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FINAL REPORT

X-RAY DIFFRACTION OF HIGHWAY MATERIALS

R. L. Handy, Project Director

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X-RAY DIFFRACTION OF HIGHWAY MATERIALS, 1966-68

R. L. Handy, Project Director

PREFACE

The attached report is a summary of our research on the most abundant
and most active clay mineral in Iowa soils: montmorillonite. The research
emphasizes swelling mechanisms and interactions with water, since these
are of prime importance in engineering. Part of the work is described
more fully in a previously submitted Progress Report by Senich, Demirel
and Handy.

The present report represents a closing phase of the research, which
has already achieved recognition at the international level. The report
has been reviewed and accepted by the International Clay Minerals Conference
for presentation in Tokyo, Japan, in August 1969, pending approval by
the Iowa Highway Research Board.

The x-ray diffraction project also contributed significantly to other
Highway Research Board projects; this will be shown in reports from these
projects.

X-RAY DIFFRACTION AND ABSORPTION ISOTHERM

STUDIES OF THE MONTMORILLONITE-WATER SYSTEM

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ABSTRACT

X-ray diffraction data during adsorption of water vapor on Na-
and Ca-montmorillonites show that interlayer expansion is continuous
but nonuniform. X-ray and adsorption isotherm data indicate an ice-like
configuration of water molecules is completed with the fourth layer of
interlayer water for the Ca-clay; a fifth layer intrudes to give a less
ordered structure. Data for the Na-clay indicate a laminar stacking
arrangement for up to three layers of interlayer water. The Na-clay
adsorbs more than twice as much water and undergoes four times as large
a volume change than the Ca-clay. The free energy change during adsorption
of water vapor on the Ca-clay is nearly twice that for the Na-clay. Free
energy changes with increasing relative pressure reflect interlayer
expansion increments.

INTRODUCTION

Adsorption isotherm and x-ray diffraction techniques were used to study the adsorption of water vapor on homoionic Na- and Ca-montmorillonites. X-ray studies were made with a Rigaku-Denki controlled atmosphere high temperature x-ray diffractometer furnace converted to serve as an adsorption chamber (Roderick and Demirel, 1966). Adsorption isotherms for the Na-clay were determined by the gravimetric method with a McBain-Baker quartz spring balance apparatus (Roderick and Demirel, 1966). Those for the Ca-clay were determined with an automatic recording electro-balance apparatus (Senich, et al., 1967). Direct expansion measurements of small cylindrical samples of the clays were also made during adsorption (Roderick and Demirel, 1963).

The homoionic montmorillonites were prepared from a commercially available Wyoming bentonite, Volclay-SPV, by ion exchange as described in detail elsewhere (Demirel, 1962).

All work was conducted at near $25^{\circ}C$; copper $K\alpha$ radiation was used in x-ray studies. The initial vacuum attained was 10^{-4}mm Hg or less in all cases.

RESULTS

Interlayer Expansion

Figure 1 presents first order basal spacings and x-ray peak widths vs relative pressure (p/p_o) for the two clays. The basal spacings change in a continuous but nonuniform manner with changes in relative pressure. Continuity is due to simultaneous existence of varying numbers of molecular layers of water between clay platelets. A pronounced hysteresis loop is evident for both clays. Variations in peak widths are, in part, due to nonconstancy of interlayer spacings. Minimum widths correspond with flatter portions of the spacing plot and indicate that most of the clay platelets are nearly at the observed spacing (MacEwan, et al., 1961). Maximum widths occur near the center of the steeper portions of the expansion plot where an expansion increment is occurring.

