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INTERSTRATIFIED CLAY SYSTEMS:

CALCULATION OF THE TOTAL ONE-DIMENSIONAL DIFFRACTION FUNCTION

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ABSTRACT

Methods are described for calculating X-ray diffraction effects from two-component interstratified clay systems. Unlike previous work, the calculations for very thick crystallites include the scattering contributions from both types of interlamellar materials.

A preliminary study of the system glycol-montmorillonite-illite indicates that, for very thick crystallites, calculated diffraction angles for most maxima are similar to those computed by other published methods; relative intensities show very large discrepancies. Calculations of the complete one-dimensional diffraction function indicate that randomly interstratified, illite-rich members of this system do not show a 001/001 diffraction maximum between about 6° and 8° 2θ. It is suggested that many natural materials may not be randomly interstratified, therefore, the widespread use of the Hendricks-Teller equation for random interstratification may be unjustified.

INTRODUCTION

Hendricks and Teller (1942), MacEwan (1956, 1958) and Mering (1949, 1950) have proposed methods for calculating one-dimensional X-ray diffraction functions for interstratified lamellar systems. It has been commonly assumed that the interlamellar electron density, for most clay systems, is negligible compared to that of the silicate layers. Therefore, little attention has been given to the problem of incorporating the effects of interlamellar scattering into calculated diffraction profiles.

Studies of the glycol-montmorillonite complex (Reynolds, 1965) indicated a fairly large diffraction contribution from the glycol layers. In fact, the F-factor for glycol exceeds that of the silicate layers at the diffraction angle of the glycol-montmorillonite-illite 001/002 peak, which is widely used for the identification and characterization of interstratified montmorillonite-illite. Clearly, it seems desirable to ascertain the extent of discrepancies that are introduced into calculated d if the scattering from the glycol layers is ignored.

The simplest and most widely used method of calculating diffraction functions has been developed by Hendricks and Teller (1942); the results apply to randomly interstratified, infinitely thick crystallites, and interlamellar scattering is ignored. Diffraction functions calculated by different methods (Mering, 1950; MacEwan, 1958) indicate a marked particle-size effect on the diffraction angles of maxima. If natural samples are of sufficiently fine particle-thickness (approximately 0.02 μ and less), then curves calculated by the Hendricks-Teller method cannot be used as a basis of comparison. A method is needed that does not share these limitations. Mering (1950) has developed such a method, but his approach can be applied only if one member of a two-component system contains no interlamellar material (e.g. dehydrated vermiculite-chlorite). MacEwan's direct Fourier transform method (MacEwan, 1958) is not restricted to such systems, but it requires modification in order to accurately incorporate the effects of interlamellar scattering.

The modified MacEwan method is described below, followed by a few calculated results for the system glycol-montmorillonite-illite. The use of a high-speed digital computer (General Electric 235) has made it possible to include the effects of interlamellar scattering in all calculations. In addition, calculations have been carried out for up to 20 layers per crystallite; these approximate "real" materials to a greater extent than do previously published diffraction functions which have been hand-calculated and therefore restricted to cases of relatively few layers. In all calculations, the structural parameters of glycol and silicate layers are as given by Reynolds (1965). The random powder Lorentz-polarization factor is used, and pure illite is considered to contain 0.7 potassium atoms per half unit cell. The basal spacing is assumed to be 10.0 Å for illite and 16.9 Å for glycol-montmorillonite. All diffraction angles given here are based on CuKα.

METHOD OF CALCULATION

MacEwan's (1956, 1958) methods form the basis of the discussion below. Most of the terminology and definitions used here are taken from his papers to facilitate the efforts of the individual reader who may wish to study the derivations of the equations and the general theory.

Consider a random interstratification of two components, A and B. The intensity, at some diffraction angle, is given by a summation over all possible spacings (MacEwan 1956, 1958).

$$\frac{I}{\Xi} = \sum F_s^2 \sigma_s \cos(2\pi R_s/d). \tag{1}$$

The Lorentz-polarization factor is indicated by Ξ; F_s is the structure factor that applies to the two end layers that are separated by the spacing R_s and σ_s is the frequency of occurrence of the array (of A and B layers) that forms the spacing R_s. If all of the layers are assumed to be identical (i.e., if the interlamellar material is ignored) then the appropriate structure factor becomes that of the 3-layer mica unit and F_s^2

may be moved outside of the summation. This procedure is easily applied to hand calculations for crystallites containing only a few layers ($N \leqq 5$). For larger values of N the calculations are most conveniently made by the computer.

