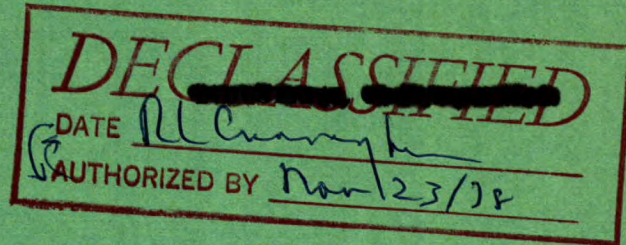


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CANADA

DEPARTMENT OF MINES AND TECHNICAL SURVEYS

OTTAWA

MINES BRANCH INVESTIGATION REPORT IR 62-46

**CLAY MINERALOGY INVESTIGATION OF
SEVENTEEN SAMPLES OF BENTONITE
SUBMITTED BY THE IRON ORE COMPANY
OF CANADA, SCHEFFERVILLE, P. Q.**

by

R. S. DEAN

MINERAL PROCESSING DIVISION

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CLAY MINERALOGY INVESTIGATION OF SEVENTEEN SAMPLES
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SUMMARY OF RESULTS

Seventeen samples of commercial bentonites were examined by X-ray diffraction. Oriented mounts of each sample were prepared from aqueous suspensions of the clay before and after it had been brought into contact with calcium-saturated ion exchange resin. They were then scanned in an X-ray diffractometer when air dry and after saturation with ethylene glycol.

Montmorillonite was the major constituent in each sample. Some expansion of montmorillonite was noted in almost all samples following ion-exchange treatment. This exchange was not complete, however, because most of the montmorillonites failed to expand fully to the basal spacing characteristic of calcium montmorillonite.

Minor quantities of cristobalite, quartz, hydrous mica, feldspar and calcite were identified during the clay mineral investigation.

Mineralogical analysis provided little information that could be considered to be significant in the pelletizing of iron ore concentrates.

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INTRODUCTION

Samples of seventeen commercial bentonites were submitted to the Mineral Processing Division, Mines Branch, on May 9, 1962, by Mr. I.S. Zajac, Ore Testing and Research, Iron Ore Company of Canada, Schefferville, P.Q. Bentonite is to be used by the company in the pelletizing of iron ore concentrates and it was hoped that mineralogical analysis of various commercial types would aid in the choice of the most suitable one.

The project was assigned laboratory number MP-MIN-302 and the individual bentonite samples were numbered B-1 to B-17 in accordance with the original sample labels.

PROCEDURE

A portion of each sample was brought into suspension by prolonged stirring in distilled water. Oriented mounts were prepared by evaporating a portion of each suspension on a glass microscope slide. For every sample a second mount was prepared from a suspension to which Amberlite IR-120 ion exchange resin had been added. The resin had previously been loaded with Ca^{++} ions and therefore produced a clay with calcium in the exchange positions.

No strict control of the particle size within the evaporated suspensions was attempted, although the aliquot was withdrawn from the upper portion of the suspension several minutes after stirring. This sampling procedure excluded most of the coarser-grained material.

The oriented mounts were scanned in a Philips X-ray diffractometer when air dry and after saturation with ethylene glycol. Iron-filtered cobalt K-alpha radiation was used. No humidity control was available; hence the results from different samples are not directly comparable. However, the air-dry untreated and air-dry, calcium-saturated mounts from each sample were run in succession so that room humidity was approximately the same.

RESULTS

Minor Minerals

Minerals present in minor or trace amounts are listed in Table 1; they are quartz, cristobalite, hydrous mica, calcite, feldspar and an unidentified mineral.

Hydrous mica was indicated by a 10\AA reflection that was not affected by glycol treatment. The remaining minor minerals were identified by their characteristic reflections. Unidentified mineral (or minerals) gave reflections corresponding to spacings of 7.59 and 5.98 \AA (Figure 9).

TABLE 1

Minor Constituents of Bentonites

Sample	Minor Constituents	Trace Constituents
B-1	-	quartz
B-2	cristobalite	-
B-3	cristobalite	-
B-4	-	-
B-5	-	cristobalite
B-6	-	hydrous mica; cristobalite
B-7	-	hydrous mica; cristobalite
B-8	-	hydrous mica; cristobalite
B-9	-	hydrous mica
B-10	-	cristobalite
B-11	-	cristobalite
B-12	quartz	hydrous mica; calcite
B-13	-	hydrous mica; calcite
B-14	-	cristobalite; quartz
B-15	-	unidentified mineral (s)
B-16	-	hydrous mica; calcite
B-17	-	feldspar

Montmorillonite

Montmorillonite is, by definition, the principal constituent of bentonites. In Table 2 the montmorillonite basal reflections from the untreated and calcium-saturated, oriented mounts are listed.

The first-order basal spacing of glycol-treated montmorillonite invariably occurred in the range 16.7 - 17.0 \AA . Higher order reflections, when observed, occurred at integral submultiples of this spacing (Figures 3 and 7).

It is apparent from Table 2 that calcium-ion saturation resulted in an increased basal spacing compared with the air-dry material. The untreated bentonite is presumably sodium montmorillonite or a variety with calcium in some of the exchange

positions. Sodium montmorillonite should give a basal spacing of about 10\AA when dehydrated. This increases to 12.4\AA with the addition of a single water layer at relative humidity values exceeding 20% (1). Within the relative humidity range 40-70%, sodium montmorillonites adsorb a second water layer and expand to $15.0-15.4\text{\AA}$. It has been found, however, that the hydration of sodium montmorillonite does not proceed in a well-defined, stepwise manner at (or above) moderate humidity conditions (2). A maximum spacing of 19\AA has been reported (3) for air-dry material in contact with a very humid atmosphere.