Senich, et al., (1967) obtained extensive x-ray data for the Ca-montmorillonite; for clarity not all the data are included in Fig. 1. Basing their calculations on the 9.14 Å spacing of pyrophyllite, they visualize the uptake of interlayer water as follows:

There is only a small increase in spacing as p/p_o goes from 0.0 to 0.015; apparently most of the vapor, less than one water molecule/unit cell as determined from adsorption isotherm data, is adsorbed on the external surfaces. Then a rapid expansion to 11.9 Å at p/p_o of about 0.08 occurs with about 2 molecules/unit cell. This spacing corresponds to one layer of water molecules. Between p/p_o of 0.08 and 0.11, a small expansion increment occurs during which hydration of the Ca ion begins. The observed spacing of 12.5 Å may be explained if the water molecules are shared by the cation and are directly between the oxygens of the two
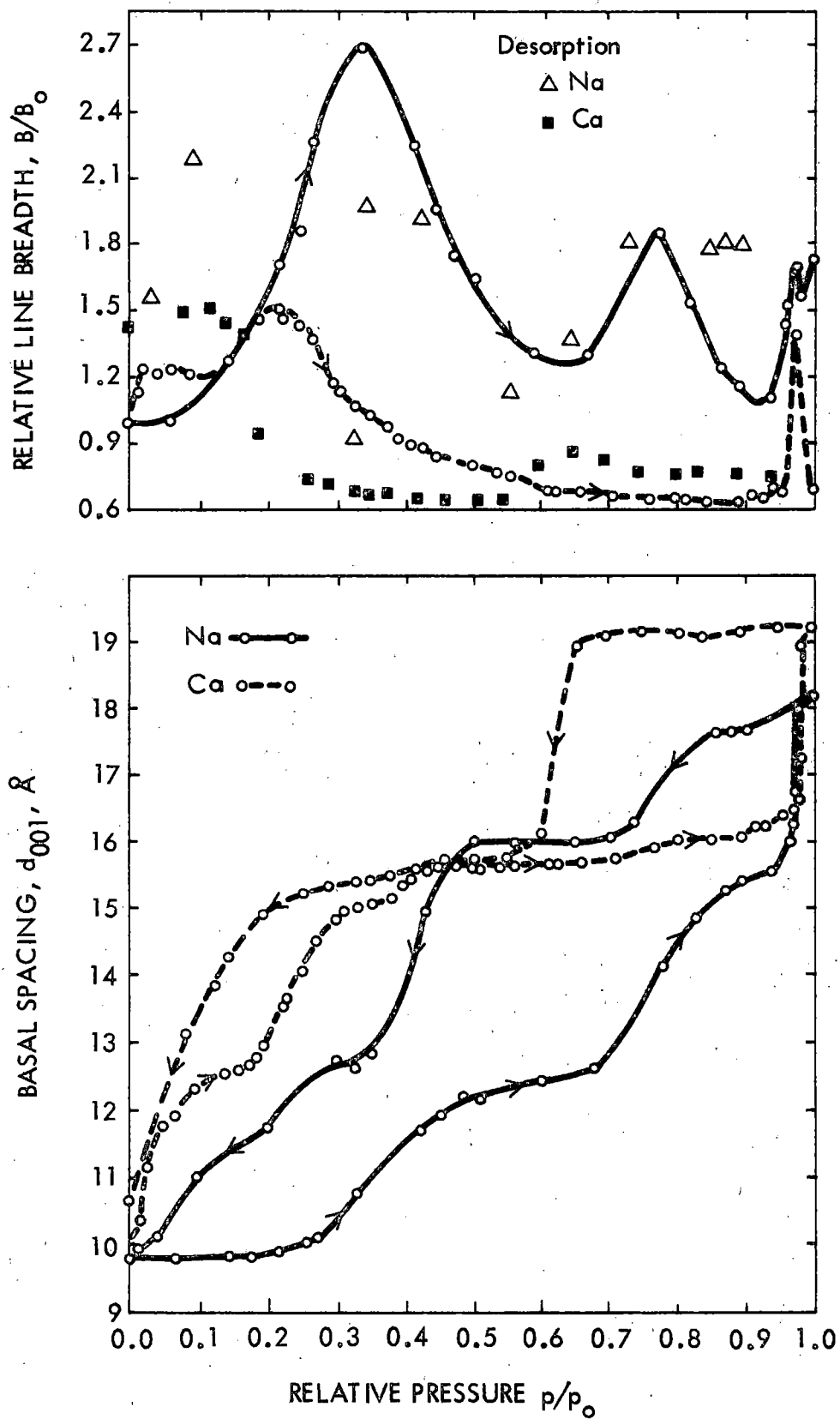
Fig. 1. First order basal spacings and line breadths of Na- and
Ca-montmorillonites versus relative pressure of water vapor.

