

SWELLING CHARACTERISTICS OF HYDROXY-ALUMINUM INTERLAYERED CLAYS*

GERALD KIDDER† and LESTER W. REED‡

Department of Agronomy, Oklahoma Agricultural Experiment Station, Oklahoma State University, Stillwater, Oklahoma 74074, U.S.A.

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Abstract—The hypothesis tested was that macroscopic swelling of montmorillonitic clays is reduced by the presence of interlayer minerals. Fine and coarse clay fractions of Camargo and Panther Creek bentonite samples were artificially interlayered by reaction of $Al_2(SO_4)_3$ and NaOH in 0.5% suspensions of the clays. All four clay fractions reacted similarly to artificial interlayering. At an Al:clay ratio of 16 meq Al/g clay the CEC was completely lost, surface area was reduced and X-ray basal spacings were altered. No macroscopic swelling occurred in samples treated with 16 meq Al/g of clay. At smaller concentrations of hydroxy-aluminum 8 and 2 meq Al/g clay, the clay properties were less drastically altered. Extraction of interlayered clays with Na citrate restored the original C.E.C., surface area, and basal spacings of all samples and resulted in some slight enhancement of C.E.C. and surface areas of the coarse fractions. Treatment with hot Na citrate resulted in an increase in swelling ability but only slight increases in C.E.C. and surface area. Evidence presented supports the hypothesis that macroscopic swelling of montmorillonitic clays is greatly reduced by interlayer materials. Reduced swelling due to interlayering occurs even when other clay properties may be slightly different from those of nontreated samples. Indications are that interlayer material occurs naturally in the clays studied and this may apply to other bentonite deposits.

INTRODUCTION

IN THE past two decades considerable attention has been focused on the occurrence, properties, and formation of hydroxy-cation materials in the interlayer spaces of expansible layer silicates (Rich, 1968). The presence of interlayer material significantly affects the chemical and physical properties of clays. Cation exchange capacity (C.E.C.) and specific surface area are reduced (Rich, 1960; Sawhney, 1960; Frink, 1965), i.r. spectra (Weismiller, Ahlrichs and White, 1967), X-ray diffraction, and differential thermal analysis patterns are altered (Carstea *et al.*, 1970). Titration curves (Schwertmann and Jackson, 1964) and several other clay properties (Davey and Low, 1968) also differ when these materials are present.

X-ray analyses have shown that interlayered clays swell and shrink less than their non-interlayered counterparts. However, commonly used X-ray analyses are limited to relatively small basal spacings and non-aqueous clay systems. For soil clays, the hydration states of major interest to

soil scientists are those in the range of macroscopic swelling, that swelling which occurs when clays come in contact with free water. The study reported here is an attempt to demonstrate that macroscopic swelling of clays is reduced by the presence of hydroxy-Al interlayer material.

EXPERIMENTAL

Clays and their preparation

The two clays used in this study were Camargo bentonite§ collected from an open-pit mine site near Camargo, Oklahoma, and Panther Creek bentonite¶ from Panther Creek, Mississippi.

Approximately 200g of each bentonite sample was suspended in 20 l. of 0.5% Na_2CO_3 by stirring portions in a commercial mixer-blender. The combined portions were agitated overnight and allowed to settle, after which the clear supernatant liquid was siphoned off and the sediment resuspended in 20 l. of deionized water. After a second wash with deionized water, the sample is dispersed (Fig. 1).

The clay fraction, $< 2.0\mu$ equivalent spherical diameter (E.S.D.), was separated by gravity

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†Graduate Research Assistant, present address: Standard Fruit Company, LaCeiba, Honduras, Central America.

‡Professor of Agronomy, Oklahoma State University.

§Obtained from the Filtrol Corporation, Jackson, Mississippi, mine near Camargo, Oklahoma.

¶Obtained from Whittaker, Clark and Daniels, Inc., New York.