If scattering contributions from interlamellar materials are to be included in the calculations, then Equation 1 must be modified and the procedure becomes somewhat more complicated. Let N be the number of silicate layers per crystallite. F_S, F_A, and F_B refer respectively to the structure factors for the silicate skeleton, interlamellar material A, and interlamellar material B. R_s is the spacing produced by some combination of S, A, and B, and D_A is the thickness of A+S and D_B is the thickness of B+S. P_A is taken as the proportion of A and P_B is the proportion of B in the clay system; $P_A+P_B=1$. The number of A and B layers required to make up any spacing R_s is given respectively by n_A and n_B. The total diffracted intensity, at some diffraction angle, is given by

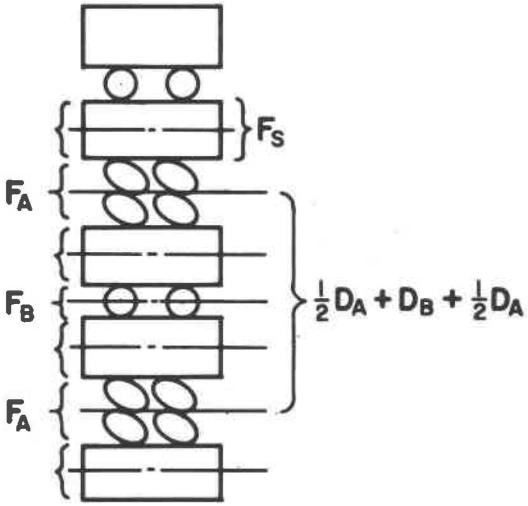

FIG. 1. Assignment of F_A, F_B, and F_S; these are Fourier transforms, respectively, of the glycol layer, the potassium layer, and the silicate skeleton.

$$\frac{I}{\Xi} = F_A^2M_1 + F_B^2M_2 + F_AF_BM_3 + F_AF_SM_4 + F_BF_SM_5 + F_S^2M_6 \quad (2)$$

where M_1, M_2, M_3, etc. are mixing functions representing summations of spacings that are bounded by A-A, B-B, A-B, etc. An example of the assignments of structure factors and spacings, R_s, is shown by Figure 1.

One subset of spacings may be considered in detail, e.g., those bounded on each end by A. The mixing function for this subset of spacings is given by

$$M_1 = \sum \sigma_{\mathrm{AA}} \cos (2\pi R_{\mathrm{AA}}/d). \tag{3}$$

An individual term from this summation has the following composition:

$$\sigma_{\mathrm{AA}} = \frac{(n_{\mathrm{A}} + n_{\mathrm{B}} - 2)!}{(n_{\mathrm{A}} - 2)!n_{\mathrm{B}}!} P_{\mathrm{A}}{}^{nA} P_{\mathrm{B}}{}^{nB}(N - n_{\mathrm{A}} + n_{\mathrm{B}}) \tag{4}$$

where

$$R_{\mathrm{AA}} = (n_{\mathrm{A}} - 1) D_{\mathrm{A}} + n_{\mathrm{B}} D_{\mathrm{B}}.$$

The factorial expression is the number of ways that a given assemblage of A and B layers can be written such that an A occurs on each end. The expression

$$P_{\mathrm{A}}{}^{nA} \cdot P_{\mathrm{B}}{}^{nB}$$

gives the probability of occurrence of the assemblage and $N - n_{\mathrm{A}} + n_{\mathrm{B}}$ is a correction required by the stipulation of a finite crystallite containing N silicate layers.

