THERMAL AND X-RAY INVESTIGATIONS OF KOWAK CLAY IN NORTHWESTERN TANZANIA AND ITS POSSIBLE INDUSTRIAL USE

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ABSTRACT

A study of some properties of clays collected from selected sites in Kowak deposit in Tarime District was carried out in order to assess their suitability as raw materials in ceramic and its related industries. The silica (SiO_2) content in the clays is predominant, and is about 66.89% followed by alumina (Al_2O_3) that is 20.2%. Haematite (Fe_2O_3) was found to be the third in abundance with an average of 3.58%. Other constituents are present in small proportions. Water loss at 105 ^{o}C lies between 2.70% and 2.76%. DTG, TG, XRD techniques and chemical analyses studied by AAS method were used to determine the minerals present in the deposit. Two clay minerals, namely, illite and kaolinite were dominant. The non-clay minerals, referred to as "impurities" found in clays include quartz, pyrope and potash-feldspar ($K_2O.Al_2O_3.6SiO_2$) in the form of microcline. Illite, kaolinite, quartz and potash-feldspar were found in all sites of the deposit while pyrope was revealed in one site only. On the basis of this study, the results obtained from the chemical, thermal and mineralogical analyses, suggest that the clays from the deposit could be exploited for the manufacture of bricks, tiles and some limited ceramic ware.

INTRODUCTION

An investigation of clay from Tarime District in northwestern Tanzania was carried out. The District is endowed with both large and small deposits of minerals in different locations. One of the known deposits "the Kowak deposit", where clays occur in significant amount was studied. The clay from this deposit is used locally for the manufacture of bricks, pottery and tiles (Koepel 1986). Hitherto no detailed scientific study has been carried out on the genesis of the deposit.

In the present study, DTA, TG and XRD techniques supplemented by chemical analysis have been employed to investigate the composition of the clays. The investigation was carried out in order to identify the main constituents of the clay samples and characterize the clay minerals for possible industrial applications.

METHODS

Sampling

Five samples taken from different sites in the Kowak deposit were studied in this investigation. They were coded as samples S_1, S_2, S_3, S_4 and S_5. The samples were collected at about 1 m and 3.5 m below the earth's surface and each sample was mixed thoroughly to obtain a homogenous mixture.

Chemical analyses

Moisture content determination

Each sample was finely ground and about 20 g of the less than 100 mesh portion was dried over night in an oven at 100^{o}C – 105^{o}C. The difference in weight was used to calculate the percentage loss on drying. Duplicate determinations were carried out and averaged.

Cation determination

The procedure adopted in the determination of SiO_2 content was different from that employed in the analysis of other cations. Ten grams of each clay sample was accurately weighed into a 150 ml beaker. 50 ml of conc. Hydrochloric (HCl) acid was added and placed on a steam bath for six hours with occasional stirring and topping up with conc. HCl acid to replace that lost by evaporation. After sixteen hours heating the final volume was allowed to decrease to 25 ml. The solution was then diluted to about 50 ml with distilled water and the SiO_2 filtered into a sintered crucible G4. The residue was then washed with distilled water and all the filtrate and washings were collected in 100 ml graduated flask and reserved for the determination of metal composition while the SiO_2 content in the crucible G4 was dried in an ovenover night at 120 – 150°C. The crucible was reweighed and the difference in weight was used to determine the SiO_2 content in the samples (Vogel 1984).

The elements Al, Ti, Fe, Ca, Mg, Na, K, Cr, Mn, Pb, Zn and V were determined by AAS method using Perkin-Elmer 2380. Each volume of standard stock solution prepared contained an equivalent of 1000 ppm of the respective element was diluted so as to give an absorbance within the linear range of the metal to be determined. A hollow cathode lamp of the element to be determined was selected, placed in its position in the spectrophotometer, properly aligned and lit. Each solution of unknown concentration was aspirated and directly read its concentration. Distilled water was aspirated for zeroing the instrument. The values obtained were multiplied with dilution factor to get the actual concentration of the original sample solution. Duplicate determinations for each metal was carried out and averaged. Nitrous oxide flame was used in atomic excitation of Al, Ti, and V in which a very high temperature is vital, while air-acetylene flame was used to the rest of the metals (Vogel 1984).