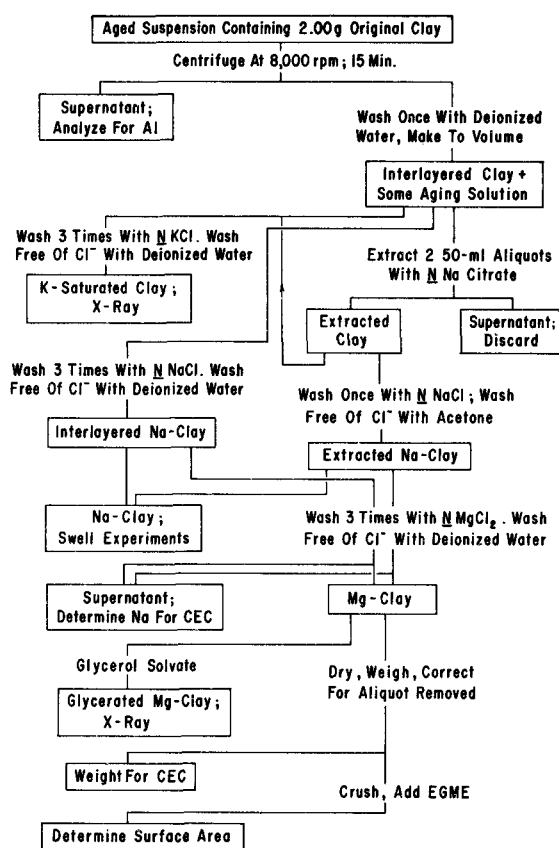


Fig. 1. Flow diagram showing steps in analysis of inter-layered clay.

sedimentation. Twenty-five cycles of suspension-sedimentation-siphoning were required for fractionation of the Camargo sample and 15 cycles for the Panther Creek sample. Further fractionation into coarse ($2.0\text{--}0.2\mu$ E.S.D.*) and fine clay ($<0.2\mu$ E.S.D.) was accomplished with a Sharples supercentrifuge (Jackson, 1956). A total of 14 centrifugation-resuspension cycles was performed in separation of the Camargo clay and seven cycles in fractionation of the Panther Creek clay. The four clay fractions were concentrated by flocculation with NaCl, washed once with deionized distilled water, and stored as suspensions.

Artificial interlayers were formed by dripping $N Al_2(SO_4)_3$ and $N NaOH$ into a vigorously agitated 0.5% suspension of clay. Each of the four clay fractions (Camargo coarse and fine and Panther Creek coarse and fine) received six different interlayer treatments consisting of the various combinations of two OH/Al molar ratios (1.5 and 2.7) and

three levels of Al (2, 8, 16 meq Al/g clay). The samples were aged in plastic bottles at a constant temperature of $22^\circ C$ for 1 yr and were shaken occasionally.

Methods of sample analysis

Five aged samples and one freshly prepared sample were extracted with hot Na citrate to determine the effect of removal of interlayer material on the clay properties. Aliquots containing 1.00g clay were heated with 100 ml $N Na$ citrate for 1 hr at $90^\circ C$, centrifuged, and the treatment repeated five times. The Na citrate extracted clay was then tested along with the interlayered samples.

Cation exchange capacity was determined (Frink, 1964) on small (0.5g) clay samples which were centrifuged for 10–15 min at 8000–10,000g to prevent loss of clay (Rollins and Pool, 1968) and as further noted in Fig. 1. The exchangeable sodium was determined by atomic absorption spectroscopy. Rapid and complete dispersion after each centrifugation was accomplished with a 1 in. rounded polyethylene plug screwed onto a Hamilton-Beach Model 33 malt-mixer in place of the usual mixing blade. A rheostat allowed the mixing speed to be easily varied as needed for dispersing the clay packed into the bottom of the plastic centrifuge tubes.

Specific surface area was determined using the ethylene glycol monoethyl ether method of Carter, Heilman and Gonzalez (1965).

For X-ray analysis, Mg-saturated and glycerol-solvated samples and K-saturated samples were air dried on Pyrex glass slides as suggested by Jackson (1956, Paragraph 4-34). Samples were X-rayed on a General Electric XRD-6 instrument with Ni-filtered CuK_α radiation generated at 50 kV and 20 mA. The optical train was $1^\circ MR$ beam, HR soller, and 0.2° detector slit.

Potassium-saturated samples were X-rayed air dry and after heating at 200° and $500^\circ C$. The degree of shift in the basal spacing was used as an indication of interlayer stability.

Swelling in unconfined conditions was carried out using the technique described by Rowell (1963). Briefly, the method consists of placing a clay suspension on a glass cover slip, allowing it to air dry, then suspending the slide containing the oriented clay sample in dilute salt solutions. The amount of water held by the clay after it had been allowed to swell was determined by weighing the clay wet and oven dry ($105^\circ C$). All swelling experiments were run at a constant temperature at $22^\circ C$.

