

Mineralogic and physico-chemical studies of Lahad Datu bentonite

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Abstract: The commencement of production of activated clay by the local industry has created the demand for bentonite (montmorillonite) clay which is the basic raw material used in the manufacturing process. In the search for this material, field augering and sampling programme were undertaken in areas which collectively form the Segama Group near Lahad Datu, Sabah.

Seven samples, representing the total variation in a montmorillonite clay deposit, have been investigated for their mineralogic and physico-chemical characteristics. The mineral is dominantly a Ca-montmorillonite clay, with quartz, feldspar and zeolite as the main impurities. Early investigations by chemical and physical properties tests showed that this material could be suitable as a bleaching clay (or as a raw material for use in the manufacture of acid activated clay). The commercial appraisal of this clay deposit still depends on many experimental studies such as trial acid activation and bleaching tests of activated products on crude oil.

INTRODUCTION

Bentonite is clay with montmorillonite as its main mineral. It has many uses in various industries which includes use to decolorize oils, fats and greases, drilling mud, ceramic material, foundry moulding, iron ore pellets, etc. (Grim, 1978).

Lately, due to the rapid expansion of the palm oil processing activities in Malaysia, there is an increase in demand for processed bentonite (activated) to be used to decolorize crude palm oil. At the moment there are several bentonite processing plants, but then the raw material used is still imported. Most of the imported bentonite are used in the production of bleaching earths and this involves as estimated foreign flow of about 20 million ringgit in foreign exchange per year. If this resource can be found locally and exploited it will not only reduce foreign capital flow but will also help support the objective of the 'National Industrial Master Plan' which calls for the wider use of local materials in industries based on natural resources.

In 1986, The Geological Survey of Malaysia pioneered in the search for this raw material. In 1988, it reported findings of bentonite (montmorillonite) clay deposits in several areas east of Sabah (Ang *et al.*, 1988).

A follow-up study was made in early 1989 around Lahad Datu, Sabah. Its main objective is to evaluate this mineral commodity through tests in the laboratory. The study involves two phases;

- (1) Mineralogical and physico-chemical study of several samples representing various quality ranges of clay mineral from several places around Lahad Datu district.
- (2) Determination of the technological properties such as its use as palm oil decolorizer or probably as a basic material for drilling mud.

However this paper will only discuss results of mineralogical and physico-chemical study of Lahad Datu bentonite.

GEOLOGICAL SETTING AND RESEARCH METHODOLOGY

Fieldworks to collect montmorillonite clay samples representing a specific range of quality were carried out in areas predetermined through literature surveys. Field augering and sampling were undertaken mainly in areas (Fig. 1) underlain by the Ayer Formation, Libong Tuffite and Tungku Formation which collectively forms the Segama Group. The Segama Group is characterised by abundant pyroclastic rocks, most of which were deposited under marine environment, and is interpreted to be Miocene in age. The Ayer Formation had been described as having been deposited in shallow, inner neritic marine environment as well as partly in deeper water, and comprises of mainly slump breccia, interbedded tuff and tuffite, tuffaceous sandstone and shale, with rare conglomerate and limestone (Leong, 1974).

The initial stage involves drying of several 1-5 cm diameter size of the sample in open air, followed by sample description (such as colour and texture). There were then crushed to sizes of <10 mm, air dried and cone quartered in two portions:

- (1) about 100 - 100 gm for wet sieving and subsequent experiments;
- (2) about 300 gm for Atterberg limits and technological properties determination.

Analysis done include mineralogical study, chemical analysis and physico-chemical properties. Mineralogic study was done using the X-ray diffraction (XRD) method with samples of <53 microns (orientated and unorientated mounts). Chemical analysis was carried out using the X-ray fluorescence (XRF). XRF was chosen because of its relative simplicity and sufficient precision. Ammonium acetate standard method were used to measure the cation exchange capacity (CEC). Some of the physico-chemical properties determined were moisture absorption (MA), ignition loss (IL), moisture content (MC), plastic limit (PL), liquid limit (LL) and surface area measurements.

