Characterization of Available Sedimentary Clay of Hobiganj District

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Abstract

Finding the proper ceramic raw materials is important for sustainable development of Bangladesh. The conventional white-ware and tiles manufacturing industries use clay as the major raw material which is generally imported from foreign country. However, due to geological position of our country we have some sedimentary clay deposits. In this study, a local clay was studied to analyse it's chemical, mineralogical composition, morphological, and thermal properties for plausible diversified applications. X-ray Fluorescence (XRF) analysis of clay showed 67.45% SiO_2 and 16.85 % Al_2O_3 as major ingredients with Fe_2O_3 and TiO_2, CaO, MgO, Na_2O and K_2O as minor impurities. X-ray Diffraction (XRD) analysis of clay revealed mineralogical composition as illite, kaolinite, quartz and rutile. Scanning Electron Microscopy exhibited clay has tiny pyramid like shape and pseudo-hexagonal structure of kaolinite in sample. Differential Scanning Calometry (DSC) showed different phase transitions such as metakaolinite phase formation occursed at 456^0C and α-β quartz transformation at 573^0C. From the thermal behaviour of this clay, it was evident that Hobiganj clay resembles ball clay type.

Keywords: *Clay Materials, XRF, XRD, SEM-EDX and DSC-TG.*

1. INTRODUCTION

Clay minerals are a group of hydrous aluminium silicates with a layered structure and very small (less than 0.005 mm) particle size. They are usually produced by weathering of rocks and occur widely in river sediments and soils. Different geologic environments produce different clay minerals from the same parent rock. Clay minerals form under a fairly limited range of geological conditions. Most clay minerals form where rocks are in contact with water, air. Generally the properties are almost common in all clay minerals. The basic structural feature of phyllosilicates is the combination of layers of pseudo-hexagonal network of SiO_2 tetrahedral (silica tetrahedral layer shown in Figure 1 (a)) and layers of cations in octahedral coordination (octahedral layer) [1-2]. Composite arrangement of each of the Al octahedral and Si tetrahedral layers result in a 1:1 structure as in kaolinite (a two-layer structure) or an octahedral layer sandwiched by two tetrahedral layers resulting in a 2:1 structure (as three-layer structure) shown in Figure 1 (b), as in montmorillonite and illite. The overall schematic representation of the common clay minerals is given in figure 1. The phyllosilicate types are divided into groups on the basis of charge on the layers and on the nature of octahedral-tetrahedral layers [3-4].

Clay minerals are very important in process industries, engineering, construction, geology, environmental, and for other miscellaneous applications. They have been widely used as the main raw materials in fabrication of diversified ceramic products for construction materials such as bricks and tiles due to many of their specific properties before and after firing. The chemical and mineral been reported to influence their ceramic properties. The main function of clay is to increase the plasticity and drying strength. Clay acts as a flux at high temperatures, its aids vitrification [5]. Depending on composition and various other technical characteristics, clay can be processed into different shapes where plasticity, strength and others parameter are varied [6]. There has been an increasing interest in utilizing clay minerals such as bentonite, kaolinite, diatomite and fullers earth for their capacity to absorb not only inorganic but also organic molecules shown in Figure 1 (a). These raw materials are mainly made from silica and alumina with some impurity. In the firing process when free silica is present in high amount it causes crack within the ceramic body due to the quartz phase transformation. At the same time high amount of alumina presence increase the refractory property of brick, tiles and other clay related ceramic body.