Swelling under applied pressures was determined by using an apparatus similar to that described by Warkentin, Bolt and Miller (1957).

*E.S.D.—Equivalent Spherical Diameter.

Equilibrium was reached after 4 hr under 1.0 and 2.0 atm, applied pressure and in 24 hr under 0.01 atm applied pressure. Measurements are reported in g of water/g of clay at 0.01 atmosphere pressure.

RESULTS

Evidence of interlayer formation in treated clays

Changes in specific surface area, C.E.C., and the amount of first order basal spacing shift exhibited by the clays were used as indications of the extensiveness and the stability of the interlayer material, Tables 1-4 and Figs. 2 and 3.

The four fractions reacted similarly to the artificial interlayering treatments. Interlayers were produced in all cases, with the greatest effect on clay properties being noted at the highest Al:clay ratio. Large amounts of hydroxy-Al material 16 meq Al/g clay reduced the C.E.C. to zero and the specific surface area to half its original value. Basal spacings for these samples were *ca.* 21 Å when Mg-saturated and glycerated, and 13 Å when K-saturated and heated at 500°C, Figs. 2 and 3. Although decreases in C.E.C. and surface area were considerable, at the low Al:clay ratio 2 meq Al/g clay, only small differences could be detected between basal spacings of treated and

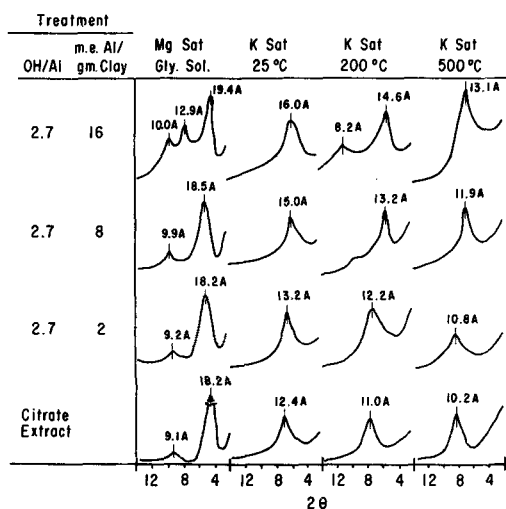


Fig. 2. Smoothed X-ray diffraction patterns of Al-layered < 0.2μ Camargo bentonite as affected by OH/Al and Al concentration after one year aging (intensities are relative).

untreated samples. At the intermediate level of Al/clay, the effect on clay properties was intermediate.

Table 1. Effect of OH/Al molar ratios on C.E.C., surface area and swelling of Camargo bentonite aged 1 year

| Sample No. | OH/Al molar ratios | Meq. Al/g clay | C.E.C. Meq/100 g | Surface area M ² /g | Swell values† g H ₂ O/g clay | |
|-----------------------------------|--------------------|----------------|------------------|--------------------------------|---|-----------|
| | | | | | Rowell | Warkentin |
| 2-0.2μ fraction | | | | | | |
| N.T.* | | | 129 | 937 | 3.00 | 2.20 |
| 1 | 2.7 | 16 | 0 | 440 | 1.60 | |
| 2 | 2.7 | 8 | 8 | 562 | 1.80 | |
| 3 | 2.7 | 2 | 87 | 787 | 2.80 | |
| 4 | 1.5 | 16 | 0 | 472 | 1.40 | |
| 5 | 1.5 | 8 | 34 | 740 | 2.20 | |
| 6 | 1.5 | 2 | 96 | 924 | 3.40 | |
| < 0.2μ | | | | | | |
| N.T. | | | 131 | 943 | 30.20 | 12.00 |
| 7 | 2.7 | 16 | 4 | 582 | 0.64 | |
| 8 | 2.7 | 8 | 47 | 774 | 0.71 | |
| 9 | 2.7 | 2 | 113 | 863 | 6.80 | 3.50 |
| 10 | 1.5 | 16 | 0 | 626 | 0.43 | |
| 11 | 1.5 | 8 | 61 | 775 | 0.80 | 3.50 |
| 12 | 1.5 | 2 | 96 | 884 | 4.40 | 5.10 |
| Citrate extracted 2-0.2μ fraction | | | | | | |
| 4 | 1.5 | 16 | 137 | 948 | 10.50 | 6.00 |
| Citrate extracted < 0.2μ fraction | | | | | | |
| 10 | 1.5 | 16 | 133 | 968 | 27.10 | 8.20 |

*N.T.—no treatment.

