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ELECTRON MICROSCOPY OF "IGUMALE" SHALE

O. AGBEDE AND P. SMART

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ABSTRACT

Igumale shale and its inclusion were analyzed using scanning electron microscopy (SEM) with its accessory, energy dispersive X-ray (EDX) system. The samples were also subjected to transmission electron microscopy (TEM) while subsidiary chemical analyses were made for allophane test. X-ray diffraction (XRD) and X-ray fluorescence (XRF) tests were conducted on the samples to complement the findings of the electron microscopy. The shale was found to have a general open structure with a crinkled lettuce effect, which suggests the appearance of montmorillonitic or mixed-layer clay. The inclusion was identified to be gypsum. It is concluded that the underlying shale was responsible for cracks on the floors and walls of buildings in the study area. The results also explain the very considerable broadening of peak in the X-ray diffraction pattern.

KEYWORDS: Microscopy, X-ray, Shale, Analysis, Diffraction.

INTRODUCTION

Igumale town is in Benue State, Nigeria. It is bounded by latitudes 6°30' - 7°N and longitudes 7°30' - 8°E and located within the equatorial climate region and at a height of 300 m above sea level. The mean maximum temperature of the region is between 26.7 - 28.9°C. Daily mean temperature is at its peak in the months of March and April while the minimum temperature occurs in the months of December and January. The mean minimum temperature is between 18.3 – 21.1 °C (Du Preez and Barber, 1965).

Igumale has high humidity and heavy rainfall. The highest relative humidity of 80 – 90 % is recorded in August during the moist south westerlies while the lowest relative humidity 60 – 70 % is recorded between November and March during the dry easterlies. The annual rainfall in this area is between 1016 - 1254 mm. The most prevalent wind directions during the year are south, south-west and west with frequencies of 20 % and 40 %. (Du Preez and Barber, 1965).

Reconnaissance survey of Igumale town showed that many of the buildings, whether traditional or modern, have developed cracks on their walls and floors. These cracks ranged in size from a few millimetres to about 10 mm wide.

The problem of cracks on buildings, which originate from the foundation, has been a major concern to the foundation engineer. X-ray diffraction analysis carried out on the fraction of the soil passing 2 μm confirmed the presence in the soil of mixed layer clays of mainly illite/smectite (Agbede and Smart, 2004a).

Barden (1972) studied the structures of a number of clay soils to establish the characteristics common to a given class, with the general aim of linking their engineering behaviour to the processes of soil formation. The study identified the chemical environment during sedimentation as the most unpredictable influence on the soil structure. It revealed that normal marine clays consistently result in a flocculated structure while estuarine and lacustrine deposits ranged from flocculated to dispersed structure. A study of the structure of artificially sedimented clays by Sides and Barden (1971) indicated that the activity of the clay, whether kaolinite, illite or montmorillonite had an important influence on the resulting structure.

Barden (1972) also presented three examples of problem soil namely, the residual soil from Malaya, the highly compressible fibrous peat from Canada and the expansive clays and clay shale from South Africa.

The structure of South East Asian marine clays from Bangkok, Singapore and Hongkong, was studied by Barden et al. (1974) using the scanning electron microscope. The micrographs revealed the deposits' flocculated open structure and compatibility both with marine environment and known geotechnical properties like sensitivity, compressibility and permeability.

An extensive study of the mineralogical composition of expansive clays was made by Ravina (1973) using the scanning electron microscope. The study showed that the non-swelling clays appeared as flat, relatively thick plates while montmorillonites had a crinkly, ridged, honeycomb-like texture.

Ogunsanwo (1985) employing the scanning electron microscope (SEM) confirmed that the microfabric of a soil derived from a fine-grained amphibolite was lateritic clay. The latter was cemented by the sesquioxides present and that its aggregation has imparted in the laterite clay a permeability value higher than expected for non-lateritic clays. Awoleye (1991) determined the mineralogy of Hong Kong granite using the scanning electron microscope and found that the main clay minerals in the deeper soils were rolled-up tubes of halloysite while very few plates of muscovite were also identified.