Mineralogical analyses

Thermoanalytical techniques

The differential thermal analyses (DTA) of clays were done by the Stanton-Redcroft model 673-4 with an attached digital volmeter connected to a PC. The temperature range for the measurement was from ambient temperature to 1000 ^{o}C. The thermocouple utilised was Pt/Pt:13% Rh. and the heating rate for all clays was maintained at 10^{o}C/minute. Calcined alumina was used as the reference material and the specimen holder was platinum.

The thermogravimetric analyses (TG) were performed using the Stanton-Redcroft TG.750 with an attached digital voltmeter and a PC. The heating operation was done from ambient temperature to 1050 ^{o}C at the heating rate of 10 ^{o}C per minute.

X-ray diffraction analysis (XRD)

X-ray diffraction patterns were recorded by the Siemens D-5005 X-ray Diffractometer. CuK_{α} radiation (λ = 1.54056Å) was employed. The samples underwent diffraction in the measuring range 2θ ranging between 2^{o} – 65^{o}.

RESULTS AND DISCUSSION

Chemical analysis

The results of chemical analysis for the five samples (S_1, S_2, S_3, S_4, and S_5) expressed in percentages, including percentage losses of water at 105^{o}C are presented in Table 1.
There was a wide variation of chemical constituents. For all the samples alumina ranked second in abundance (ranges between 17.12 and 22.57%) after silica (> 63.81%) followed by haematite while lead oxide, zinc oxide and chromate are the least in all the samples. However, Fe_2O_3, MgO and K_2O occur in large proportions compared to other oxides (Table 1). It was observed that the amount of silica in clays is much higher and vice versa for alumina when compared to the theoretical values of pure kaolinite. Pure kaolinite has a theoretical chemical composition of 46.55 wt % SiO_2, 39.49 wt % Al_2O_3 and 13.96 wt% H_2O. However, in nature kaolinite is rarely found in pure form. Two types of impurities are associated with kaolinite: impurity resulting from isomorphous substitution of an element into the kaolinite structure and impurities resulting from accessory minerals that adhere to the surface area of kaolinite. The latter type can affect some intended use of a particular clay but this may be handled by

diverse beneficiation techniques (Ekosse 2001, Kimambo 1988). The water contents obtained at 105^{o}C were less for the clays investigated compared to those reported in the literature which was in the range between 7.77 and 11.37% (Kirk-Othmer 1979). This discrepancy may be ascribed to the regularity in units arrangement of clay minerals that cause small amounts of adsorbed water to be found between/or within layers, and secondly, the variation of grain size of the clay materials. Note that increase in particle size is accompanied by decrease in surface area, hence a small amount of adsorbed water is present in clay materials. However, this water is not very important, as it only depends on the humidity (wet or dry season). Loss on ignition at 600^{o}C is crucial because it measures molecular water.

Table 1: Chemical composition (in %) of clay minerals studied.

Sample	SiO_2	Al_2O_3	TiO_2	Fe_2O_3	CaO	MgO	Na_2O	K_2O
S_1	70.01	17.12	0.10	3.63	0.34	0.41	0.03	0.50
S_2	70.22	18.00	0.12	3.66	0.36	0.39	0.04	0.50
S_3	64.01	22.29	0.11	3.46	0.38	0.37	0.03	0.48
S_4	63.81	22.57	0.11	3.51	0.41	0.40	0.03	0.39
S_5	66.42	21.02	0.12	3.63	0.98	0.35	0.03	0.46
Sample	Cr_2O_3	MnO	PbO	ZnO	V_2O_5	H_2O	LOI	Total
S_1	0.007	0.04	0.0033	0.001	0.003	2.76	5.11	100.07
S_2	0.923	0.04	0.0039	0.002	0.003	2.64	5.30	101.2
S_3	0.0121	0.039	0.0031	0.005	0.003	2.67	5.56	99.90
S_4	0.0141	0.04	0.0038	0.002	0.003	2.88	5.72	99.89
S_5	0.0132	0.04	0.0035	0.002	0.003	2.70	4.22	99.99

Table 2: Mineralogy of samples as determined by XRD. M=major; m = minor, T = trace.