†Rowell swell in 5 × 10⁻³ N NaCl, Warkentin swell at 0.01 atmosphere pressure 10⁻⁴ N NaCl.

Table 2. Effect of OH/Al molar ratios on C.E.C. surface area and swelling of Panther Creek bentonite aged 1 year

| Sample No. | OH/Al molar ratios | Meq. Al/g clay | C.E.C. Meq/100 g | Surface area M ² /g | Swell values† g H ₂ O/g clay | |
|--------------------------------------|--------------------|----------------|------------------|--------------------------------|---|-----------|
| | | | | | Rowell | Warkentin |
| 2-0.2μ fraction | | | | | | |
| N.T.* | | | 91 | 740 | 3.60 | 2.10 |
| 13 | 2.7 | 16 | 0 | 346 | 1.20 | |
| 14 | 2.7 | 8 | 0 | 471 | 0.80 | |
| 15 | 2.7 | 2 | 58 | 649 | 3.70 | |
| 16 | 1.5 | 16 | 0 | 456 | 1.00 | |
| 17 | 1.5 | 8 | 11 | 554 | 0.92 | |
| 18 | 1.5 | 2 | 59 | 708 | 5.60 | |
| < 0.2μ fraction | | | | | | |
| N.T. | | | 108 | 868 | 15.80 | 9.80 |
| 19 | 2.7 | 16 | 0 | 590 | 0.50 | 3.40 |
| 20 | 2.7 | 8 | 42 | 619 | 0.91 | 3.40 |
| 21 | 2.7 | 2 | 85 | 781 | 12.90 | 6.30 |
| 22 | 1.5 | 16 | 0 | 570 | 0.45 | 4.00 |
| 23 | 1.5 | 8 | 46 | 742 | 1.10 | 3.80 |
| 24 | 1.5 | 2 | 68 | 855 | 4.30 | |
| Freshly interlayered 2-0.2μ fraction | | | | | | |
| 25‡ | 2.7 | 16 | 0 | 150 | | |
| Citrate extracted 2-0.2μ fraction | | | | | | |
| 16 | 1.5 | 16 | 97 | 770 | 24.00 | 8.20 |
| 25‡ | 2.7 | 16 | 91 | 760 | 26.60 | |
| Citrate extracted < 0.2μ fraction | | | | | | |
| 19 | 2.7 | 16 | 104 | 912 | 34.00 | |
| 22 | 1.5 | 16 | 103 | 926 | 34.40 | 13.30 |

*N.T. — no treatment.

†Rowell swell in 5×10^{-3} N NaCl Warkentine swell at 0.01 atm in 10^{-4} N NaCl.

‡Same as sample No. 13.

Table 3. Effect of aluminum in solution and OH/Al molar ratios on first order X-ray basal spacings of Camargo bentonite aged 1 year

| Sample No. | OH/Al molar ratios | Al in solution (% of added) | 1st. order basal spacing (Å) | | | |
|---------------------------------|--------------------|-----------------------------|------------------------------|------|--------------|-------|
| | | | Mg. glycerol | 25°C | K Sat. 200°C | 500°C |
| 2-0.2μ fraction | | | | | | |
| N.T.* | | 0 | 17.8 | | 10.8 | 10.0 |
| 1 | 2.7 | 1 | 19.3 | 17.0 | 14.4 | 13.5 |
| 2 | 2.7 | 0 | 19.0 | 15.5 | 12.6 | 10.4 |
| 3 | 2.7 | 0 | 18.2 | 13.4 | 12.6 | 10.9 |
| 4 | 1.5 | 45 | 21.2 | 16.0 | 14.0 | 13.2 |
| 5 | 1.5 | 42 | 18.8 | 12.7 | 11.9 | 10.6 |
| 6 | 1.5 | 13 | 18.4 | 12.7 | 11.9 | 10.6 |
| < 0.2μ fraction | | | | | | |
| N.T. | | 0 | 18.2 | 11.3 | 10.6 | 10.1 |
| 7 | 2.7 | 0 | 19.4 | 16.0 | 14.6 | 13.1 |
| 8 | 2.7 | 0 | 18.5 | 15.0 | 13.2 | 11.9 |
| 9 | 2.7 | 0 | 18.2 | 13.2 | 12.3 | 10.8 |
| 10 | 1.5 | 27 | 20.5 | 16.2 | 14.2 | 13.1 |
| 11 | 1.5 | 26 | 18.0 | 14.2 | 12.7 | 11.3 |
| 12 | 1.5 | 0 | 18.2 | 13.0 | 11.4 | 10.5 |
| Citrate extracted sample 2-0.2μ | | | | | | |
| 4 | 1.5 | 0 | 18.2 | 12.4 | 11.7 | 10.2 |
| 10 | 1.5 | 0 | 18.2 | 12.4 | 11.0 | 10.2 |