Smart and Tovey (1982) presented an atlas of soil micrographs of soils and sediments. Welton (1984) presented an atlas which included both SEM micrographs and EDX (energy dispersive) spectra for

I. O. Agbede, Department of Civil Engineering, University of Agriculture, Makurdi, Nigeria.
P. Smart, Department of Civil Engineering, The University of Glasgow, Scotland.

most of the common minerals found in sedimentary rocks. He concluded that the most reliable way to identify minerals through the SEM is to compare their characteristic morphologies (as shown in the atlas) with the elemental compositions determined by the EDX system.

The main techniques for examining microstructure are X-ray diffraction, the polarizing microscope and the electron microscope. The study of microstructure has been accepted as necessary for a basic understanding of the geotechnical properties of clay (Barden et. al, 1974). The objective of this paper is to use the scanning electron microscopy to study the behaviour of Igumale shale.

MATERIALS AND METHODS

Shale samples and their inclusions were collected from Igumale. The specimens were air-dried, treated with chisel and hammer, trimmed to size and mounted on an aluminium stub with carbon glue. The latter would improve the electrical contact between the specimen and the stub before being examined with the scanning electron microscope. The scanning electron microscope used in this study was a Leica Cambridge S360, version V03.03, 1992 model, which was available in the Department of Geology and Applied Geology, University of Glasgow. The entire process is referred to as "mounting". The specimen surface was vacuum coated with a layer of gold at 15 mA and 0.085 torr for about five minutes. This was to render the surface electrically conducting to prevent it charging and hence distorting the view under the electron microscope. Contamination of the coated specimens was avoided both by keeping them in a sealed plastic box and by minimizing direct handling. The EDX system used was equipped with a pre-programmed marker system to aid in the rapid identification of the displayed peaks.

Qualitative mineralogical analysis by X-ray diffraction (XRD) was employed to confirm the presence of megascopic minerals like clay minerals and quartz. X-ray diffraction was performed with a Phillips PW 1050/35, kW diffractometer using CoK_{α} radiation and Fe filtration. The instrument was equipped with facilities for varying the scanning voltage and current. Both the chart speed and slits could be adjusted. In order to contain the peak within the chart, the scale was adjusted to 1×10^{3} cps. Specimens were prepared using the standard routine method in the University of Glasgow. A small representative sample of the material was ground to a fine paste with acetone. A thin slurry was prepared and smeared onto a semi-porous ceramic slide and allowed to dry at room temperature. The specimen was then placed in the sample chamber for scanning. The minerals were identified by their characteristic basal spacing and also by comparing the diffraction traces to standard traces for minerals in the Department of Geology and Applied Geology, University of Glasgow.

A quick test was used to determine whether allophane was present in the soils from the study area. The allophane was detected by treating the soil with sodium fluoride solution. The fluoride ions complex ('mobile' or reactive alumina) displaces its hydroxyl groups, so that the pH of the suspension rises as shown in the following equation.

$$Al(OH)_3 + 6F^{=} \rightarrow Al(F)_6^{3-} + 3OH^{-}$$

Approximately 1N solution of Sodium Fluoride (NaF) was made up by preparing a saturated solution and drawing off 50 ml of the supernatant. One gm of air-dried soil was placed in a 100 ml beaker. The pH electrode was placed in readiness above the soil and the 50 ml NaF solution was added. The pH reading was taken immediately. Further pH readings were taken at 30 seconds intervals, with stirring at the time of measurement. Continuous stirring was achieved using a magnetic stirrer. As the rate of change slowed down, the intervals were decreased to 1 minute. The pH was observed against time for 10 minutes.

