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Use of different analytical techniques to characterize Odukpani clays in Nigeria

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Abstract

A combination of analytical techniques such as atomic absorption spectroscopy (AAS), X-ray diffraction (XRD), infra red spectral (IR) analysis, energy dispersive analysis of X-ray (EDAX), differential thermal analysis (DTA) and thermogravimetric analysis (TGA) were employed to characterize clays from Odukpani, Cross River State, Nigeria. The samples were also subjected to physico-chemical tests. The results obtained show that the silicon content was the highest and that of manganese the lowest. The silica (SiO_2) content was found to be 47.52% followed by alumina (Al_2O_3) 34.01%, iron oxide (Fe_2O_3) 2.38% and trace amounts of other elements such as Ca, Mg, Na and Mn (0.038, 0.188, 1.78 and 0.00%, respectively). The X-ray diffraction studies showed that the clay deposits consist predominantly of kaolinite and quartz with trace amounts of illites and biotite minerals. The infra red spectral analysis between 400 and 3700 cm^{-1} revealed interesting wave numbers and absorption bands. EDAX analysis of the clay samples reveals that Al and Si, were in the ratio of 1:2 whereas other elements like K, Ti and Fe were below detection limits. The thermal analysis revealed thermograms that provided valuable information on the purity of the starting materials and the mode of the reactions of the various clay samples.

Keywords: Odukpani clays, atomic absorption spectroscopy, infra-red spectral and energy dispersive analysisof X-ray, differential thermal and thermogravimetric analysis.

INTRODUCTION

Kaolinite structural layers have been investigated mostly from crystallographic studies, X-ray analysis, thermal analysis and infra red spectral analysis (Szabo et al., 1974; Kotoky et al., 2006) and reported to compose of mixture of minerals. Thus, their thermal analysis may be difficult if the reactions of different minerals overlap each other and if the reactions typical of a single mineral in the mixture are changed by solid state reactions (Muller-Vonmose and Muller, 1974). It is therefore, necessary to supplement DTA and TGA used in studying the reactions of clay with other techniques such as IR, XRD and EGA (Smith, 1972; Reynolds and Walker, 1993).

Nurchol et al. (1997) investigated the mineralogical and chemical properties of manganese nodules using XRD and AAS in Java clay soils from different materials. The results obtained from the investigation revealed that the predominant soil clay materials in the samples were kaolinites. Similar findings have also been reported by Kotoky et al. (2006). Studies on kaolinite clay, especially phase changes as a result of heat treatment, are well understood and documented. Most of the research efforts in this area are directed towards the formation of the meta kaolinite (between 600 - 900 °C), the spinel (900 - 1100 °C) and mullet (1200 - 1400 °C) and their structures (Szabo et al., 1974).

Clays are of immersed geological, industrial and agricultural importance (Murray, 1963; Ekosse, 1994). The mineral assemblage of clays helps in understanding and management of erosion and flood related problems (Kotoky et al., 2006), and in the construction of tunnels, road cuts, fills and dams (Oden et al., 2001). Depending on the physical and chemical characteristics, clays may find application in a number of industries such as plastics, paint, ceramics, ink, catalysts, pharmaceutical and fibre glass among others (Worall, 1975; Murray, 1980; Emufu-

