

Some Mineralogical and Physico-Chemical Properties of Fuller's Earths from Tertiary Sediments in South Korea

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Abstract: Fuller's earth deposits from Miocene sedimentary sequences in Gyeong Sang-do contain up to 95% Ca-montmorillonite accompanied by cristobalite, clinoptilolite, mordenite, quartz, feldspar and X-ray amorphous material. Differential thermal analysis, infrared and electron microscopic data are given for the montmorillonite component. The ease with which the exchangeable calcium of the montmorillonite could be replaced by sodium (to give a product with properties similar to that of a bentonite) was monitored by the Atterberg liquid limit test. Some samples tested as possible binders for foundry moulding sands gave results that compared favourably with material currently being used for this application. Many of the samples also met the OCMA specifications for clays used in drilling muds.

INTRODUCTION

The description 'fuller's earth' is usually applied to clay deposits in which the main constituent is montmorillonite and the principal exchangeable cation is calcium. Clay deposits consisting of montmorillonite in which the main exchangeable cation is sodium are termed 'bentonites'. Both fuller's earth and bentonite are important industrial raw materials, their main areas of application being as binders in foundry moulding sands and for iron ore pelletizing, as bleaching agents for oils and fats, and as suspension aids in the oil-well drilling industry. Korean domestic consumption of fuller's earth and bentonite has increased dramatically over the last few years as a result of rapid industrial development.

Fuller's earth was first described from Tertiary sediments of Korea by Kim J. D. et al. (1970) and some geological and mineralogical data were reported by Kim O. J. et al. (1976). Between 1978 and 1981, the senior author and colleagues from the Korea Institute of Energy and Resources (KIER) carried out a systematic field survey of these fuller's earth occurrences

(Kim J. W. et al., 1978; 1980; 1981); this included a drilling programme to estimate the size of individual deposits.

This paper describes the mineralogical composition and physico-chemical behaviour of fuller's earths from deposits in the Yonil, Gampo and Ulsan areas, Gyeong Sang-do, which were identified during the KIER field survey. Results from some use-related tests are also reported and compared with those obtained from commercial grades of fuller's earth and bentonite available in the United Kingdom.

GEOLOGICAL BACKGROUND

The fuller's earth beds, which range in thickness from a few cm to several metres, occur in Miocene sedimentary sequences exposed in an area along the south-eastern coast between Pohang and Ulsan. The Miocene sediments, which rest unconformably on rocks of the Cretaceous Gyeongsang System, are divided into a lower Yangbug Group (predominantly waterlain ashes, tuffs and other volcanic detritus) and an upper Yonil Group (fine-grained sandstones and shales with little evidence of volcanoclastics). Sediments of the Yangbug Group were deposited in fresh water whereas those of the Yonil Group were deposited in a shallow, off-shore marine environment (Kim B. K., 1965). Most of the fuller's earths are associated with

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Table 1. Sample details

Sample No.	Location (Sheet and claim No.)	Stratigraphic unit	Lithology of host rock	Maximum burial depth
G-40	Gampo, No. 40	Haseori Andesitic Tuff	Andesitic tuff and detrital sediments	unknown
G-40-1	"	"	"	"
G-66	Gampo, No. 66	Eoil Formation	Ash layer and detrital sediments;	2000-2300m
G-68	Gampo, No. 68	Hyodongri Volcanics	Tuff and volcanics	2000m
J-2-40	Gampo, No. 56	Eoil Formation	Ash layer and detrital sediments;	2000-2300m
			volcanics	
J-2-70	"	"	"	"
K-1	Gampo, No. 39	Haseori Andesitic Tuff	Andesitic tuff and detrital sediments	unknown
U-34	Ulsan, No. 34	"	"	"
U-41	Ulsan, No. 41	"	"	"
Y-3-1	Yonil, No. 3	Upper Basaltic Tuff	Basaltic tuff	800-900m
Y-12	Yonil, No. 12			
Y-16-1	Yonil, No. 16	Upper Basaltic Tuff	Basaltic tuff	900m
Y-16-2	Yonil, No. 16	Upper Basaltic Tuff	Basaltic tuff	900m
Y-27	Yonil, No. 27	"	"	"
Y-33	Yonil, No. 33	Upper coal-bearing formation	lignite, sandstone, shale and ash layer	900m

the volcanoclastic sediments of the Yangbug Group (Table 1). Mineralogical and geochemical evidence suggest that they formed by alteration of fine-grained, glassy volcanic ash during the early stages of burial diagenesis (Moon, in preparation). Estimated burial depths range from a few hundreds of metres to 2700 m (Kim J. W. et al., 1978); exact depths cannot be determined because of the lateral impersistence of many of the beds which leads to difficulties in relating sequences from one locality to another.

MINERALOGICAL COMPOSITION OF SAMPLES

Representative portions of the fuller's earths were ground to pass a 100 mesh (125 μ m) screen and examined by X-ray diffractometry (XRD). 'Randomly-oriented' cavity mounts were used. Diffractometer operating constants were: radiation: Co-K α at 40 kV and 40 mA; slits: divergent 1, receiving 0.1 $^\circ$, anti-scatter 1 $^\circ$; scanning speed: 2 $^\circ$ (2 θ /min).

