

Characterisation of Bidor Kaolinite and Illite

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ABSTRAK

Dua jenis mineral lempung dari kawasan Bidor di Perak telah dikaji. Daripada kaji pembelajaran sinar-X, mineral-mineral itu dikenalpasti sebagai kaolinit tak teratur dan polimorf illit 2 M. Morfologi, sifat permukaan, struktur liang dan sifat penyerapan inframerah mineral-mineral itu diperiksa. Dasar-dasar untuk pencaman mineral-mineral itu dibincangkan.

ABSTRACT

Two types of commercial clay minerals from the Bidor region of Perak were studied. From the X-ray diffraction study, these clays were identified as disordered kaolinite and 2 M polymorph of illite. The morphologies, the surface properties, the pore structures and the infrared absorption properties were examined. The basis for the identification of these clays is discussed.

INTRODUCTION

Clay is formed by the disintegration and chemical decomposition of rocks. The type of clay that is deposited in a particular locality generally depends on the geochemical environment. Reasonably pure kaolinite and illite minerals are mined in the Bidor-Tapah region of Perak. Although commercial exploitation of these minerals has been carried on for a number of years, there seem to be a lack of proper characterization of these minerals. The detailed structure and characteristics of these minerals are not known. This paper attempts to fill the gaps in the knowledge of these materials so that non-traditional uses may be found for them.

The kandite group of minerals consists of hydrated aluminosilicate with general composition of $\text{Al}_2\text{O}_3 : \text{SiO}_2 : \text{H}_2\text{O}$ in the ratio of 1 : 2 : 2. They belong structurally to the non-expandable 1 : 1 layer silicate family. Some of the members

classified under this group are kaolinite, dickite, nacrite, disordered kaolinite and halloysite.

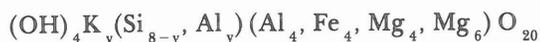
Kaolinite has low isomorphous substitutions, and the water generally exists as hydroxyl groups. It consists of sheets of SiO_2 tetrahedras bonded to sheets of Al_2O_3 octahedras in such a manner that they are stacked one above another in the c-axis. The theoretical composition of kaolinite in terms of oxides are as follows: SiO_2 , 46.54; Al_2O_3 , 39.50%; H_2O , 13.96%.

Disordered kaolinite has essentially a similar chemical composition to kaolinite. They are of lower crystallinity, principally resulting from the random layer displacement parallel to the b-axis. In the X-ray diffraction pattern, some of the reflections of the kaolinite are not observed. A whole series of kaolinite, ranging from the well crystalline to the totally disordered variety may exist in nature. Some isomorphous replacements may have occurred in the octahedral layer. The

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α -angle may be altered and the structure may become pseudo-monoclinic (Grim, 1968).

Illite has been used as a general term to describe the mica-like minerals with a 10Å interlayer spacing and a non-expanding lattice. The chemical composition is similar to that of muscovite. The general formula as given by Grim (1968) is:



where y varies from 1 to 1.5. The formula suggests the presence of both the trioctahedral and the dioctahedral types of structure. Illite usually consists of a 1 M_d (monoclinic disordered) muscovite structure. The 2 M muscovite structure has also been found in some samples. In general, most illite are of mixed layer structures. The basic structural unit of muscovite is two layers of tetrahedral silica sheets separated by a layer of octahedral alumina sheets.

Apart from chemical analysis, x-ray diffraction study is the most important method for the determination of the identity of the clays. The morphologies of a clay is determined by the type and the crystalline state of the minerals. This can be revealed by the electron micrograph of the suitably prepared clays. The type of clay is also characterised by the thermal behaviour, the cation exchange capacity, the surface area, the pore structure and other physical properties. However, these properties do vary from sample to sample of the same clay. Some of these properties are studied and reported for the local clays in this paper.

MATERIALS AND METHODS

Sample Materials

Kaolinite and illite for the study were given by two private companies within Malaysia.