Sample	Quartz	Illite	Kaolinite	Microcline	Pyrope
S_1	√ M	√ M	√ m	√ m	√ m
S_2	√ M	√ M	√ m	√ m	
S_3	√ M	√ m	√ m	√ m	
S_4	√ M	√ m	√ m	√ m	
S_5	√ M	√ m	√ m	√ m	

X-ray Diffraction analysis

X-ray results are given in Table 2. Quartz, illite, kaolinite and microcline [K-feldspar-$KAlSi_3O_8$] are present in all samples. Among these, quartz and illite are seen to be predominant while the rest occur in minor quantities. However, for sample S_1 pyrope [Mg-feldspar – $Mg_3Al_2(SiO_4)_3$] was the only accessory mineral present. These results are in good agreement with both chemical and thermal analyses. The concentration values for silica which is of the average of 69.01% and aluminium 20.2% obtained by chemical analysis agree with quartz (major), kaolinite and illite (minor) contents in the samples. The data obtained by thermal analysis are discussed below; they also show the correlation with the mineralogical composition. The high percentages of SiO_2 is a sign of quartz dominance in all samples.

Thermoanalytical characterisation

The differential thermal analysis (DTA) results are presented in Table 3. The thermogravimetry (TG) and differential thermogravimetry (DTG) curves labeled, (a) and (b), respectively, for each sample are plotted in the same Figure. Their thermograms are presented in Figs. 1 - 5 for samples S_1 to S_5, respectively. Both DTG and TG curves of samples S_1 and S_2 largely resemble. The differential thermal analysis curves of S_1 and S_2 show broad endothermic peaks at 98°C and 92°C, respectively, which are due to the loss of adsorbed water while dehydroxylation peaks occur at 484°C and 579°C (S_1) and at 579°C, 688.5°C and 724.7°C (S_2). Broad exothermic peaks which are results of the burning off of organic matter present in S1 appear at 260°C and 323°C while the endo/exothermic peaks appear between 854°C and 917.7°C. The peaks observed indicate the presence of illite and quartz in these samples, observations which are supported by X-ray analysis. The thermogram curves of these samples given in Figs. 1 and 2 show two distinct features, namely, the abrupt weight losses, which occur in two stages in both samples and the gradual weight losses. The first stage for S_1 occurs between 25°C and 194°C associated with broad weak endothermic peak at 98°C and accompanied with weight loss of 2.2% while for S_2 it occurs between 25°C and 140°C associated with broad endothermic peak at 92°C and weight loss of about 1.5%. In the second stage, the weight loss for S1 and S_2 of about 2.2% and 1.8%, respectively, occurs between 440°C and 654°C for S_1 and between 427°C and 684°C for S_2 both associated with an endothermic peak at 579°C. The reaction at these temperature ranges is due to the dehydroxylation of illite. The weight loss of about 0.6% which occurs between 654°C and 817°C for S_1; and between 688.5°C and 724.7°C for S_2 is due to the water bonded to magnesium in an octahedral position of dioctahedral illite (Grim 1968). The large sharp endo/exothermic peaks between 854°C and 917°C for S_1 are not associated with any weight loss but they may be due to reorganisation and rearrangement of new phases of illite. For S_2, a gradual weight loss which continues to 684°C is due to dehydroxylation of illite (Grim 1968). The XRD patterns of these samples confirm these observations.