RESULTS AND DISCUSSION

1. Mineralogical study

All samples can be categorised as having montmorillonite as their main

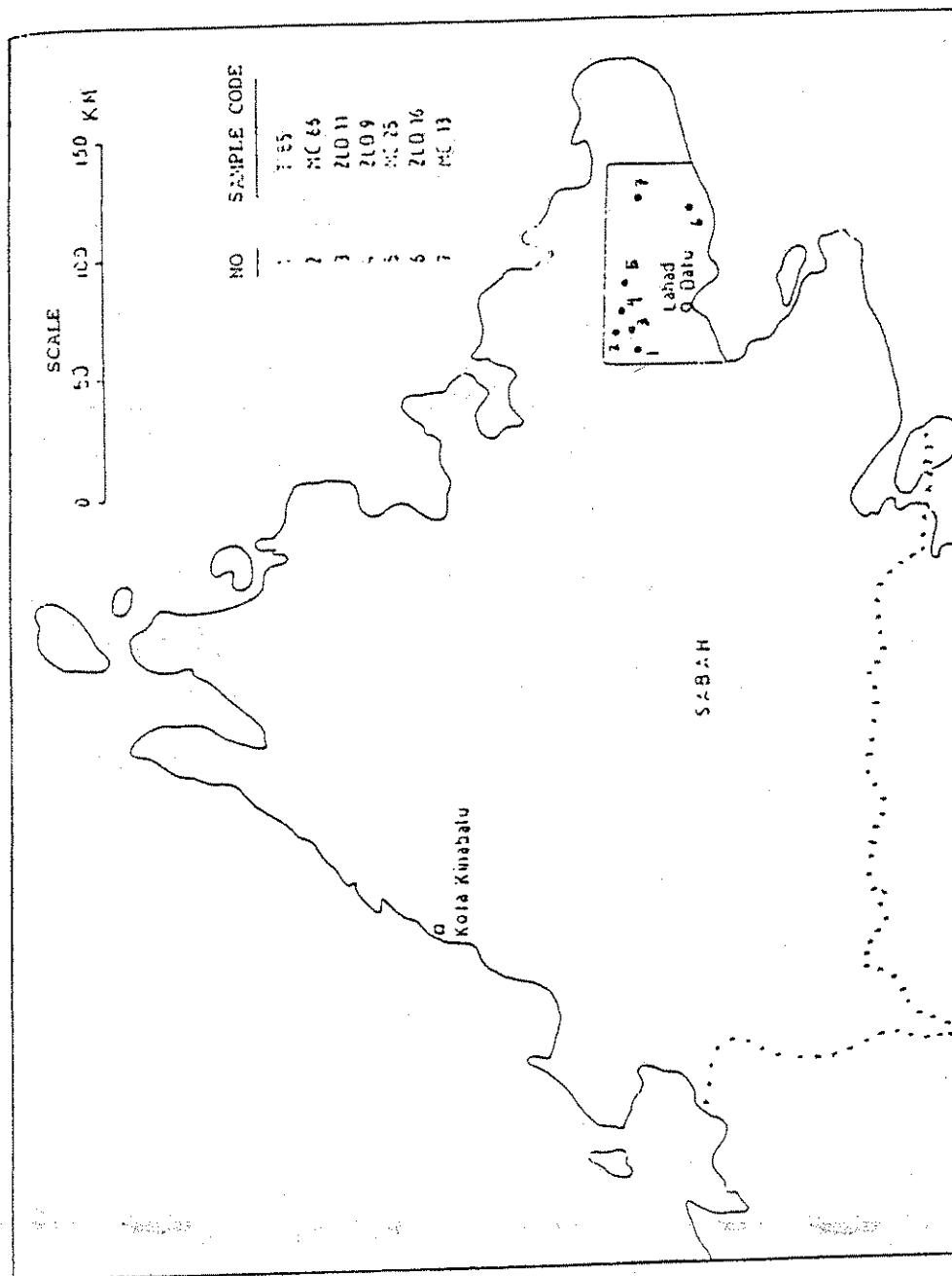


Figure 1: Sample location map of area investigated.

mineral. Mineralogical compositions of the samples are shown in Table 1. Diffraction traces illustrating these mineral assemblages are shown in Fig. 2.

Almost all of the samples contain a small and appreciable amount of zeolite (probably mordenite), feldspar (probably albite), and at times kaolinite, mica and hornblende as the trace minerals. Smectite was dominant in sample MLP 1, MLP 3, and MLP 5 and was a major component in samples MLP 2, MLP 4, MLP 6 and MLP 7.

XRD examination of powder mounts of bentonite provide an indication of the smectite species present. The position of the α (060) spacing shows whether the smectite is dioctahedral (1.49-1.50 Å) or trioctahedral (1.52-1.54 Å). Dioctahedral smectite include montmorillonite, the most common species, beidellite, containing predominantly Al in structure sites; and nontronite a Fe-rich dioctahedral smectite. Trioctahedral smectites are less common; saponite is a trioctahedral smectite that contains mainly Mg in structure sites. Base spacing α (060) determination done on a fraction of a Lahad Datu bentonite showed clearly peaks at 1.50 Å indicating predominantly dioctahedral character of the smectite.

