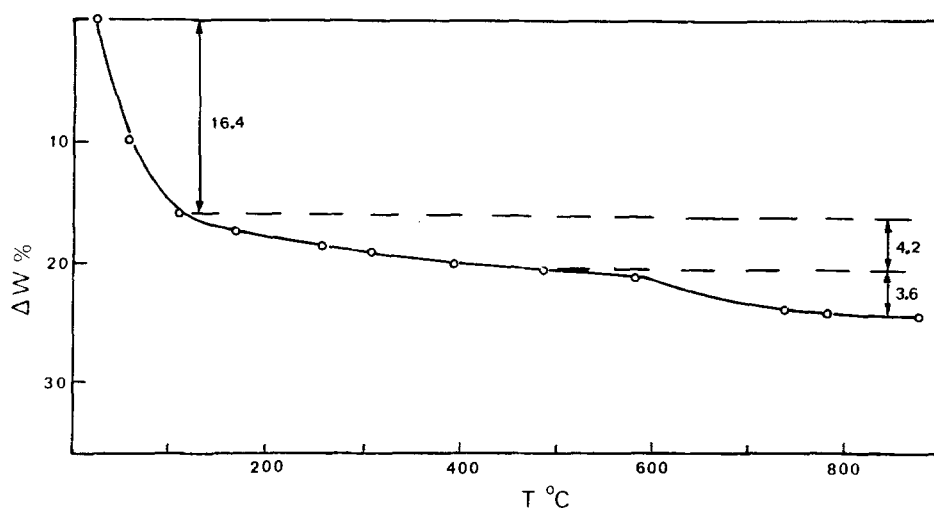

Figure 2.   Weight change of zirconium montmorillonite, expressed as percentage of sample weight at room temperature and 50% R.H., when heated for periods of 12 hr at successively higher temperatures, T.
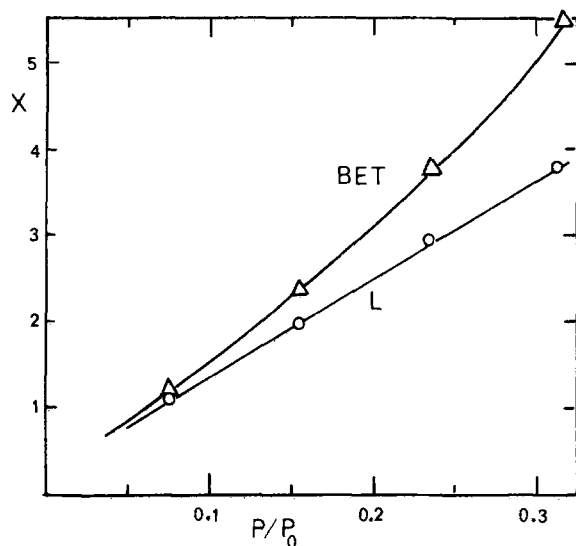
Figure 3.   Plots of $X = P/P_0V$ (curve L) and $X = P/(P_0 - P)V$ (curve BET) for hydroxy-Zr-montmorillonite heated at 300°C/20 hr, vs. relative pressures, P/P_0. X is expressed in units of $g\ cm^{-3} \cdot 10^3$. The linearity of the Langmuir plot L and curvature of the BET plot are evident.

were determined from the values of V_m, taking 16.2 Å² as the area occupied/N_2 molecule. The results indicate that the high surface area of the heated hydroxy-Zr-montmorillonite is due predominantly to micropores in the interlayer spaces.

Hydroxy-zirconium complexes with reduced charge montmorillonites

Hydroxy-zirconium complexes were prepared using reduced charge montmorillonites. The amount of zirconium taken up by the reduced charge montmorillonites is shown in Figure 4 where Zr atoms/formula unit are plotted against layer charge per formula unit. The slope of the line corresponds to about 1.85 Zr atoms per unit change of layer charge. Again we find an effective charge near +0.5 for each Zr atom.

