MINERALOGY OF SOME INDIAN CLAYS*

By M. Ramakrishna Rao

(*National Metallurgical Laboratory, Jamshedpur, India*)

Received April 3, 1956

(Communicated by Sir C. V. Raman)

Abstract

Mineralogical compositions of five Indian clays have been determined by the petrographic, X-ray, electron-microscopic and differential thermal analysis methods. The relative importance of the methods is discussed and the procedures are described.

Introduction

A study of the mineralogical composition of five samples of Indian clays, used in the ceramic and refractory industries, has been made. The importance of such a study lies in the fact that to a large extent the working properties of the clays depend on their mineralogical composition, degree of crystallinity and grain size.

To determine the mineralogical composition of the clays, techniques complementary to one another, are generally required. As the grain size of most clay minerals is of the order of a few microns or less, the petrographic microscope does not have sufficient resolving power to distinguish the individual crystals. However, if the crystal size is coarse enough, as is the case with some dickites and kaolinites, the petrographic microscope can be used for their identification. On the other hand, it is possible to distinguish various types of clay minerals by X-ray diffraction procedures. The chief limitation of the X-ray method is that it is often difficult or impossible to detect impurities present in amounts less than 5% of the total material. It is here that the petrographic microscope has an advantage over the X-ray diffraction method.

The electron microscope has been of great help in determining the morphology, degree of crystallinity and grain size, which aid in distinguishing the clay minerals. Differential thermal analysis has been of great value for the study of clay minerals, but here also, it is not always possible to detect small percentages of impurities present in the clays. In the present paper, the results are given of a correlated study using the above techniques.

---

* This investigation was made by the author as part of his work on a Colombo Plan Fellowship at the Physical and Crystal Chemistry Section, Mineral Dressing and Process Metallurgy Division, Mines Branch, Department of Mines and Technical Surveys, Ottawa, Canada.

EQUIPMENT AND PROCEDURES

Petrographic Study

The clays were examined under a petrographic microscope by the powder method, using Shillaber's oils of known refractive indices. The samples were examined as received and also after washing away the finer and lighter fractions.

Electron Microscopic Study

An R.C.A. electron microscope of the electromagnetic type was used in this study. The fine clay suspensions were mounted on "formvar" films by standard procedures. The strength of the "formvar" solution used was 0·1% in dichloro-ethane. The films were shadowed by chromium evaporation *in vacuo*. The samples were examined at an initial magnification of 10,000.

Differential Thermal Analysis

Differential thermal analysis equipment has been described by many workers with some variation in details.[1] A brief description of the experimental arrangement used in the present work is detailed below. Sketches of the palladium block specimen holder are shown in Fig. 1.

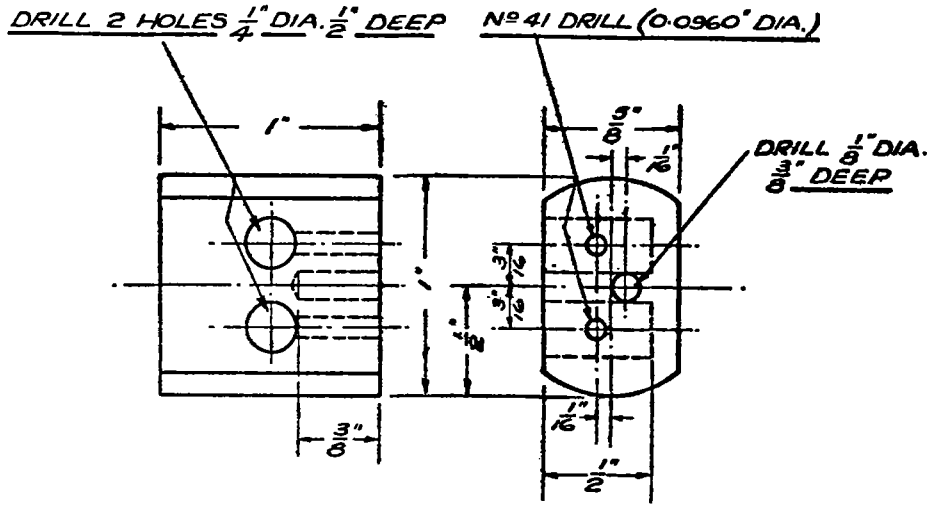

FIG. 1. Palladium Specimen Holder for D.T.A.