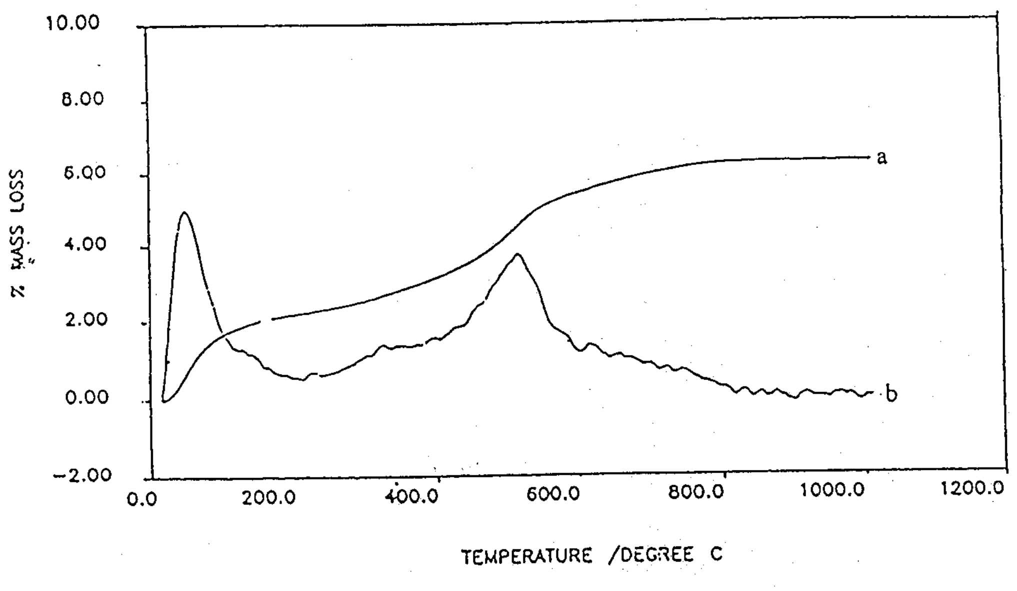

Figure 1: TG(a) and DTG(b) curves for sample S_1.

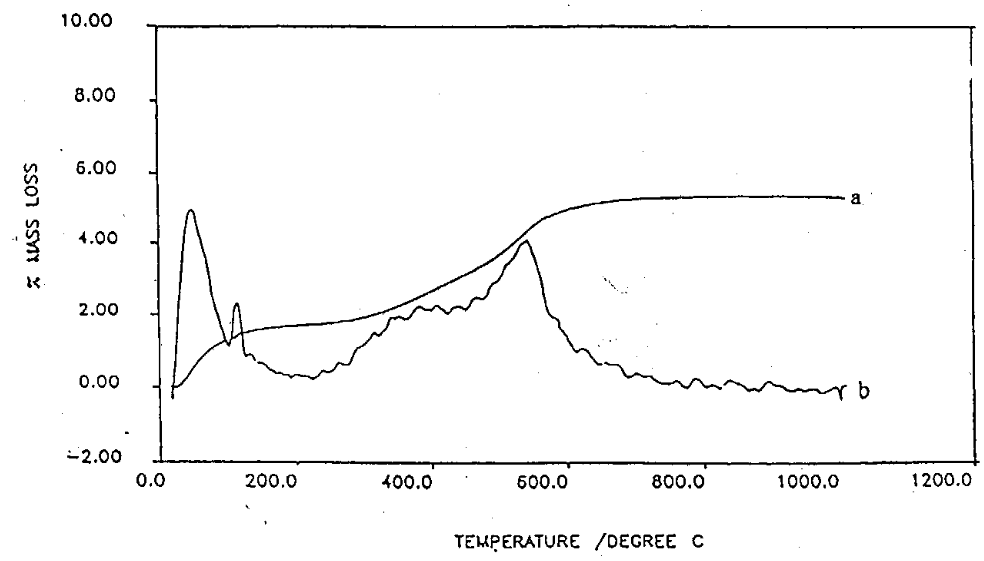

Figure 2: TG(a) and DTG(b) curves for sample S_2.