clay surfaces, while the cation is in the base of tetrahedrons in the hexagonal framework of the mineral surface.

A second layer of water, leading to a total of 5.5 molecules/unit cell, leads to a 15.1 $\overset{o}{A}$ spacing at p/p_o of about 0.38. Two hexagonal water networks stacked in a laminar fashion would give a 14.7 $\overset{o}{A}$ spacing, while a laminar stacking including the cation would give 15.6 $\overset{o}{A}$. The 15.1 $\overset{o}{A}$ is an average value of 14.7 $\overset{o}{A}$ and 15.6 $\overset{o}{A}$ peaks; the broad line widths in this region support this view.

In the p/p_o range of 0.38 to about 0.42, another expansion to 15.6 $\overset{o}{A}$ occurs with perhaps the start of an ice-like configuration with formation of tetrahedrons with the water molecules of the hexagonal network. The stable 15.6 $\overset{o}{A}$ spacing is associated with a total uptake of 7.5 molecules/unit cell.

A four water-layer ice-like configuration causing a 16.5 $\overset{o}{A}$ spacing can be obtained with 12 water molecules/unit cell. A 16.5 $\overset{o}{A}$ spacing is attained at p/p_o of 0.98; adsorption data show about 12 molecules/unit cell at this point. The combination of minimum peak width and maximum intensity supports the hypothesis of an ice-like configuration of least disorder. The cation fits loosely in holes and does not directly affect the spacing.

Apparently a fifth layer of water enters between the configuration above p/p_o of 0.99, giving a less ordered structure but causing a minimum peak width at 19.2 $\overset{o}{A}$. The final number of water molecules/unit cell is about 14.

The ice-like configuration is completed in a very limited range of p/p_o near saturation. The configuration proposed is not in basic contradiction

with the ice-structure proposed by Macey (1942) and Demirel (1962), nor with the NMR studies of Wu (1964).

The x-ray data obtained by Roderick and Demirel (1966) for the Na-montmorillonite are not as extensive as that obtained later for the Ca-clay, and do not allow as detailed an analysis. There is very little change from the initial 9.82 $\overset{o}{A}$ spacing of Na-montmorillonite as p/p_o increases to about 0.20. Adsorption isotherm data show that, at this point, about one molecule/unit cell has been adsorbed primarily on external surfaces. An increment of expansion then occurs with a second leveling and a minimum peak width at p/p_o of 0.65. The basal spacing is 12.5 $\overset{o}{A}$ with six molecules of water per unit cell. There is no indication of a stable 11.9 $\overset{o}{A}$ spacing. The increase from 9.8 $\overset{o}{A}$ to 12.5 $\overset{o}{A}$ is near that for a monolayer of water molecules (2.8 $\overset{o}{A}$) in which waters are directly between basal oxygens of the mineral surfaces.

A second increment of expansion occurs with a leveling off and minimum peak width at p/p_o of 0.94, and a 15.5 $\overset{o}{A}$ spacing. The total water uptake is 12.5 molecules/unit cell. Again, there is no indication of an intermediate state corresponding with the 15.1 $\overset{o}{A}$ spacing of Ca-montmorillonite. The 15.5 $\overset{o}{A}$ spacing corresponds to another 2.8 $\overset{o}{A}$ water layer.