As a first indication of allophane content, the pH after 10 minutes was considered and the following interpretation made: The allophane content is negligible if pH < 9.0, low if pH is 9.0 to 9.8, medium if pH is between 9.8 and 10.5, and high if pH > 10.5. The rate of fall of pH also gives an indication of the amount of allophane present (Flowers, 1995 - personal communication).

Further investigation, using the transmission electron microscope (TEM) was carried out in the Deparment of Physiology, University of Glasgow, to shed more light on the status of the amorphous material. The samples selected were S1P6, S2P6 and S3P6, which all belong to the same profile as S2P6 which had responded most positively to the allophane test. Though it was desirable to study many samples, only these three samples were available at this stage of the study.

Exactly 0.100 g of clay fraction (< 2 μm) of each sample was ultrasonically dispersed for 5 minutes in 50 ml of distilled water. With the aid of a pipette, a drop of suspension was carefully placed onto Formvar film which was supported by a copper grid ready for observation under the Zeiss electron microscope. Each specimen was examined at different magnifications between 7,000x and 85,000x. Observations were made at every stage and photographs taken where necessary.

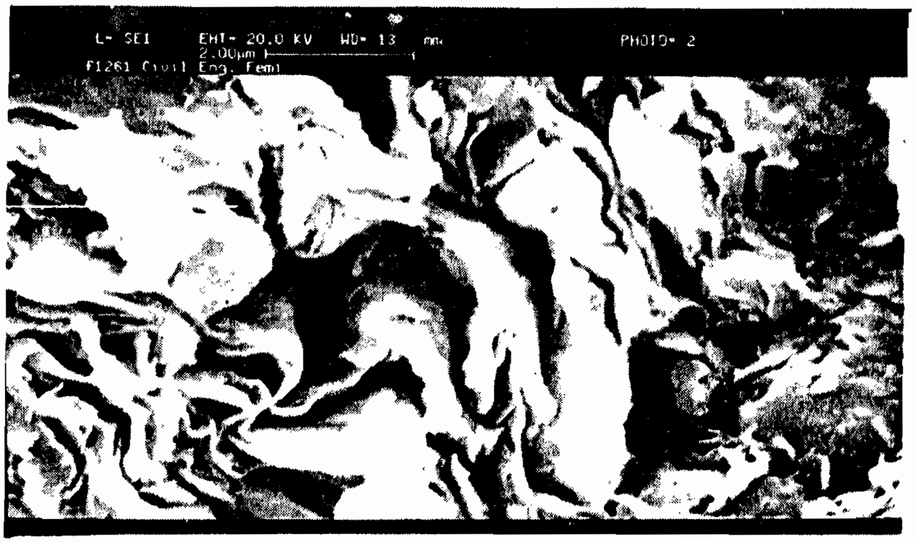
RESULTS AND DISCUSSIONS

Table 1 summarizes the X-ray diffraction analyses of shale and its inclusions. The table showed that shale was predominantly made of quartz and clay minerals (kaolinite and mixed layer illite/smectite) while the inclusion was essentially gypsum. The mineral composition was analyzed by Agbede and Smart (2004b) using the method of Schultz (1964). Thus, about two thirds of the clay comprises clay minerals

Table 1: Summary of X-ray analyses on shale and inclusion

Sample	Minerals			
	Quartz	Clay minerals	K feldspar	Gypsum
Shale	20.0	63.0	6.5	3.5
Shale inclusion	-	-	-	100.0

Figure 1 shows the scanning electron micrograph of the shale with a general open structure. It is possible that the clay was more open in its natural state but has closed up during the air drying process of sample preparation (Barden, 1972). The crinkled lettuce leaf effect seems to be characteristic of the appearance of montmorillonitic and mixed-layer clays under the scanning electron microscope. This micrograph is similar to that presented by Barden (1972) for an expansive clay from South Africa.



7.300X

Fig. 1: Scanning electron micrograph of shale. It shows general open structure of shale. The crinkled lettuce appearance is characteristics of montmorillonitic or mixed-layer clay. Bar scale is 2µ.

