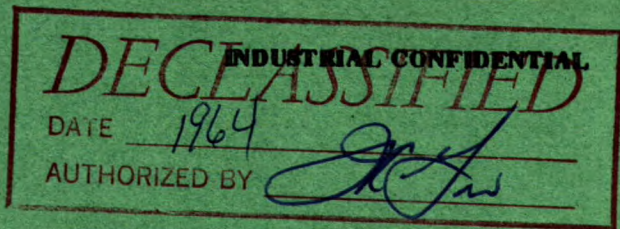


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CANADA

DEPARTMENT OF MINES AND TECHNICAL SURVEYS

OTTAWA

MINES BRANCH INVESTIGATION REPORT IR 64-4

**THE MINERALOGY OF THREE SAMPLES
SUBMITTED BY MEDICINE HAT BRICK
AND TILE COMPANY LIMITED**

by

J. G. BRADY, R. S. DEAN & L. K. ZEMGALS

MINERAL PROCESSING DIVISION

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SUMMARY OF RESULTS

The mineralogical compositions of three clay samples from Manitoba were investigated for Medicine Hat Brick and Tile Company, Limited, Medicine Hat, Alta. The samples were obtained under the supervision of L. O. Lindoe, Director of Research for the Company, from power-auger drill holes.

The major constituents of the samples were shown by X-ray diffraction analysis and differential thermal analysis to be kaolinite and quartz. Although the proportions of these materials varied between samples, in general, they are alike mineralogically.

X-ray diffraction indicated that the samples also contain a mixed-layer clay mineral and minor amounts of one or more of such minerals as hematite, dolomite, anatase, gibbsite, pyrite, potash feldspar and calcite.

It was shown by differential thermal analysis that two of the samples would be difficult to use for production of clay products. One sample contains an excess of oxidizable material, probably pyrite and carbonaceous material, and the other contains an excess of quartz. Each of these materials would probably cause difficulty in the firing process. Dilution of the samples by suitable materials would probably make them satisfactory.

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INTRODUCTION

Three 1 pound samples were submitted by L. O. Lindoe, Medicine Hat Brick and Tile Company, Limited, Medicine Hat, Alta. for investigation by differential thermal analysis (DTA) and X-ray diffraction analysis. The samples were obtained in Manitoba, from auger holes in the N. W. quarter of Section 3, Township 23, Range 15, west of the Principal Meridian.

The work is of a confidential nature and it was agreed that it should remain so until about May 1st, 1967, or until the company has had time to explore the area and decide on definite action. It was stated by the Company that the Mines Branch of the Manitoba Department of Mines and Natural Resources would also withhold the information from the public until May 1st, 1967.

The X-ray diffraction analysis and interpretation was carried out by R. S. Dean, the DTA and interpretation by L. K. Zemgals, and co-ordination of the work and results and conclusions by J. G. Brady.

SAMPLES INVESTIGATED

The following descriptions of the samples were given by Mr. Lindoe in a letter of November 19, 1963;

Sample 38, TH 63-38, 12-32, (Lab No. 1465), "has a PCE of between 19 and 20, fires (to) a good red to at least cone 12 and (shows) no sign of pyrite".

Sample 42, TH 63-42, 29-43, (Lab No. 1466), "has a PCE of between 20 and 23, (and) fires nearly white. A little pyrite (is) evident in the fresh sample and very evident at cone 20".

Sample 42, TH 63-42, 43-53, (Lab No. 1467), "has a PCE of 25, (and) fires nearly white. (There is) no evidence of pyrite in the fresh sample but some at cone 25".

Mr. Lindoe stated that the samples were quite plastic but dried extremely well. No physical properties were determined in the Mineral Processing Division, beyond the verification of the PCE's. These were found to be: No. 1465, Cone 17; No. 1466, Cone 20; No. 1467, Cone 26.

DIFFERENTIAL THERMAL ANALYSIS

Procedure

The samples for DTA were ground to pass through a 100-mesh Tyler laboratory screen. DTA curves were obtained in an atmosphere of air. A curve for No. 1466 was also obtained in an atmosphere of nitrogen to eliminate the carbonaceous material peaks and to bring out the clay mineral peak. In addition, all samples were investigated for approximate quartz content. Usually the small peak caused by the reversible inversion of quartz at 574°C is masked by the very much larger one due to an irreversible clay heat effect. Consequently, the presence of quartz was checked by first heating the sample to approximately 700°C, cooling to 400°C, and then heating again to approximately 650°C. Quantitative determinations of the amounts of kaolinite and quartz were made by measuring the areas under the appropriate peaks and comparing these with curves obtained from standard materials. The appropriate quartz peak occurs at about 574°C and the significant kaolinite peak at about 550 to 620°C.