A final expansion occurs with a leveling off and minimum peak width at p/p_o of about 0.99, and an 18.2 $\overset{o}{A}$ spacing. This corresponds to a third molecular layer of water and a total of 18.5 molecules/unit cell. No intermediate 16.5 $\overset{o}{A}$ stable spacing was observed as was with the Ca-clay. Additional adsorption, with very little expansion, leads to about 29 molecules/unit cell at saturation.

The data for the Na-clay do not permit postulation of a configuration for the interlayer water. The peak width variation for the Na-clay is much more pronounced than for Ca-clay. Roderick and Demirel (1966), from analysis of peak width variations, find evidence that some sort of laminar stacking arrangement occurs, for up to three molecular layers of interlayer water on Na-montmorillonite, rather than an ice-like configuration.

Free Swelling

Figure 2 presents results of free swell due to adsorption of water vapor. The portions below p/p_o of 0.4 do not represent the true expansion. Since the specimens were molded at a p/p_o of 0.4 and no overall shrinkage occurred on evacuation to a p/p_o of 0.00, the adsorption of a p/p_o of 0.4 evidently proceeds mainly with interlayer expansion into the intermicellar pores. For p/p_o above 0.4, the expansion isotherms are continuous with slight slope changes which correspond approximately with those for the x-ray data for interlayer spacings. The porosity of montmorillonites having the same associated cation seems to have no appreciable effect on swelling due to water vapor adsorption (Roderick and Demirel, 1963).

As shown in previous discussion, the Na-clay had considerably more total water adsorbed at any spacing than did the Ca-clay. The free swelling data show the volumetric expansions are about 480% and 120% for the Na- and Ca-clays, respectively. The volumetric expansion due to interlayer swelling, from x-ray data, are about 85% for the Na-clay and 90% for the Ca-clay. The expansion of the Ca-montmorillonite is primarily due to intermicellar swelling.