Montmorillonite was found to be the major phase in all the samples. The d (001) spacings of the montmorillonites were between 15.0 and 15.4 Å , indicating that the exchange sites were occupied predominantly by divalent cations (Ca $^{2+}$, Mg $^{2+}$). The d(060) spacings were all 1.500 \pm 0.01 Å , signifying that the montmorillonites were dioctahedral, i. e. in the octahedral layer

Al, Fe $^{3+}$ >Mg $^{2+}$, Fe $^{2+}$. As shown in Table 2, other minerals were identified in appreciable to minor amounts, these including cristobalite, feldspar, quartz, and the zeolites clinoptilolite and mordenite.

Montmorillonite contents of the powdered samples were calculated from ethylene glycol monoethyl ether (EGME) surface area values (Carter et al., 1965). This method is based on the formation, under vacuum, of a stable monolayer of polar EGME molecules on the surface of each individual montmorillonite crystallite. Ca-saturated montmorillonites give EGME surface areas in the region of 800m 2 /g-other 'non-swelling' clay minerals such as kaolinite, halloysite, mica and chlorite give values <50m 2 /g, and nonclay minerals values <5m 2 /g. Amounts of montmorillonite in the present samples were obtained simply by comparing their surface area values with that of a pure Ca-montmorillonite (800m 2 /g), these ranging from 95% for Y-3-1 down to 45% for G-68 (Table 2).

In many of the samples, totals of X-ray identifiable minerals fell far short of 100%. For instance, in Y-12 only Ca-montmorillonite and quartz were identified (Table 2). Surface area measurements indicated 49% montmorillonite, and the height of the main quartz peak on the diffractometer chart suggested about 25% of this mineral. The deficit of about 25% must be due

Table 2. Summary of mineralogical compositions of fuller's earths determined by X-ray diffraction analysis and surface area measurements on powdered (<100 mesh) samples.

Sample No.	Description of hand specimen	Surface area m ² /g	Montmorillonite content (%)	major	appreciable	minor
G-40	Pale green/buff fragmentary clay	365	46	Ca-mont.	clinoptilolite	mordenite feldspar quartz cristobalite
G-40-1	Buff blocky clay	418	52	Ca-mont.	clinoptilolite	cristobalite feldspar
G-66	Pale green/grey fragmentary clay	545	69	Ca-mont.		feldspar quartz
G-68	Pale grey fragmentary clay	360	45	Ca-mont.	feldspar	quartz
J-2-40	Purple-pale green waxy clay	575	72	Ca-mont.	quartz	
J-2-70	Pale green fragmentary waxy clay	531	66	Ca-mont.		quartz cristobalite
K-1	Cream fragmentary clay	431	54	Ca-mont.	feldspar	cristobalite
U-34	Green fragmentary clay	492	62	Ca-mont.	feldspar	mordenite
U-41	Pale grey blocky to fragmentary clay	613	77	Ca-mont.	cristobalite	quartz
Y-3-1	Pale green blocky waxy clay	764	95	Ca-mont.		quartz
Y-12	Pale pinkish buff blocky clay	392	49	Ca-mont.	quartz	
Y-16-1	Buff blocky clay	536	67	Ca-mont.	cristobalite	clinoptilolite
Y-16-2	"	491	61	Ca-mont.	cristobalite	clinoptilolite
Y-27	Pale greyish green fragmentary clay	378	47	Ca-mont.	clinoptilolite	mordenite feldspar quartz
Y-33	Pale yellow/green clay with tendency towards laminar fracture	673	84	Ca-mont.	cristobalite	quartz

to the presence of X-ray amorphous aluminosilicates. Deficits of approximately the same order of magnitude occur in samples G-66 and K-1 and it is likely that such material is present to a lesser extent in the remaining samples. This X-ray amorphous material may be partially altered volcanic glass or imperfectly crystallized alteration products.

CHARACTERIZATION OF THE MONTMORILLONITE

Differential thermal analysis (DTA) curves and infrared (IR) spectra were determined on selected samples. In the absence of chemical analyses, DTA curves and IR spectra can provide some indication of the structural-chemical composition of the montmorillonite, in particular the nature and relative amounts of octahedral cations. The morphology and texture of the montmorillonites as observed by scanning

and transmission electron microscopy are also discussed in this section.

DTA curves

DTA curves (Fig. 1) were obtained on Stanton Redcroft equipment using ~0.15g sample, 15°C/min heating rate and calcined alumina as the inert reference.

DTA curves of montmorillonites are usually divided into three regions: (a) the low-temperature region (<300°C) within which adsorbed and exchangeable cation co-ordinated water are released; (b) the dehydroxylation region (400-750°C); (c) the high-temperature region (>800°C), where new phases crystallize from the dehydroxylated clay.

(a) The low-temperature region. All the montmorillonites in Fig. 1 show a large endotherm due to expulsion of water sorbed on the surface of the montmorillonite particles and loosely bound within the interlayer region of the montmorillonite crystallites. A shoulder

on the high-temperature side of this endotherm, which becomes progressively better developed on going from Y-33 to J-2-70, represents expulsion of water molecules co-ordinated to the divalent exchangeable cations.