Clay fraction of less than 2 micron was prepared as follows: To two liters of a 5.0% clay

suspension was added 10 ml of a 10% sodium hexametaphosphate solution and 1 ml of 1 N NaOH solution. After mixing, the mixture was poured into a 2 L measuring cylinder for settling. Stoke's law was employed to calculate the rate of sedimentation. The upper 10 cm portion of the clay suspension was carefully decanted after 8 hours. The fine clay portion was collected through centrifugation and dried at low temperature.

Ammonium saturated clay for the cation exchange capacity determination was prepared as follows: The fine clay fraction was stirred continuously with 0.5 M ammonium acetate solution for 4 hours, after which the supernatant solution was collected and centrifuged. Fresh ammonium acetate solution was then used and the stirring repeated twice more with the final stirring lasting 7 hours. The NH_4^+ saturated clay was then washed thoroughly with distilled water until no ammonium ion was detectable in the washing. The clay was then dried for 12 hours before being analysed.

Methods

Chemical analysis of the clays was carried out following the procedures described by Bennet and Reed (1971). The $\text{SiO}_2 : \text{Al}_2\text{O}_3$ ratio was checked by x-ray fluorescence using a Philip type PW1410/10 machine. The cation exchange capacity determination was performed using ammonium acetate by the Nesslerisation method (Standard Methods, 1965).

The X-ray diffraction studies was performed with a Philips Model PW1080/00 diffractometer using $\text{Cu K}\alpha$ radiation. Transmission electron micrographs were obtained with a Philips EM201C electron microscope. Adsorption of nitrogen was carried out with a conventional glass volumetric apparatus with a vacuum better than 10^{-5} Torr at liquid nitrogen temperature. All samples were evacuated for at least 10 hours at high vacuum before adsorption was conducted.

RESULT AND DISCUSSION

X-ray Diffraction Pattern

Kaolinite

The data for the x-ray diffraction pattern is given in Table 1. The calculated angles and the d-spacings for the sample are obtained on a model triclinic structure with the following unit

cell dimensions: $a = 5.14 \text{ \AA}$, $b = 8.93 \text{ \AA}$, $c = 7.39 \text{ \AA}$, $\alpha = 91.8^\circ$, $\beta = 104.5^\circ$ and $\gamma = 90^\circ$. The diffractogram is shown in *Fig 1a*. It can be seen that all the major kaolinite reflections can be accounted for from the diffractogram. The appearance of the (060) reflection of the sample at $d = 1.489 \text{ \AA}$ indicates that the sample is a dioctahedral mineral. This reflection provides a direct measurement of the b-parameter of the unit cell.

TABLE 1
The observed and calculated 2 theta angles and the d-spacing of the kaolinite sample

Angle (obs.)	Angle (cal.)	d(obs.)	d(cal.)	hkl	Intensity
8.90*	—	10.01	—	—	m
12.39	12.37	7.14	7.158	001	ws
14.01*	—	6.26	—	—	m
16.87*	—	5.23	—	—	m
17.83	17.86	4.975	4.966	100	m
19.91	19.87	4.459	4.468	020	m
20.43	20.40	4.347	4.352	110	w
20.90*	—	4.250	—	—	w
21.27	21.25	4.177	4.181	111	w
24.88	24.88	3.576	3.579	002	vs
26.69	26.73	3.340	3.334	120	S
27.93	27.92	3.194	3.195	121	w
29.97*	—	2.981	—	—	w
35.00	35.10	2.563	2.556	130	m
35.46	35.43	2.531	2.533	131	w
36.03	36.09	2.494	2.494	112	m
37.75	37.73	2.383	2.384	003	m
38.47	38.58	2.333	2.340	131	m
39.30	39.32	2.292	2.291	013	w
45.53	45.52	1.992	1.992	203	m
51.01	51.08	1.788	1.787	004	w
55.23	55.23	1.666	1.663	204	w
60.00	60.02	1.542	1.541	313	w
62.36	62.34	1.489	1.489	060	w