The sample under study is placed in a cavity in the specimen holder and an inert reference material, calcined alumina, is placed in another cavity. Two connected thermocouples are placed one in each cavity and the leads of this differential couple are connected to a preamplifier and then to a Leeds

and Northrup Recorder. Another thermocouple is placed in a separate cavity close to the specimens. The leads of this couple are connected to a Leeds and Northrup Program Controller. The horizontal tube furnace carrying the specimen holder is now heated at the rate of 12° C. per minute. The rate of temperature rise is controlled by the Program Controller. The inert material in the palladium block is stable throughout the heating range, whereas the clay sample undergoes a succession of endothermic or exothermic reactions during heating. This results in the setting up of differential e.m.f.s which are recorded on the Leeds and Northrup Recorder, appearing as peaks on either side of the centre line of a strip chart. However, as soon as each reaction is over the temperature of the specimen equalises with that of the inert material, and the differential thermocouple record returns to the centre of the strip chart.

X-Ray Diffraction

X-ray examination was carried out by the powder diffraction techniques using North American Philips Co. high angle goniometer. The technique is described in detail by Klug and Alexander.[2] The salient features are as follows:

An X-ray beam impinges on the smooth surface of a finely pulverised specimen mounted in a rotating sample holder. The diffracted X-ray beam is picked up by a Geiger-Muller counter, scanning at a rate of $2\theta = 1°$ per minute, amplified and recorded on a moving chart from which θ values can be obtained and hence the corresponding d-spacings.

Results

X-Ray Diffraction

The results of X-ray examination of these five clays are given in Table I. Filtered Cu K radiation was used throughout. The d-spacings in Angstrom units are given for each clay. By comparison of the values with those in the A.S.T.M. Card Index of Powder Diffraction Patterns and also the available lieterature,[3] each set of the lines was attributed to a specific mineral constituent. The intensities of the kaolinite and mica lines showed some variations from those given by some of the previous workers. However, this could be expected, as the clays and micas do tend to exhibit preferred orientation. The intensities are estimated approximately from the magnitude of the peaks. Quartz, even when present in small amounts, gives much stronger peaks than kaolinite as, for instance, in the Rajhara and Jabbalpur clays. In such cases the strongest peak of the kaolinite is taken as 100, with which other peaks of lower intensities are compared, while the quartz lines of higher intensity are denoted as " very strong". The X-ray diffraction patterns of these clays are