The curves were recorded on a Leeds and Northrup X₁ - X₂ recorder. A heating rate of 12°C/min. was used.

Results

DTA curves are reproduced in Figure 1. Endothermic reactions peak downward and exothermic reaction peaks point upward. The sample (No. 1466) run in nitrogen was placed in a different sample-holder and furnace than those run in air. The peaks obtained in air are larger, because the sample-holder takes more material than the sample-holder used for the nitrogen run. The peak temperatures and the mineral content of the samples are summarized in Tables 1 and 2.

Discussion of Results

DTA curves obtained in air show in a general way the temperatures and extent of the various endothermic or exothermic reactions which take place when the material is fired in a kiln with an oxidizing atmosphere. The rate of temperature increase of the DTA is much faster (12°C/min.) than that of a kiln and so, normally, the reaction temperatures obtained commercially are slightly lower than the ones shown on the DTA curves.

DTA indicates that all samples contained a kaolin group clay mineral (probably kaolinite). The amount of oxidizable materials varied from none (No. 1465) and small (No. 1467) to extremely large (No. 1466). In sample No. 1466, a small endothermic

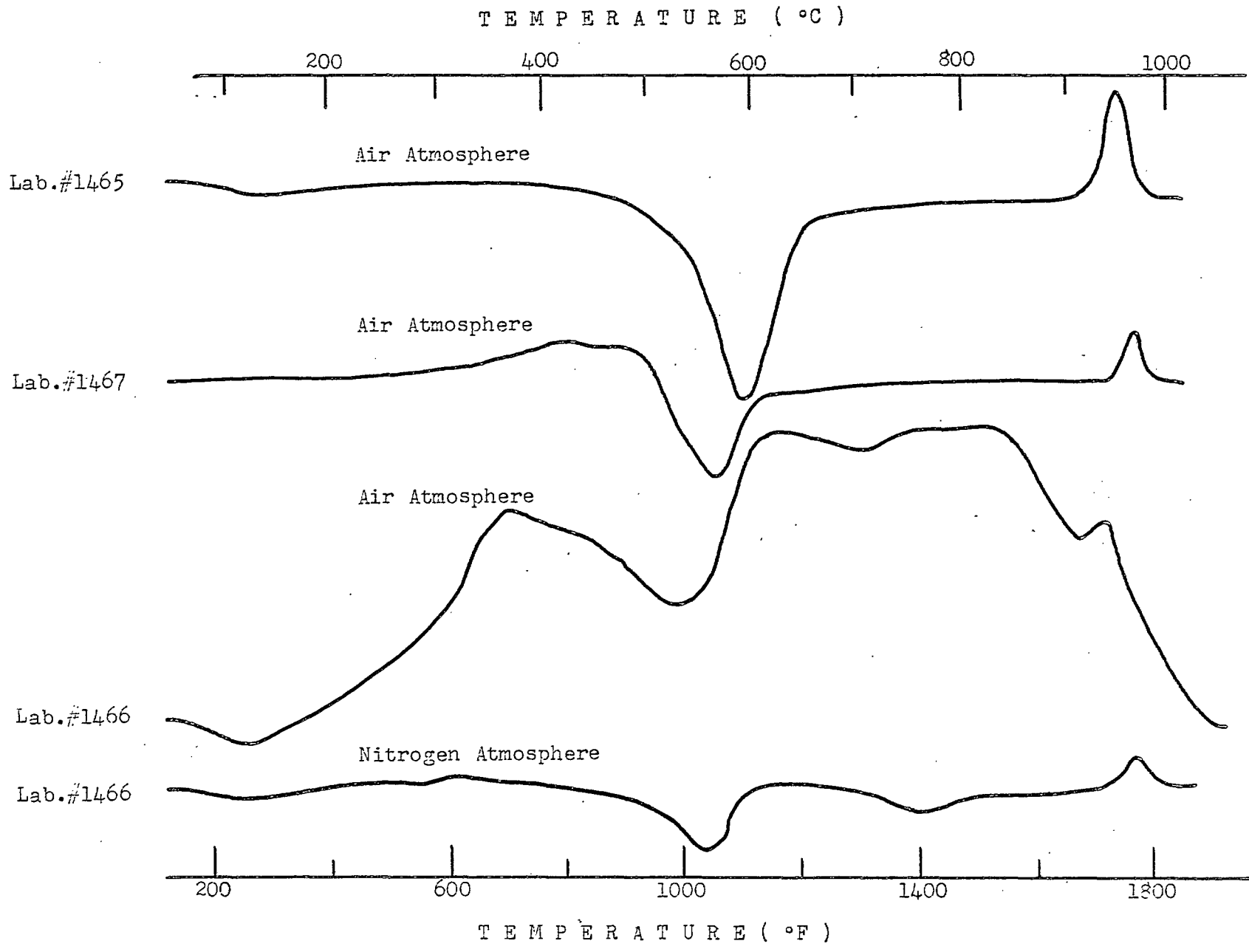


Figure 1. D T A Curves.

TABLE 1

Summary of DTA Results

Sample and Atmosphere	Clay Peaks, °C	Carbonaceous and other Oxidizable Material Peaks, °C	Remarks
No. 1465 Clay 12-32, TH 63-38 Air	115,585,950 - Kaolin clay mineral	—————	No evidence of oxidizable material from the appearance of the DTA curve.
No. 1466 Clay 29-43, TH 63-42 Air	545,945 (see remark)- Kaolin clay mineral	360,620,760,820- Very large amount of oxidizable material, probably high temperature carbonaceous material and pyrite	The oxidation peaks interfere with the clay peaks (545°C and 945°C). The exothermic peak at 820°C suggests the final burn-out of oxidizable material.
No. 1466 Clay 29-43 TH 63-42 Nitrogen	115,560,975 - Kaolin clay mineral 575 - Secondary clay mineral	—————	Small endothermic peak at 290°C suggests some gibbsite and at 765°C small amount of dolomite.
No. 1467 Clay 43-53 TH 63-42 Air	565,960 - Kaolin clay mineral and a suggestion of secondary clay mineral	410,480 - Small amount of oxidizable material, possibly pyrite.	A very sandy clay with small amount of oxidizable material.