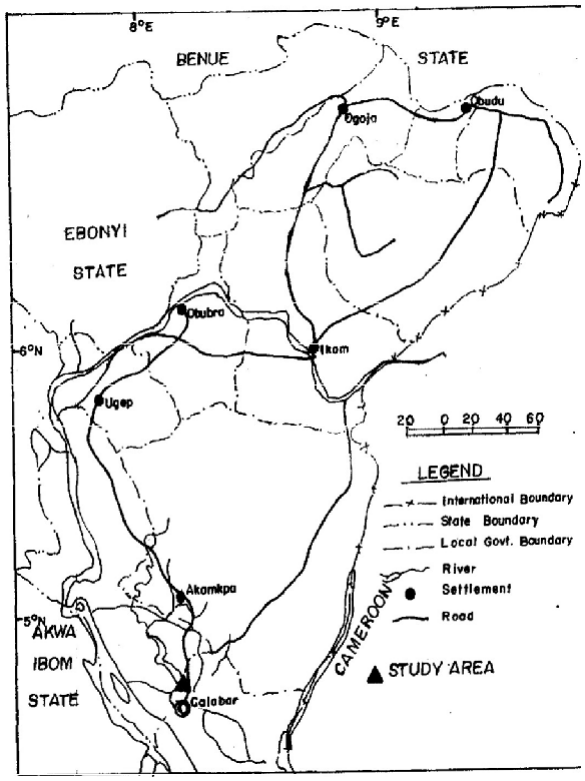

Figure 1. Generalized map of Cross River state, Nigeriashowing study area (Ekwueme et al*.,* 1995).

rieta et al., 1992).

The physical, chemical and mineralogical characteristics of Odukpani clay deposits and their brick forming pro-perties have recently been reported (Attah et al*.,* 2001; Oden et al*.,* 2001). The results obtained for these depo-sits and those from Calabar, Cross River state, Nigeria revealed that their properties are related to several appli-cations (Attah et al*.,* 2001). Thus, the present study is designed to use different analytical techniques to charac-terize Odukpani clays with the view to assessing their che-mical composition and relating them to their suitability foruse in the paint, bricks, ceramics, paper and refractory in-dustries.

MATERIALS AND METHODS

Materials

Fresh clay samples were collected from 10 different locations within the Ikot Omin clay deposits at Odukpani, south eastern Nigeria (Figure 1). The samples were collected along a pit sank in the clay deposit and at a depth intervals of 10 cm with the aid of a shovel and digger and hand picked to minimize the possibility of contamination. About 2.0 kg of each sample was collected and placed in small polythene bags. 1.0 kg of each sample was dried, pulverized and sieved before analysis.

Methods

A sub-sample of 1.0 g from each of the dried samples was digested in a sterilized polypropylene bottle using a mixture of concentrated HCl and HF acids (Analar grade) in a ratio of 7:1, respectively. The mixture was heated in a thermostated water bath at a temperature range of 50 - 60 $^{\circ}$C for 2 h. The resulting milky solution was cooled in tightly covered bottles under tap water and 10 ml of saturated boric acid (Analar grade) solution added. The sample solution was well covered and returned to the water bath that was preheated to about 70 $^{\circ}$C. Heating continued until clear sample solution was obtained. The solution was finally made up to 250 ml with distilled water in a plastic volumetric flask. The standard solutions and aliquots of the diluted clear digest were used for elemental analysis. Standard curves were used to establish the relationship between intensity and concentration (Mann et al., 1974; Underwood and Day, 1988; Emufurieta et al., 1992). Another set of sample solutions were prepared with a dilution factor of 100. Some of the samples were duplicated and analysed to check for precision and accuracy.

The recommended standard methods of A.O.A.C (1990) were used for the elemental quantitative analysis. Sodium and potassium levels were determined using flame analyser Jenway PFP-f and an atomic absorption spectrophotometer model 1233 with air-acetylene flame was used to analyse iron, manganese, magnesium, calcium, silicon, aluminium, titanium and phosphorus.

A Mettler-Toledo TG850 thermo-analyser was used to record DTA and TGA curves simultaneously. The thermo-analytical investigation was carried out in a high purity dried nitrogen gas with a flow rate of 5.0 L/h under continuous evacuation at 1.33 x 10^{-6} mbar between 0 - 1000 $^{\circ}$C. The heating rate was 10 $^{\circ}$C/min. Al_2O_3 was used as reference material. The fourier transform infra red spectra of the samples were recorded between 400 and 4000 cm^{-1} on IF566V/S beam spectrometer. Measurements were carried out at room temperature by diffused reflectance method (mixture of the sample with KBr in a ratio of approximately 1:20). The KBr window using Mir infra-red source operated at 5 mbar vacuum at room temperature with a voltage of 220 V x 10 A single phase and a frequency of 50 Hz was used.