Figure 2 shows an EDX analysis of the shale. The major elements contained in it are Si, Al, K, Ca, Mg, and Fe The percentages of the elements compare well with those presented by Welton (1984) for illite-smectite.

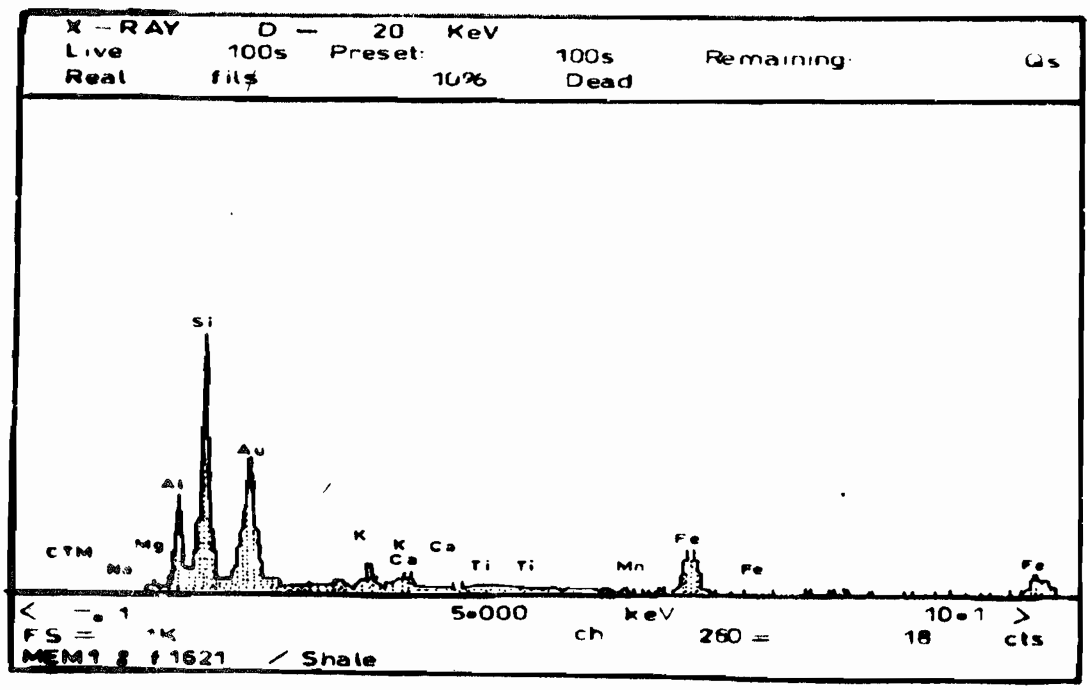
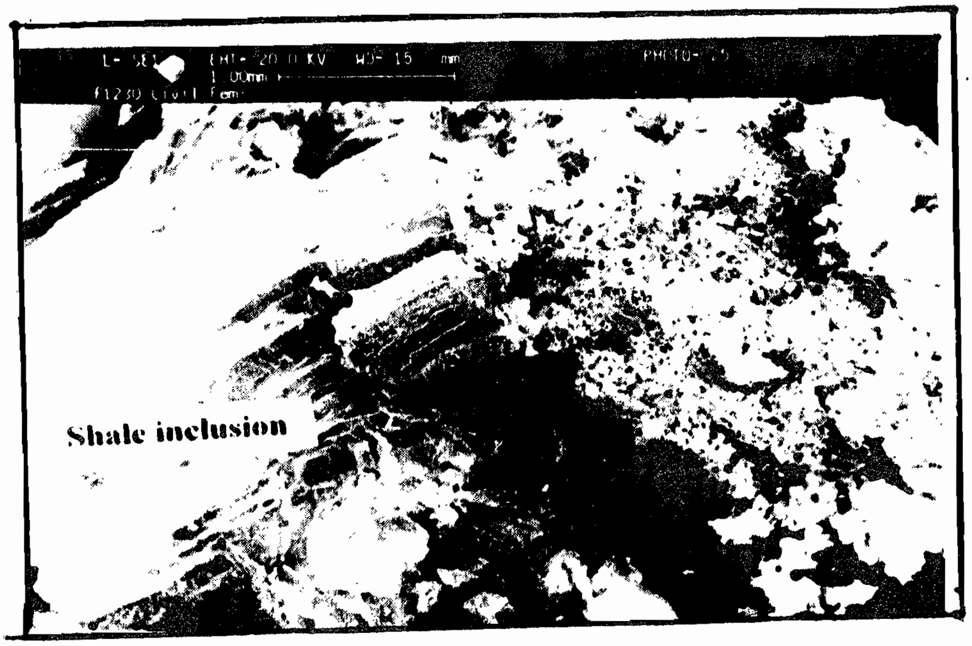