TABLE I

X-Ray Diffraction Data on Indian Clays

Travancore-China Clay[1]			Chaibasa Clay[2]			Orissa Clay[3]			Jubbalpur Clay[4]			Rajhara Clay[5]		
I	*d*	Mineral	I	*d*	Mineral	I	*d*	Mineral	I	*d*	Mineral	I	*d*	Mineral
100	7·155	Kaolinite	100	7·166	Kaolinite	100	7·144	Kaolinite	100	7·155	Kaolinite	100	7·166	Kaolinite
15	4·446	do	30	5·001	Muscovite	10	4·47	Muscovite	5	4·984	Muscovite	25	4·443	do
20	4·354	do	35	4·471	do	15	4·255	Quartz	12	4·471	do	100	4·266	Quartz
17	4·172	do	10	4·358	Kaolinite	40 5	3·576 3·945	Kaolinite Kaolinite Muscovite	25	4·258	Quartz	20	4·163	Kaolinite
14	4·130	do	5	4·256	Quartz	5	3·844	Kaolinite	15	4·163	Kaolinite	8	3·843	do
8	3·837	do	5	4·044	Muscovite	5	3·735	do	10	3·863	do	8	3·704	do
75	3·576	do	8	3·883	do	8	2·562	Kaolinite Muscovite	5	3·735	do	55	3·576	do
5	3·346	Quartz	10	3·735	do	10	2·491	Kaolinite	70	3·584	do	V.S.	3·343	Quartz
3	3·099	Kaolinite	25	3·670	Serpentine ?	10	2·461	Quartz	8	3·492	do	8	3·027	Talc
14	2·561	do	50	3·578	Kaolinite	10	2·377	Kaolinite	V.S.	3·445	Quartz	15	2·560	Kaolinite
8	2·527	do	60	3·343	Quartz Muscovite	10	2·279	Kaolinite Quartz	5	3·027	Kaolinite Talc	5	2·526	do
12	2·489	do	40	3·202	Muscovite	5	2·238	Quartz	5	2·985	Muscovite	8	2·495	Kaolinite Talc
8	2·379	do	5	3·064	Kaolinite	8	2·125	Quartz Kaolinite	10	2·562	Kaolinite Muscovite	25	2·458	Quartz
20	2·339	do	20	2·995	Kaolinite Muscovite	8	1·989	Muscovite Kaolinite	8	2·492	Kaolinite	8	2·376	Kaolinite

12	2·287	do	10	2·862	Muscovite	5	1·974	Quartz	10	2·458	Quartz	15	2·336	do
3	2·180	do	5	2·791	do	18	1·819	do	8	2·381	Kaolinite	20	2·281	Kaolinite Quartz
5	1·992	do	5	2·740	Kaolinite	10	1·665	Kaolinite	12	2·335	do	5	2·238	Quartz
5	1·983	do	15	2·564	Kaolinite Muscovite Serpentine	15	1·642	Muscovite	12	2·279	Quartz Kaolinite	15	2·132	do
3	1·938	do	10	2·495	Kaolinite	5	1·451	Quartz	5	2·238	Quartz	15	1·981	do
3	1·834	do	5	2·390	do	5	1·381	do	8	2·129	Quartz Muscovite	50	1·819	do
3	1·786	do	5	2·340	do	8	1·375	do	10	1·972	Quartz	15	1·674	do
6	1·659	do	5	2·296	do	8	1·371	do	20	1·819	do	12	1·661	Quartz Kaolinite
3	1·616	do	5	2·246	do	5	1·337	Muscovite Sericite ?	10	1·672	do	25	1·542	Quartz
2	1·541	do	5	2·204	do	5	1·287	Muscovite	10	1·667	Kaolinite	8	1·487	Kaolinite
12	1·489	do	5	2·127	do	5	1·255	Quartz	10	1·542	Quartz	5	1·453	Quartz
2	1·456	do	15	1·993	Muscovite				8	1·492	Kaolinite	12	1·382	do
2	1·371	do	5	1·658	Kaolinite				8	1·382	Quartz	12	1·377	Quartz Talc
2	1·307	do	5	1·503	Muscovite				10	1·377	Quartz Talc Muscovite	15	1·373	Quartz
			5	1·351	do				8	1·371	Quartz Kaolinite	5	1·258	do
									5	1·255	Quartz	5	1·183	do

1. Supplied by Ceramic Expert, Kundra.
2. Supplied by Baidyanath Sarda, Chaibasa.
3. Supplied by Orissa Industries Ltd.
4. Supplied by Perfect Potteries Ltd.
5. Supplied by Reliance Firebrick and Pottery Co., Ltd.

reproduced in Fig. 3. These patterns were recorded for reproduction purposes with the recorder chart moving at the rate of 9″ per hour. These records show a slightly more irregular background than the originals, from which the *d*-values were calculated, which were recorded at 36″ per hour.