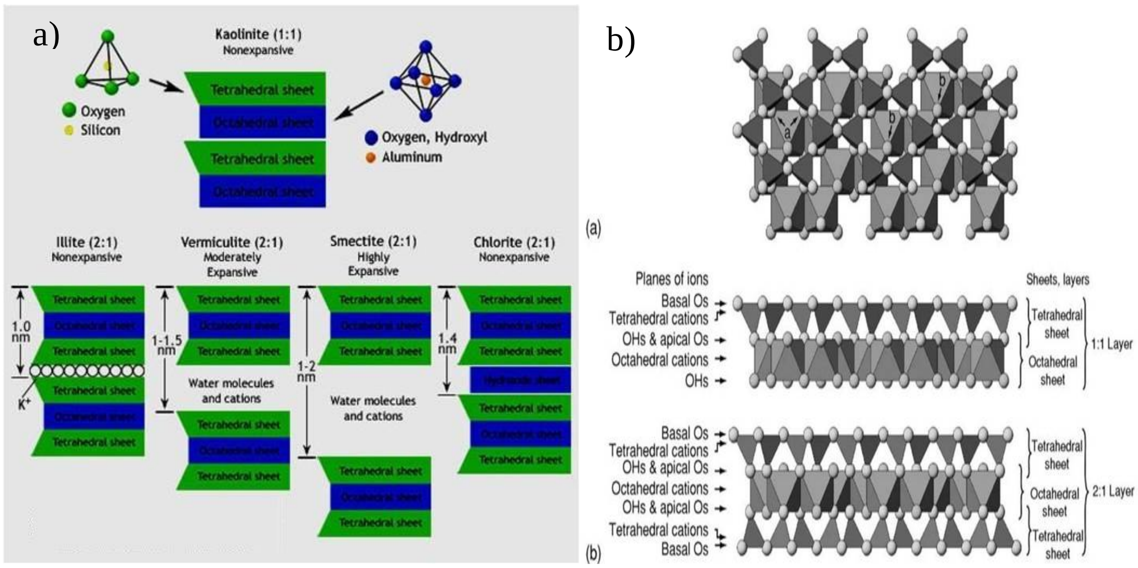

Figure 1. Structure of different clay minerals

2. MATERIALS AND METHOD

Geological studies reveal clay to be of two different types based on the way they were deposited. The types of clays which are found to be at the place of their origin are called residual Clay. Typically these types of clays are deposited along the igneous rocks from which they were formed and are obtained in relatively pure state. Based on their in-situ nature, they are found to have coarse particle size with a wide particle size distribution. Due to this, these clays show lower plasticity. China clay is an example of residual clay, which is highly pure, has larger particle size and lower plasticity. The other type is sedimentary clays which are deposited by transportation from their origin by natural agencies like water, wind etc. Sedimentary clays are seldom obtained in pure state, due to impurities that are picked up during transportation and are retained in the deposits. The grinding action of clay particles in water, and wind results in very fine particle sizes, giving the sedimentary clay very high plasticity. Ball clay is an example of sedimentary clay, which is not highly pure, but has a finer particle size and very good plastic property.

Geological surveys indicated that Bangladesh has deposits of both some residual and sedimentary types of clays. A number of places across the country have been identified as the sources of various types of clay. Notable locations are Bijoypur in Mymensingh, Barapukuria and Maddhyapara in Dinajpur etc [7]. Beside this location there are also some locations in Hobiganj district where huge amount of clay deposit were found. The clays that are available in these sources are mainly Red Clay, Black Clay, Brick Clay etc. In this work local Hobiganj clay is used as principle research materials. Hobiganj clay occurs abundantly in some particular localities of the district of Hobiganj in Bangladesh. The predominant color of Hobiganj clay formation is reddish yellow. Generally the clay is light grayish white to bluish white with light yellow and slightly soap to feel, massive and soft to medium hard shown in Figure 2. The natural clay was mixed as powder materials which were subsequently pressed to form cylindrical tablet sample of 15 mm in diameter as well as 2 mm in thickness by uniaxial die pressing.

A study was made on the natural clay of three different deposits of Hobiganj district. The aim of the present research is the study on physical, chemical properties of natural Hobiganj clay and their firing behavior. Within this research the methods used for the identification and quantification of natural clay for structural materials. X-ray fluorescence analysis may give detail about chemical composition of raw materials. After study the chemical composition of natural clay, necessary oxides are added for structural materials composition if modification needed. X-ray diffraction leads to an understanding of the structural characteristics of the clay mineral. Chemical compositions of Hobiganj clay collected from different area of Hobiganj district were investigated using X-ray Fluorescence Spectrometer. The different phases of Hobiganj clay were identified by using PAN-Analytical X-ray Diffractometer. Different phase % were identified by High Score plus Software. FE-SEM sample was taken as powder form for morphological information. Thermal behavior and weight loss of clay sample were studied by (DSC-TG) apparatus.

3. RESULTS AND DISCUSSION

3.1. X-ray fluorescence characterization

X-ray fluorescence (XRF) is the emission of characteristic "secondary" (or fluorescent) x-rays from a material that has been excited by bombarding with high-energy x-rays or gamma rays. The phenomenon is widely used for elemental analysis and chemical analysis of clays [7]. Figure 2 shows the general appearance of Hobiganj clay when it was collected from Hobiganj district of Bahubal Thana. Basically, this Hobiganj clay looks like blackish type.

Figure 2. Graphical image of Hobigonaj clay

Table 1 shows that the clay contains a small amount of CaO, MgO, Na_2O and K_2O which acts as fluxes. The presence of Fe_2O_3 and TiO_2 bearing materials impair the effectiveness of industrial raw materials, affect their utility for various applications. Traditionally, iron is removed by physical separation techniques, but hydrometallurgical treatment such as acid washing is the more effective and widely employed process. Sometime iron oxide is also having helpfulness in brick and tiles for absorbing infrared radiation from sunlight. For making good quality of brick and tiles, it is very important to make sure the proper composition of clay raw materials.