*non-kaolinite reflection

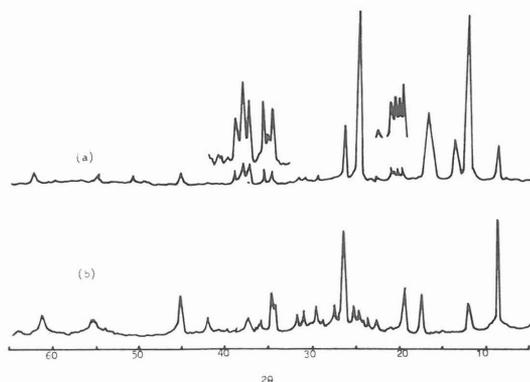


Fig. 1. X-ray diffractograms for a) kaolinite, b) illite.

Hinckley (1963) used the peaks between the two θ angles of 19° and 22° to calculate the crystallinity of kaolinite. Well crystallised kaolinite has high $1\bar{1}0$ and $11\bar{1}$ reflections which yield a high crystallinity index. The peaks in this range for the sample show poorer resolutions. This, together with the broadening of the peaks of the other non-basal reflections suggest that the sample is disordered in nature. The direction of the peak broadening resembles the data published by Robertson *et al.* (1954) for disordered kaolinite, suggesting that a seminar b-axis displacement occurred with the sample studied. Furthermore, a comparison of the kaolinite mineral with the data of Brindley (1961) indicates the sample has a crystallinity in between the well crystallised and the completely disordered kaolinite.

The diffractogram of the kaolinite sample studied showed a number of peaks due to the presence of other minerals. The peak appearing at 10.01 \AA is assigned to the (002) reflection of a mica-type mineral. This assignment is supported by the other 2 M muscovite reflections: (004) at 4.98 \AA , (110) and (111) at 4.46 \AA , (024) and (006) at 3.33 \AA , (200) at 2.56 \AA and (001) at 1.99 \AA . Many of these peaks overlap with the kaolinite reflections. The (020) reflection of kaolinite at 4.46 \AA should be lower than the ($1\bar{1}0$) peak at 4.35 \AA . The relative height of this peak is a likely result of the overlapping with the (110 and 111)

reflections of the mica-type mineral. The overlapping of reflections in this region also resulted in the high background noise observed. Consequently, the crystallinity method of Hinckley (1963) cannot be applied. This mica-type mineral is similar to the illite mineral described later. The ratio of the peak heights of the (001) reflection of the kaolinite to the (002) reflection of the mica-type mineral is 10 : 1.

The peak at 4.26 \AA is assigned to the (110) reflection of quartz which is its second most intense reflection. The most intense reflection of quartz, the (101) reflection, appears at 3.34 \AA . This peak overlaps with the ($1\bar{2}0$) reflection of kaolinite. The peak at 1.817 \AA is assigned to the (112) reflection of quartz.

Two broad peaks at 6.26 \AA and 5.23 \AA were not accounted for. These are non-clay reflections. The peak at 6.26 \AA may be associated with the mineral lepidocrocite (Rooksby, H.P., 1961).

Illite

The x-ray diffractogram for the illite sample is shown in Fig. 1b. The assignment of the reflections is shown in Table 2. The assignment was based on the data of Bradley and Grim (1961). The characteristic mica basal reflections (001) are readily identified from the diffractogram. These include the peaks at 10.01 \AA (002), 4.95 \AA (004) and 3.326 \AA (006). Other major reflections are also clearly seen. The appearance of the (060) reflection at $d = 1.506 \text{ \AA}$ shows that the mineral is dioctahedral. This is supported by the strong (004) reflections at $d = 4.95 \text{ \AA}$.

Bradley and Grim (1961) showed that for synthetic muscovites, the 2 M polymorph gives seven distinct reflections besides the basal (006) reflection at 3.33 \AA between the θ angles from 20° to 35° . Whereas the 1 M polymorph gives only two distinct reflections besides the basal (003) reflection at 3.33 \AA . A comparison of the diffractograms of the Bidor sample with these diffractograms suggests that the sample is of 2 M polymorph (2 layer monoclinic structure).