The differential thermal curves of these clays are given in Fig. 2. All these clays show broad endothermic peaks between 586–610° C. and a comparatively sharp exothermic peak between 975 and 990° C., characteristic of kaolinite. The endothermic peak is thought to be due to the loss of combined water and the exothermic peak due to the crystallisation of alpha alumina or mullite, or both.[4] A small exothermic peak at 450° C. in the Rajhara clay appears to be due to the oxidation of some organic matter. During

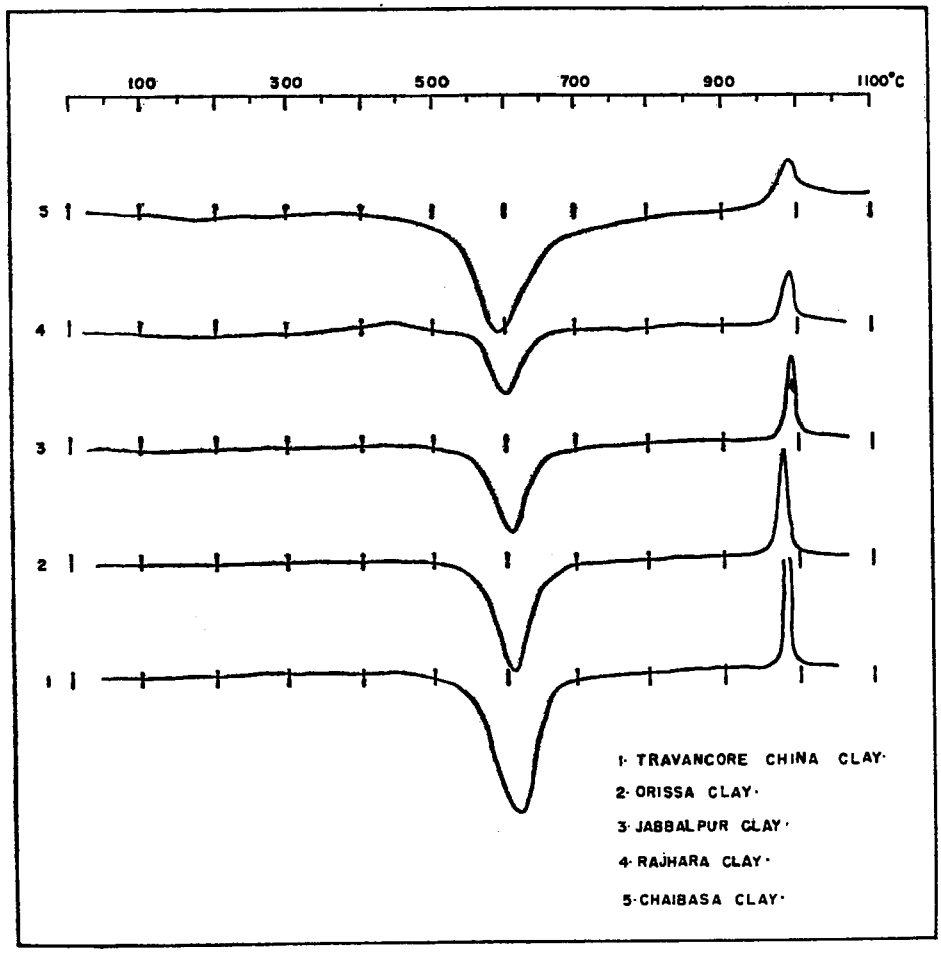

FIG. 2. Differential Thermal Curves.

cooling all the clays showed a small exothermic peak at 573° C. which is attributed to the β to α inversion of quartz.