Mielenz and King (1955) indicate that in the presence of liquid water the volumetric expansion of Ca-montmorillonites is 125%, i.e,, little or
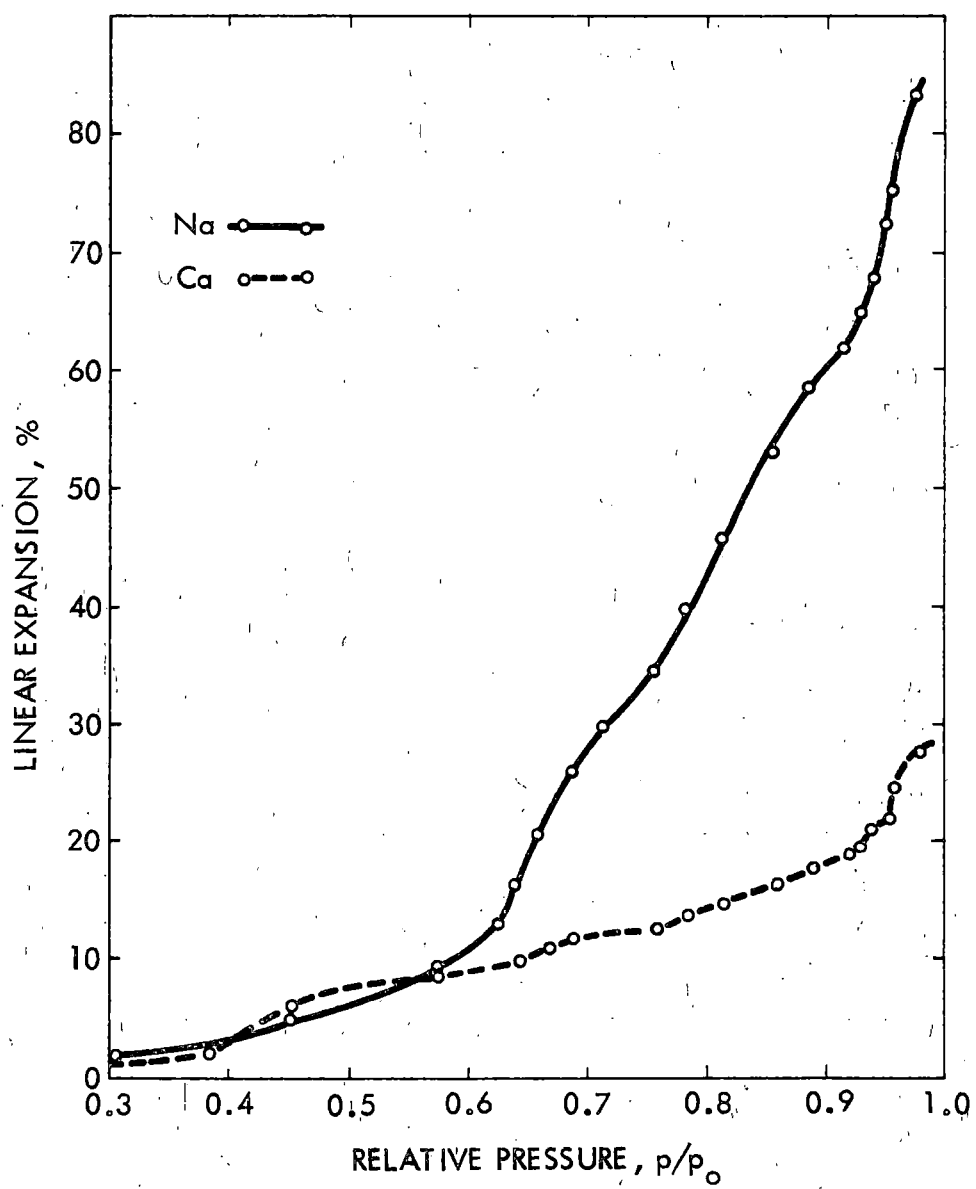
Fig. 2. Expansion isotherms of Na- and Ca-montmorillonites.

no further expansion beyond that which occurs due to vapor adsorption. Na-montmorillonites, however, give volumetric expansions 3 to 3.3 times as great as those due to vapor adsorption. X-ray data indicate this additional swelling in the presence of liquid water is due to lattice expansion (Demirel, 1962).

Sorption Isotherms

Figure 3 presents the first adsorption isotherm cycle for two and three successive cycles for the Ca- and Na-montmorillonites respectively. The Ca-clay displays a hysteresis loop above p/p_o of 0.20, while the Na-clay has a more pronounced hysteresis over the entire p/p_o range. Senich, et al., (1967) report a drift on successive cycles for Ca-montmorillonite; the isotherms do not coincide. Roderick and Demirel (1966) found successive adsorption curves were in very good agreement with Na-montmorillonite at p/p_o above 0.20 while desorption curves showed much less agreement.