The differential thermal analysis results of S_3 and S_4 (Table 3) show broad weak endothermic peaks at 63°C and 60°C respectively; associated with the loss of free adsorbed water. This may be attributed to the presence of a crystallised kaolinite or dehydrated halloysite in the samples (Grim 1968). Allophane and hydrated halloysite are ruled out because they show well-developed peaks at around 100°C (Grim 1968). Small sharp peaks due to dehydroxylation of crystal lattice are observed at 578°C. This is in good agreement with the reported value of 583°C for well crystallised kaolinite (Grim 1968), though it is slightly lower by ca. 0.8%. The cause of this observation is likely to be due to small particle sizes of the samples. From the survey of clay minerals by Grim (1968) and Brindley (1961), it is concluded that dehydration temperature decreases with decreasing particle size. The main endo/exothermic peaks between 854°C and 908°C (S_3) and between 734°C and 788°C (S_4) are more rounded than the well-crystallised kaolinite. According to Bentor *et al.* (1963) and Mackenzie (1970 a; b) all features are in agreement with the declared clay composition of kaolinite with some illite, results which are supported by XRD analysis. The thermograms of these two samples (Figs. 3 - 4) bear great similarity to one another; both show initial weight loss below 200°C (0.17% for S3 and 0.12% for S_4). This is followed by a limited gradual weight loss up to ≈ 500°C (weight loss of ca. 0.42% and 0.03% for S_3 and S_4, respectively). Above this temperature, a rapid loss of lattice water (hydroxyls) takes place and terminates at ~800°C for S_4. The reaction taking place is due to dehydroxylation of illite. Sample S_3 shows an extended gradual weight loss of endo/exothermic peaks between 854°C and 908°C, which may be due to reorganisation and rearrangement of new phases of illite. These results are confirmed by X-ray analysis data.

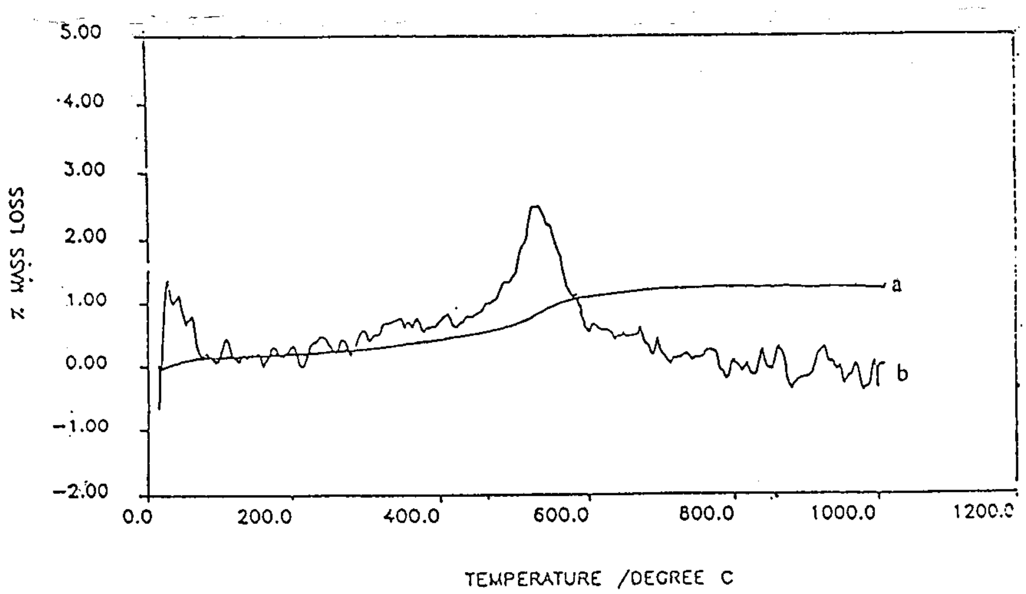

Figure 3: TG(a) and DTG(b) curves for sample S_3.