Fig. 2 EDX Spectrum for Shale

The good comparison suggests that Igumale shale is a mixed-layer clay thus supporting the results of the X-ray diffraction. This suggests that the underlying shale could undergo expansion and shrinkage in the rainy and dry seasons respectively. Such foundation movement will normally cause damage to all structural elements supported including floors and both leaves of cavity wall (BRE Digest 361, 1991).

Table 2 summarizes the geochemical composition of shale and its inclusion. Figure 3 shows the general view of the inclusion under the scanning electron microscope. The crystallized form of this material can be readily observed. Figure 3 compares favourably with that presented by Welton (1984) for gypsum coated with palladium. The result of the EDX analysis, therefore, complements the findings of the X-ray diffraction analysis. Thus, inclusion in the shale is essentially gypsum. The presence of sulphur, which could not be ascertained by the X-ray fluorescence (XRF) analysis has been confirmed by the EDX analysis at a single point.



7,300X

Fig. 3: Scanning electron micrograph of inclusion in the shale.

Table 2: Geochemical composition of shale and the inclusion

Sample	SiO_2	Al_2O_3	Fe_2O_3[1]	TiO_2	MnO	MgO	CaO	Na_2O	K_2O	P_2O_5	L.O.I[2]	Total
Shale	55.13	20.32	7.64	0.86	0.02	1.52	1.18	0.00	1.99	0.20	11 14	100.00
Inclusion	7 54	2.71	10 79	0.13	0.00	0.39	22.78	0 00	1 07	0.15	13.31	58.87

1 Total Fe as Fe_2O_3
2 Loss of ignition at 950 °C

Gypsum reacts chemically with free lime in cement to destroy the cementing properties of concrete and this will probably call for the use of sulphate resisting cement (Institution of Civil Engineers, 1976). Construction work at Igumale employs ordinary Portland cement. Thus the presence of gypsum in the foundation soil could probably lead to a deterioration of the concrete foundation over a long period of time. The engineering properties of gypsum/anhydrite change as a consequence of groundwater, pressure and heat. Gypsum and anhydrite may experience dissolution in the near surface zone and along the discontinuities, creating karst terrains to depths related to present and/or past groundwater levels (Yitmaz, 2001) This could lead to some noticeable settlement of the soil and subsequently any structure constructed on it Agbede and Smart (2004b) showed that the gypsum content increased with depth, which implied that all the shale within the foundation had gypsiferous inclusions.

Ground water table fluctuates in Igumale with the seasons. The hydration of the anhydrite (gypsum) may lead to some swelling. Dissolution of gypsum near surface could be explained by the near absence of gypsum in the soil profile at the surface as reported in Agbede and Smart (2004b). These are probably responsible for the unusual swelling and shrinkage of the foundation soil which could lead to the formation of cracks. Cracks, which show signs of stress, may also emanate from the interaction between the soil and the structure. The structure itself, when properly examined may throw some light on soil behaviour and subsequent interaction with the superstructure. The soil structure is the 'window' of the past and the 'crystal ball' for the prediction of future engineering performance (Smith, 1985)

Table 3 summarizes the results of the allophane test and indicate that the allophane content is negligible to low. The highest pH value of 9.23 suggests that amorphous materials are probably present (Flowers, 1995 - personal communication).