(b) The dehydroxylation region. Montmorillonites may be described as showing 'normal' or 'abnormal' dehydroxylation behaviour depending on the temperature range in which dehydroxylation occurs (Mackenzie, 1970). Normal montmorillonites show a single

dehydroxylation endotherm between 650–720°C, abnormal varieties show either a single endotherm at approximately 550°C or a dual endothermic system with peaks at approximately 550 and 650°C. The reasons for these differences in dehydroxylation behaviour have not yet been explained satisfactorily; they must, however, be related to variations in bonding energy between different hydroxyl groups in the lattice and this could also result from differences in relative amounts of Al, Fe (III, II) or Mg in the octahedral sheet or, possibly, differences in the distribution (random vs. ordered) of these cations within the octahedral sheet.

Only Y-3-1 shows well-defined 'abnormal' dehydroxylation behaviour. The remaining four samples show some degree of 'abnormal' behaviour (e.g. the shoulder at 554°C on the curve of Y-33), but generally the dehydroxylation behaviour is 'normal'. (The sharp exotherm at 469°C on the curve of U-41 is not related to dehydroxylation, but is caused either by the combustion of about 1% pyrite impurity or oxidation of Fe (II) present in the montmorillonite lattice to Fe (III).)

(c) The high-temperature region. Grim & Kulbicki (1961) divided montmorillonite into two types based on the shape of the DTA curve in this region. Those showing an endotherm at approximately 850°C followed immediately by an exotherm (giving an S-shaped peak system) were termed "Wyoming-type" and those where the endothermic and subsequent exothermic effects were separate (by up to 200°C) were termed "Cheto-type". These two types were further distinguished by the nature of their high-temperature recrystallization products. Wyoming-type montmorillonites developed mullite and cristobalite simultaneously about 200°C after the S-shaped peak; in Cheto-type montmorillonites, crystallization of B-quartz was related to the appearance of the exothermic peak.

Of the present samples, Y-3-1 is a good example of Wyoming-type high-temperature behaviour—this is also shown by G-66 and, possibly, J-2-70, although here the exothermic component of the S-shaped system is poorly, if at all, developed. U-41 exhibits Cheto-type high-temperature behaviour. Y-33 shows a rather sharp endothermic peak at 874°C followed by a further

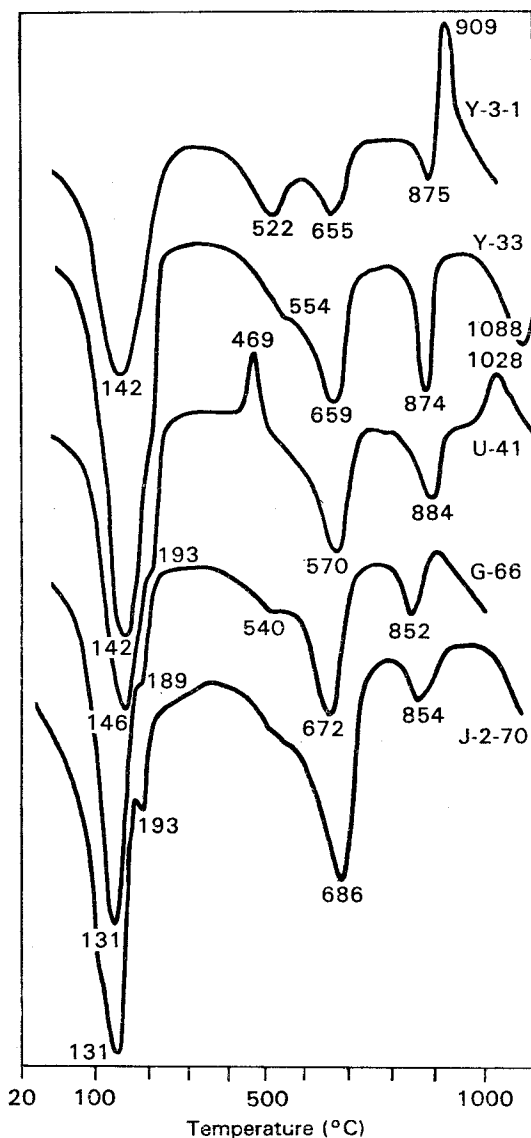


Fig. 1 DTA curves of selected fuller's earths.

endotherm at 1088°C and does not fit into either of the above categories.

In spite of work by Schultz (1969), who placed montmorillonites in a number of categories based on a combination of their dehydroxylation and high-temperature behaviour, there is much scope for a systematic study of montmorillonite DTA behaviour in relation to structural-chemical composition. Such a study may also have much practical value, as it has been suggested (Hofman, 1959) that the long-term stability of montmorillonite used as a binder for foundry moulding sands may be a function of its dehydroxylation temperature.

IR spectra

IR spectra were obtained on a Perkin Elmer Model 577 Grating Spectrophotometer, samples being examined as dispersions in KBr disks (2 or 0.5mg sample/300mg KBr).

Fig. 2 shows the 1400–300 cm^{-1} region of the spectra of four of the samples. Frequency ranges of absorption bands can be assigned to particular cation-anion vibrational modes following Farmer (1974). For instance, all four spectra show an Al-OH-Al bending vibration between 918 and 920 cm^{-1} , this being best developed in J-2-70. Samples Y-16-1 and Y-3-1 show an Al-OH-Fe (III) vibration at 883 cm^{-1} . An Al-OH-Mg vibration at 848–850 cm^{-1} is shown by J-2-70 and G-68. It would appear, therefore, that the octahedral sheets of Y-16-1 and Y-3-1 are richer in Fe and poorer in Mg than those of J-2-70 and G-68.