As mentioned in the experimental section, the highly reduced charge montmorillonites did not disperse in zirconyl chloride solution, and therefore were dispersed in a mixture of acetone and water before adding the zirconyl chloride solution. To examine the possible effect of acetone on the formation of the hydroxy-zirconium complexes, the initial montmorillonite was treated with 0.1 M zirconyl chloride solution both with and without the addition of acetone. The amount of zirconium taken up by the montmorillonite in the presence of acetone was larger than the amount taken up without acetone by about 0.1 Zr atom/formula unit. This amount, which corresponds to the intercept on the Zr axis in Figure 4, may be adsorbed on interlayer and external surfaces as neutral species such as $Zr_4(OH)_{16}$. The basal spacing of the Zr-montmorillonite prepared in the presence of acetone also was larger than that pre-
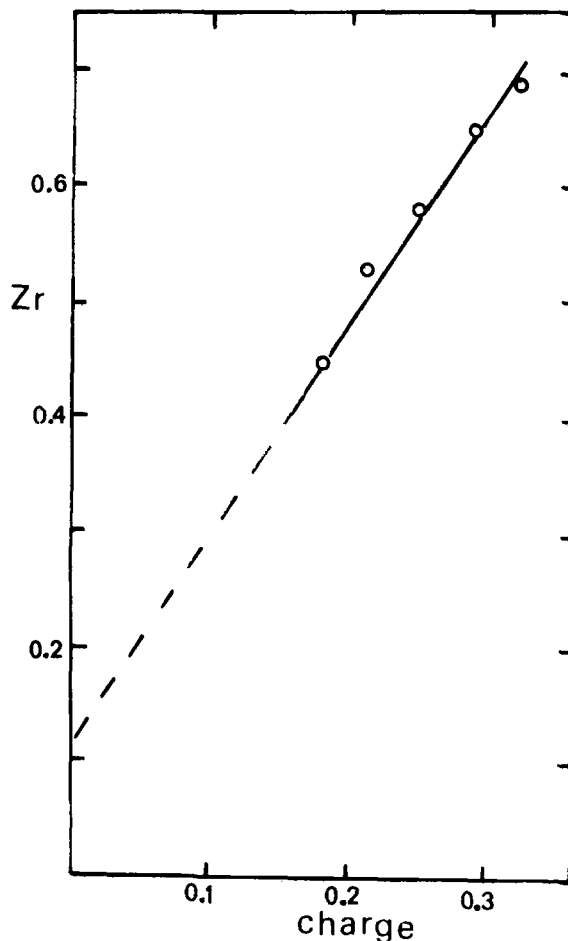

Figure 4.   Results for reduced charge montmorillonites. Number of Zr atoms per formula unit plotted against layer charge per formula unit.

pared without acetone and the difference persisted when the samples were heated. Therefore, it seems likely that the larger spacing obtained when acetone is used in the preparation may be related to the form or arrangement of the zirconium complexes rather than the inclusion of acetone molecules which would not remain in the heated samples.

The basal spacings of the Zr-montmorillonites with reduced charges are shown with respect to temperature in Figure 5. Curves 1–4 correspond to exchange capacities of 47.0, 57.6, 67.0, and 86.2 meq/100 g clay; curve 4 corresponds to the montmorillonite with normal charge. At the lower temperatures, the spacing increases as the charge diminishes, but the differences diminish as the temperature increases, and disappear at 400°C. The increase of spacing with diminution of charge is consistent with the decrease of electrostatic attraction between the layers and the interlayer ions.

Figure 6 shows the surface areas of the reduced charge montmorillonites after heat-treatment at 300° and 500°C plotted against the CEC. Contrary to the
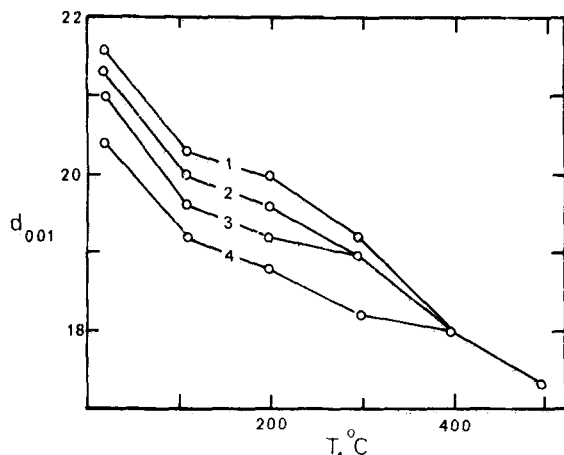
Figure 5. Basal spacings, d(001), in Å, of reduced charge, zirconium montmorillonites vs. temperature. The curves shown correspond to cation exchange capacities as follows: (1) 4.70, (2) 5.76, (3) 67.0, (4) 86.2 meq/100 g clay.

Figure 7. Probable form of the $[Zr_4(OH)_{14}(H_2O)_{10}]^{2+}$ complexes.

original expectation, the surface area tends to decrease as the layer charge (i.e., CEC) decreases, even though below 400°C the basal spacing increases with decrease of layer charge (see Figure 5). The main conclusion, however, is that the surface area remains almost constant when the layer charge is diminished from about 90 to about 50 meq/100 g clay.