Table 3: pH of soil samples in allophane test.

Time	pH of sample							
(min.)	S2P5	S3P5	S4P5	S5P5	S1P6	S1CS	S2CS	S3CS
0.00	8.74	8.88	8.68	8.76	8.89	8.70	8.77	8.89
0.50	8.89	8.86	8.89	8.88	8.95	8.89	8.93	8.85
1.00	8.92	8.88	8.89	8.88	8.99	8.93	8.98	8.88
2.00	8.98	8.90	8.90	8.89	9.06	9.00	9.04	8.92
3.00	9.02	8.91	8.95	8.91	9.09	9.02	9.07	8.94
4.00	9.04	8.93	8.95	8.91	9.12	9.02	9.10	8.96
5.00	9.06	8.94	8.97	8.92	9.15	9.04	9.12	8.98
6.00	9.08	8.96	8.99	8..93	9.17	9.06	9.14	9.00
7.00	9.10	8.97	9.00	8.94	9.18	9.08	9.15	9.00
8.00	9.11	8.98	9.01	8.94	9.20	9.09	9.17	9.02
9.00	9.12	8.99	9.02	8.95	9.21	9.09	9.18	9.03
10.00	9.12	9.00	9.03	8.95	9.23	9.11	9.19	9.04

Figures 4 and 5 were chosen to illustrate the main types of particles observed during the transmission electron microscopy.

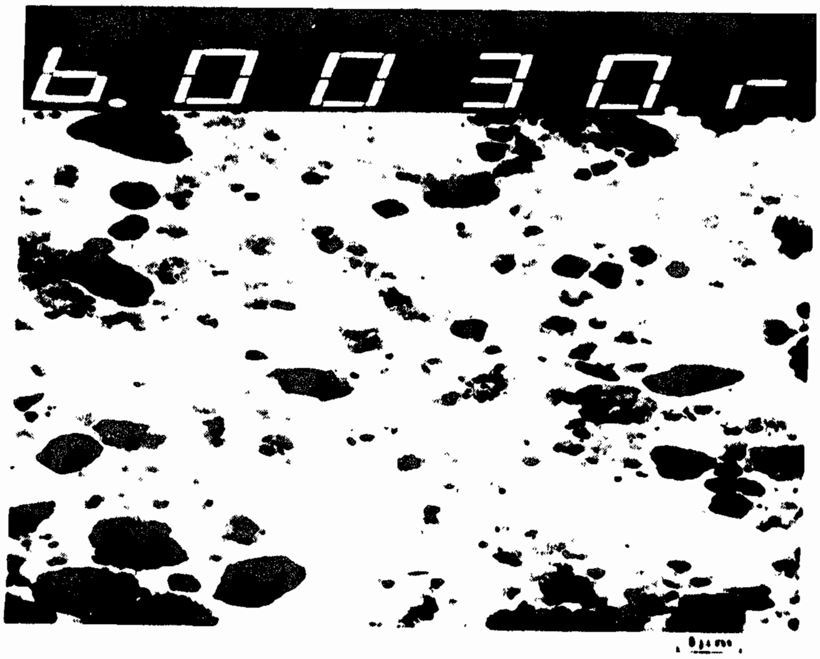
(1) Nearly hexagonal plates could be observed in all the three specimens. These particles are about 1 μm in diameter, on the average. They are almost spherical subrounded and correspond to code 21 according to the chart in Soil Survey of England and Wales (SSEW). The particles often have slightly fuzzy edges and are electron dense. This suggests the presence of kaolinite (Avery and Bullock, 1977).