The X-ray studies were performed with a Rich-Siefert model 3000-TT X-ray powder diffractometer. About 0.5 g of the dry milled clay samples was placed in an aluminium holder and analysed with PXRD. Then analysis was carried out using CuKα radiation at 40 kV and 30 MA and at a scan rate of 2 $^{\circ}$ per min. The interpretation of the diffractograms obtained for each sample was done by comparing the peaks obtained with those of standard minerals established by Brown (1965) and joint committee on powder diffractogram standards (1980).

The energy dispersive analysis of X-ray (EDAX) was carried out on the samples using a scanning electron microscope (SEM) fitted with a link 1515 spectrometer. For elemental analysis, the sample film was placed firmly in a waxed and gold coated plate. The EDAX patterns were obtained with the help of a computer attached to the instrument.

For each experimental condition, 2 to 3 measurements were performed to estimate the repeatability. The repeatability was quite good and the data presented represent the results obtained beyond the experimental error.

RESULTS AND DISCUSSION

Results

Table 1 shows the elemental composition of Odukpani clay samples obtained using AAS and flame photometry. It is observed that aluminium and silicon are the predominant elements in the clay samples while calcium, sodium, phosphorus, magnesium and manganese are in minor quantities. From the EDAX pattern of the clay samples

Table 1. Elemental composition of Odukpani clay samples (elements, %).

Samples	Al	Si	Fe	Ti	K	Ca	Na	P	Mg	Mn
Sw_1	31.12	55.35	10.41	2.00	1.12	0.000	0.60	0.0003	0.0006	0.0003
Sw_2	32.35	56.42	9.12	0.11	2.21	0.0045	0.20	0.0003	0.1402	0.0004
Sw_3	30.14	56.43	11.11	0.11	1.26	0.0046	1.60	0.0004	0.1281	0.0005
Sw_4	39.11	61.11	8.10	0.42	3.05	0.0035	1.00	0.0002	0.1265	0.0002
Sw_5	30.54	60.26	4.94	1.21	2.53	0.0027	0.60	0.0004	0.1129	0.0003
Sw_6	27.48	57.59	9.31	3.09	2.11	0.0028	0.80	0.1303	0.1205	0.0003
Sw_7	27.06	58.24	7.76	3.84	2.75	0.0039	0.60	0.1204	0.1254	0.0012
Sw_8	28.29	60.22	7.0	2.38	2.21	0.0029	0.80	0.1001	0.1254	0.0004
Sw_9	29.16	59.22	6.08	3.09	3.09	0.0030	1.00	0.1118	0.1260	0.0005
Sw_{10}	28.17	58.37	7.35	3.36	2.85	0.0036	1.50	0.1213	0.1233	0.0004
Ave	29.34	58.32	8.12	1.95	2.32	0.0032	0.90	0.0586	0.1229	0.0011