*N.T. — no treatment.

Table 4. Affect of aluminum in solution and OH/Al molar ratios on first order X-ray basal spacings of Panther Creek bentonite aged 1 year

| Sample No. | OH/Al molar ratios | Al in solution (% of added) | Mg. glycerol | Basal spacings (Å) | | |
|-----------------------------|--------------------|-----------------------------|--------------|--------------------|-------|-------|
| | | | | K Sat. | | |
| | | | | 25°C | 200°C | 500°C |
| 2-0.2μ fraction | | | | | | |
| N.T.* | 0 | 0 | 17.1 | 11.5 | 10.3 | 9.9 |
| 13 | 2.7 | 0 | 27.1 | 17.0 | 14.5 | 13.4 |
| 14 | 2.7 | 0 | 20.1 | 16.4 | 14.4 | 13.2 |
| 15 | 2.7 | 0 | 18.4 | 13.1 | 14.0 | 10.9 |
| 16 | 1.5 | 45 | 22.6 | 15.9 | 13.6 | 11.8 |
| 17 | 1.5 | 31 | 19.4 | 14.2 | 12.8 | 10.6 |
| 18 | 1.5 | 0 | 18.5 | 12.4 | 11.8 | 9.8 |
| < 0.2μ fraction | | | | | | |
| N.T. | | 0 | 17.6 | 11.0 | 10.3 | 9.9 |
| 19 | 2.7 | 0 | 21.8 | 16.8 | 14.0 | 13.0 |
| 20 | 2.7 | 0 | 19.2 | 15.4 | 13.2 | 12.3 |
| 21 | 2.7 | 0 | 18.2 | 13.1 | 11.1 | 10.7 |
| 22 | 1.5 | 40 | 22.1 | 16.8 | 14.4 | 13.3 |
| 23 | 1.5 | 28 | 18.8 | 13.2 | 11.5 | 11.2 |
| 24 | 1.5 | 0 | 18.2 | 13.2 | 10.9 | 10.4 |
| Freshly interlayered 2-0.2μ | | | | | | |
| 25† | 1.5 | 0 | 22.1 | | 14.7 | 14.2 |
| Citrate extracted 2-0.2μ | | | | | | |
| 16 | 1.5 | 0 | 18.2 | 12.2 | 10.6 | 10.0 |
| 25 | 2.7 | 0 | 18.2 | 12.1 | 11.0 | 10.2 |
| Citrate extracted ∞ 0.2μ | | | | | | |
| 19 | 2.7 | 0 | 18.2 | 12.3 | 11.0 | 10.2 |
| 22 | 1.5 | 0 | 18.0 | 12.1 | 10.4 | 10.0 |

*Not treated.

†Same as sample No. 13.

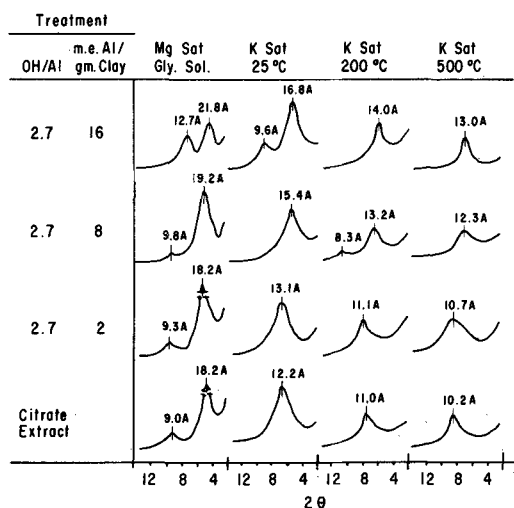


Fig. 3. Smoothed X-ray diffraction patterns of Al-interlayered < 0.2μ Panther Creek bentonite as affected by OH/Al and Al concentration after one year aging (intensities are relative).