The structure factors for A do not include the silicate layers and therefore possible interactions between A and S must be considered. Given any specific assemblage, for example A-S-B-S-A, there are three silicate end layer interactions, namely, A-S, S-A, and S-S. For the first two $R_s = D_{\mathrm{A}} + D_{\mathrm{B}} + D_{\mathrm{A}}/2$, and for the third, $R_s = D_{\mathrm{A}} + D_{\mathrm{B}} + D_{\mathrm{A}}$. The frequency of occurrence for each is given by (4). The asymmetrical arrays always occur in pairs of equal R_s, therefore they may be considered as a single R_s whose $\sigma_{\mathrm{AS}} = 2\sigma_{\mathrm{AA}}$. These interactions are summed as follows:

$$M_4 = \sum \sigma_{\mathrm{AS}} \cos (2\pi R_{\mathrm{AS}}/d)$$

and

$$M_6 = \sum \sigma_{\mathrm{AA}} \cos (2\pi R_{\mathrm{SS}}/d).$$

An analogous argument can be developed for the arrays with B end layers, giving rise to summations M_2 and M_5 (see Eq. 2). Spacings with S-S ends (separated by a core containing a B on each end) are included in the M_6 summation.

The spacings terminated by A-B must be treated somewhat differently. The A-B terms are included in M_3, but the factorial expression of (4) becomes

$$2\,\frac{(n_{\mathrm{A}} + n_{\mathrm{B}} - 2)!}{(n_{\mathrm{A}} - 1)!(n_{\mathrm{B}} - 1)!}. \tag{5}$$

It is necessary to multiply by two because all arrays, that can be written with an A on one end and a B on the other, have a mirror image. The spacing for a particular term is given by

$$R_{\mathrm{AB}} = (n_{\mathrm{A}} - \tfrac{1}{2})D_{\mathrm{A}} + (n_{\mathrm{B}} - \tfrac{1}{2})D_{\mathrm{B}}.$$

The terms bounded by silicate layers are included in the M_6 summation. For these terms σ_{SS} is given by σ_{AB}, and R_{SS} is given by

$$R_{\mathrm{SS}} = n_{\mathrm{A}}D_{\mathrm{A}} + n_{\mathrm{B}}D_{\mathrm{B}}.$$

The S-A and S-B interactions are included in M_4 and M_5, respectively, except that pairing of the asymmetrical arrays (B-S-A-S-A-S and S-A-S-A-S-B) has already been accounted for by the "two" in (5). Therefore, $\sigma_{\mathrm{AB}} = \sigma_{\mathrm{AS}} = \sigma_{\mathrm{BS}}$.

$$R_{\mathrm{AS}} = (n_{\mathrm{A}} - \tfrac{1}{2})D_{\mathrm{A}} + n_{\mathrm{B}}D_{\mathrm{B}},$$

and

$$R_{\mathrm{BS}} = n_{\mathrm{A}}D_{\mathrm{A}} + (n_{\mathrm{B}} - \tfrac{1}{2})D_{\mathrm{B}}.$$

Each of the summations is multiplied by its appropriate F·F factor and the results are summed to provide the intensity of the diffraction function at some specific diffraction angle (Eq. 2).

It is necessary to discuss briefly the distribution of the zero terms among summations M_1, M_2, and M_6. The zero terms arise because each of the individual layers is zero distance from itself. The zero term in M_1, for example, is represented by a single layer A. This can be considered as a zero spacing bounded on each end by A/2. Therefore σ_s for the zero terms is divided by two before inclusion in the appropriate summation. In an N layer case, the distribution of the zero spacings is as follows:

Summation	Zero Term
M_1	$P_{\mathrm{A}}(N-1)/2$
M_2	$P_{\mathrm{B}}(N-1)/2$
M_6	$N/2$

The mathematical model used here is necessarily limited. It is assumed that the theoretical diffracting substance consists of an array of crystallites of identical thickness (N). Natural materials, on the other hand, will doubtless contain a distribution of thicknesses. This distinction is important at small values of N, for substantial differences are evident in "apparent *d*" and peak symmetry and breadth among calculated profiles for cases of N = 3, 4, 5, and 6. However, as N is increased beyond 10 or 11, further changes in the calculated profiles are minimal. For these reasons, the simple model used here becomes unrealistic if it is applied to cases of small N, perhaps prohibitively so.

RESULTS

One-dimensional diffraction functions have been calculated for several compositions in the system glycol-montmorillonite-illite. The results are summarized by Table 1 and Figures 2 and 3. Table 1 shows computed intensities and apparent spacings for several diffraction maxima. The results refer to very thick crystallites ($N = 20$). The column labelled "MacEwan" was computed according to the methods discussed by MacEwan (1958) for finite crystallites in which the interlamellar material is ignored. The results show that the higher angle peaks give very similar values by all three methods. The agreement is less satisfactory at lower diffraction angles. Errors in calculated $d(001/002)$ amount to approximately 10 percent of the range 0 to 100 percent illite. The relative intensities show very poor agreement among the various methods; so poor, in fact, that intensity data that do not incorporate interlamellar scattering are of little interpretive value.