TABLE 2

Approximate Kaolin and Quartz Percentage
from DTA Analysis

Sample	Kaolinite, %	Quartz, %
No. 1465 Clay 12-32, TH 63-38	35	31
No. 1466 Clay 29-43, TH 63-42	21	35
No. 1467 Clay 43-53, TH 63-42	20	75

peak suggests gibbsite (290°C), a second clay mineral (575°C) and dolomite (765°C). The shape of the kaolinite peak for No. 1467 suggests also the presence of another clay mineral.

The presence of kaolinite in the samples is indicated by a small endothermic peak due to the loss of absorbed water at approximately 110-150°C, by a broad endothermic reaction at approximately 550-600°C, due to the breakdown of the clay crystal structure and by a final exothermic reaction in the 950-980°C range. The DTA curves suggest that No. 1465 contains the greatest amount of kaolinite and that very little other clay mineral is present. The curves for No. 1466 and No. 1467 indicate the presence of kaolinite as well as some other clay mineral. This is particularly true of No. 1466.

Carbonaceous material and/or pyrite usually produce an intense exothermic reaction in the 300-500°C temperature range. Occasionally a very large quantity of high-temperature carbon burns out up to 800°C and so interferes with the clay reaction at 550-600°C, (No. 1466). Pyrite in clay usually breaks down at approximately 450°C and its final breakdown usually occurs after the carbon has been removed. Difficulty is encountered in determining the relative amounts of pyrite and carbon in a sample by DTA. Sample No. 1466 contains an excessive amount of oxidizable

material which is probably both carbonaceous material and pyrite. These materials would probably introduce a problem in firing (No. 1466) because of the large amount of oxygen required to burn them out. In producing clay products it is likely that any clay similar to No. 1466 should be well diluted by clays containing little oxidizable material such as No. 1465 or No. 1467.

All samples contain quartz, the percentages of which are shown in Table 2. The very small peaks caused by the quartz reaction at 574°C are obscured by the large clay reaction so that they are not apparent in Figure 1. Samples No. 1465 and No. 1466 contain moderate to large quantities of quartz, and No. 1467 contains about 75 per cent of it.