Swelling experiments

Preliminary studies of macroscopic swelling, using the techniques of Warkentin *et al.* (1957), revealed differences in swelling characteristics of the fine and coarse fractions of untreated clays. The coarse clay (2.0-0.2μ E.S.D.) produced swelling pressures considerably lower than predicted by theory (Warkentin *et al.*, 1957; Warkentin and Schofield, 1962), while the fine clays (< 0.2μ E.S.D.) swelled to values very near theoretical. Jonas and Roberson (1968) reported that coarse fractions of montmorillonite expanded less than fine fractions and concluded that higher structural charge density of the coarse fractions was responsible for their reluctance to expand in atmospheres of high relative humidity. Specific surface area and C.E.C. measurements of the clays used in this study showed, however, that the charge density of the coarse and fine clay fraction was the same. Incomplete removal of salt (Bolt, 1956) was dismissed as the reason for lessened swell when a sample of Panther Creek clay washed 20 times with deionized distilled water failed to swell more

than less washed samples. Lack of parallel orientation was also dismissed as the cause of the problem, since this geometric arrangement would increase rather than decrease the swelling pressure.

Two differences in unconfined swell (Rowell's method, 1963) of the fine and coarse fractions were also observed. (1) The fine clay swelled considerably as the concentration of the salt solution decreased, whereas the coarse clay showed very little swelling. Just before dispersion the fine clays held 15–30g water/g clay; the coarse clays held 3–5g water/g clay. (2) The fine clays dispersed at higher salt concentrations than did the coarse clays, Fig. 4. Charge densities of the two fractions being essentially the same, both would be expected to have the same osmotic forces (repulsive forces?) acting between the layers. These results suggest that attractive forces not accounted for in the parallel charged plate model of Bolt (1956) were acting in the coarse clay system to prevent swelling.

The artificially interlayered coarse clay fractions did not swell, as predicted from results obtained with their non-treated counterparts. Little or no swelling occurred in artificially interlayered fine clay samples with the high Al:clay ratio, 16 meq/g clay. This would be expected from the complete blockage of C.E.C. sites in those samples, since without exchangeable ions there would be no osmotic force acting to separate the layers. The same effect, however, was noted with samples treated with 8 meq Al/g clay, even though half as much of the original C.E.C. remained. The binding

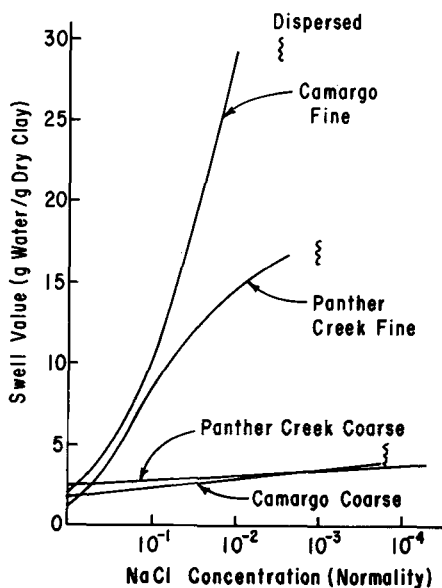


Fig. 4. Swell of Na-clays before artificial Al-interlayering.

effect of the interlayer material was apparently stronger than the repulsive force resulting from the presence of exchangeable ions, and separation of the layers was prevented. At the lowest Al:clay ratio a 20–85% reduction in swell values (a term used by Rowell (1963), to denote g water held/g clay) of the fine clay was observed, demonstrating the effect of small amounts of interlayer material on clay swelling.

Striking results of unconfined swell of the citrate extracted samples afforded an explanation of several of the observations discussed and provided evidence to support the hypothesis that interlayer material causes reduction in clay swelling. As the data in Table 1 and 2 show, the citrate-extracted samples had the largest swell values of any samples, even larger than the original untreated samples. Although C.E.C., surface area, and X-ray data showed some differences between the extracted and original samples, the differences were not nearly as great as those found for swell values.

The large increase in swell values of the coarse fractions upon citrate extraction, taken with the concomitant slight increase in C.E.C. and surface area, indicates that the agents preventing swell probably occupy only a small area of the layer surfaces and do not satisfy all of the cation exchange sites.