A study of the observed basal reflections of the montmorillonites following calcium saturation suggests that, in most cases, the exchange of calcium for sodium was incomplete. At relative humidity values exceeding 1%, pure calcium montmorillonite should have a basal spacing of at least 14\AA (1,4). This approximate spacing was recorded in many instances (samples B-1, B-8, B-9, B-10, B-12, B-13, B-14 and B-16) of which sample B-13 furnishes an excellent example. In this sample montmorillonite, which was either unhydrated (10\AA) or contained a single water layer (12.4\AA) (Figure 1), expanded uniformly to 14.6\AA following Ca^{++} saturation (Figure 2). The persistence of the weak 10.0\AA reflection after glycolation (Figure 3) suggested that the material which remained unexpanded was hydrous mica.

The diffraction data suggest that partial replacement of sodium by calcium has resulted, in many cases, in the adsorption of monomolecular layers of water within the montmorillonite interlayer spaces. A basal spacing of about 12.4\AA was given by samples B-3, B-6, B-7 and B-17 following calcium saturation (Figure 5). The superstructure reflections at $22 - 23.3\text{\AA}$ suggest that most of the montmorillonite in these samples, which is not uniformly hydrated to a spacing of 12.4\AA , has an arrangement that consists of regular alternations of 12.4 and 10.0\AA layers. This may be considered to be a regular mixed-layer structure having a fundamental basal spacing periodicity of approximately $10.0 + 12.4\text{\AA} = 22.4\text{\AA}$.

Samples which gave basal spacings intermediate between fully collapsed montmorillonite (9.5\AA) and montmorillonite containing single water layers (12.4\AA) were probably composed of randomly interstratified mixtures of these two hydration states (5) (see Figure 4). This interpretation is offered to explain the positions of the first-order basal reflections from calcium-saturated montmorillonites B-2, B-4 and B-5. The superstructure reflections from these three samples also suggest the presence of some regularly interlayered material.

A basal spacing of $15.0 - 15.4\text{\AA}$, representing two water layers, is stable in calcium montmorillonite over a wide range of relative humidity conditions above 20% (1). This

TABLE 2

Basal Spacings of Montmorillonites

Sample	Super-structure d (Å)	First Order Reflections		Higher Order Reflections	
		d (Å)	I	d (Å)	
B-1 untreated	22	11.3	ms	5.03	3.12
B-2 calcium saturated		14.9	vvs		3.05
B-2 untreated	21.4 (diffuse)	10.8	s		
B-2 calcium saturated		11.5	s		
B-3 untreated	23	9.9-11.7	w	4.89	3.14
B-3 calcium saturated		12.2	w		3.09
B-4 untreated	23	10.8	ms		3.16
B-4 calcium saturated		11.1	ms		3.19
B-5 untreated	21-26	9.8	w		3.18
B-5 calcium saturated		11.9	m		3.15
B-6 untreated	23.3	10.0	w		3.18
B-6 calcium saturated		12.4	ms		
B-7 untreated	22	10.9	m		3.17
B-7 calcium saturated	22.3	12.4	w		3.19
B-8 untreated		12.4	m		
B-8 calcium saturated		14.6	m		
B-9 untreated	22.3	11.2	m	4.98	3.16
B-9 calcium saturated	21.4	13.9	s		3.04
B-10 untreated		10.7-11.5	w	4.93	3.20
B-10 calcium saturated		14.9	m		
B-11 untreated		11.7	s		3.14
B-11 calcium saturated		13.3	s		
B-12 untreated		11.7	w		
B-12 calcium saturated		14.0	w		
B-13 untreated		12.4	w		
B-13 calcium saturated		14.6	w		
B-14 untreated		11.2	s	5.0	3.12
B-14 calcium saturated		14.6	s	5.03	3.06
B-15 untreated		14.7	w		
B-15 calcium saturated		14.7	w		
B-16 untreated		12.2	m		
B-16 calcium saturated		14.3	m		
B-17 untreated	22	9.9-10.5	w		
B-17 calcium saturated		12.4	m		

degree of expansion was approached by only a few samples, notably B-10 and B-1. The latter sample also gave integral high-order basal reflections for this expanded spacing (Figure 6).

Sample B-15, which showed no expansion following the ion-exchange treatment, (Figures 8 and 9) may have some cation other than sodium in the exchange position. The physical properties of this bentonite were also somewhat different from the other samples in that it could be more readily dispersed in distilled water.

As shown in Table 2, a large variation occurred in the intensities of the first-order basal reflections given by the various montmorillonites. It was thought that these intensity variations may have been due, in part, to the presence in some samples of amorphous material, which could weaken montmorillonite reflections by dilution. However, dissolution of free alumina from sample B-12 by the sodium hydroxide method (6) resulted in no appreciable increase in the relatively weak montmorillonite basal reflections obtained from this sample (Figures 10 and 11). It appears, therefore, that variations in the intensities of the montmorillonite reflections are probably related to the crystallinity of the material or amorphous silica rather than to the presence of amorphous aluminous impurities.

CONCLUSIONS

Montmorillonite was the major mineral constituent of all samples. Much variation was observed in crystalline swelling properties and the crystallinity of the various montmorillonites but little can be deduced from these data concerning the physical behaviour of the bentonites.