Table 1. Semi-quantitative mineral composition of samples from XRD.

Sample	Min. Code	Smectite (montmo.)	Qtz	Feldspar	Zeolite	Other
MC 25	MLP 1	****	**	tr	nd	tr (il)
MC 66	MLP 2	***	**	*	*	tr (m, hb)
T 85	MLP 3	****	**	*	nd	tr (m, il)
ZLD 9	MLP 4	***	**	*	*	tr (m)
ZLD 11	MLP 5	****	*	*	*	tr (m, k)
ZLD 13	MLP 6	***	**	*	*	tr (k, il)
ZLD 19	MLP 7	***	**	nd	nd	* (k)

Key:

**** - dominant
 *** - major
 ** - appreciable
 * - minor
 tr - trace
 nd - not detected

il - illite
 m - mica
 k - kaolinite
 hb - hornblende

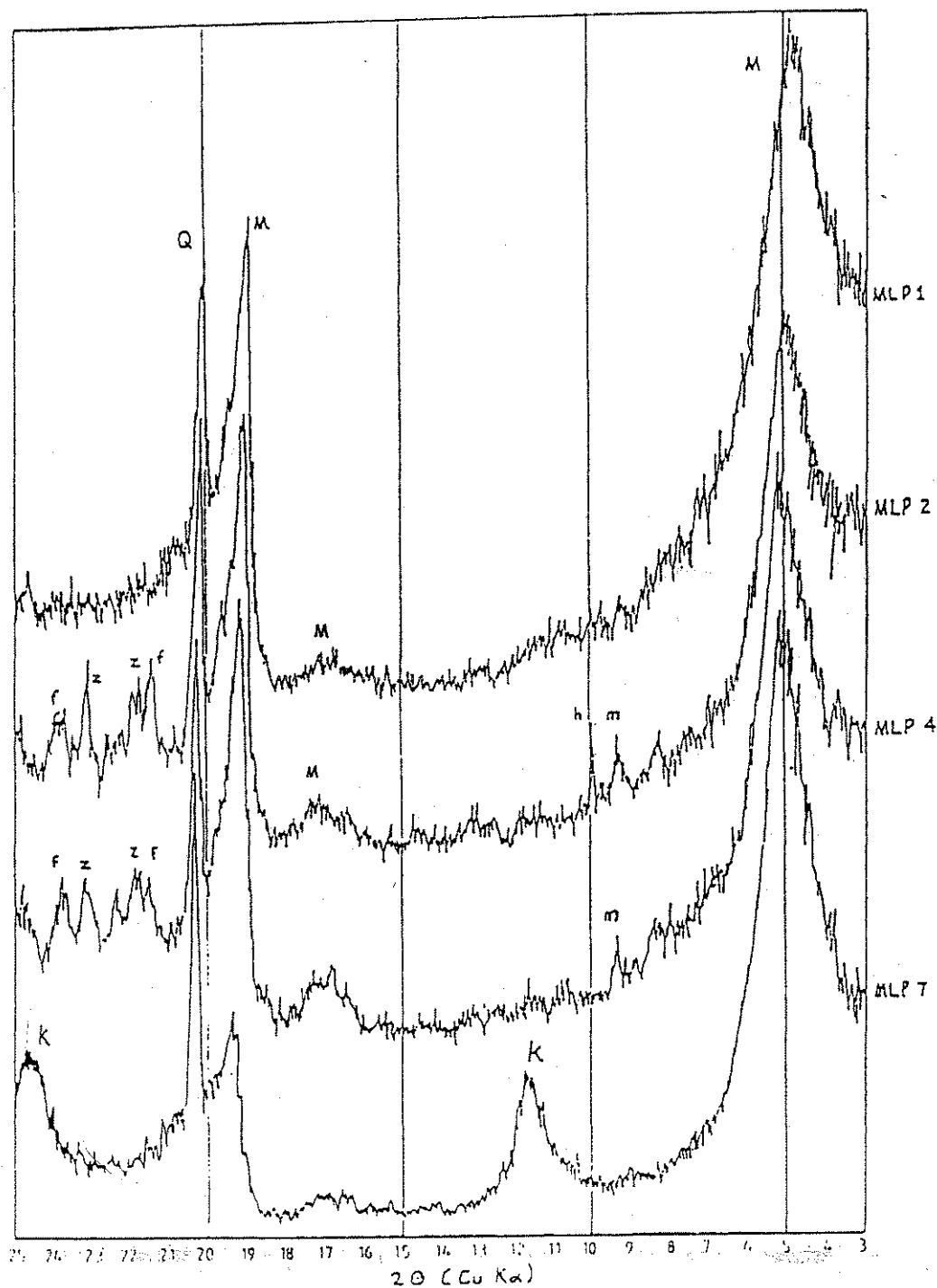


Figure 2: X-ray diffraction (XRD) traces of Lahad Datu clays.
 M = montmorillonite, m = mica, k = kaolinite,
 Q = Quartz, f = feldspar, z = zeolite, h = hornblende.

2. Chemical Study

(a) Major-element chemical analyses

Four of the samples, MLP 2, MLP 3, MLP 5 and MLP 6, were analysed for major elements by X-ray fluorescence (XRF). Results are shown in Table 4. The high SiO_2 values in sample MLP 3 indicates high quartz content as also shown by XRD analysis.

As a whole (in Table 2), SiO_2 content in Lahad Datu bentonite were high, almost all had $>55\%$ and one sample nearly 63% while Al_2O_3 content were $<20\%$. This when compared to the Wyoming bentonite whose SiO_2 content is 55.4% and Al_2O_3 is 20.1% , shows that the Lahad Datu bentonite has a very high adsorption power due to the big difference in SiO_2 and Al_2O_3 content. Lahad Datu bentonite also shows higher K_2O and Fe_2O_3 content. This high K_2O content can be attributed to the presence of minerals such as feldspar, mica and zeolite. CaO recorded in Table 2 existed in the exchangeable cation form as found in smectites.

(b) Cation-Exchange Capacity (CEC)