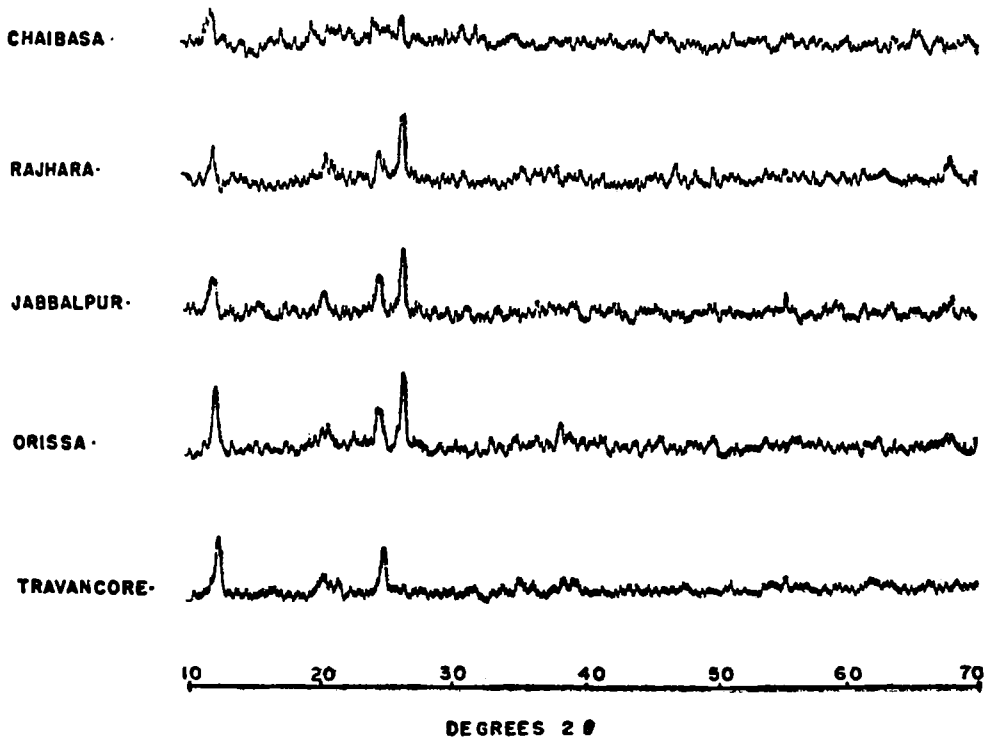

FIG. 3. X-Ray Diffraction Patterns of Indian Clays.

The electron micrographs of these clays are shown in Figs. 4–8. The Travancore-China clay is extremely well crystallised, and shows equant or elongated crystals of six-sided cross-section. The Jabbalpur clay also shows many such well-formed crystals besides the coarsely formed irregular plates. The Orissa clay shows a few subhedral crystals with the irregularly formed plates predominating. The Rajhara clay is mostly composed of irregularly formed coarse plates with some smaller subhedral to anhedral crystals. The shape of the crystals in all these clays is suggestive of kaolinite with a possibility of the coarser plates being dickite. A recent publication[5] shows that kaolinite could occur in tubular forms. However, such forms were not seen in the present study. The Chaibasa clay is very coarsely crystalline, showing large irregular plates. Some of these could possibly be mica.

Under the petrographic microscope the clay mineral, in most cases, appears as aggregates of minute plates and needles, with an average refractive index of 1·562, and with moderate to weak birefringence. In the Chaibasa

clay, some of these small plates, under high magnification, appear to be vermicular. The impurities present in these clays are as follows:

Travancore-China clay	A small amount of quartz with traces of rutile, zircon, apatite, hydrated iron oxide and muscovite.
Chaibasa clay	Appreciable amounts of muscovite and kyanite, small amounts of serpentine and quartz, and a trace of hæmatite.
Orissa clay	Small amounts of quartz and muscovite, with traces of rutile, limonite, apatite, dolomite, zircon, sericite and orthoclase.
Jabbalpur clay	Small amounts of quartz and sericite (muscovite) and talc, with traces of rutile, apatite, calcite and gibbsite.
Rajhara clay	A considerable amount of quartz with a small amount of talc, traces of apatite, calcite, and hydrated iron oxides.