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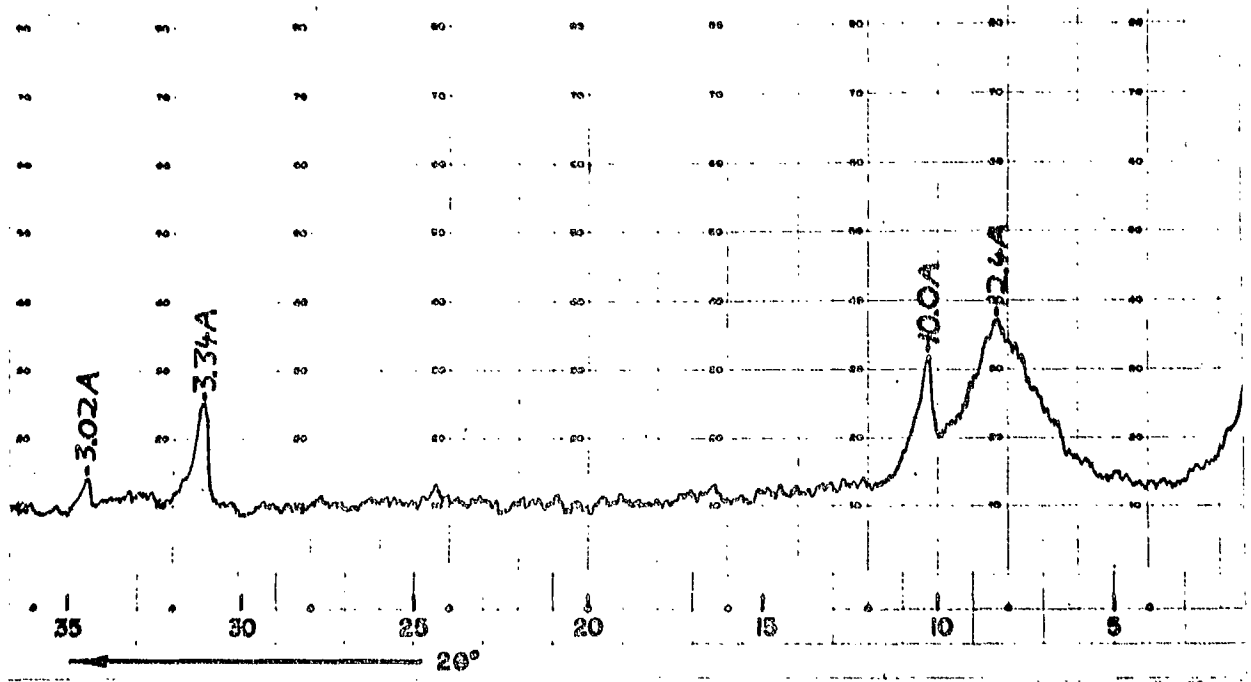


Figure 1. X-ray diffractogram of bentonite B-13, oriented mount, untreated.

Co/Fe radiation
 Scale Factor = 1
 Time Constant = 16 sec
 Slits - 1°
 Scanning Speed = 1°/min
 Montmorillonite - 12.4; 10.0; 3.34Å
 Hydrous Mica - 10.0 and 3.34Å, (in part)
 Calcite - 3.02Å

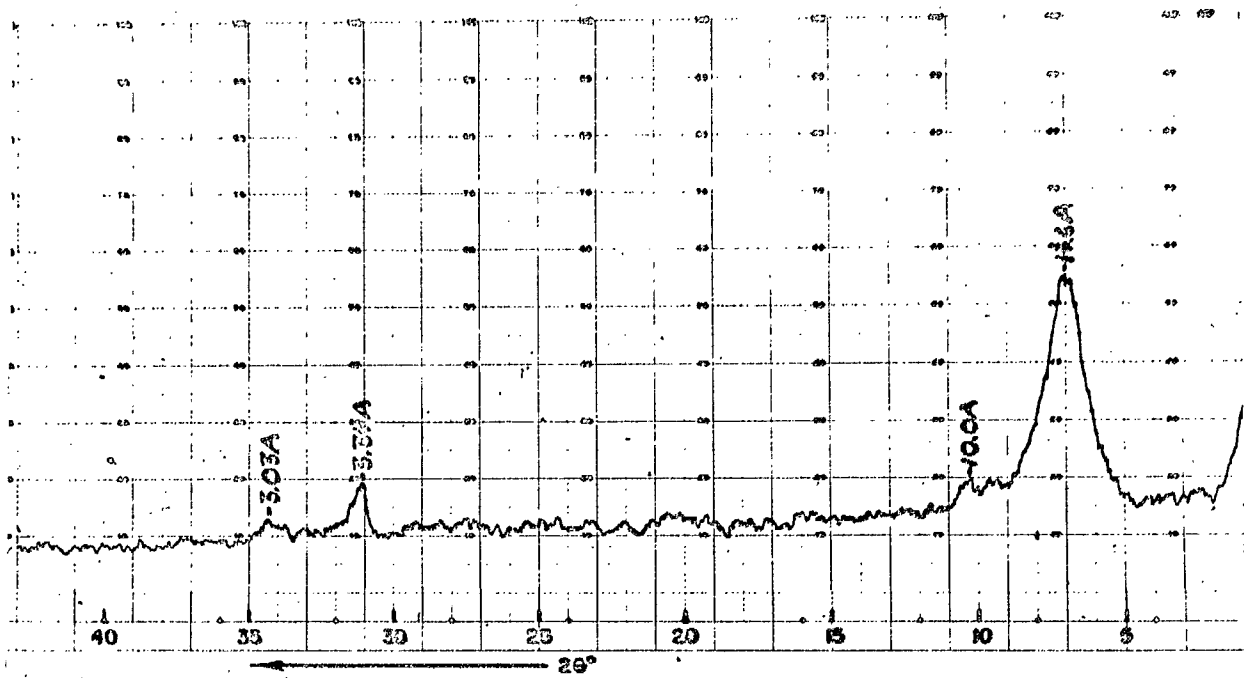


Figure 2. X-ray diffractogram of bentonite B-13, oriented mount, Ca⁺⁺ saturated

Co/Fe radiation

Scale Factor = 1

Time Constant = 16 sec

Slits - 1°

Scanning Speed = 1°/min

Montmorillonite 12.4; 10.0; 3.34Å (in part)