TABLE 2
The 2 theta angle and d-spacing of the Illite sample

Obs. Angle	d(obs.)	hkl	Intensity
8.84	10.01	002	s
12.35*	7.17	—	w
17.92	4.950	004	m
19.79	4.486	110, 111, 111	m
22.85	3.880	113	w
23.80	3.738	023	w
24.85	3.583	—	w
25.48	3.496	114	w
26.80	3.326	024, 006	s
27.85	3.203	114	w
29.90	2.988	025	w
31.25	2.862	115	w
32.10	2.788	116	w
34.55	2.596	—	w
34.90	2.570	200	m
37.65	2.389	133, 204	w
37.69	2.132	136	w
45.55	1.991	010	m
61.50	1.508	060	w

*non-illite reflections.

The broad reflection at 7.17 Å is due to (001) reflection of the poorly crystallised kaolinite as impurity. This is supported by the presence of another non-illite broad reflection at 3.58 Å (The (002) reflection of kaolinite). There is still some ambiguity in the identification of this sample from the x-ray diffraction pattern. It shows that the sample is a mica-type mineral. The chemical composition and the loss on ignition lies in between that of well crystallised muscovite and illite. Theoretical chemical composition of muscovite is SiO₂, 45.2%; Al₂O₃, 38.5%; K₂O, 11.8%. Illite is known to have more SiO₂ and water with less Al₂O₃ and K⁺, although muscovite with 31.8% SiO₂ and 25.8% Al₂O₃ are also known. However, because the term "illite" is not a specific name but a general term for clay mineral constituents of argillaceous

sediments belonging to the mica group, the name seems appropriate.

Morphology

The transmission electron micrographs (TEM) for the kaolinite sample and the illite sample are shown in *Figs. 2a* and *2b*.

Comparison of the TEM micrograph for the kaolinite sample with the micrograph of well crystallised kaolinite confirms that the sample is not well crystallised. Most crystals do not exist as well defined hexagonal plates, though straight well defined incomplete dimensions are still observed. The angles between edges confirm the hexagonal origins of these crystals. The average particle size is less than 2 microns in diameter.