TABLE 1. DIFFRACTION MAXIMA FOR TWO COMPOSITIONS IN THE SYSTEM GLYCOL-MONTMORILLONITE-ILLITE

	0.7 Mont.–0.3 Illite						0.3 Mont.–0.7 Illite					
	This paper 20-layer case		MacEwan 20-layer case		Hendricks-Teller infinite crystallite		This paper 20-layer case		MacEwan 20-layer case		Hendricks-Teller infinite crystallite	
Peak	d	I	d	I	d	I	d	I	d	I	d	I
001/001	16.83	9,150	16.83	30,000	16.65	32,000	—	—	—	—	—	—
001/002	8.72	780	8.88	150	8.77	170	9.43	670	9.63	960	9.55	1,060
002/003	5.53	700	5.52	1,260	5.52	1,520	5.26	290	5.25	618	5.24	678
003/004	4.29	70	—	—	—	—	—	—	—	—	—	—
003/005	3.371	2,561	3.370	2,010	3.371	31,442	3.353	1,791	3.353	1,978	3.353	15,463

Figure 2 shows a portion of the continuous one-dimensional diffraction profiles for the compositions treated in Table 1. The differences among the profiles in the region of $2\theta < 11°$ should be noted. The diffraction profile at $2\theta < 7°$ is not shown for 0.3 montmorillonite-0.7 illite because no peak appears in this region; the background rises smoothly and steeply toward lower diffraction angles.

Figure 3 shows calculated diffraction profiles (right-hand side) for a series of compositions of randomly interstratified glycol-montmorillonite-illite ($N = 11$). The left-hand side of Figure 3 shows portions of

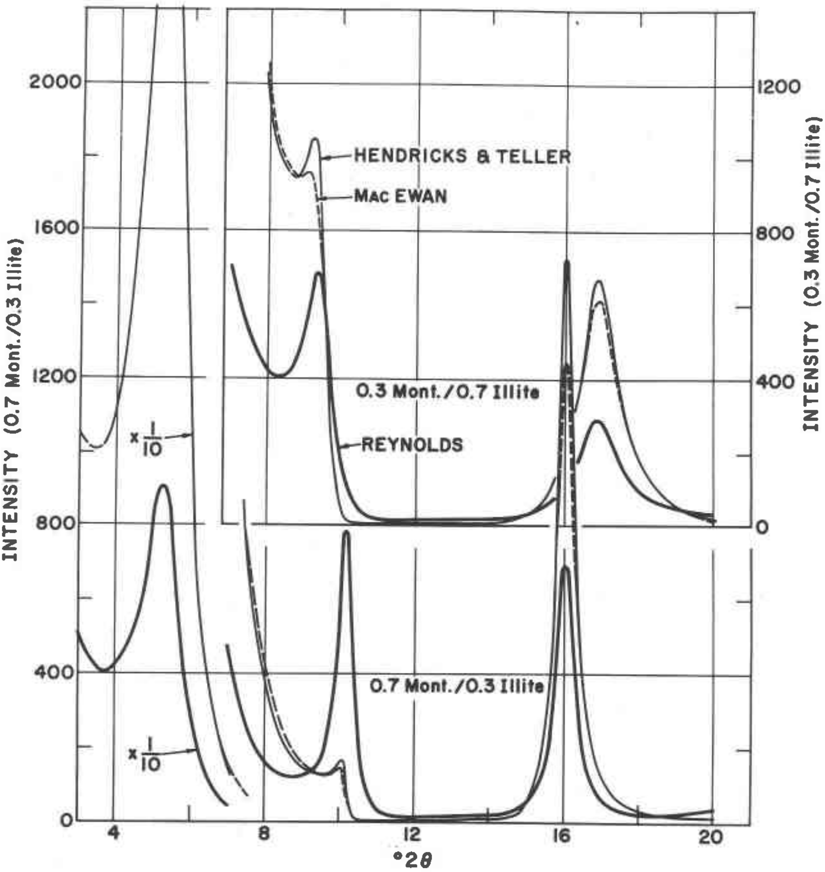

FIG. 2. Comparison of the results for various methods of calculating the diffraction function. Curves computed by the MacEwan- and Hendricks-Teller-methods are coincident except where otherwise indicated. These calculated diffraction patterns show maxima for the 001/001, 001/002, and 002/003.