Hydrous mica 10.0; 3.34Å (in part)

Calcite - 3.03Å

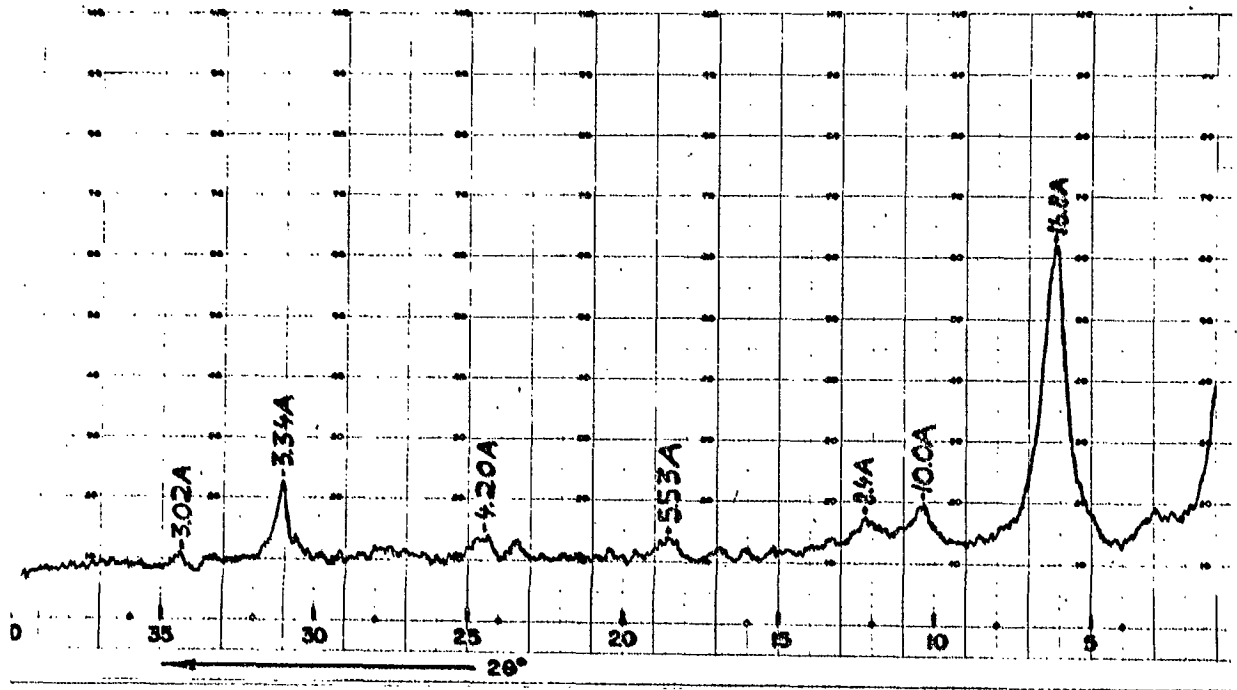


Figure 3. X-ray diffractogram of bentonite B-13, oriented mount, Ca^{++} saturated, glycolated

Co/Fe radiation

Scale Factor = 1

Time Constant = 16 sec

Slits - 1°

Scanning Speed = $1^\circ/\text{min}$

Montmorillonite - $16.8; 8.4; 5.53; 4.20; 3.34\text{\AA}$
(in part)

Hydrous Mica - $10.0; 3.34\text{\AA}$ (in part)