None of the remaining bands in the spectra in Fig. 2 provide any specific information on the composition of the octahedral sheet. The absorption at 795–798 cm^{-1} may be due either to cristobalite or quartz—the former being more likely when there is a strong vibration also at 623 cm^{-1} .

Electron microscopy

Transmission electron micrographs were obtained from dispersions of the samples using a Philips 201 electron microscope; specimens were prepared by dropping dilute aqueous suspensions on to a carbon-coated support grid. Scanning electron microscopy was carried out on gold-coated fracture surfaces using a Cambridge Stereoscan. IIA. Typical micrographs

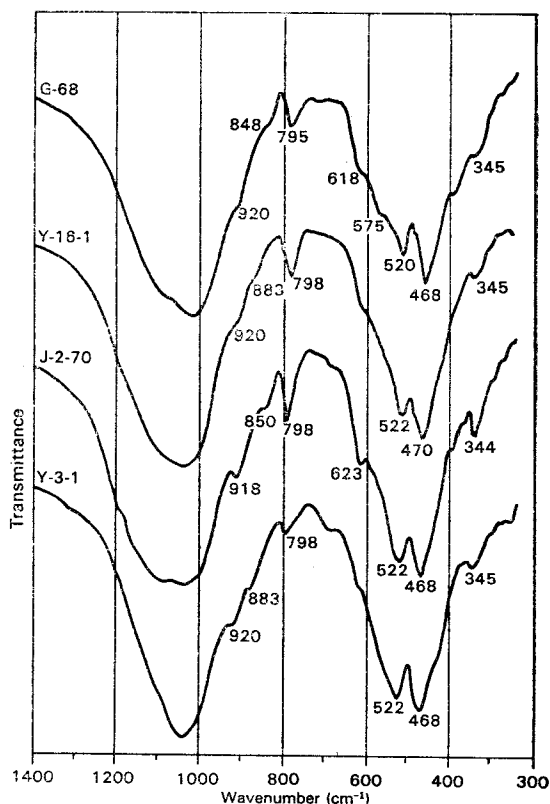


Fig. 2 IR spectra of selected fuller's earths.

are shown in Fig. 3.

The transmission electron micrograph of sample Y-33 (Fig. 3a) illustrates the typical appearance of the montmorillonite. It occurs as large thick aggregates of thin plates which, at the extremities of the aggregates, curl and twist. Once liberated from the aggregates, these plates break down into smaller and thinner plates—some so thin that they can hardly be distinguished from the background. Sample G-66 (Fig. 3b) shows similar behaviour. In the bottom right-hand corner of the micrograph there is a granular particle aggregate; small rounded grains are also scattered throughout the micrograph. This sample contains a large proportion of X-ray amorphous material and it is possible that these are unaltered glass spherules. In sample U-41 (Fig. 3c) the montmorillonite aggregates and plates appear to be breaking down ultimately to lath-like particles (not uncommon for montmorillonites