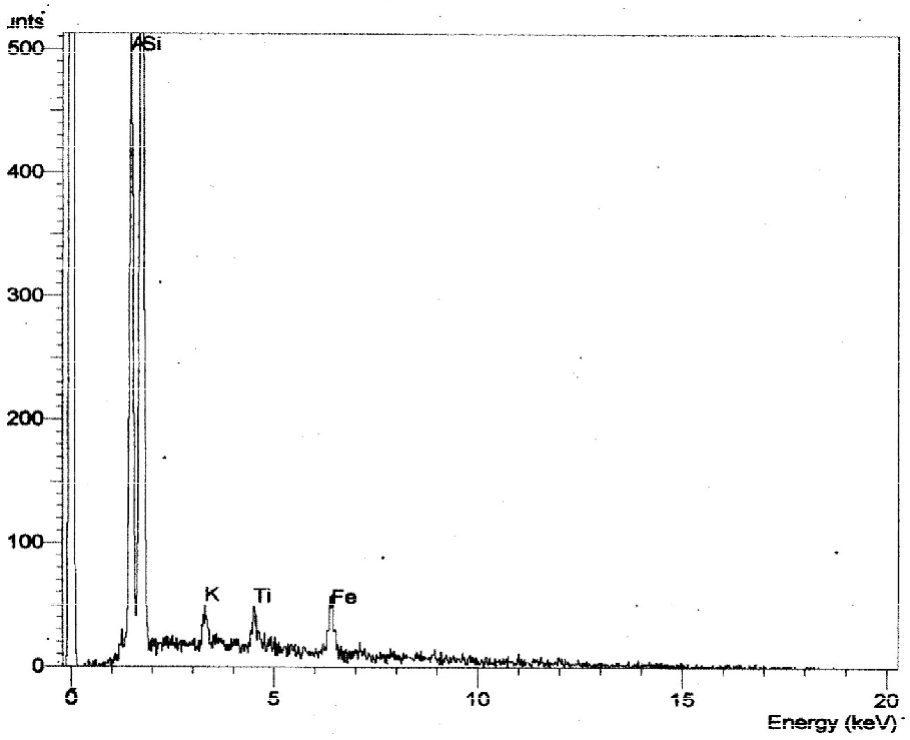

Figure 2. EDAX pattern of the clay samples.

(Figure 2), it is observed that aluminium and silicon is in the ratio of 1:2 and the particle size observed to be 0.046 mm. The chemical composition of the clay samples, shown in Table 2, reveals that the oxides of P_2O_5, MnO, TiO_2 and K_2O were in very low concentration in all the clay samples studied.

The results of the IR spectra obtained from the samples under study (Figure 3) reveal spectra with bands between 400 and 1200 cm^{-1} and an OH absorption band between 3400 and 3700 cm^{-1} (Szabo et al., 1974).

From the X-ray powder diffractometer results, shown in Table 3, it is observed that Odukpani clay samples is composed of different types of minerals with kaolinite as the predominant mineral with minor amount of illites and quartz.

The results of thermo analytical experiments of Odukpani clay in nitrogen atmospheres are enumerated in Table 4 and the DTA and TGA thermogram patterns of the clay samples at a temperature range of 0 - 1000 $^{\circ}C$ shown in Figure 4.

DISCUSSION

The results of the chemical analysis are similar to those

Table 2. Chemical composition of clay samples from Odukpani, south eastern Nigeria.

Oxides (%)	SW_1	SW_2	SW_3	SW_4	SW_5	SW_6	SW_7	SW_8	SW_9	SW_{10}
SiO_2	49.51	48.17	46.83	48.20	46.83	46.79	46.83	46.97	46.96	47.53
Al_2O_3	35.37	34.59	34.02	34.02	32.32	35.22	32.32	34.81	33.52	34.62
TiO_2	0.001	0.00	0.002	0.001	0.00	0.002	0.00	0.00	0.001	0.002
Fe_2O_4	2.62	2.47	2.40	2.33	2.16	2.17	2.19	2.19	2.22	2.15
MgO	0.01	0.23	0.21	0.21	0.19	0.20	0.21	0.21	0.21	0.20
MnO	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
CaO	0.00	0.00	0.06	0.06	0.05	0.05	0.04	0.04	0.04	0.04
Na_2O	1.62	0.54	1.32	2.69	1.62	2.93	1.62	1.18	2.18	2.16
K_2O	0.51	0.39	0.96	0.77	0.64	0.32	0.71	0.58	0.57	0.60
P_2O_5	0.01	0.01	0.02	0.02	0.31	0.15	0.61	0.50	0.52	0.52
Loss on ignition	12.50	13.00	12.00	12.00	12.50	12.60	12.60	12.60	12.00	12.00
Total	100.54	99.40	97.84	100.29	96.62	100.43	97.13	99.08	98.21	99.80