Cation exchange capacities were determined using ammonium acetate standard method. In the present study the total CEC was measured in order to give additional information about the purity of the sample, since the material is mainly a mixture of montmorillonite (CEC = 70 to 150 meq/100 g), kaolinite (CEC = 3 to 15 meq/100 g) and other minor non-clay minerals. It was also expected that the

Table 2. Chemical Analysis by X-ray Fluorescence (XRF).

	MLP 2	MLP 3	MLP 5	MLP 6	Wyoming USA*
SiO_2	59.14	62.69	60.54	60.13	55.40
Al_2O_3	17.70	14.86	16.81	15.24	20.10
Fe_2O_3	9.39	5.57	8.51	8.18	3.70
MgO	1.46	1.34	1.27	1.77	2.49
CaO	1.37	1.38	1.50	1.34	0.49
Na_2O	-	-	-	-	2.76
K_2O	2.55	2.17	1.25	3.01	0.60
MnO	0.22	0.06	0.03	0.19	-
P_2O_5	0.11	0.11	0.11	0.12	-
LOI	9.39	12.89	10.92	9.98	13.50
TOTAL	101.3	101.1	100.9	99.9	99.0

total CEC would measure the capability of the clay to exchange with sodium, producing a Na-bentonite product. The nature of the exchangeable cations, which could affect the capacity to exchange with sodium, was investigated in five selected samples.

Based on the results of observations made, it can be concluded that the Lahad Datu bentonite has low to high CEC value, as shown in Table 3. The high CEC value shown by MLP 5 might be due to the presence of zeolite whose CEC value is higher than smectite. CEC values in the samples tested decreases in the order $MPL\ 5 > MLP\ 1 > MLP\ 4 > MLP\ 3 > MLP\ 2$.

Table 3. Cation Exchange Capacity (CEC) data

Mineral Code	CEC (meq/100 gm)
MLP 1	134.3
MLP 2	35.0
MLP 3	47.4
MLP 4	53.8
MLP 5	158.0

3. Physico-Chemical

(a) Moisture Adsorption (MA), Ignition Loss (IL) and Moisture Content (MC)

The MA values are approximately in accordance with the mineralogical composition given by XRD (Table 4). In general, the samples with high montmorillonite content present higher MA, but is not perfect proportionality (due to the inaccuracy of the XRD results). The MC and IL values also vary in accord with the mineral composition of the material.

(b) Plastic Limit (PL) and Liquid Limit (LL).