These results might suggest the presence of small amounts of interlayer material in the original bentonitic clays. Such an occurrence is somewhat unexpected, since interlayer materials might be thought to be products of clay weathering. The clays used in this study came from supposedly unweathered bentonite deposits and, theoretically, should not contain such materials (preliminary examination of these clays for carbonates showed none to be present). This effect has also been noted by Rowell (1963), who reported that removal of iron oxide (0.58% by weight) from the $< 0.05\mu$ fraction of Wyoming bentonite increased the swell value by about 10%.

DISCUSSION AND CONCLUSIONS

Despite a large measured surface area and high cation exchange capacity, the coarse clay fractions ($2.0\text{--}0.2\mu$) of the two bentonite samples studied swelled very little before dispersing. Conversely, the fine clays swelled to large volumes before dispersing in dil. NaCl solutions, a behavior suggesting that different forces are active in the two fractions.

Since the fine and coarse fractions had essentially the same charge densities, in like solutions the osmotic (repulsive?) forces would be the same for the two fractions. The different swell behavior

observed must then be explained by dissimilar attractive forces.

Results suggest that the attractive force in the coarse clay is strong, whereas that of the fine clay is much weaker. As the repulsive force increases (i.e. NaCl concentration decreases), the strong, attractive force in the coarse clay allows the layers to expand very little (absorbing from 2 to 4g water/g clay). When the repulsive force becomes greater than the attractive force, the clay suddenly goes from a state where the layers are probably an average of ca. 80 Å (Fink *et al.* (1968), Warkentin *et al.*, (1957)) apart to a dispersed state. On the other hand, the weaker, attractive forces of the fine clay allows water to enter rather easily and the layers expand to large average distances before dispersing. Finally, the repulsive force becomes greater than the attractive force and the fine clay disperses.

The strong, attractive forces of the coarse clay are suspected to be randomly distributed islands of interlayer material which bind adjacent layers together by electrostatic bonds. Results from samples treated with hot Na citrate lend strength to this explanation. After such treatment, samples Nos. 4, 16, and 25 attained swell values of the same order of magnitude as the untreated fine clays. These results show that use of methods such as that of Fink, Rich and Thomas (1968) is probably possible only with samples freed of interlayer materials.

When interlayer material is absent, the clay swells as described for the fine clay. The clay takes up about 30 times its weight in water before finally dispersing. In such a system a long-range attractive force holds the clay particles together before dispersion. Numerous investigators (see van Olphen, 1963; Mungan and Jessen, 1963; Rowell, 1965; Low, 1968) have advanced explanations for the formation and stability of clay gels. The results of this study do not allow the favoring of one model over another. It is obvious, however, that removal of materials from the surfaces of the silicate clays, especially those of large E.S.D., enhances their ability to swell.

Of particular significance is the marked effect on swelling produced by small amounts of interlayer material, which affect other clay properties only minimally. This appeared most dramatically in the swelling of the coarse clays after citrate extraction.

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Résumé—L'hypothèse soumise à vérification était que le gonflement macroscopique des argiles montmorillonitiques est réduit par la présence de minéraux interfeuilletés. Des fractions argileuses fixes et grossières d'échantillons de bentonite de Camargo et Panther Creek ont eu leurs espaces interfeuilletés artificiellement remplis en faisant réagir $Al_2(SO_4)_3$ et NaOH dans des suspensions d'argile à 0,5%. Les quatre fractions argileuses ont réagi de la même manière au cours de ce traitement. Pour un rapport Al/argile de 16 me Al par g d'argile, la C.E.C. disparaît complètement, la surface est réduite et les distances basales déterminées aux rayons X sont modifiées. Aucun gonflement macroscopique n'est observable avec les échantillons traités avec 16 me Al par g d'argile. A des concentrations d'hydroxy-aluminium plus basses, 8 et 2 me Al par g d'argile, les propriétés de l'argile sont altérées moins profondément. Lorsqu'on extrait par le citrate de sodium les argiles traitées, on observe pour tous les échantillons le retour aux valeurs d'origine de la C.E.C., de la surface et des distances basales, en aboutissant même à une légère augmentation de la C.E.C. et de la surface des fractions grossières. Le traitement avec le citrate de sodium chaud entraîne une augmentation de l'aptitude au gonflement, mais seulement un faible accroissement de la C.E.C. et de la surface. Cette observation confirme donc l'hypothèse selon laquelle le gonflement macroscopique des argiles montmorillonitiques est fortement réduit par les matériaux interfeuilletés. Cette réduction du gonflement due à certaines insertions interfeuilletés s'observe même quand d'autres propriétés de l'argile ne sont que légèrement différentes de celles des échantillons non traités. Il y a des indications pour penser que certains matériaux interfeuilletés sont présents naturellement dans les argiles étudiées, ce qui peut s'appliquer à d'autres dépôts de bentonite.