Sample No. 1467 would probably be difficult to extrude and the products might crack with rapid cooling after firing. Dilution of this sample by a clay containing less quartz and more clay material will probably be necessary for the manufacture of clay products.

X-RAY DIFFRACTION ANALYSIS

Procedure

Finely ground portions of each of the three samples (Nos. 1465, 1466 and 1467) were examined by means of the Guinier focusing X-ray powder camera.

Other portions of these samples were dispersed in distilled water and centrifuged briefly at fairly low speeds. The fine-grained material remaining in suspension was recovered by flocculation with acetic acid.

Free iron oxides were removed from the fine-fraction (clay) concentrate of No. 1465 by the dithionite-citrate method of Mehra and Jackson(1) before any further work on this sample was attempted. Upon completion of this treatment, a change in colour of the suspension from red to white occurred. The treated clay was collected by centrifugation and washed with a 2 per cent acetic acid solution.

Oriented clay mineral mounts were prepared by evaporating suspensions of the fine-fraction concentrates to dryness on borosilicate-glass slides. These were scanned with a North American Philips High Angle X-Ray Diffractometer when air-dry, glycol-saturated, and after heating for one-half hour at 580°C.

The remainder of the fine-fraction clay concentrates of all three samples were dried at about 100°C and examined with the Guinier X-ray powder camera. The powders were subsequently

heated for one-half hour at 580°C and then subjected to the differential dissolution (NaOH) treatment of Hashimoto and Jackson(2). After washing, portions of the resultant suspensions were evaporated on borosilicate-glass slides. These oriented clay mounts were heated for one-half hour at 580°C and then scanned with the X-ray diffractometer.

Results and Discussion

The relative abundance of the various mineral constituents of the three samples, as estimated from the overall intensity of their X-ray diffraction patterns, is given in Table 3.

TABLE 3
X-Ray Diffraction Analyses

Mineral	Sample		
	No. 1465	No. 1466	No. 1467
Quartz	B	B	A
Kaolinite	B	B	C
Mixed-Layer Clay	C	C	E
Hematite	D	-	-
Dolomite	G (?)	E	G
Anatase	F	F	G
Gibbsite	-	F	-
Pyrite	-	F	G
Potash Feldspar	G	G	G (?)
Calcite	-	G (?)	-

Estimated abundance of minerals, from "A" (very abundant) to "G" (trace)

The close relationship of the three samples to each other is reflected by the similarity of their principal mineral constituents. Most abundant among the clay minerals were members of the kaolin group. As shown in Fig. 2, oriented mounts of the fine-fraction concentrates yielded intense first and second order basal reflections. The exact positions of these peaks, 7.14 and 3.55\AA respectively, were determined from another scan using a lower recorder sensitivity. The sharpness of the basal reflections, together with the presence of the appropriate general reflections in the powder photographs of the fine-fraction concentrate, indicate that the bulk of this material is kaolinite (3). Although the kaolinite in all samples appeared to be of the fairly well-ordered variety, some variation in the degree of kaolinite ordering was evident. According to the scale of Murray and Lyons(4), No. 1466 and No. 1465 displayed the greatest and least degree of kaolinite ordering respectively.

The mixed-layer clay mineral (or minerals) yielded irregular peaks or bands of fairly low intensity at "d" spacings of about 9.3\AA or greater (Fig. 2). Ethylene glycol saturation appeared to have little effect upon the configuration of these reflections. Heat treatment at 580°C resulted in the formation of a wide band extending from the vicinity of the $9\text{-}10\text{\AA}$ region to some indefinite larger value (Fig. 3).

The failure of the heat treatment to collapse the mixed-layer material to a basal spacing of about $9.4\text{-}10\text{\AA}$ suggests that the mica-like layers (approximately 10\AA thick) are separated in some instance by interlayer material (such as the "brucite layers" of chlorites). The absence of definite peaks in the X-ray diffractograms of the heated samples indicates that the distribution of interlayer material is neither regular nor uniformly random. Probably, the interlayer complexes are either regularly or randomly distributed (or absent) within individual crystallites, the overall effect being the formation of a wide composite band of basal reflections within the low theta angle region.