In general, the steeper portions of the adsorption curves correspond with interlayer expansions shown by x-ray data. The mechanism proposed by Barrer and MacLeod (1954) explains the form of the adsorption curve. They also attribute the steeper portions of the desorption curves to removal of interlayer adsorbate. However, comparison of present x-ray data and sorption isotherms show that the steeper portions of desorption curves, i.e. near saturation and in the p/p_o range 0.65 to 0.55 for the Na-clay and near saturation and p/p_o range 0.40 to 0.25 for the Ca-clay, correspond with ranges of stable basal spacings. That is, the greater portion of the water being desorbed is from the external surfaces. The
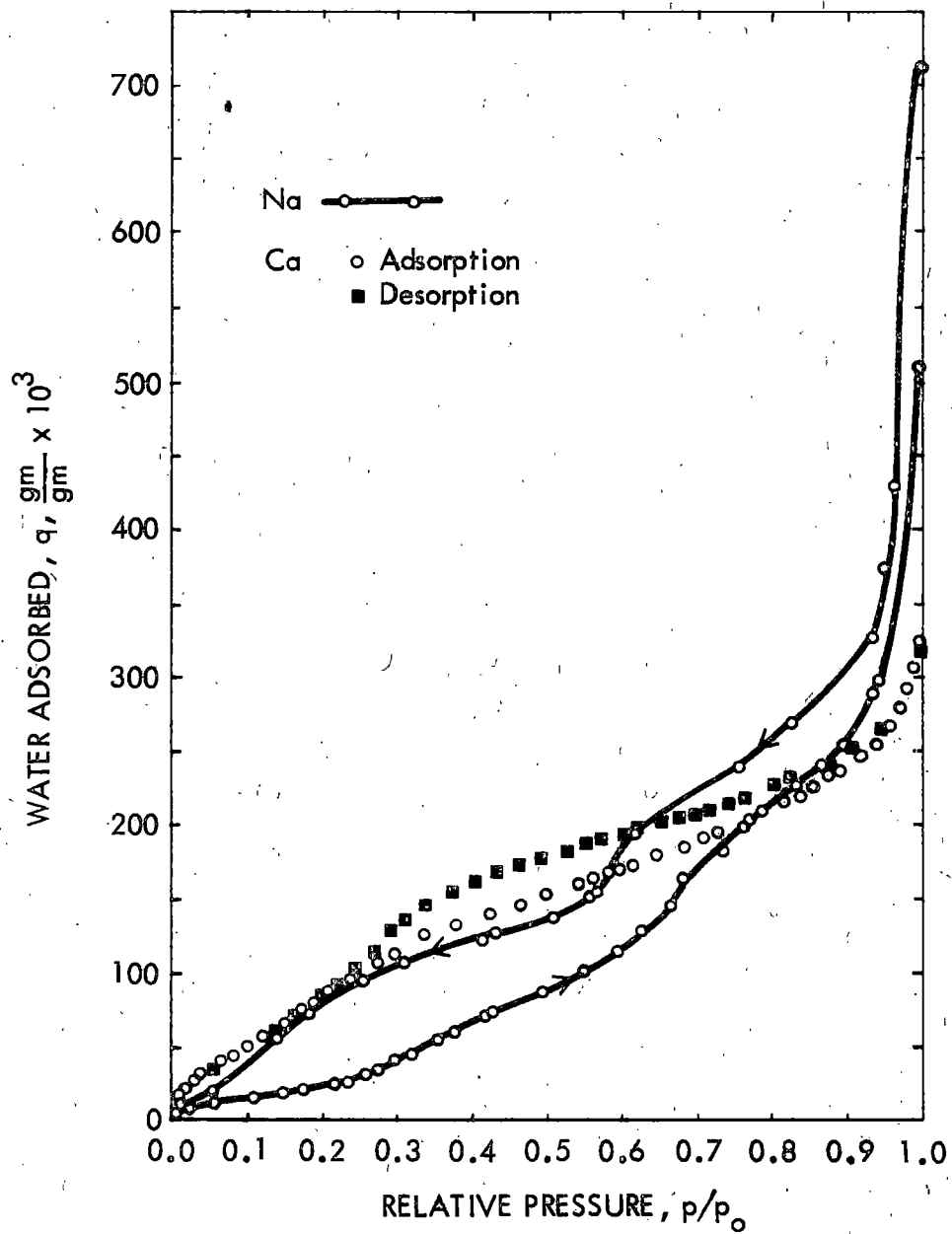
Fig. 3. Sorption isotherms of Na- and Ca-montmorillonites.

hysteresis explanation of Barrer and MacLeod (1954) for nonpolar gases
and vapors, i.e., destruction of a thixotropic structure, would apply
to these areas of the desorption curves. The final steep portions of
the desorption curves correspond to the removal of part of the interlayer
water.