X-ray diffraction patterns from a series of glycerated montmorillonites that had been incompletely saturated with lithium and heated (see Greene-Kelly, 1955). An exact comparison between observed and calculated diffraction phenomena is not possible here, because glycerol and glycol produce interlamellar complexes which differ from each other in thickness and in the distribution of scattering centers. Therefore, values for *d* have been omitted from the calculated profiles. They have been included on the diffraction patterns only to establish that a compositional range is represented between almost fully collapsed and almost fully expanded montmorillonite.

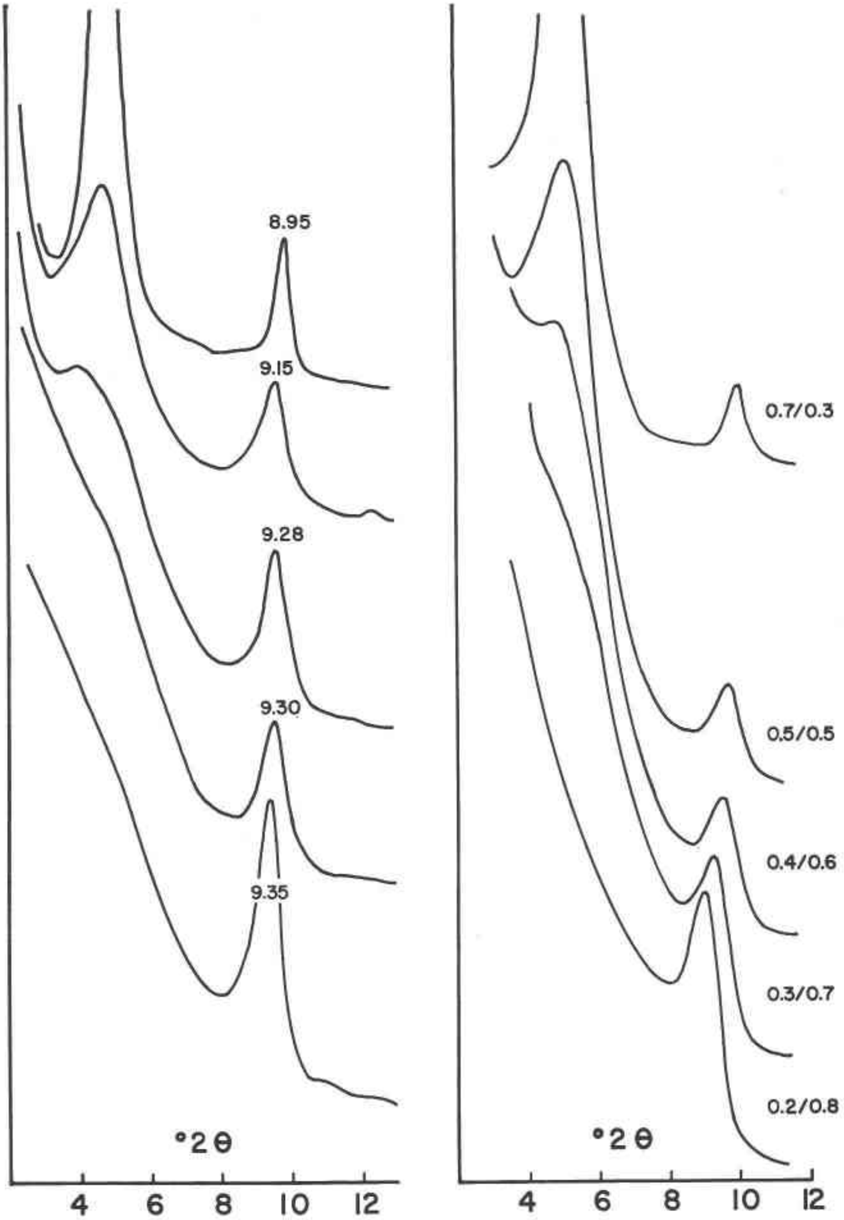

FIG. 3. Comparison between X-ray diffraction patterns from partially collapsed, glycerol-solvated montmorillonites (left-hand side) and computed one-dimensional diffraction profiles for the random interstratification of montmorillonite (glycol)-illite. Numbers on the computed curves refer to fraction montmorillonite/fraction illite.