The NaOH treatment resulted in the dissolution of dehydroxylated kaolinite and interlayer alumina. The distinct basal reflections which were recorded at about 9.8\AA following the subsequent 580°C heat treatment of No. 1467 and No. 1465 (Fig. 4) indicated that the interlayer material within the mixed-layer system was aluminous, that is this non-collapsing phase was an "intergradient" (Al) rather than a normal (Fe-Mg) chlorite. Sample No. 1466, on the other hand, showed incomplete contraction to 9.8\AA after similar treatment, suggesting the presence of some Fe-Mg interlayer complexes.

A comparison of the X-ray powder photographs of the centrifuged samples with the powdered, unfractionated samples yielded some information regarding the particle size distribution of the various minerals. Kaolinite, anatase and gibbsite appeared to be concentrated within the finer fractions, whereas

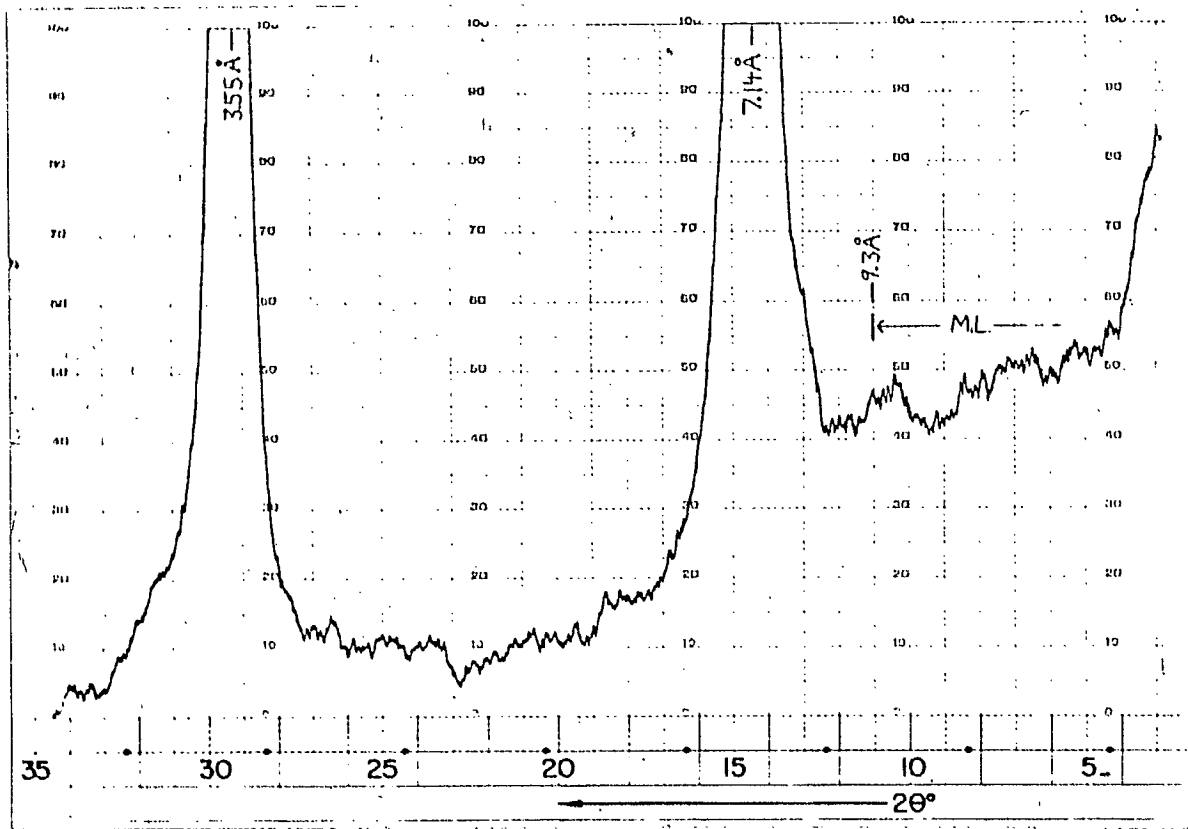


Figure 2. X-Ray Diffractogram of Sample No. 1465,
Oriented Fine-Fraction Concentrate (free
iron oxides removed)

Co/Fe radiation
 Scale Factor = 1
 Time Constant = 16 sec
 Slits - 1°
 Scanning Speed = $1^\circ/\text{min}$
 Kaolinite - 7.14; 3.55Å
 M.L. - Mixed-Layer Clay Mineral(s)