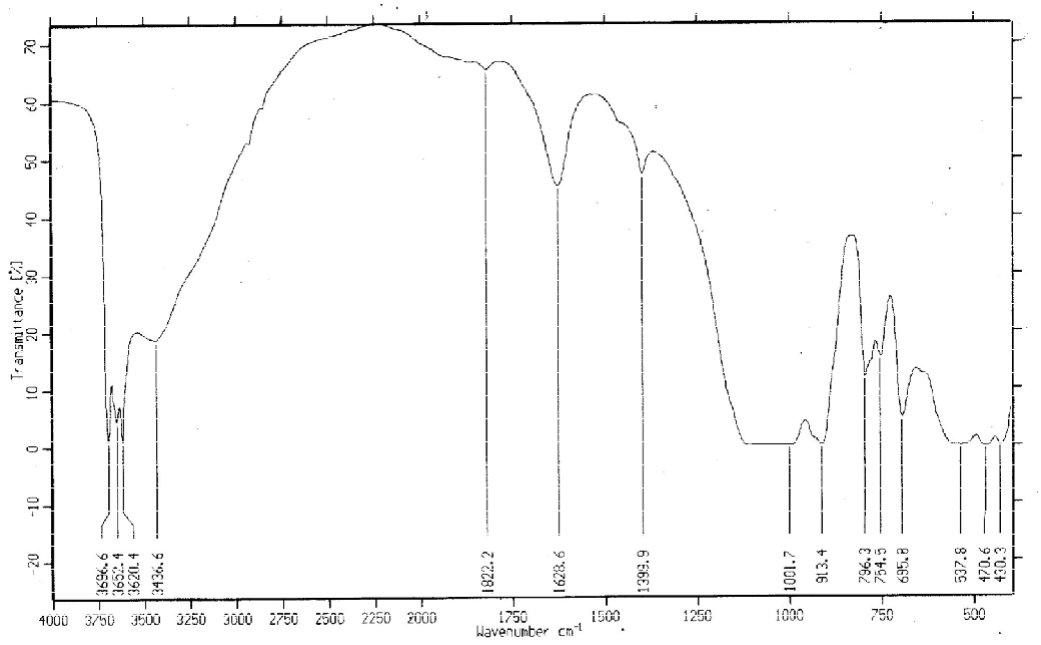

Figure 3. IR spectra of the clay samples.

Table 3. Average mineralogical composition (%) of the clay samples.

Minerals (%)	SW_1	SW_2	SW_3	SW_4	SW_5	SW_6	SW_7	SW_8	SW_9	SW_{10}	1	2	3	4
Kaolinite	88	86	86	89	84	83	86	89	94	96	91	96	85	85
Illites	8	6	4	6	7	7	6	7	4	5	3	3	15	3
Quartz	1	3	1	2	3	2	3	1	1	1	6	2	tr	4
Felspar	1	2	3	3	3	4	3	2	1	-	-	-	-	2
Others	2	3	5	-	3	6	2	1	-	-	-	-	-	8

1) Average mineralogical composition of Ibadan clays (Emufurieta, 1988).
2) Average mineralogical composition of Kaduna (Kankara) kaolin (Emufurieta, 1988).
3) Average mineralogical composition of the China clay (Huber, 1985).
4) Recommended value by NAFCON (1985 kaolin tender document).

Table 4. Thermoanlaytical DTA and TGA data for Odukpani clay samples.

S/N	ATM	Heating rate (^{o}C/min)	Max Temp (^{o}C)	Weight of Sample (mg)	Weight loss (%)	DTA			TGA	
						Peak Endo	Peak endo	Peak exo	Peak	
1	N_2	5 5	1000 900	27.52 3.7389	13.5862	530	620	900		480
2	N_2	5 5	1000 900	27.52 3.8389	13.6134	520	630	900	110	500
3	N_2	5 5	1000 900	28.30 3.6758	13.7128	540	620	90	105	490
4	N_2	5 5	1000 900	38.30 3.900	13.7920	540	635	900		570
5	N_2	5 5	1000 900	27.13 3.6710	13.7933				110	500
6	N_2	5 5	1000 900	28.00 3.1132	14.1245	540	620		900	540