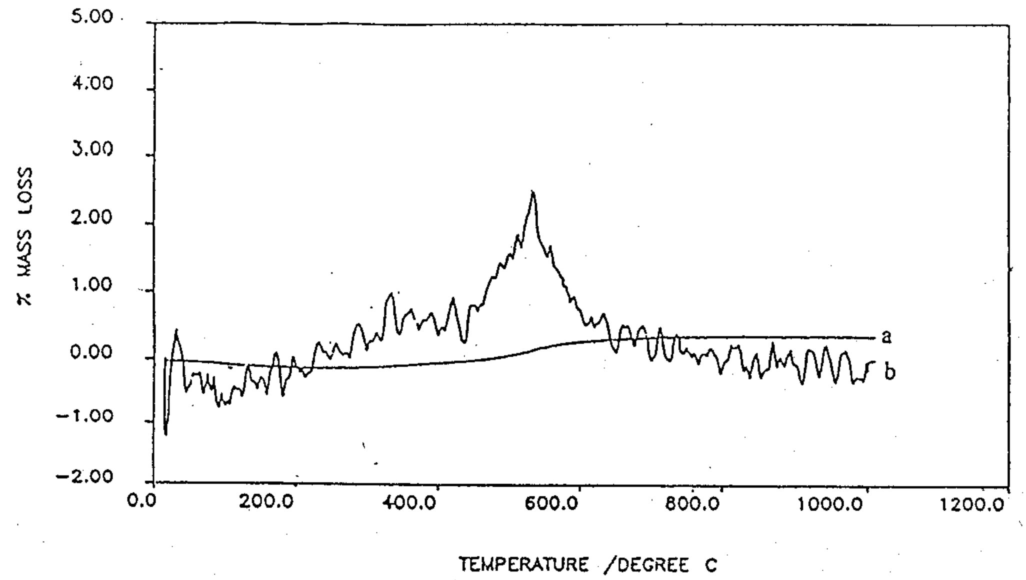

Figure 4: TG(a) and DTG(b) curves for sample S_4.

The differential thermal analysis results of S5 (Table 3) show a broad weak endothermic peak at 88.6°C, a small sharp endothermic peak at 738.6°C and a large sharp endo/exothermic peak with a shoulder (at 902.5°C) occurring between 891°C and 959°C. The only plausible interpretation for this observation would be the presence of two clay minerals – kaolinite and illite which take structural reorganization at different temperatures. These details are revealed in the TG curves and confirmed by XRD analysis. The thermogram curve of the sample (Fig. 5) shows abrupt weight loss of about 1.1% between 25°C and 161°C. This weight loss is associated with a broad weak endothermic peak at 88.6°C. Slight gradual weight loss of about 0.3% which occurs between 161°C and 290°C is associated with a loss of adsorbed water which is driven off with difficulty, while the other loss of about 1.3% that occurs between 290°C and 471.5°C is due to burn off of organic matter present in this sample and lattice water belonging to kaolinite. Another abrupt weight loss of about 1.9% observed between 471.5°C and 743.7°C is due to dehydroxylation of kaolinie and illite. The weight losses are almost completed at 800°C with a corresponding endo/exothermic effect regarded to be due to illite clay transformations.