Free Energy Changes

The free energy of immersion of a nonporous wettable surface in a
saturated vapor may be expressed as:

$$\Delta F = \gamma_{sl} - \gamma_{so} + \gamma_{lv} \tag{1}$$

where γ_{sl} is the solid-liquid interfacial tension, γ_{so} the surface tension
of the solid in vacuum, and γ_{lv} the surface tension of the liquid in
contact with its own vapor. For an adsorbent consisting of a noninteracting
fine powder wettable by the liquid, capillary condensation occurs before
final saturation and Eq. (1) becomes (Craig, et al., 1956):

$$\Delta F = \gamma_{sl} - \gamma_{so} . \tag{2}$$

For materials consisting of interacting solid particles such as
montmorillonites, Hirst (1948) and Demirel (1962) have shown that the
free energy is:

$$\Delta F = (\gamma_{sl} - \gamma_{so}) + \alpha \Delta V \tag{3}$$

where α is the interstitial surface area per cm^2 of total surface and ΔV
is the free energy change per cm^2 of interstitial surface due to separation
of surfaces against the force of interaction. The values given in Eq. (3)

will be designated the "free energy of wetting" of the solid. This may

be calculated from adsorption isotherm data by Bangham's free energy

equation (Bangham, 1937):

$$\Delta F = - \frac{RT}{M\Sigma} \int_0^1 \frac{q}{p/p_o} \, d(p/p_o) \tag{4}$$

where R is the gas constant, T the absolute temperature, M the molecular

weight of water, Σ the specific surface of the montmorillonite, q the

grams of water adsorbed per gram of clay, and p/p_o the relative vapor

pressure.

The free energies of wetting for the Na- and Ca-montmorillonites were

determined from the adsorption isotherm data by graphical integration of

q/p_o vs p/p_o plots and by using specific surface areas (from crystallographic

data) of 748 m^2/g and 759 m^2/g for the Na- and Ca-montmorillonite,

respectively. The free energies of wetting for three successive adsorption

cycles on the Na-clay were - 40.55 $\pm$ 2.43, - 36.15 $\pm$ 2.17 and - 37.50 $\pm$

2.24 ergs/cm^2 (Roderick and Demirel, 1966). Those for two successive

cycles with the Ca-clay were - 69.91 $\pm$ 2.36 and - 69.66 + 2.72 ergs/cm^2

(Senich, et al., 1967). These are in close agreement with earlier values

of - 34.76 $\pm$ 1.91 for Na-montmorillonite and - 76.61 $\pm$ 4.30 for

Ca-montmorillonite (Demirel, 1962).

Note that the Ca-clay, with less than half the total water adsorbed

by Na-clay, has nearly twice as large a free energy change. This may be

indicative of the formation of a more ordered configuration of the

interlayer water.

If the values of the integral $\Sigma \Delta F = - RT/M \int_0^{p/p_o} \frac{q}{p/p_o} d(p/p_o)$ for

increasing values of p/p_o, as determined by graphical integration, are

plotted against p/p_o on a log-log scale, a series of straight lines is obtained. For the Na-clay three linear portions are obtained (Roderick and Demirel, 1966), and for the Ca-clay, six linear portions (Senich, et al., 1967). Comparison to x-ray data shows that the breaks in the log-log plots correspond quite closely with the beginning of each increment of interlayer expansion. The increasing slope changes of the log $\Sigma\Delta F$ vs log p/p_o plots apparently reflect the differences in interaction energies at increasing increments of expansion.

Figure 4 presents plots of $\Sigma\Delta F$ vs interlayer separations at the same p/p_o. A series of sharp breaks in the curves are noted, corresponding with those discussed above. For the Na-montmorillonite, each segment of the curve corresponds with an expansion increment; each break occurs at very nearly an integral multiple of 2.8 $\overset{o}{A}$, the thickness of a water molecule. This gives additional evidence of a laminar stacking of the water layers.