Calcite - 3.02\AA

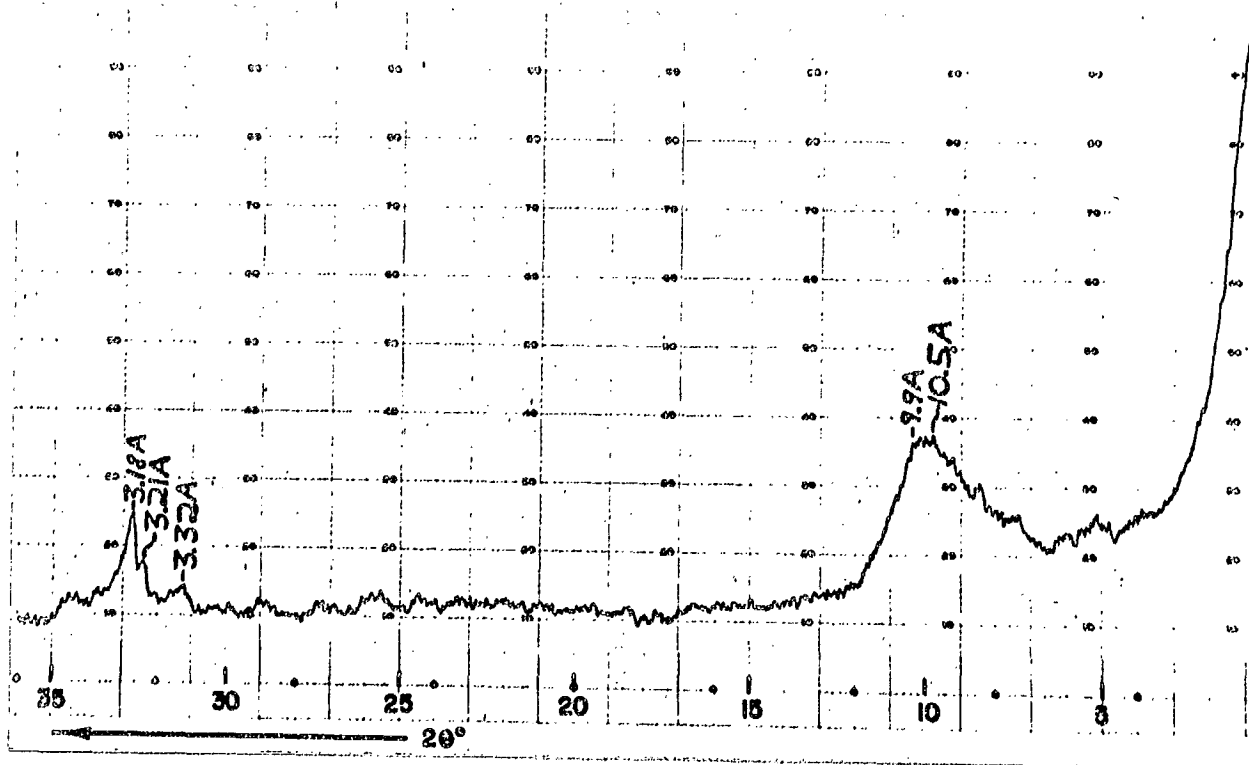


Figure 4. X-ray diffractogram of bentonite B-17, oriented mount, untreated.

Co/Fe radiation

Scale Factor = 1

Time Constant = 16 sec

Slits - 1°

Scanning Speed = $1^\circ/\text{min}$

Montmorillonite - 9.9, 10.5; 3.32Å ?

Feldspar - 3.21; 3.18Å

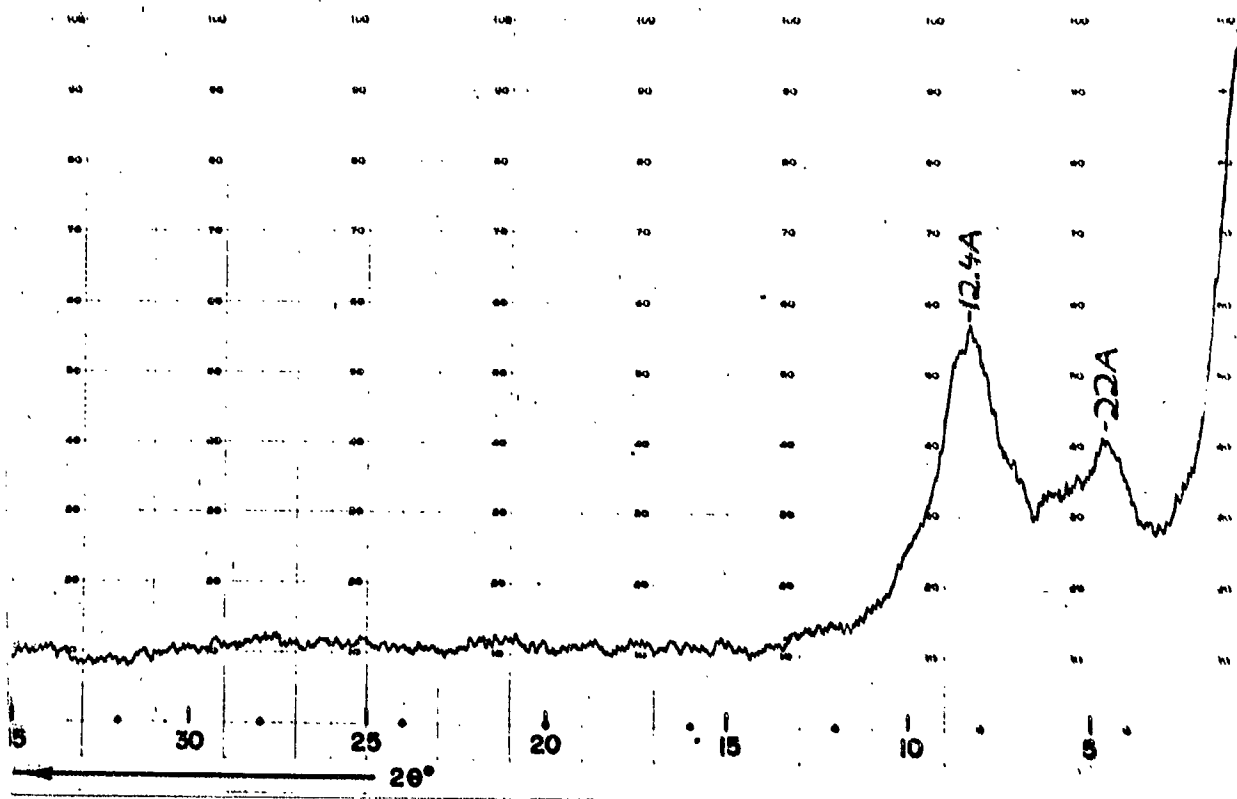


Figure 5. X-ray diffractogram of bentonite B-17, oriented mount, Ca^{++} saturated

Co/Fe radiation
Scale Factor = 1
Time Constant = 16 sec
Slits - 1°
Scanning Speed = $1^\circ/\text{min}$ °
Montmorillonite - 22; 12.4Å