Table 3: DTA peaks of clay minerals

	Endothermic peaks(maxima)		**Exothermic peaks(maxima)**		**Endo/Exothermic peaks**	
	Temperature °C	**Magnitude**	**Temperature °C**	**Magnitude**	**Temperature °C**	**Magnitude**
S_1	98	broad large				
			260	broad weak		
	484	broad weak				
	579	small sharp			854-917.7	large and sharp
S_2	92	broad weak				
	579	small				
	688.6	large				
	724.7	large				
S_3	63	broad weak				
	578	Small sharp	313	broad weak		
			785	broad weak		
					854-908	large and sharp
S_4	60	broad weak				
	578	small sharp				
					734-788	large
			907.6	small sharp		
S_5	88.6	broad weak				
			430.4	broad weak		
			607.6	large		
	738.6	small sharp				
					891-959	large and sharp

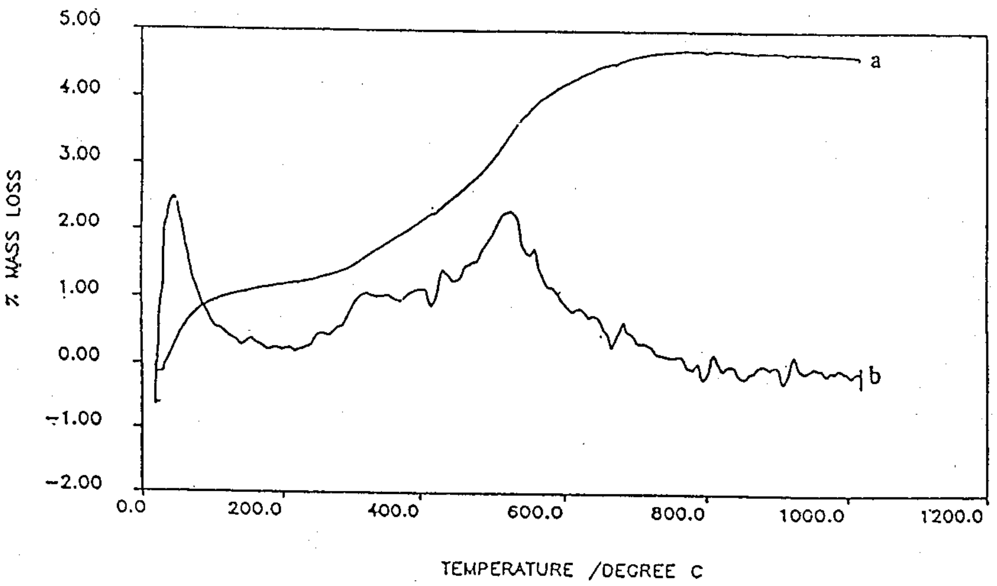

Figure 5: TG(a) and DTG(b) curves for sample S_5.

CONCLUSION

The study has indicated that the chemical composition of the clay minerals present in the deposit is made up of mainly silica, with an average of 66.89%, followed by the alumina, which is on the average of 20.2%. Hematite is the third in abundance with an average of 3.58%. Kaolinite and illite are the only clay minerals found in the deposit. Non-clay minerals found are quartz, pyrope and k-feldspar.

The clay minerals obtained are considered suitable in the manufacture of bricks and tiles. They could find other applications in ceramic industry. However, in order to optimize their properties for specific applications, they must be beneficiated accordingly. The colouring oxide, Fe_2O_3 which imparts the red pigmentation to the burned clay products is present in reasonable quantity, the amount in the clay samples ranges between 3.46% and 3.63%. On this basis, therefore, making the raw materials from this deposit be suitable in the manufacture of certain types of colouring ceramic products. The low concentration of Pb in the deposit makes the kaolin to be used in both pharmaceutical and paper industries (Ekosse 2001). However, the high percentage of haematite rules out the application in paper industries and in the production of whiteware like porcelain due to the red colouring imparted by Fe_2O_3 unless the clay is beneficiated. The presence of silica in a large proportion (range between 25 – 50%) is an advantage for use of raw materials in ceramic products, because of its ability in minimizing shrinkage on the drying and firing of ceramic products. Similarly, the absence of large proportions of organic matter is an added advantage for ceramic production.

This study has given preliminary results of the constituents of the deposit to ascertain some uses of these clays. Further investigations are underway to determine other properties such as plasticity, mechanical strength, particle size distribution, mineral structure etc in order to substantiate further the use of these clays in industries.

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