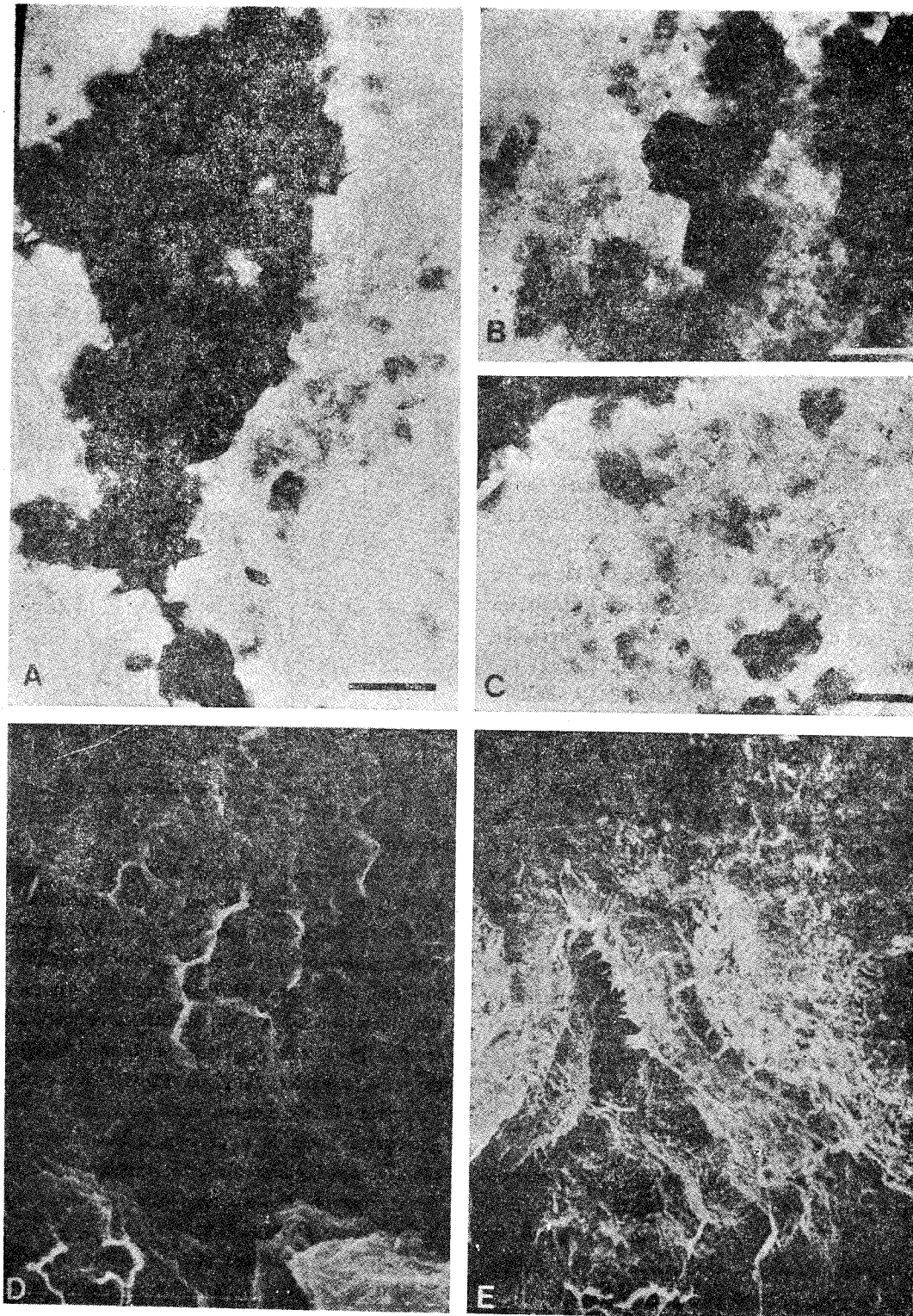


Fig. 3 Transmission (a-c) and scanning (d-e) electron micrographs of selected fuller's earths. (a) Y-33; (b) G-66; (c) U-41 (scale bar=1 μ m on all three micrographs); (d) Y-3-1 (\times 4000); (e) Y-3-1 (\times 500).

which have been thoroughly dispersed). On the left-hand side of the micrograph, particles undergoing incipient alteration are seen.

Under the scanning electron microscope the montmorillonite shows characteristic "honeycomb" structure (Fig. 3f). At low magnification (Fig. 3e), shard-like particles may be discerned with thin ribbons of montmorillonite growing out from their surfaces.

PHYSICO-CHEMICAL BEHAVIOUR OF THE MONTMORILLONITES

A number of 'physico-chemical tests were carried out on the bulk samples. Some of these tests, e.g. strengths of prepared sand/clay bodies and viscosities and filtrate losses of dilute clay suspensions, provided data that could be compared directly with specifications for particular applications. Other tests, such as measurements of the amount of methylene blue dye absorption and Atterberg liquid limits of the bulk samples, when considered in conjunction with the grade (montmorillonite content), provided an indication of the extent to which the primary montmorillonite aggregates dispersed in water, i. e. the degree to which the desirable technical properties of the montmorillonite would be developed in a water medium. Measurement of the liquid limits of the original samples after incremental additions of sodium carbonate also indicated the ease with which these predominantly Casaturated montmorillonites (fuller's earths) could be exchanged to their Na-forms—which could then be considered for the range of applications covered by natural Na-montmorillonites or bentonites.

Most of these tests were also carried out on a number of commercial montmorillonite samples. Test results on these are tabulated with results from the present samples where relevant.

Hydrocyclone separation

A laboratory hydrocyclone (Bain and Morgan, 1983) was used to produce upgraded products from samples G-66, Y-12 and Y-33. Montmorillonite contents, as determined from EGME surface area values, increased as follows:

Sample	Original montmorillonite content	Montmorillonite content in product
	(%)	(%)
G-66	69	91
Y-12	49	57
Y-33	84	97

Such separations are not normally carried out in commercial practice because of the difficulties and expense involved in recovering the montmorillonite from suspension (certain white bentonites from Texas, USA, and Milos, Greece, are treated in this manner to produce high-grade, white sorptive fillers for 'personal care products (toothpaste etc.) but the volume of production is extremely low). However, the high-shear conditions encountered by the clay suspension on passing through the hydrocyclone can lead to a large degree of aggregate breakdown. By comparing liquid limits of original samples with hydrocycloned products it is possible to monitor this (see section on liquid limit determinations). Thus, if the extent of aggregate breakdown was appreciable for any of the present samples it would be worth considering incorporating some means of shearing (e. g. low-moisture extrusion) into any possible processing plant for the deposit.

Methylene blue dye adsorption

In the absence of equipment for determining EGME surface areas, measurement of the methylene blue exchange capacity of a fuller's earth or bentonite can provide an estimate of the amount of montmorillonite present. The test procedure is simple, requires very little apparatus, and can therefore be carried out in a field laboratory. It is ideal, for instance, for recognition of montmorillonite-rich horizons in borehole core sequences as relatively large numbers of samples can be dealt with in a working day.

Although the mechanism of methylene blue absorption by montmorillonite is by exchange with the original cations on the clay surface, this method does not provide a true cation exchange capacity (CEC) value (Hang and Brindley, 1970). Two factors militate against this.

1. The methylene blue cation is raft-shaped and is normally absorbed with its largest face (135\AA^2) in

contact with the montmorillonite surface. However, for most montmorillonites the area available at each exchange site is only of the order of $110\text{--}120\text{\AA}^2$. Monolayer cover by the methylene blue cations thus occurs before the CEC is satisfied.

2. Because of the relatively large size of the methylene blue cation it is not always able to reach exchange sites at the centres of large montmorillonite aggregates.