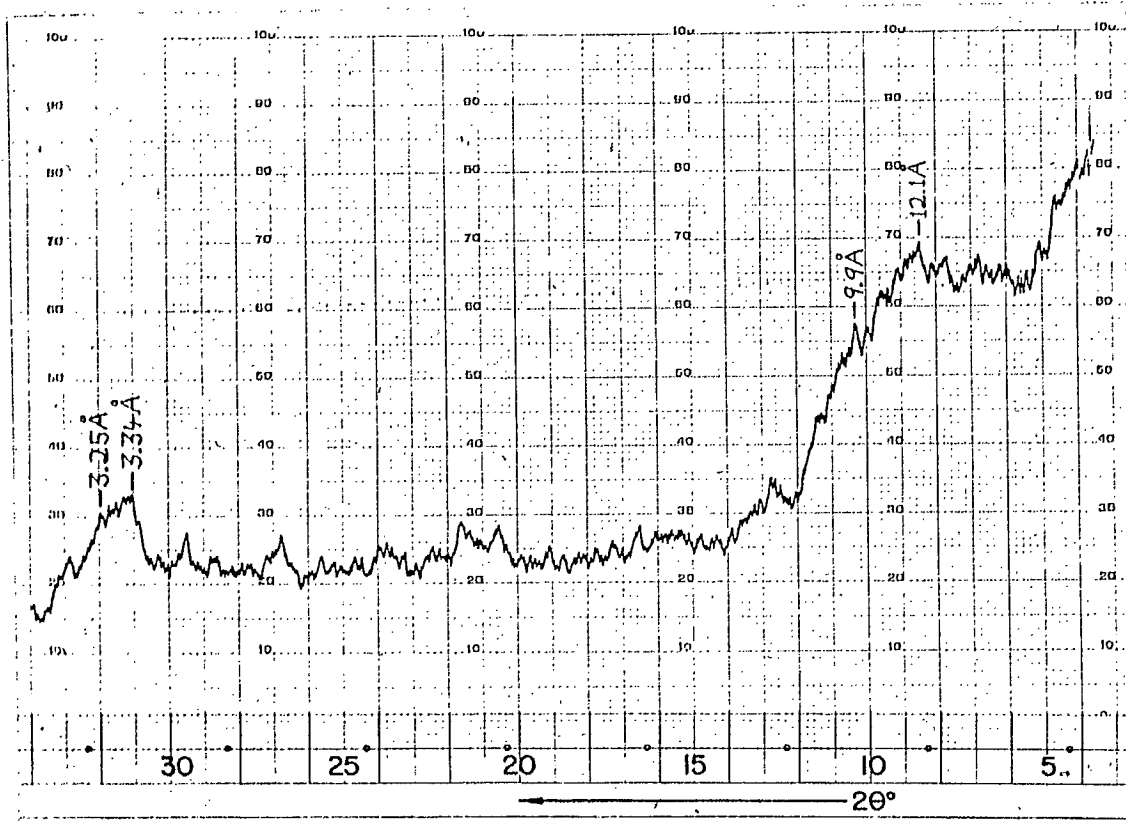


Figure 3. X-Ray Diffractogram of Sample No. 1465,
Oriented Fine-Fraction Concentrate,
Heated for One-Half Hour at 580°C

Co/Fe radiation
 Scale Factor = 1.
 Time Constant = 16 sec
 Slits - 1°
 Scanning Speed = $1^\circ/\text{min}$
 All Reflections - Mixed-Layer
 Clay Mineral(s)