The general similarity between the two sets of curves should be noted. The 001/001 first appears as a well-defined maximum near the middle of the compositional range. Further increases in the expanded component cause an increase in intensity, but little change in diffraction angle. In no case is an 001/001 maximum present whose diffraction angle is intermediate between that of the 001/002 and the glycol (or glycerol)-montmorillonite 001. The assumed model of random interstratification appears to apply quite well to the partially collapsed montmorillonite series shown in Figure 3.

DISCUSSION

None of the methods tested here produced diffraction maxima, for any composition, in the region between the 2θ value for the 001/002 and about 6°. Using the modified MacEwan method, the 001/001 first appears at a composition of about 0.4 montmorillonite-0.6 illite, but its apparent spacing, for a 20-layer case, is approximately 18Å. Apparently the breadth of the peak has caused it to be displaced (toward lower diffraction angles) by the rapidly increasing Lorentz-polarization and structure factors. This effect is markedly enhanced at finer crystallite sizes and has been noted by MacEwan (1958) and Mering (1950). With increasing montmorillonite content, the 001/001 increases in intensity and its diffraction maximum migrates to about 16 Å and then to 16.9Å for pure montmorillonite. This behaviour is not indicated by curves of the silicate mixing functions (see MacEwan, *et al*, 1961, p. 404–405), although these curves generally confirm the absence of large changes in diffraction angle with composition. The mixing-function maxima are displaced if they are multiplied by $F^2\Xi$. Consequently, it is somewhat misleading to compare mixing function profiles with X-ray diffraction patterns, for, of course, the X-ray diffractometer records the complete one-dimensional diffraction function. The important point here is that randomly interstratified members of the glycol-montmorillonite-illite system do not produce diffraction maxima between the 001/002 and a position very near that of the glycol-montmorillonite 001. Therefore, glycolated samples that produce asymmetrical illite 001 profiles or maxima between about 8 and 6° 2θ cannot be construed as examples of random interstratification. If such samples are not randomly interstratified, then it is a questionable procedure to interpret their other diffraction maxima on the basis of any of the published curves for this system, for all of these curves are based on models of random interstratification. Many diffraction patterns of mixed-layered clays do show asymmetrical 001/002 profiles or a definite maximum between $2\theta = 8°$ and $2\theta = 6°$; this implies that non-random interstratification is common and perhaps typical.