The plot for the Ca-montmorillonite is in agreement with the expansion mechanism discussed earlier. The first segment corresponds with uptake of the first monolayer of water and the second segment with hydration of the Ca ion to give a 12.5 $\overset{o}{A}$ spacing. The third segment corresponds with a second layer of water; the fourth with the start of an ice-like configuration; and the fifth with completion of the ice-like configuration with four layers of water. The sixth segment corresponds with entrance of a fifth water layer leading to a less ordered structure. The largest free energy change occurs during the formation of the proposed ice-like configuration.
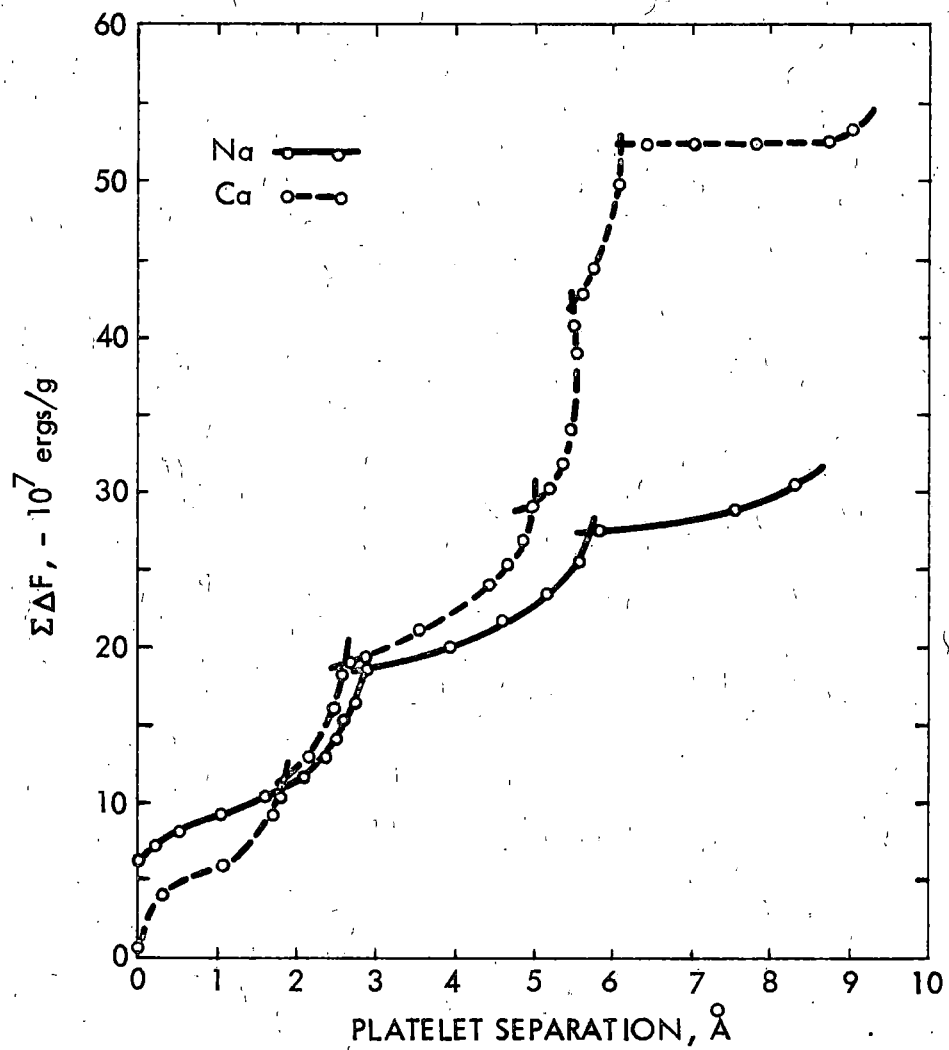
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Fig. 4. Free energy change versus interlayer separation of Na- and Ca-montmorillonites.

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