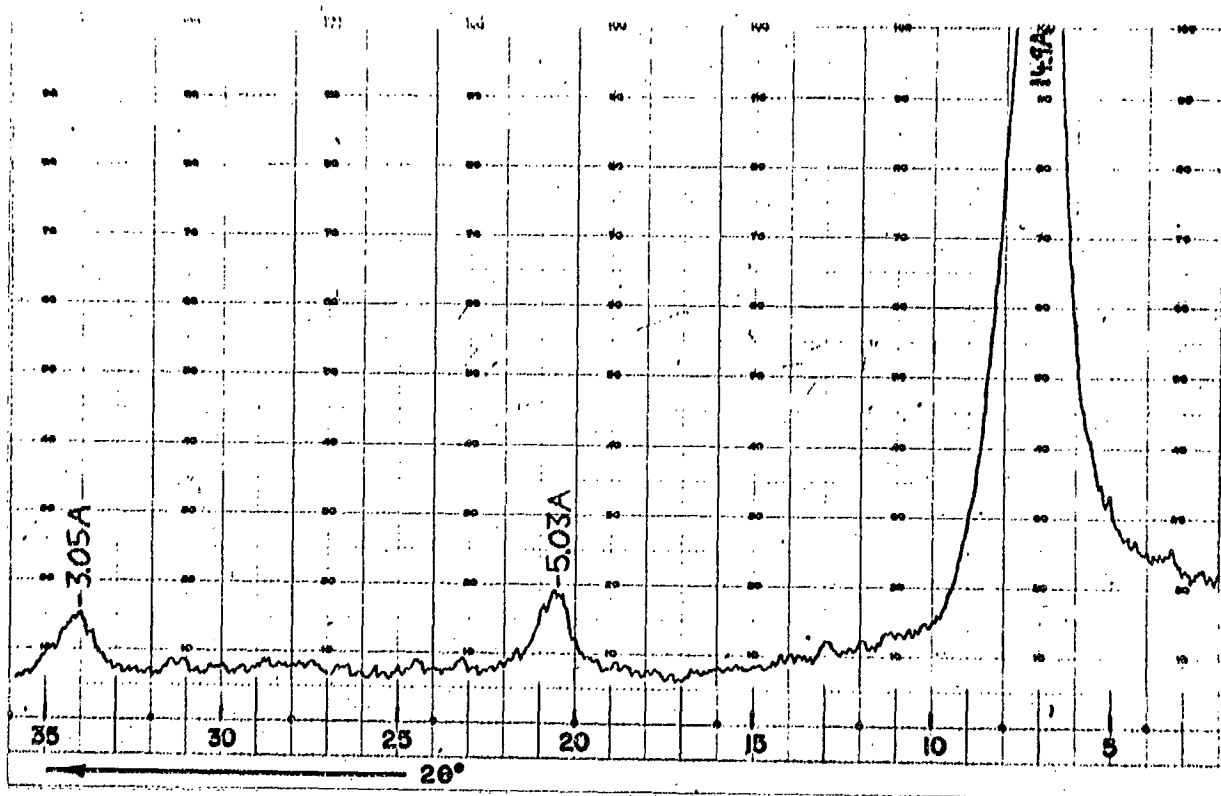


Figure 6. X-ray diffractogram of bentonite B-1, oriented mount, Ca⁺⁺ saturated

Co/Fe radiation
Scale Factor = 1
Time Constant = 16 sec
Slits - 1°
Scanning Speed = 1°/min
Montmorillonite - 14.9; 5.03; 3.05A

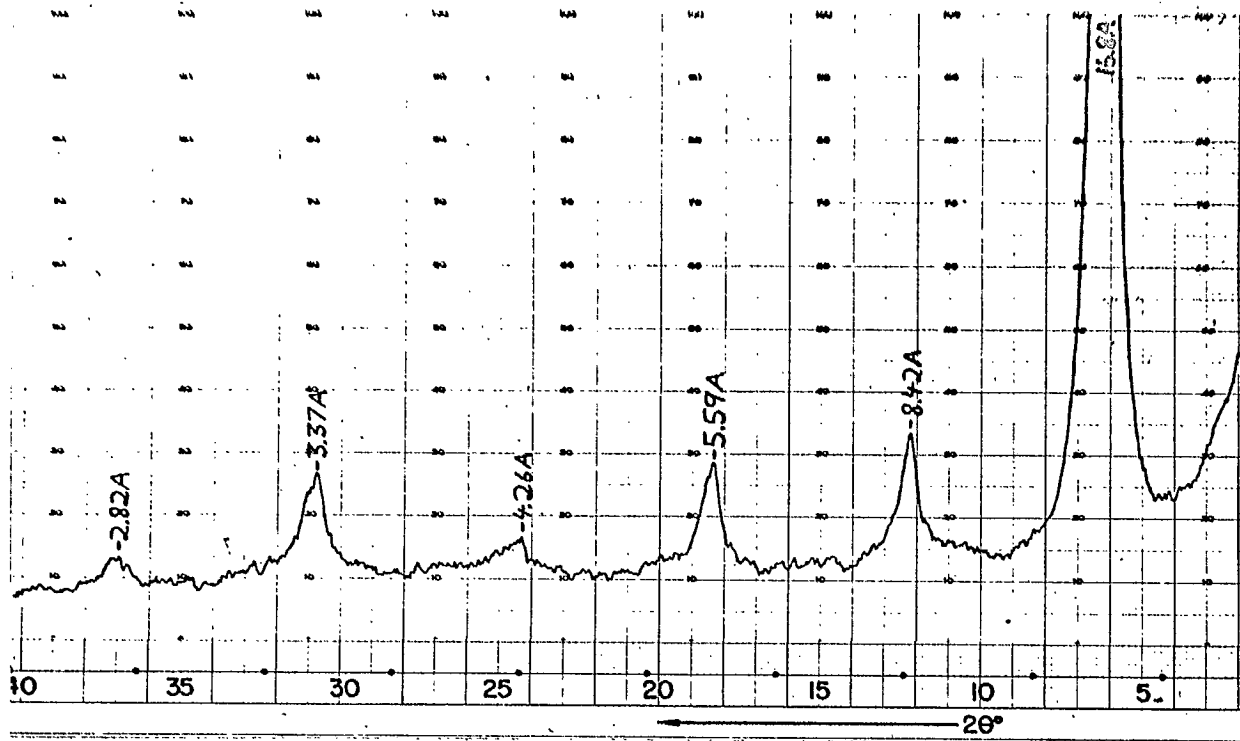


Figure 7. X-ray diffractogram of bentonite B-1, oriented mount, Ca^{++} saturated, glycolated