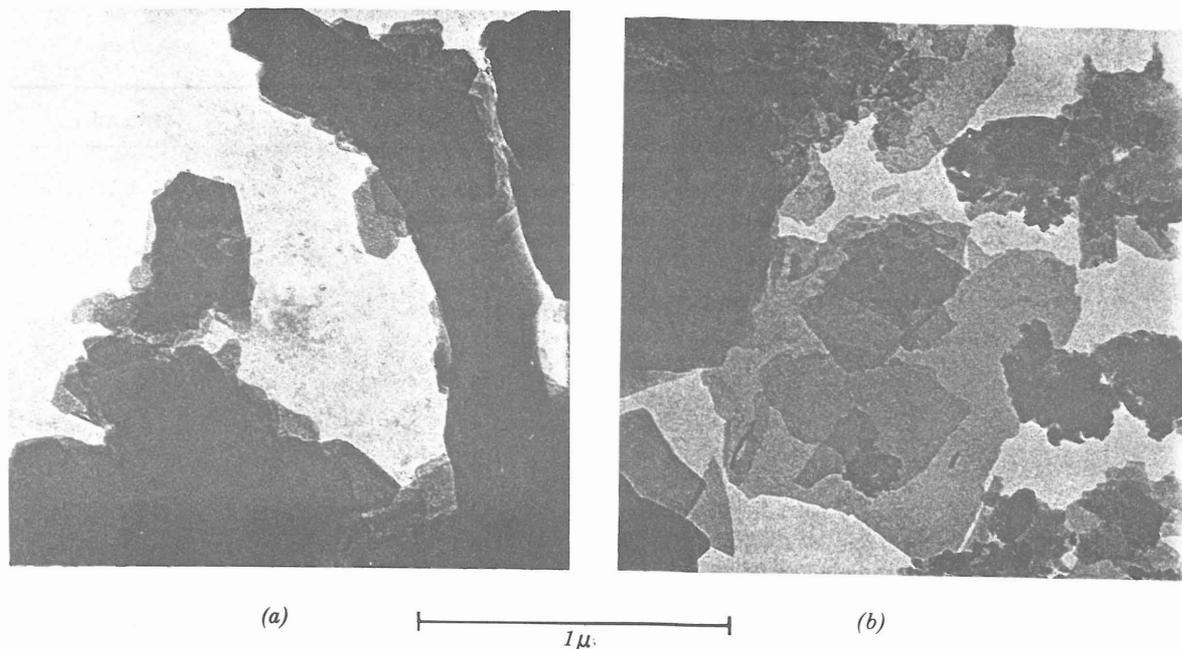


Fig. 2. Transmission electron micrographs for a) kaolinite, b) illite. (48000 X).

The TEM micrograph of the illite shows that the sample has no fixed crystal shapes.

Surface and Pore Structure

The nitrogen adsorption-desorption isotherms for the kaolinite and illite samples are shown in Fig. 3. Both the isotherms are of sigmoid shape with an inflexion point at low relative pressure region, a gentle slope at intermediate pressure region. These are typical type IV isotherms according to the BET classification. Small hysteresis are observed for both the samples at relative pressure above 0.45. According to the de Boer classification (1968), these are type A hysteresis which are characterised by steep and narrow hysteresis loops. This type of hysteresis is usually obtained with cylindrical pores. This is consistent with the computer prediction performed for kaolinite by Christian *et al.* (1981) who showed that cylindrical pore model provides a reasonable fit for both branches of the isotherms of kaolinite.

Pore analysis performed using the method of Gregg and Sing (1967) assuming cylindrical

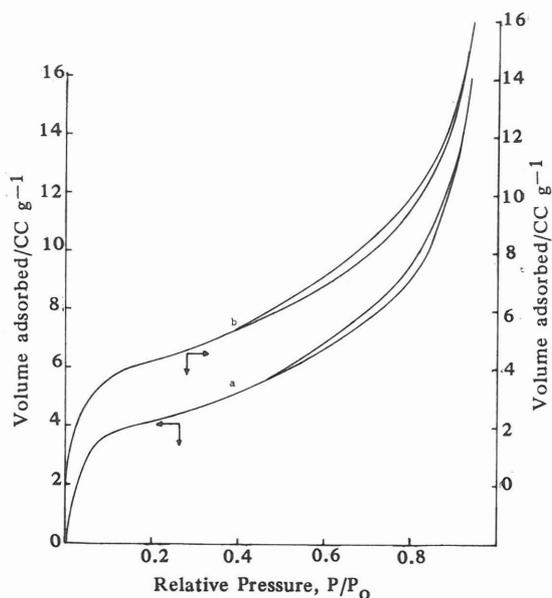


Fig. 3. Nitrogen adsorption-desorption isotherms for a) kaolinite, b) illite. (at liquid nitrogen temperature)

pore show that for both the samples of clays, a large proportion of the pores falls in the range between 23 Å to 40 Å. Detailed analysis shows that micropores may exist in the illite sample.

Both the samples produced straight lines for the BET plots between relative pressure regions of 0.05 to 0.35. From these plots the BET surface areas of these clays are determined to be 12.7 m²g⁻¹ for the kaolinite and 15.2 m²g⁻¹ for the illites. The value for kaolinite is comparable to reported values for other kaolinite while the value obtained for the illite sample seems to be lower than the surface areas reported for illite of other origins, which ranges from 40 – 60 m²g⁻¹.

Cation Exchange Capacity

The cation exchange capacity (CEC) of the kaolinite sample used of particle size less than 2 μ is 3.8 meq/100 g. This value is comparable to the value reported for this mineral of other origin. However, the exchange capacity for the illite sample, 4.4 meq/100 g for the < 2 μ fraction is rather low compared to the reported values of other illite. Since the surface area is dependent upon the particle size, this low value may not be surprising in view of the comparatively low surface area of the sample.