Methylene blue exchange capacities of the bulk samples together with those of the hydrocyclone-upgraded products are given in Table 3. In Fig. 4 these results are plotted against the montmorillonite contents of the samples obtained from EGME surface areas. The line running from the origin to the value of 97 meq/100g at 100% montmorillonite represents the maximum amount of methylene blue that can be absorbed by a montmorillonite with a surface area of $800\text{m}^2/\text{g}$.

Fig. 4 shows that there is a very poor correlation between methylene blue exchange capacity and montmorillonite content. Samples G-40, G-66 and G-68 plot more or less on the line, suggesting that either there was very little original aggregate formation

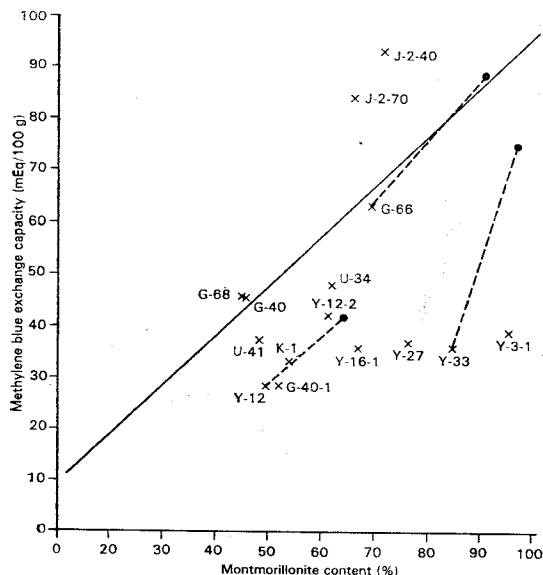


Fig. 4 Plots of methylene blue exchange capacity vs. montmorillonite content for the fuller's earths. \times =original sample, \bullet =hydrocyclone product.

in these samples or that any aggregates broke down easily under the low-energy conditions used for this test. All the other samples (except J-2-40 and J-2-70—see below) were still aggregated to greater or lesser extents. This would not seriously affect the physico-chemical behaviour of samples G-40-1, K-1, U-34, U-41 and Y-16-2 but could be significant for samples Y-16-1, Y-27, Y-31 and Y-33.

Samples J-2-40 and J-2-70 plot above the line in Fig. 4. This anomalous behaviour could be due to the methylene blue cations adopting a different packing arrangement on the montmorillonite surface. This has, in fact, been postulated for some Na-montmorillonites (Hang and Brindley, 1970) but there is no reason to believe, from XRD evidence, that the present two samples are other than Ca-montmorillonites ($d(001) \sim 15.4\text{\AA}$). No explanation can be given at present for the high MBEC of these two samples but it will be seen that they also give consistently higher values than the other samples for all the tests described below.

Plots of methylene blue exchange capacity against montmorillonite content for the three hydrocyclone-upgraded products show: (i) the dispersion characteristics of sample G-66 are not, as would be expected, changed by hydrocycloning; (ii) perhaps surprisingly, those of sample Y-12 are not affected; (iii) the plot of the product from Y-33 moves nearer to the line suggesting that some aggregate breakdown occurred on hydrocycloning.

Atterberg liquid limits

Bain (1971) has shown that Atterberg plastic and liquid limits may be of particular value in the identification and assessment of a range of industrial clays. The plastic limit (PL) is defined as the minimum % water (on a dried-at- 105°C basis) required to roll the clay into 1/8-inch diameter rods without crumbling. The liquid limit (LL) is defined as the water content, again as a % of the oven-dried weight, of a thick clay slurry at the point where it begins to flow when jarred in the cup of a Casagrande apparatus. These values roughly define the lower and upper limits between which the clay exhibits 'plastic' behaviour.

Liquid limit values for montmorillonites vary widely and depend both on the exchangeable cation present

Table 3. Methylene blue exchange capacities and liquid limits of the fuller's earths.

Sample	mbec meq/100g	original	Liquid limit % sodium carbonate addition				
			2	3	4	5	6
G-40	45.5						
G-40-1	28.8						
G-66	63.5						
G-66	63.5	227					
hydrocyclone product	88.0	282				478	
G-68	45.7	175	240	253	215	222	221
J-2-40	94.2	330					
J-2-70	84.3	326	455	466	496	496	448
K-1	33.5						
U-34	48.0	149					
U-41	39.5						
Y-3-1	39.3	152	248	294	367	428	412
Y-12	28.4	100					
hydrocyclone product	42.0	123				194	
Y-16-1	36.1	150	250	254	263	267	267
Y-16-2	42.3						
Y-27	37.4						
Y-33	36.4	136					
hydrocyclone product	75.0	216				640	
Berkbond 2 (SM)			252				
Berkbent DM (SM)				328			
Berkbent CE (SM)					480		
Wyoming Bentonite (SM)						(580)	
Wyoming Bentonite (CS)						(550)	
Mediterranean Bentonite (CS)						477	

and the state of aggregation of the clay. Bentonites usually give values in the range 600-750 whereas fuller's earths give values between 100 and 250. Liquid limits have been used for assessing the suitability of montmorillonites for foundry use (Navarro & Taylor, (1959).