(2) Finer plates than reported in 1 above were also present in the specimens but they were lighter than the hexagonal plates. A large population (40% by volume) of electron transparent thin plates, (0.02 μm in diameter) were observed. The larger plates in this population were about 1 μm diameter.

(3) Thin and sharp-cornered plates.

(4) A negligible quantity of an atypical particle which looks somewhat like halloysite, but is not really tube shaped.

(5) About 1 % of finely-divided electron dense particles (0.005 μm in diameter) is scattered among the above. These are probably iron oxides and their hydroxides or other unidentified compounds.



20,000X

Fig. 4: Transmission electron micrograph of dispersed particles from clay fraction of S3P6. This is a general view; the large particles seen here are atypical. The large plate at the top left is atypical.

85,000X

Fig. 5: Transmission electron micrograph of dispersed particles from the clay fraction of S1P6. The magnification shows plates down to 0.02μ diameter at the mid top. It also shows atypical amounts; a suspected halloysite tube; finely divided 'iron oxide' (just below the tube); and a group of plates possibly containing amorphous material (top left).

About half of the clay fraction, probably kaolinite, consists of electron-dense particles measuring about 1 μm diameter. Most of the remainder of the clay fraction consists of thin plates of montmorillonite or mixed-layer clay minerals which measure between 1 and 0.02 μm diameter, and occasionally 0.002 μm thick. These plates probably stack randomly in the soil. There probably was some amount of amorphous material present and a very slight amount of very finely-divided electron-dense material (probably iron oxide/hydroxide) and other unidentified compounds.

The peak broadening observed in X-ray diffraction traces is explicable as follows: if it is taken that the thickness of the particles in 2 above is 0.002 μm, the thinness of the particles seen in the TEM will cause the corresponding peaks in the XRD to become broader. Consider an extreme case using cobalt radiation, the following calculation gives the width at half height, B, based on Scherrer's equation (Brown and Brindley, 1980).

$B = K\lambda / L \cos\theta$

where K = constant = 0.91

λ = wavelength = 1.79 Å (for cobalt)

L = crystal thickness = 0.002 μm = 20 Å

$2\theta = 6.05^{\circ}$ for d = 17 Å for smectite.

$$\text{Then } B = \frac{0.91 \times 1.79}{20 \times 0.9986} = 0.082 \text{ (radians } 2\theta) = 4.7^{\circ}\ (2\theta)$$

This is the width at half height. Half of this is 2.35° which implies that the lower and upper limits at half line are: $6^{\circ} \pm 2.35^{\circ} = 3.65^{\circ}, 8.35^{\circ}$.

The corresponding d-spacings are 12.3 Å and 28.4 Å, respectively. The actual broadening will be less than this, because the majority of the particles will be more than 20 Å in thickness.

CONCLUSIONS

The following points summarize the findings in this study.

1. Transmission electron microscopy (TEM) revealed that more than half of the clay fraction in Igumale shale consists of electron-dense particles about 1 μm diameter, probably kaolinite.
2. Most of the remainder of the particles consists of thin plates between (1 - 0.02 μm in diameter) and occasionally about 0.002 μm thick, suggestive of montmorillonite or mixed-layer clay minerals.
3. There was a very slight amount of finely-divided electron-dense material present in the soil, tentatively identified as iron oxide/hydroxide.
4. The scanning electron micrograph of shale showed a general open structure with a crinkled lettuce effect, which suggests the appearance of montmorillonitic or mixed layer clay.
5. The inclusion in the shale is essentially gypsum ($CaSO_4.2H_2O$). This suggests that heave and other engineering problems associated with gypsum cannot be ruled out in Igumale. (Ruwaih, 1984).
6. The allophane test and the Transmission Electron Microscopy (TEM) showed that there was no significant quantity of amorphous materials in the soil samples and that the clay particles were extremely small. When pieced together, the results explained the very considerable broadening of peaks, which had been troublesome in the X-ray diffraction analyses.

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