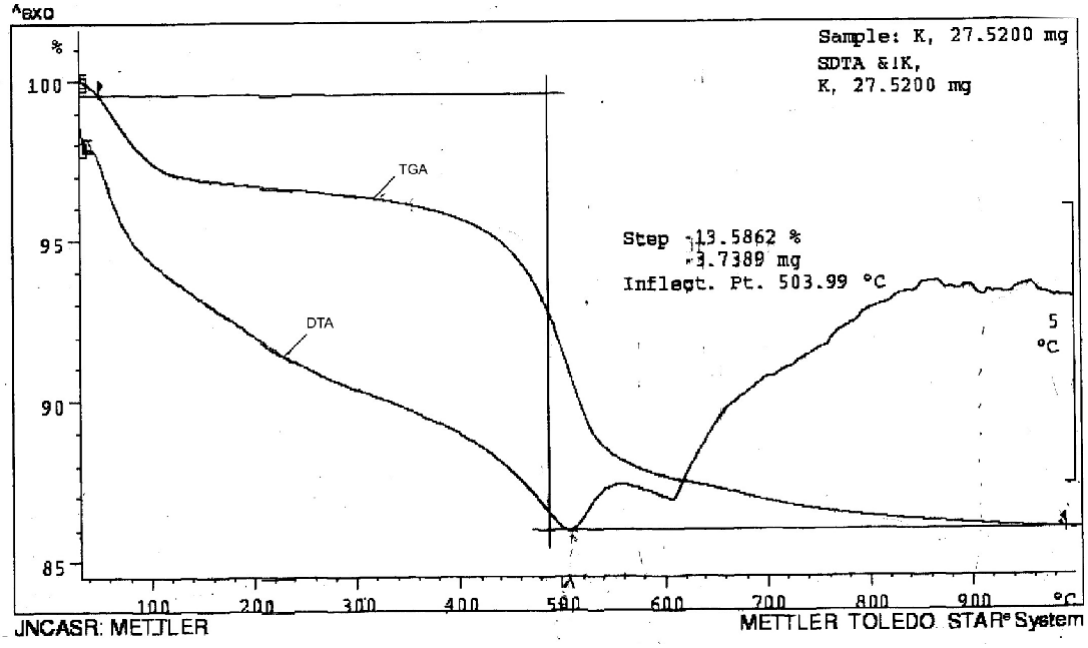

Figure 4. DTA and TGA thermogram patterns of the clay samples.

of previous workers (Oden et al., 2001). The observed large amount of silica, alumina and iron contents suggests that the clays could be used for a variety of purposes. It is observed from Table 2 that the dominant components of the clay samples (SiO_2, Al_2O_3 and H_2O) clearly defined them as hydrated alumino-silicate type. The average silica + alumina + water (SiO_2 + Al_2O_3 + H_2O) contents in the clay samples constitute about 88.76% (made up of 47.53% SiO_2, 34.08% Al_2O_3 and 7.20% H $_2$O). Potassium oxide (0.605%), iron III oxide (2.289%) and sodium oxide (1.786%) are among the major significant impurities found in the clay samples. The % of other oxides such as calcium oxide (0.038%), magnesium oxide (0.19%), manganese oxide (0.001%), phosphorus pentaoxide (0.266%) and titanium dioxide (0.001%) are comparatively lower than those of aluminium and silicon. A comparison of the total percentage of Al_2O_3, SiO_2 and H_2O in Odukpani clay samples (88.76%) shows that it could be used in paints manufacturing industry (Paynes, 1961).

A comparative analysis of the SiO_2/Al_2O_3 ratio for the clay samples (2:1) shows that the Odukpani clays fall into clays recommended for refractory work (Worall, 1975). For good refractory characteristics, clay should have a percentage composition of Al_2O_3, between 30 and 50% with a limited amount of Fe_2O_3, T_1O_2 and CaO (Ryan,

1976).