SUMMARY

The principal constituent in all these clays is kaolinite. It is fine-grained and very well crystallised in the Travancore-China clay. In Jabbalpur, Orissa and Rajhara clays, the kaolinite occurs mostly as coarse irregular plates with some fine euhedral to subhedral crystals. The Chaibasa clay shows the coarsest plates, some of which seem to be muscovite. Amongst the impurities, quartz occurs in all these clays in varying amounts, the Rajhara clay containing the largest amount. Muscovite occurs in a significant amount in the Chaibasa clay, and in small amounts in Orissa, Jabbalpur and Travancore-China clays. Kyanite occurs in an appreciable amount in Chaibasa clay, along with a small amount of serpentine. Small amounts of talc occur in the Rajhara and Jabbalpur clays. The Rajhara clay contains some organic matter. Other impurities occurring in very small amounts or traces are rutile, hæmatite, apatite, zircon, orthoclase, calcite, dolomite, gibbsite and hydrated iron oxides.

ACKNOWLEDGEMENTS

I take this opportunity to thank Dr. F. W. Boswell for his valuable help in the electron microscopic study. My thanks are due to Dr. A. T. Prince and Dr. N. F. H. Bright, for helpful suggestions during the course of the investigation and also during the preparation of this publication, and to Mr. R. H. Lake, for his help in conducting the differential thermal analyses.

REFERENCES

1. Grim, R. E. .. *Clay Mineralogy*, McGraw-Hill Book Co, Inc., New York, 1953.
2. Klug, H. P. and Alexander, L. E. *X-Ray Diffraction Procedures*, John Wiley & Sons, Inc., New York, 1954.
3. Kerr, P. F., Hamilton, P. K. and Pill, R. J. *et al.* *Analytical Data on Reference Clay Minerals*, American Petroleum Institute, Project 49, Preliminary Report No. 7, 1950.
4. Grim, R. E. .. *Clay Mineralogy*, McGraw-Hill Book Co., Inc., New York, 1953.
5. Stourdze, U. Y., Nicot, B. N. F. and Goulart de Andrade, E. "Tubular Morphology of Some Brazilian Kaolinites," *Am. Mineral.*, 1956, **41**, 67–75.