In the present study, the measurements of PL and LL were carried out for three samples in order to obtain additional information on the nature and quality of the material. The results (Table 5) show that the Atterberg limits can give a good indication of the clay purity. Clays with high montmorillonite showed high Atterberg limit values. The three samples fall close to the Ca-montmorillonite area in the clay identification chart (fig. 3) outlines by Bain (1971).

Table 4. Moisture Adsorption (MA), Ignition Loss (IL) and Moisture content (MC) values.

Sample	Min. Code	MA	MC	IL
MC 25	MLP 1	16.89	7.14	10.43
MC 66	MLP 2	17.20	7.95	9.39
T 85	MLP 3	11.85	4.72	12.89
ZLD 6	MLP 4	14.36	6.08	7.97
ZLD 11	MLP 5	17.69	5.66	10.92
ZLD 13	MLP 6	15.08	9.67	9.98
ZLD 16	MLP 7	12.58	4.68	11.72

Table 5. Plastic Limit (PL), Liquid Limit (LL) and Plasticity Index (PI).

Mineral code	LL	PI	PI
MLP 1	114.2	58.8	55.4
MLP 2	112.7	45.3	67.4
MLP 5	111.0	49.7	61.3

(c) Surface area measurement

The Quantasorb area meter (nitrogen and the BET method) was used to measure the surface area of selected samples in order to analyse:

- (1) the possible variations in the measurements related to the mineral composition of the samples;
- (2) the relative grain size, chemical activity and adsorption capacity, by comparison with other known clays.

The results obtained (Table 6) show a relationship between mineral composition and the surface area. Clays with high montmorillonite showed high surface area values. Values measured were found to be within the montmorillonite clay range except sample MLP 6. Olphen (1979) quotes values from 48 to 97 m²/g for several non-sodium montmorillonite clays (under variable experimental conditions).