With the exception of J-2-40 and J-2-70, the present samples show liquid limit values between 100 and 227 (Table 3) which, as noted above, are typical for fuller's earths. Samples from the Gampo area give higher liquid limits in relation to montmorillonite content than those of the Yonil area, indicating that the former disperse more readily in water. The increase in liquid limit from original sample to hydrocyclone overflow product is greater for Y-33 than for G-66 or Y-12, which confirms the suggestion made previously that the hydrocyclone is effectively breaking down most

of the primary particle aggregates in sample Y-33.

Liquid limits of some of the bulk samples following sodium carbonate treatment are also given in Table 3. Samples Y-16 and G-68 show very poor response to sodium carbonate addition, the maximum liquid limits reached being in the range 250-270. Sample Y-3-1 shows a more normal response and shows a maximum liquid limit at 5% sodium carbonate addition—the amount theoretically required to replace completely all the Ca ions at exchange sites by Na ions.

For sample J-2-70, the maximum liquid limit was reached after 4% sodium carbonate addition. This observation, taken in conjunction with the high liquid limit of 326 exhibited by the original sample, suggests that about 20% of the exchange positions in the natural clay are occupied by Na ions.

Also recorded in Table 3 are the liquid limits of a

number of commercial montmorillonites supplied by Steetley Minerals Ltd (SM) and Colin Stewart Minerals Ltd (CS). Berkbond 2, Berkent DM and Berkent CE are all sodium carbonate treated varieties of natural Ca-montmorillonite extracted from Lower Cretaceous sediments at Woburn, Bedfordshire, UK. Berkbond 2 is produced for foundry moulding sand uses and contains 2% sodium carbonate. Berkent DM is supplied for use in the drilling mud industry (3% sodium carbonate) and Berkent CE is for civil engineering applications (4-5% sodium carbonate). Liquid limits of two natural Na-montmorillonites from Wyoming, USA are given. The last sample in Table 3 (Mediterranean Bentonite) is a sodium carbonate exchanged montmorillonite from Milos, Greece.

From Table 3 it can be seen that after 2% sodium carbonate addition G-68, Y-3-1 and Y-16-1 give liquid limits very close to that of Berkbond 2 and might therefore be considered suitable for foundry moulding sand applications.

Y-3-1 gives liquid limits after 3% sodium carbonate addition that approach those of the drilling mud and civil engineering Berkent grades. The hydrocyclone product from Y-33 gives an extremely high liquid limit of 640 indicating that exposure to high-shear conditions raises the level of physico-chemical performance of this clay to that of a natural sodium-montmorillonite.

Liquid limits of J-2-70 after sodium carbonate exchange are comparable to those of Berkent CE.

Bonding properties

The bonding properties of samples J-2-70, Y-3-1 and Y-16-1 in mixtures with sand were determined using the specialized equipment and test procedures described in BCIRA standard testing procedures (1967).

Results on the three samples (with 1% sodium

carbonate added) are given in Table 4. The results were obtained on test pieces made from a standard sand (Chelford Grade 60) following 5% addition of clay. 3.25% by weight of water was added to the sand/clay mix and this milled for 5 minutes prior to preparation of the test pieces. Results for Berkbond 2 (used mainly in iron foundries) and Wyoming Bentonite (used mainly in steel foundries) test pieces prepared under identical conditions are also given in Table 4.

From Table 4 it is seen that Berkbond 2 has a high green strength and low dry strength whereas Wyoming Bentonite has a low green strength but high dry strength. Green and dry strengths of Y-3-1 compare closely with those of Berkbond 2. Samples J-2-70 and Y-16 show low green strengths which are almost identical to that of Wyoming Bentonite and their dry strengths also approach the values shown by this sample.

Sample Y-3-1 gives a higher shatter index—a measure of the potential toughness of the sand/clay mix—than Berkbond 2 or Wyoming Bentonite. Sample J-2-70 and Y-16 give significantly lower values for this test. All three samples give acceptable results for the compactability test.

On the basis of the above tests, all three samples would be expected to perform more than adequately as binders for foundry moulding sands. The high dry strengths shown by J-2-70 and Y-16-1 suggest also that they would be suitable binders for pelletizing iron ore.

Viscosity and filter loss

Measurement of viscosity and filtrate loss of a dilute suspension provide data which are essential to the evaluation of montmorillonites for use in oil-well drilling muds. Two main specifications apply—those of the American Petroleum Institute (API) and the Oil Companies Materials Association (OCMA).

Table 4. 'Binding' properties of the samples in a 5% mixture with sand

Sample	Green strength (lb/in ²)	dry strength (lb/in ²)	shatter index (%)	compactability (%)
J-2-70	6.8	97	62	62
Y-3-1	11.3	71	82	66
Y-16	6.5	105	62	59
Berkbond 2	12.1	50	80	62
Wyoming Bentonite	6.6	115	75	62

These are set out below.

API

Viscosity: Minimum 8 cp plastic viscosity to be given by 10g clay in 350 ml water.

Filtrate loss: Maximum 14.0 ml to be given by 10g clay in 350 ml water.

OCMA

Viscosity: Minimum 15 cp apparent viscosity to be given by 6.5g clay in 100 ml water.

Filtrate loss: Maximum 15.0 ml to be given by 7.5g clay in 100ml water.