DISCUSSION

The basic species in zirconyl chloride solutions are tetrameric hydroxy cations $[Zr_4(OH)_{16-n}(H_2O)_{n+8}]^{n+}$ (Muha and Vaughan, 1960). It is reasonable to assume that these tetrameric cations are involved in the exchange reaction with the interlayer cations of montmorillonite. From the results obtained, the charge per zirconium atom is close to 0.5 and corresponds to the tetrameric complex, $[Zr_4(OH)_{14}(H_2O)_{10}]^{2+}$; two of the four zirconium atoms presumably retain single positive charges and the other two are neutral. The four zirconium ions can be hydrolyzed independently and such a tetrameric cation can be represented schematically as
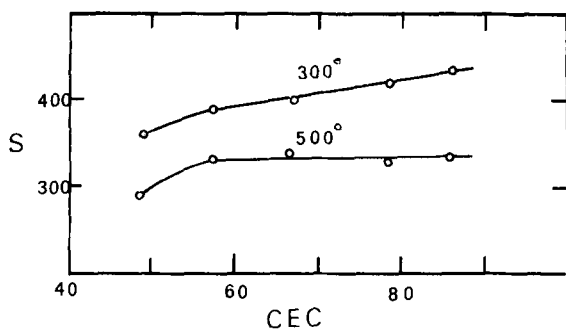

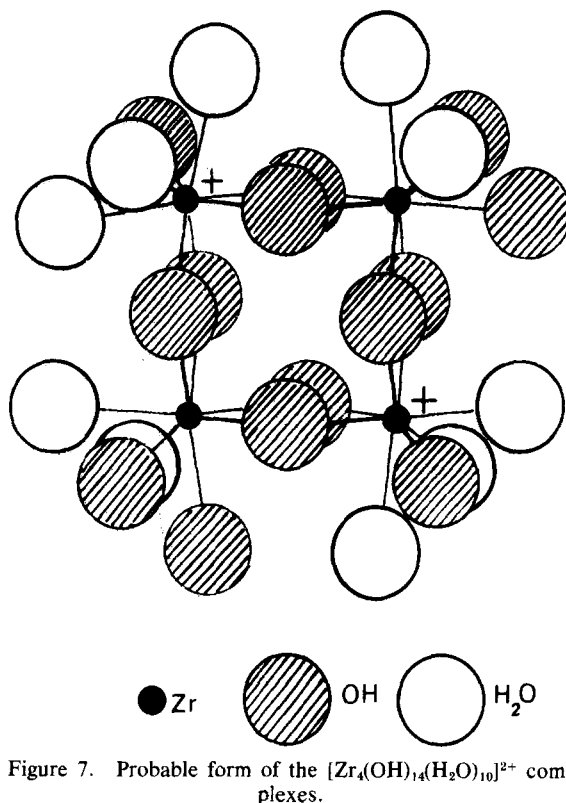Figure 6. Surface area S, in m²/g, of reduced charge, Zr-montmorillonites after heating at 300° and 500°C.

shown in Figure 7. The overall dimensions of this complex, estimated from the structural data reported by Clearfield and Vaughan (1956), are ~10 Å for the overall square configuration and 4.5 Å for the thickness, and include the van der Waals radii of the oxygen atoms. A complex with these dimensions can be fitted into the interlayer space of the expanded montmorillonite with either a double layer of flat-lying complexes, or a single layer of complexes standing normal to the layer. Both arrangements give a basal spacing near 19 Å, and it is difficult to determine the more likely arrangement because of the limitations of the available data. With either arrangement, the pore volume in the interlayer space can be estimated on the basis that one square complex cancels two negative charges of the silicate layers. It follows that 0.32 square complex is exchanged per unit cell. The interlayer space of the 18.4 Å montmorillonite complex is 8.8 Å thick since the silicate layer of montmorillonite is 9.6 Å in thickness. The interlayer volume for one unit cell of the montmorillonite is 5.2 × 9.0 × 8.8 Å³, or 412 Å³. In a unit cell, 0.32 'molecule' of square complex is exchanged and the volume occupied by one square complex is 450 Å³. Thus the volume occupied by the complex per unit cell is 144 Å³. Therefore only one-third of the interlayer space volume is occupied by the square complexes, and ⅔ of the interlayer space volume can be regarded as pore volume prior to any decomposition of the hydroxy-Zr-montmorillonites.

The high surface area of the hydroxy-Zr-montmorillonites is attributable to the loose packing of the hydroxy-zirconium complexes in the interlayer spaces. From the standpoint of porosity it makes no difference to the calculation whether the hydroxy-Zr units lie flat on or stand normal to the layers. However, it is a valid question why more than half of the interlayer volume remains open. A close packing of the hydroxy-Zr units lying in a *single* flat configuration on the silicate surfaces is geometrically feasible. A possible explanation is that when the hydroxy-Zr units are adsorbed on to the dispersed montmorillonite surfaces, the layers come together with their attached hydroxy-Zr units and close-packing is unlikely to take place. Consequently, we can think of a double layer of hydroxy-Zr complexes mismatched so that they leave a large fraction (about ⅔) of the interlayer volume open to gas adsorption. Therefore, although a single layer of hydroxy-Zr units is geometrically possible, a sufficient mismatch of the bulky units occurs to establish a double layer of these units. The immobility of the hydroxy-Zr units may be attributed to the fact that they carry two units of positive charge and these will be located preferentially to satisfy the negative charges on the silicate layers. A similar picture may explain why with reduced layer charges the complexes still maintain the same (or even slightly larger) basal spacings; the slightly larger spacings reflect the weaker electrostatic forces.