Co/Fe radiation
Scale Factor = 1
Time Constant = 16 sec
Slits - 1°
Scanning Speed = $1^\circ/\text{min}$
Montmorillonite - 16.8; 8.42; 5.59; 4.26;
3.37; 2.82A

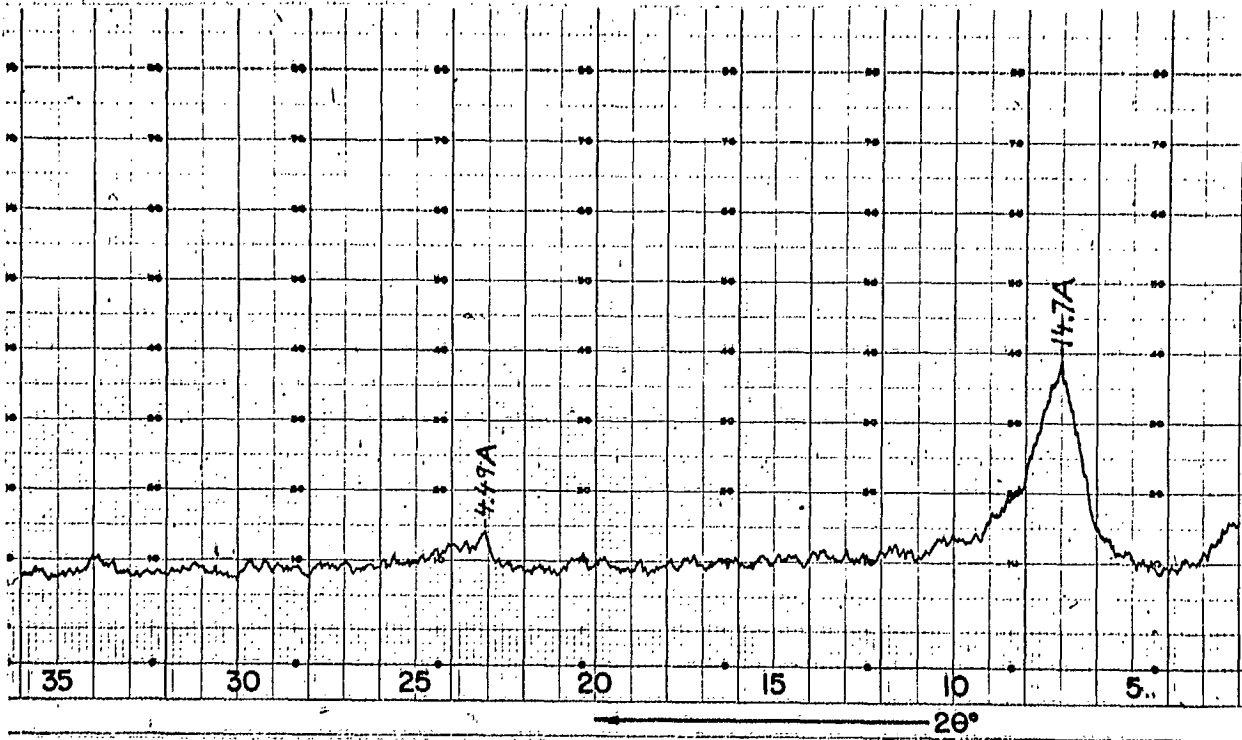


Figure 8. X-ray diffractogram of bentonite B-15, oriented mount, untreated

Co/Fe radiation
Scale Factor = 1
Time Constant = 16 sec
Slits - 1°
Scanning Speed = $1^\circ/\text{min}$
Montmorillonite - $14.7; 4.49\text{\AA}$