FIG. 4. Travancore China Clay, × 20,000

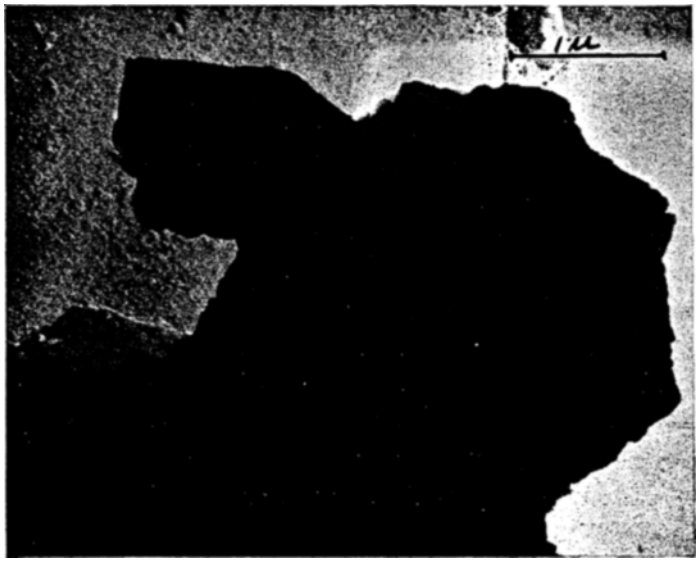

FIG. 5. Chaibasa Clay, × 20,000

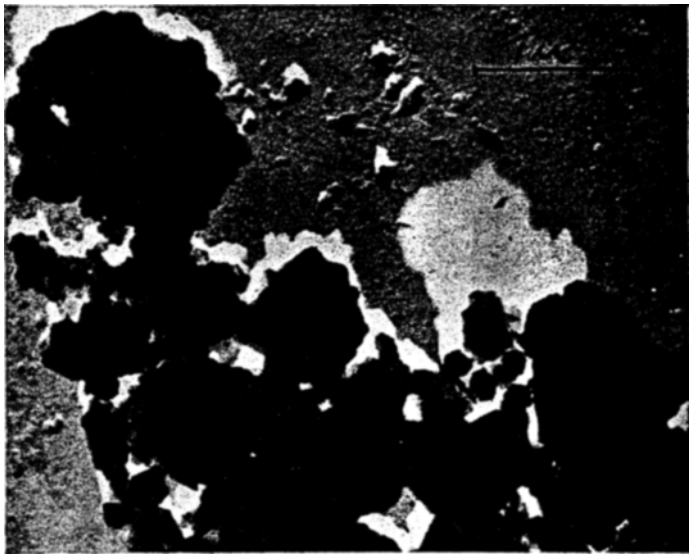

FIG. 6. Orissa Clay, × 20,000

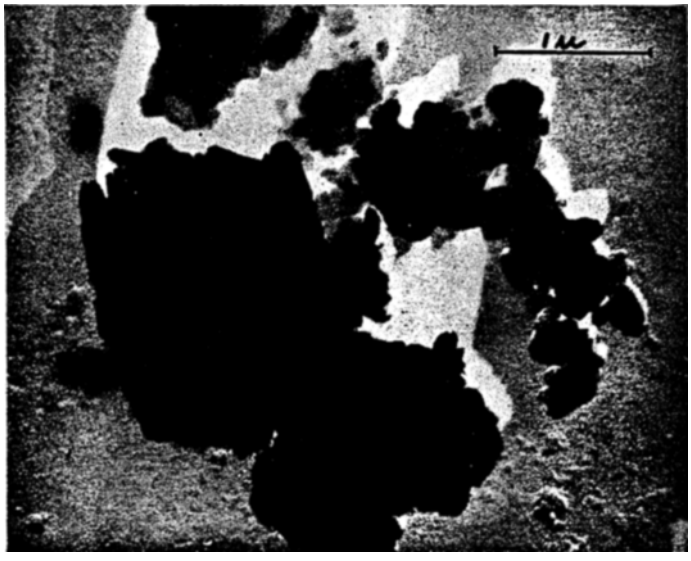

FIG. 7. Jabbalpur Clay. × 20,000

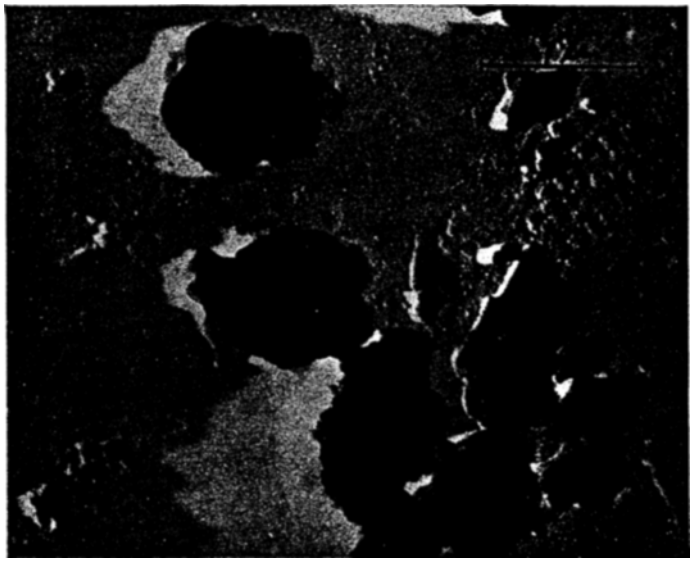

FIG. 8. Rajhara Clay. × 20,000