The cation exchange capacity of a clay may be caused by isomorphous substitution (Neal *et al.*, 1977) or by broken bonds. Clays of the same type but of different origins may exhibit widely differing cation exchange capacity. The pre-treatment procedure, the pH, the particle sizes, the crystallinity, lattice imperfection and the presence of impurities may profoundly affect the cation exchange capacity. It has been shown that the CEC of kaolinite increased 400% when the particle size was reduced from 10 – 20 μ to 0.1 – 0.5 μ (Harmon & Franlini, 1940) and a similar increase was observed with illite when the particle size was reduced from 1 – 0.1 μ to less than 0.06 μ (Grim, Bray 1936). The differing CEC values of the samples may thus be understood.

Other Properties

Differential thermal analysis was carried out on the kaolin sample. The characteristic

endothermic peak of kaolinite was observed at around 500° with another sharp exothermic peak at just below 1000°. Infrared spectrum of the kaolin sample showed the four kaolinite peaks at 3622, 3655, 3670 and 3700 cm⁻¹ corresponding to the –OH vibrations. These properties are consistent with kaolinite (Robert & White, 1966).

Only two peaks at 3620 and 3700 cm⁻¹ are clearly identifiable in the infrared spectrum of the illite sample. The peak at 3700 cm⁻¹ is caused by the presence of kaolinite as impurities (Beutelspacher *et al.*, 1976). These spectra are shown in Fig. 4. The poor resolutions of the spectra at this range is likely to be caused by instrumental precision, although we cannot rule out the inherent poor resolutions of the sample. These spectra indicate that the nature and concentration of the hydroxyl groups differ in kaolinite and illite.

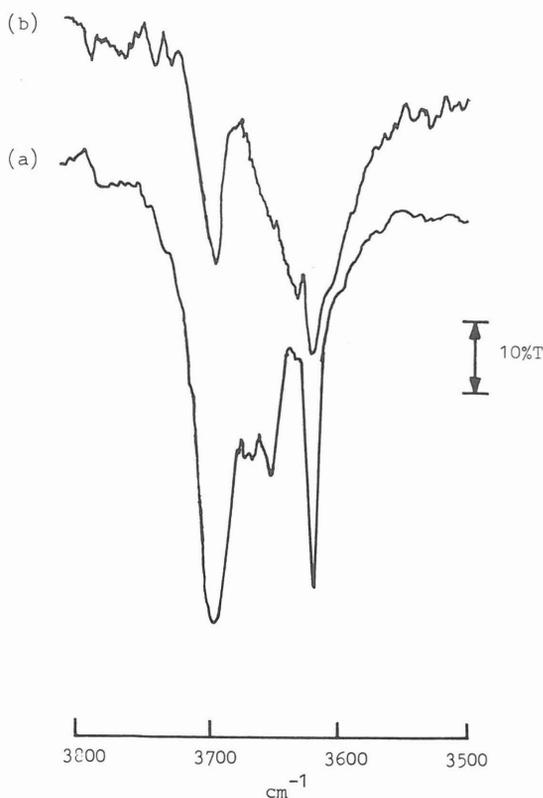


Fig. 4. Infrared spectra of a) kaolinite, b) illite.

CONCLUSION

From the x-ray diffraction studies, it is concluded that the Bidor kaolinite is a reasonably pure disordered kaolinite. The pore is cylindrical in shape and of diameter ranging from 20 to 40 Å. The surface area is in the region of $13 \text{ m}^2 \text{ g}^{-1}$ and has a cation exchange capacity of 3.8 meq/100 g. These and other characteristics are typical of kaolinites of other origin. The Bidor illite sample was identified to have a 2 layer monoclinic structure (2 M polymorph). No fixed crystal shape was observable from the electron micrograph of the sample. It has a rather low surface area ($15 \text{ m}^2 \text{ g}^{-1}$) and low cation exchange capacity ($4.4 \text{ meq}/100 \text{ g}^{-1}$) when compared to illite of other origins.

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