Kurzreferat—Es wurde die Hypothese untersucht wonach makroskopische Quellung montmorillonitischer Tone in der Gegenwart von Zwischenschichtmineralem vermindert wird. Feine und grobe Tonfraktionen aus Camargo und Panther Creek Bentonit Proben wurden künstlich durch die Reaktion von $Al_2(SO_4)_3$ und NaOH in 0,5% Suspensionen der Tone mit Zwischenlagerung versehen. Alle vier Tonfraktionen reagierten ähnlich zur künstlichen Zwischenlagerung. Bei einem Al:Ton Verhältnis von 16 meq Al/g Ton ging die Kationenaustauschkapazität (C.E.C.) vollkommen verloren, die Oberfläche wurde vermindert und die Röntgen Basiszwischenräume wurden verändert. In Proben, die mit 16 meq Al/g Ton behandelt wurden trat keine makroskopische Quellung auf. Bei kleineren Konzentrationen von Hydroxy-Aluminium 8 und 2 meq Al/g Ton, waren die Eigenschaften des Tones weniger drastisch verändert. Extraktion von zwischengelagerten Tönen mit Na-Citrat stellte die ursprüngliche C.E.C., Oberflächeninhalt und Basiszwischenräume von allen Proben wieder her und ergab in manchen eine Leichte Zunahme der C.E.C. und der Oberflächeninhalte der groben Fraktionen. Behandlung mit heissem Na-Citrat ergab eine Zunahme in Quellungsfähigkeit jedoch eine geringe Zunahmen in C.E.C und Oberfläche. Das vorgelegte Beweismaterial stützt die Hypothese wonach makroskopische Quellung montmorillonitischer Tone durch-zwischenlagerstoffe weitgehend vermindert wird. Verminderte Quellung infolge von Zwischenlagerung erfolgt sogar wenn die anderen Toneigenschaften etwas verschieden von denen der unbehandelten Proben sind. Es bestehen Anzeichen dafür, dass Zwischenlagerungsstoffe in den untersuchten Tönen natürlich vorkommen und das mag auch bei anderen Bentonitablagerungen der Fall sein.

Резюме — Проверены предположения об уменьшении макроскопического разбухания монтмориллонитовых глин при наличии межслоевых минералов. Межслоевые промежутки тонких и грубых глинистых фракций бентонитовых образцов из Камарго и Пантер Крик искусственно насыщались в результате реакции $Al_2(SO_4)_3$ и NaOH в 0,5% суспензиях глин. Все четыре глинистые фракции вели себя одинаково при образовании смешанно-слоистых фаз. При соотношении Al и глины, равном 16 м — экв Al/г глины способность к обмену катионов была полностью утрачена, площадь поверхности уменьшилась и базальные межплоскостные расстояния (по рентгеновским данным) изменились. Макроскопическое разбухание не происходило в образцах, обработанных 16 м — экв Al/г глины. При меньших концентрациях гидрокси алюминия (8 и 2 м — экв Al/г глины) глинистые свойства не были изменены столь резко. Обработка смешанно-слоистых глин лимоннокислым Na восстанавливала первоначальную способность к обмену катионов, площадь поверхности, базальные межслоевые расстояния всех образцов и приводила к некоторому увеличению катионного обмена и площади поверхности грубых фракций. Обработка горячим цитратом Na приводила к увеличению способности к разбуханию и только к незначительному увеличению способности к обмену катионов и площади поверхности. Полученные данные подтверждают гипотезу о значительном снижении разбухания монтмориллонитовых глин с межслоевым материалом. Уменьшение разбухания благодаря присутствию межслоевого материала происходит даже тогда, когда другие глинистые свойства могут только незначительно отличаться от таких необработанных образцов. Установлено, что в изученных глинах встречается смешанно-слоистый материал; это же может быть и в других бентонитовых месторождениях.