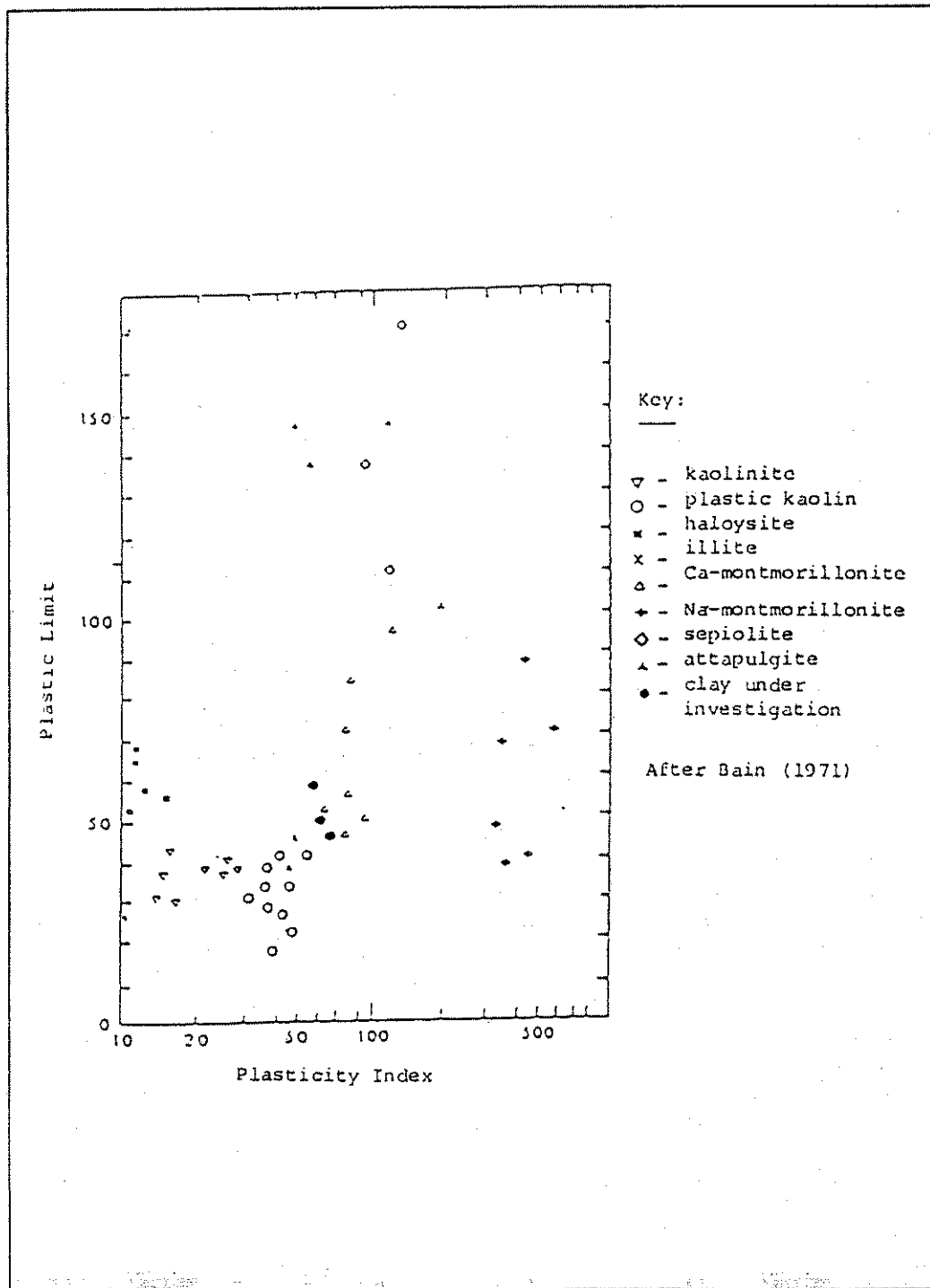


Figure 3: Plastic limit versus plasticity index.

Table 6. Surface Area Measurement

Mineral Code	Surface area (m ² /g)
MLP 2	50.2
MLP 3	77.7
MLP 4	70.6
MLP 6	23.6

The textural nature of the material, constituted of dense aggregates of montmorillonite, retaining the texture and volume of the original rock, is the possible reason for such low surface area results (especially MLP 6). This textural nature may also affect the availability of surface area for chemical reactions (including possibly cation exchange).

CONCLUSION AND RECOMMENDATIONS

Results of XRD tests on several samples taken from different locations in the Lahad Datu area, Sabah, showed the presence of montmorillonite. Qualitatively the content of montmorillonite mineral (smectite) varies from sample to sample, that is from low to medium high. This existing is believed to be of the Ca-bentonite type. Besides montmorillonite, other mineral such as quartz, zeolite, feldspar, kaolinite, mica/illite, chlorite and hornblende are present as impurities in the clay.

Results from chemical and physico-chemical properties analysis of selected samples showed the possibility of the Lahad Datu clay as a suitable bleaching clay. However, further studies must be made to confirm this. Qualitative composition of the minerals present, and its suitability as bleaching clay through tests by direct exposure to crude palm oil (CPO) are recommended.

However, the clay must be activated with acid before use so that the bentonite will have an adequate and high adsorption ability. The acid activation process can be done by addition of hydrochloric acid or sulphuric acid at a certain rate to leach out other compounds such as CaO, MgO, Fe₂O₃, Na₂O and K₂O so that the percentage of SiO₂ will increase compared to other compounds in the bentonite. Higher SiO₂ percentage, and higher SiO₂ percentage compared to Al₂O₃ in the bentonite will make bentonite more active.

REFERENCES

- ANG, N.K., KAMURADIN MD. SLAR, AND TUNGAH SURAT, 1988. Report on Investigation of Bentonite (Montmorillonite) Resources in Sabah, East Malaysia. Geological Survey Malaysia.

- BAIN, J.A., 1971. A Plasticity Chart as an aid to the Identification and Assessment of Industrial Clays. *Clay Mineral.*
- BRINDLEY, G.H. AND BROWN, G. (Ed.), 1980. Crystal Structures of Clay Minerals and their X-ray Identification. *Mineralogical Society*, London.
- GRIM, R.E., 1962. *Applied Clay Mineralogy*. McGraw-Hill, New York.
- GRIM, R.E. AND GUVEN, N., 1978. *Bentonites*. Geology, Mineralogy, Properties and Uses: Developments in Sedimentology 24. Elsevier Scientific Publishing Company, New York.
- HIGHLEY, D.E., 1972. Fuller's Earth (Mineral Dossier No. 5). Mineral Resources Consultative Committee, London.
- LEONG, K.M., 1974. The Geology and Mineral Resources of the Upper Segama Valley and Darvel Bay Area, Sabah, Malaysia. Geological Survey Malaysia Memoir 5 (Revised).
- OLPHEN, H. AND FRIPIAT, J.J. (eds.), 1979. *Data handbook for Clay Materials and other non-metallic minerals*. Pergamon Press, Oxford, 346 p.
- WIEDERMAN, L.H., 1981. *JAOCS* 58, 159.

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