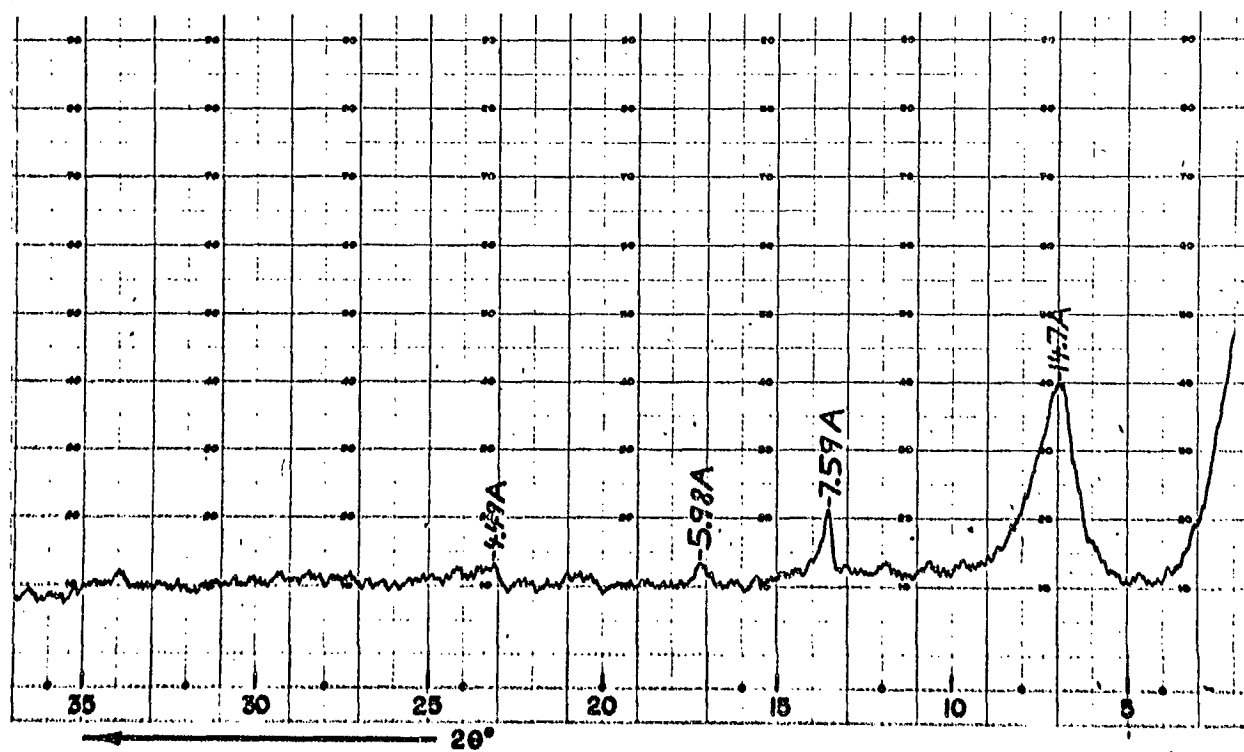


Figure 9. X-ray diffractogram of bentonite B-15, oriented mount, Ca^{++} saturated

Co/Fe radiation

Scale Factor = 1

Time Constant = 16 sec

Slits - $1^\circ/\text{min}$

Montmorillonite - 14.7; 4.49A

Unidentified mineral - 7.59; 5.98A



Figure 10. X-ray diffractogram of bentonite B-12, oriented mount, glycolated

Co/Fe radiation
Scale Factor = 1
Time Constant = 16 sec
Slits - 1°
Scanning Speed = 1°/min
Montmorillonite - 16.7 Å
Hydrous Mica - 10.0; 3.34 Å (in part)
Quartz - 4.26; 3.34 Å (in part)

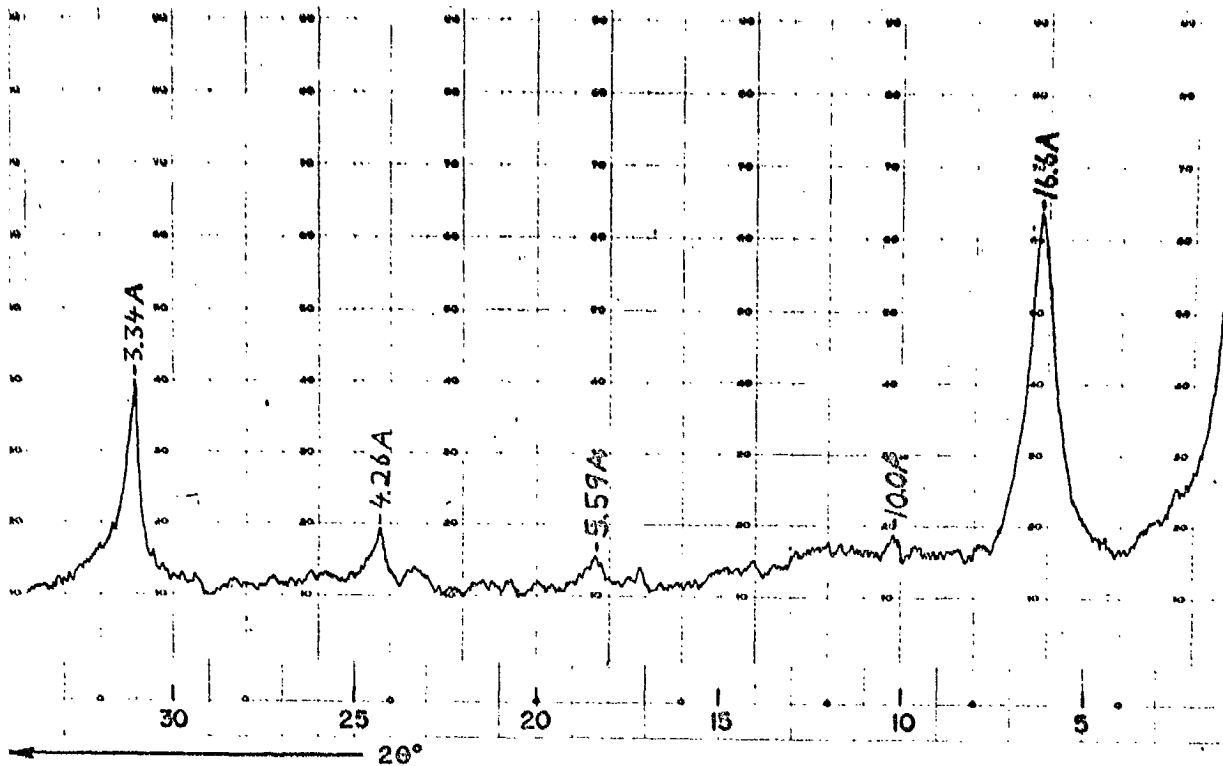


Figure 11. X-ray diffractogram of bentonite B-12, boiled for 2.5 minutes in 0.5N NaOH solution, oriented mount, glycolated.

Co/Fe radiation
Scale Factor = 1
Time Constant = 16 sec
Slits - 1°
Scanning Speed = 1°/min °
Montmorillonite - 16.6; 5.59 Å
Hydrous Mica - 10.0; 3.34 Å (in part)
Quartz - 4.26; 3.34 Å (in part)