The oxides of sodium, potassium and magnesium are the main fluxing and ion exchange materials in clays. Thus, the vitrification and ion exchangeable materials of these clays are expected to be low. This however, is an added advantage for its use in brick making since a high level of CaO can cause undesirable expansion and subsequent cracking in structures (Obaje and Ekpenyong, 1997).

X-ray diffraction investigation

The results of mineralogical analysis of the clay samples in the present investigation, presented in Table 3, show that the clay samples are predominantly kaolinitic with some quantities of illites, quartz and felspar. Kaolinite alone constitutes between 83 to 96%, illites varies from 4 to 8%, quartz ranged from 1 to 4% and other minerals ranged from 1 to 6%. A simple comparison with the mineral composition of some well known clay deposits indicates that the investigated deposit is similar to Kaduna and China clay deposits with very small variations in the mineral contents. The clay samples are all of sedimentary origin and seem to have gone through different levels of transformation before deposition, which does affect their physical properties like plasticity and shrinkage.

Infra red (IR) spectral studies

Figure 3 shows the IR spectra of the clay samples stu-dies. On the basis of the frequency of vibrations in the low infra red region between 400 and 1200 cm^{-1}, (430.8, 470.4 Si- O, 538.6 Al-O-Si, 695.8, 753.2, 795.9 vs Si-O-Si, 913.4 Al-O -H, 1008.0, 1033.2 Si-O, 1104 vs Si-O-Si) the bands are associated with the stretching vibrations of S-O and Al-O tetrahdral vibration, Al, Fe and Mg octahe-dral and Si-O-Si octahedral vibrations. 4 types OH absor-ption bands were observed in the IR spectra of the clay samples within the infra red region of 3500 - 3700 cm^{-1}. These are 3696.6 cm^{-1} for free OH groups situated at the surface of dioctahydral layer, 3652.4 cm^{-1} for interparticle hydrogen bonded OH groups situated at dioctahydral sur-face, 3620.4 cm^{-1} for hydrogen bonded OH groups situa-ted between the layers and 3936.6 cm^{-1} for intra particle hydrogen bonded OH groups situated at the unoccupied position of the tetrahydral layer. The results obtained in this study compares favourably well with those reported in the literature (Szabo et al., 1974; Velda, 1992).

Thermal analysis

The results of thermoanalytical analysis of Odukpani clays in nitrogen atmosphere presented in Table 4 and Figure 4 show that the DTA and TGA curves changed in the nitrogen atmosphere. The DTA thermograms showed 2 peaks, an endothermic and exothermic between 0° to 1000°C. The main endothermic peak which is asymmetric with a maximum at 540°C can be associated with the removal of last traces of OH in the form of H_2O which can exist in the lattice even above 600°C. At 900°C, a sharp exothermic peak appeared which probably indicates a new spinel-type phase. This is in agreement with the findings of Szabo et al. (1974). The TGA results reveal a single broad loss of mass in the region of 400 to 550°C. The total loss of 13.59% corresponds to the removal of water molecules in the kaolinite groups (calculated loss of mass of 13.95%). The dehydroxylation of clays occurs within this temperature range. No loss was observed above 550°C indicating a complete separation of the 2 weight loss steps on heating to a constant temperature of 500°C (Pekene and Sharp, 1974).

Conclusions

Clays from Odukpani, south eastern Nigeria have been characterized using AAS, XRD, FTIR, EDAX and DTA/TGA methods of analysis. From the results obtained, the following conclusions have been drawn:

i. The samples contain high contents of alumina (Al_2O_2) and silica (SiO_2) with minor contents of P_2O_5, MgO, K_2O, MnO and TiO_2.

ii. The samples are predominantly kaolinitic with minor contents of illites, quartz and felspar. The samples are amorphous at 550°C

iii. EDAX patterns revealed the ratio of Al:Si to be 1:2 with a mean particle size of 0.046mm.

iv. A comparison of Odukpani clays with specification of some industrial clays shows that the samples can be recommended for use in the plastics, paint, ceramics, refractory and fertilizer industries among others.

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