REFERENCES

Bittel, R., Boursat, C. and Platzer, R. (1959) Étude de la fixation du zirconium par la montmorillonite acide: *Bull. Groupe Fr. Argiles* **11**, 9–19.

Brindley, G. W. and Ertem, Gözen (1971) Preparation and solvation properties of some variable charge montmorillonites: *Clays & Clay Minerals* **19**, 399–404.

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

Clearfield, A. and Vaughan, Ph. A. (1956) The crystal structure of zirconyl chloride octahydrate and zirconyl bromide octahydrate: *Acta Crystallogr.* **9**, 555–558.

Hofmann, U. and Klemen, R. (1950) Verlust der Austauschfähigkeit von Lithiumionen an Bentonit durch Erhitzung: *Z. Anorg. Allg. Chem.* **212**, 95–99.

Jeffery, P. G. (1975) *Chemical Methods of Rock Analysis* 2nd edition: Chapter 50. Pergamon Press, Oxford.

Medlin, J. H., Suhr, N. H. and Bodkin, J. B. (1969) Atomic absorption analysis of silicates employing LiBO$_2$ fusion: At. Absorpt. Newsl. **8**, 25–29.

Muha, J. M. and Vaughan, Ph. A. (1960) Structure of the complex ion in aqueous solutions of zirconyl and hafnyl oxyhalides: *J. Chem. Phys.* **33**, 194–199.

Westerlund-Helmerson, U. (1966) The determination of chloride as silver chloride by atomic absorption spectroscopy: *At. Absorpt. Newsl.* **5**, 97.

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

Резюме—Реаксий обмена Na-монтмориллонита с растворами цирконилового хлорида образуют продукты с основными промежутками около 18 Å, которые устойчивы при температуре до 500°C и имеют поверхностные площади порядка 300–400 м²/г. Ионы Na обмениваются с тетраметрическими окси-катионами $[Zr_4(OH)_{14} \cdot nH_2O]^{2+}$. Большая поверхностная площадь относится за счет пористости, образуемой устойчивыми "столбиками" окиси циркония, формирующимися в результате дегидроксилирования комплексных катионов. Изотермы адсобций азота относятся к типу Лангмуира и согласуются с адсорбцией в межслойных микропорах. Монтмориллониты с пониженным зарядом, формирующиеся под воздействием процедуры Хофмана-Клемена, имеют или подобные или немного меньшие поверхности.

Resümee—Austauschreaktionen von Na-Montmorillonit mit Zirkoniumchloridlösungen ergeben Produkte mit Basisabständen von fast 18 Å, die bis 500°C beständig sind und Oberflächenmaße in der Gegend von 300–400 m²/g. Die Na Ionen werden mit tetrameren Hydroxylkationen $[Zr_4(OH)_{14} \cdot nH_2O]^{2+}$ ausgetauscht. Die große Oberfläche wird der Porosität zugeschrieben, die von den stabilen Zirkoniumoxydsäulen stammt, welche durch Dehydroxylierung des komplexen Kation geformt wurden. Die Stickstofadsorptionsisothermen gehören zum Langmuirtyp und stimmen mit der Adsorption in den Zwischenschichtmikroporen überein. Montmorilloniten mit verminderter Ladung, welche durch Anwendung der Hofmann-Klemenmethode hergestellt wurden, geben entweder ähnliche oder etwas kleinere Oberflächen.

Résumé—Les réactions d'échange de montmorillonite-Na avec des solutions de chlorure de zirconyl donnent des produits avec des espacements de base d'à peu près 18 Å qui sont stables jusqu'à 500°C et qui ont des surfaces externes de l'ordre de 300–400 m²/g. Les ions de Na sont échangés avec des cations hydroxy tétramériques $[Zr_4(OH)_{14} \cdot nH_2O]^{2+}$. La grande étendue de la surface externe est attribuée à la porosité formée par les "pilliers" stables d'oxide de zirconium, eux-mêmes formés par la déshydroxylation du cation complex. Les isothermes d'adsorption de nitrogène sont du type Langmuir, et sont consistants avec l'adsorption dans les micro-pores interfeuillets. Les montmorillonites à charge réduite, formées par l'application du procédé Hofmann-Klemen, produisent des surfaces externes soit semblables, soit un peu plus petites.