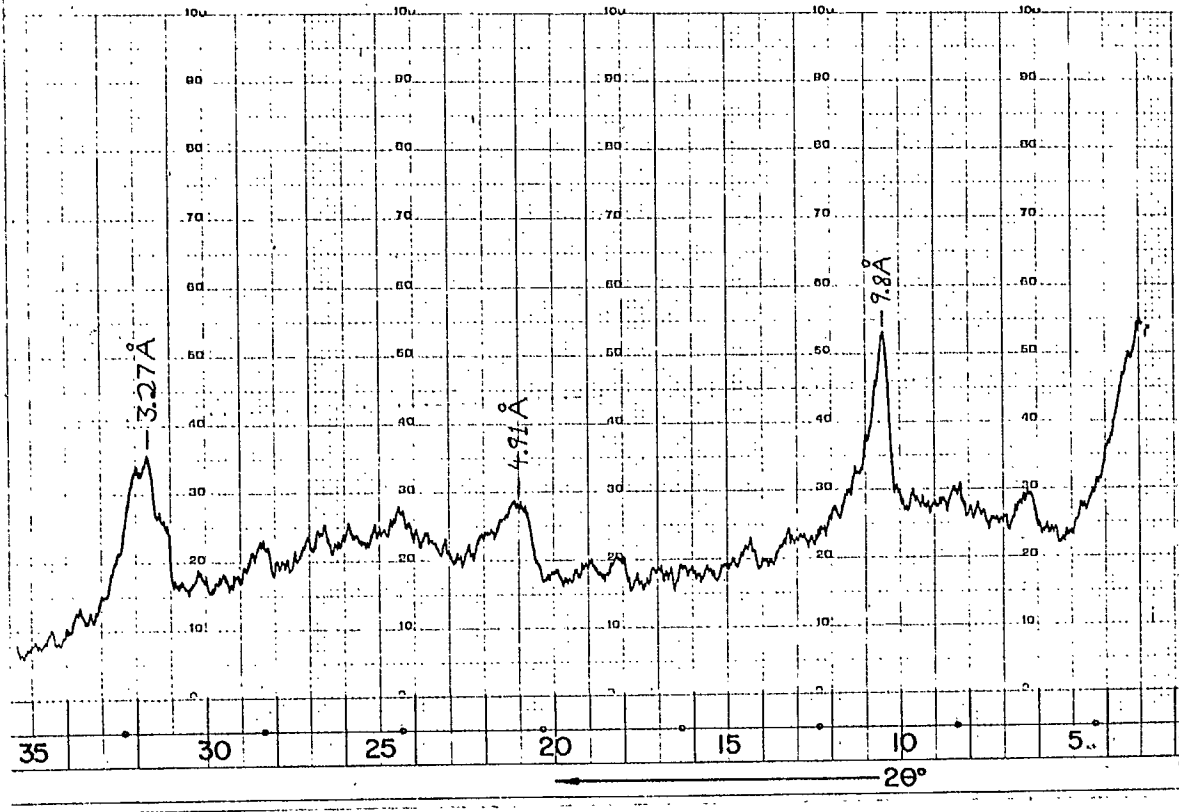


Figure 4. Fine-Fraction Concentrate of Sample No. 1465, Boiled in Excess 0.5N NaOH Solution for 2.5 Minutes after Heating for One-Half Hour at 580°C. Oriented Mount of Washed Residue Heated for One-Half Hour at 580°C

Co/Fe radiation
 Scale Factor = 1
 Time Constant = 16 sec
 Slits - 1°
 Scanning Speed = 1°/min
 All Reflections - collapsed Mixed-Layer Clay Mineral(s)

the opposite was true of quartz, potash feldspar and pyrite. The variation of quartz content with particle size was very pronounced, as only minor and trace amounts of quartz were detected within the fine-fraction concentrates of No. 1467 and the remaining two samples respectively. Although the exact particle size range within the fine-fraction concentrates was not determined, these probably contained few particles coarser than 10 microns (equivalent settling diameter).

CONCLUSIONS

The major constituents of clay samples No. 1465, No. 1466 and No. 1467 are shown by X-ray diffraction and differential thermal analyses to be a kaolin group clay mineral (kaolinite) and quartz. Although the proportions of these materials vary between samples, in general, they are alike mineralogically.

X-ray diffraction analysis indicates that the samples contain a mixed-layer clay mineral. In addition, it indicates they contain minor amounts of one or more of such minerals as hematite, dolomite, anatase, gibbsite, pyrite, potash feldspar and calcite.

DTA indicates that No. 1466 contains an excessive amount of oxidizable substances, probably carbonaceous material and pyrite. The quantity is sufficient to cause difficulty in firing, unless the material is diluted by clays containing little or no oxidizable material. Sample No. 1467 contains about 75 per cent quartz, which is excessive, and it will probably require dilution with a material containing less quartz and more clay minerals.

The X-ray diffraction study indicated that kaolinite, anatase and gibbsite were concentrated in the fine-fraction (probably less than 10 microns diameter) whereas the opposite was true of quartz, potash feldspar and pyrite.

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