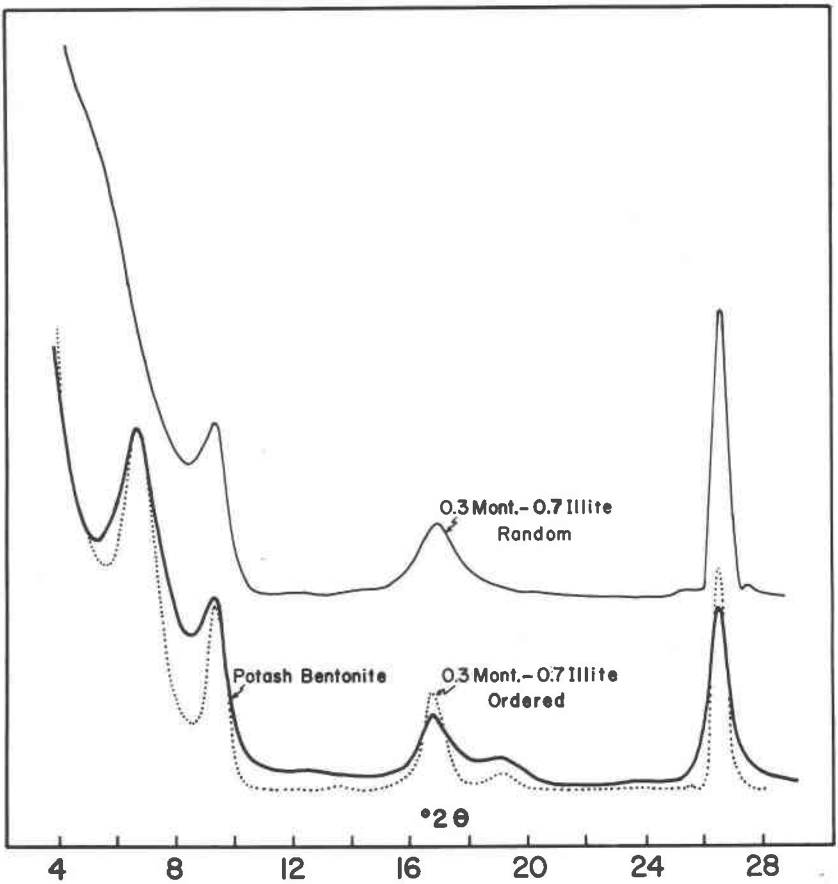

FIG. 4. Comparison between the X-ray diffraction pattern from a potash bentonite (solid lower curve), and the computed profile calculated for a case of complete ordering (regular alternation) of 0.3 montmorillonite-0.7 illite (dashed curve). The calculated profile for the same composition, but for conditions of random interstratification, is given by the uppermost curve.

NON-RANDOM INTERSTRATIFICATION

A preliminary study has been made of diffraction phenomena from non-randomly interstratified systems. Figure 4 shows a comparison between (1) the observed diffraction pattern from an oriented and glycol-solvated potash bentonite (Kinnekulle), and (2) the calculated one-dimensional profile for a composition of 0.3 montmorillonite-0.7 illite, in which it is assumed that no two successive interlamellar regions are occupied by the glycol complex, i.e., the tendency toward ordering is complete. The method of calculation here was somewhat altered from the methods described above. A subsidiary computer program was used to compute the σ terms (e.g., Eq. 4) for conditions of regular alternation. The calculated profile at $2\theta > 10°$ is based on $N = 11$, but the profile at $2\theta < 10°$ represents the average of profiles computed for $N = 8, 9, 10$, and 11[1]. This procedure eliminates background ripples which are severe at low diffraction angles (see MacEwan and Ruiz Amil, 1959, p. 99). Figure 4 also shows a diffraction profile computed for a condition of random interstratification of 0.3 montmorillonite-0.7 illite ($N = 11$). The intensities at low diffraction angles, for both calculated curves, have been corrected for the effects of a one-degree beam divergence (sample length = 2 cm). This correction simulates some of the experimental conditions under which the observed diffraction pattern was obtained.

The very close correspondence between observed and computed diffraction profiles (ordered case) should be noted. These two profiles are well correlated with respect to (1) rate of background rise at low diffraction angles, (2) relative intensities for all diffraction maxima, and (3) equivalence of diffraction angles for all maxima. Conversely, it can be seen that the random model, and the Hendricks-Teller method (see Fig. 2), fail utterly to provide realistic comparisons with the observed diffraction pattern. These relationships strongly suggest that (1) materials such as the potash bentonite of Figure 4 are examples of ordered interstratification, and (2) at large values of N, the mathematical model developed in this paper provides a valid simulation of reality.

CONCLUSIONS

1. A modified version of MacEwan's method, which allows incorporation of interlamellar scattering effects, provides calculated one-dimensional diffraction profiles which correlate well with X-ray diffraction patterns obtained from some types of natural materials. These correlations have, at present, only been established for cases of large N ($N \geqq 10$ silicate layers per crystallite).

2. For very thick crystallites ($N = 20$), the different methods tested here give similar values for calculated d in the system glycol-montmorillonite-illite; analytical data are probably not in error by more than 10 percent if the interlamellar material is ignored. Intensity data, provided by calculating the scattering from the silicate layers only, are so poor that they are of little diagnostic value.

3. For one potash bentonite, good agreement has been obtained be-

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[1] Except for the absence of background ripples, and somewhat greater peak breadth, this averaged profile is virtually identical to one computed for $N = 11$.

tween calculated and observed diffraction profiles by basing the calculations on the assumed condition of a regular alternation of glycol-montmorillonite and illite units.

4. Randomly interstratified montmorillonite (glycol)-illite does not produce a 001/001 diffraction maximum between $2\theta \approx 8°$ and $2\theta \approx 6°$. Diffraction maxima in this range indicate a tendency toward regular interstratification (ordering). Significant errors could be introduced if other portions of such diffraction patterns are interpreted by means of models which assume random interstratification.

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