Apparent and plastic viscosities were measured on the present samples using a direct-reading Fann viscometer. The plastic viscosity of clay suspension is a mechanical phenomenon created by friction between the clay particles, between these and the liquid surrounding them, and by the liquid itself. The apparent viscosity is a measure of these effects and also the attractive forces existing between the particles. For montmorillonite, these forces may be considerable and are dependent on the chemistry of the suspension. Thus the plastic viscosity reflects the extent of disaggregation of the clay whereas the apparent viscosity also takes into account the electrochemical state of the suspension.

Filtrate losses were measured by recording the total volume of fluid leaving the clay suspension whilst it was held at a pressure of 100 lbs/in² for 30 minutes.

Table 5 gives the viscosities and filtrate losses shown

by 5% suspensions of the sodium carbonate treated clays in water. No attempt was made to prepare suspensions with concentrations corresponding to either the API or OCMA specifications as it was considered more instructive to compare the results for the present samples with those given by the commercial samples under the same preparation conditions. The commercial montmorillonites give apparent viscosities of between 19 and 27 cp. Apparent viscosities of J-2-70 and U-34 approach this range and these two samples would easily meet the OCMA viscosity specification. Y-16-1 and, possibly, Y-3-1 might meet the OCMA viscosity specification. Y-61-1 and, possibly, Y-3-1 might also meet this specification at 5% sodium carbonate addition.

The API plastic viscosity specification is a more rigid specification aimed mainly at natural sodium-montmorillonites (bentonites). By appropriate chemical treatment (based essentially on the addition of sodium carbonate but also with extra reagents such as magnesium oxide), it is possible to ensure that a natural calcium-montmorillonite gives an apparent viscosity sufficient to meet the OCMA specification but, as can be seen for the Berkbent grades in Table 5, plastic viscosities then tend to be very low (0.5-2 cp compared with 13.5 cp for Wyoming Bentonite). All the present samples give plastic viscosities greater than those shown by the Berkbent grades but only J-2-70 would

Table 5. Viscosities and filtrate losses of the samples.

Sample	Sodium carbonate added(%)	plastic viscosity cp	apparent viscosity cp	filtrate loss ml/30min
G-68	4	3.5	7.5	20.2
	6	3.5	7.5	20.0
J-2-70	4	6.5	13.7	12.2
	5	7.5	17	10.8
U-34	3	8	15.2	17.6
Y-3-1	4	3.5	6.2	28.4
	5	2.5	9.7	20.4
Y-16-1	4	3.5	8.7	19.2
	5	4.	11.5	18.2
Berkbent DM	(3)	2	23	15.6
Berkbent CE	(4)	0.5	26.7	17.4
Wyoming Bentonite	—	13.5	25.5	7.8
Mediterranean Bentonite	(?4)	8	19.5	10.0

give a plastic viscosity approaching the API specification.

Filtrate loss from J-2-70 would meet API and OCMA specifications. Values shown by the remaining samples, although not unreasonably high for sodium carbonate exchanged montmorillonites, are outside both specifications.

Only J-2-70 therefore appears to meet completely the specifications for a drilling mud although, if the OCMA specifications are used, U-34, Y-16-1 and Y-3-1 might just meet the requirement for viscosity but not that for filtrate loss. Most of the sodium carbonate exchanged clays would be suitable for civil engineering applications as they show moderate apparent viscosities which could be improved with suitable chemical treatment. Filtrate losses also are not so critical for this application so the values shown by the present samples would also be acceptable.

CONCLUSIONS

Preliminary mineralogical and technical data have been determined on fuller's earths occurring in three localities, Gampo, Ulsan and Yonil, in South-eastern Korea.

A dioctahedral montmorillonite, whose exchange sites are occupied mainly by divalent cations, comprises 45-95% of the samples. The most common accessory mineral is cristobalite, although substantial amounts of quartz, feldspar, clinoptilolite and mordenite occur. It is also possible that significant amounts of X-ray amorphous material are present in the samples.

Dispersion characteristics of the clays, as monitored by methylene blue exchange capacities and Atterberg liquid limits, vary between the three localities. Samples

from Gampo generally show the best dispersion behaviour (that of samples J-2-40 and J-2-70 being notable in this respect) and those from Yonil the worst. Generally, samples showing the best dispersion behaviour also gave the best response to sodium carbonate addition.

Three samples tested as possible binders for foundry moulding sands performed adequately, giving results that compared favourably with material being used for this purpose. These samples would probably also be suitable as binders for iron ore pelletizing.

Only sample J-2-70 meets the API specification for drilling muds but a number of other samples would probably meet the less rigid OCMA specifications and most would be suitable for civil engineering applications.

Detailed mineralogical and chemical analysis of these samples is currently in progress and this should lead to a better understanding of the relationship between composition and technical performance.

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三紀層中에서 産出되는 酸性白土에 關한 鑛物學的 組成 및 物理化學的 性質에 關하여 문 회 수 · D. J. Morgan

慶尙道 地域의 三紀層中에 胚胎되어진 酸性白土는 主로 Ca-몽모리로나이트로 구성되며 이의 組成比는 95%까지에 이른다. 이에 수반되는 鑛物은 크리스토파라이트, 石英, 長石, 三井石鑛物 및 非結晶質이 있다. 示差熱分析, 적외선 및 전자현미경에 의한 이들의 기본적인 特性을 기재하였고 物理的性質을 涉性限界 및 양이온교환능을 측정기재하였다. 이들 資源의 이용가능한 용도범위를 고찰하였다.