Table 1. Chemical composition of Hobiganj natural clay raw material

Component ID	SiO_2 %	Al_2O_3 %	Fe_2O_3 %	TiO_2 %	CaO %	MgO %	K_2O %	Na_2O %	P_2O_5 %	ZrO_2 %	Cr_2O_3 %
HOBI-11	67.45	16.85	7.52	2.02	0.03	0.98	4.53	0.33	0.06	0.02	0.07

3.2. XRD characterization

Figure 3 shows XRD pattern of Hobiganj natural clay sample. In this sample different phases are present. The clay sample looks like the ball clay type. In this clay sample the intensity of silica or quartz is the highest it means high amount of silica is present within this sample. The kaolinite mineral has alumina [8-9]. The Hobiganj clay sample has Al_2O_3 which is around 16.45 % of its weight. In this sample iron oxide content is 7.52 %. In this clay the main phases found are illite, kaolinite, quartz and rutile (Titanium oxide-TiO_2).

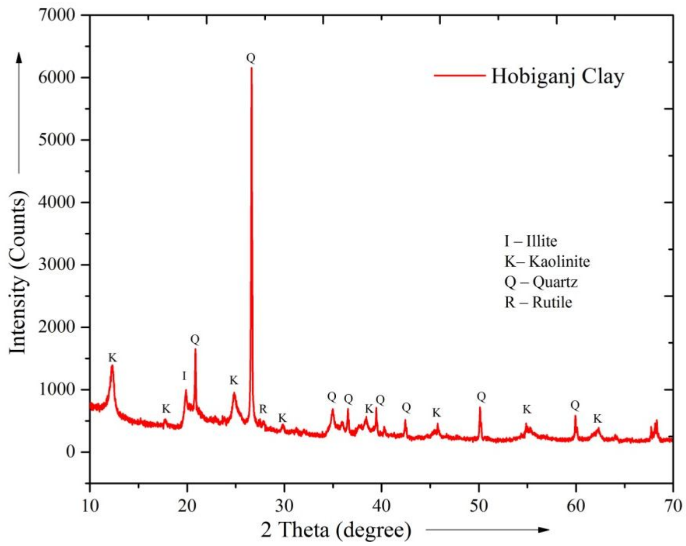

Figure 3. XRD Analysis of Hobiganj Clay

3.3. SEM-EDX Characterization

The Scanning Electron Microscopy (SEM) provides detailed images of individual grains of clay minerals and EDX provides detection of major and minor elements at points on grain surfaces, allowing highly reliable identification from crystal form and composition, as well as direct observation of particle packing and size [10]. Morphologies observed by SEM can also be useful in identification of clay minerals. Clay materials show a variety of morphologies, including platy, pseudo-hexagonal particles, booklets and vermicular stacks. Hobi-11 is look like ball clay. The figure shown below is Hobiganj clay. At first, we investigated the natural clay sample for morphological view.

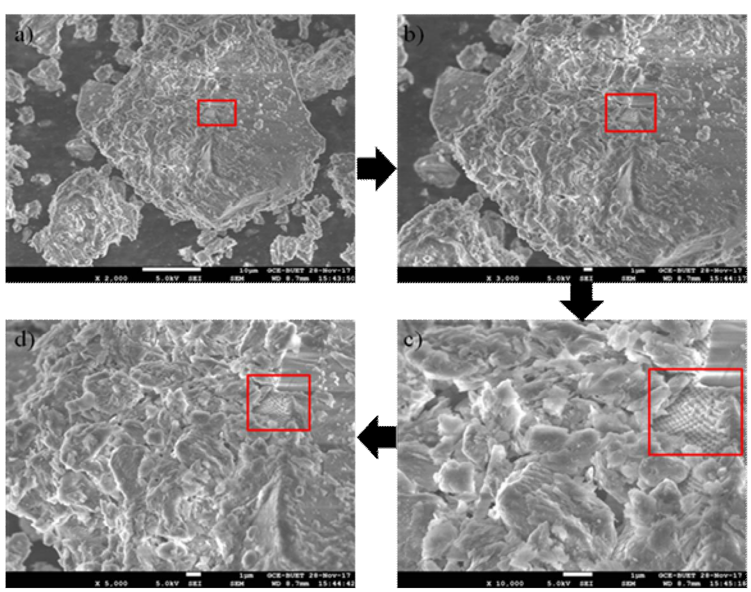

Figure 4. FESEM micrograph of Hobiganj clay

From FESEM micrographs (Figures 4 and 5), clearly give information that the Hobiganj clay has tiny pyramid like shape and pseudo-hexagonal structure. This pyramid like shape may be the tetragonal or octahedral sheet structure. Morphological investigation of this clay sample revealed also huge illites like particles.

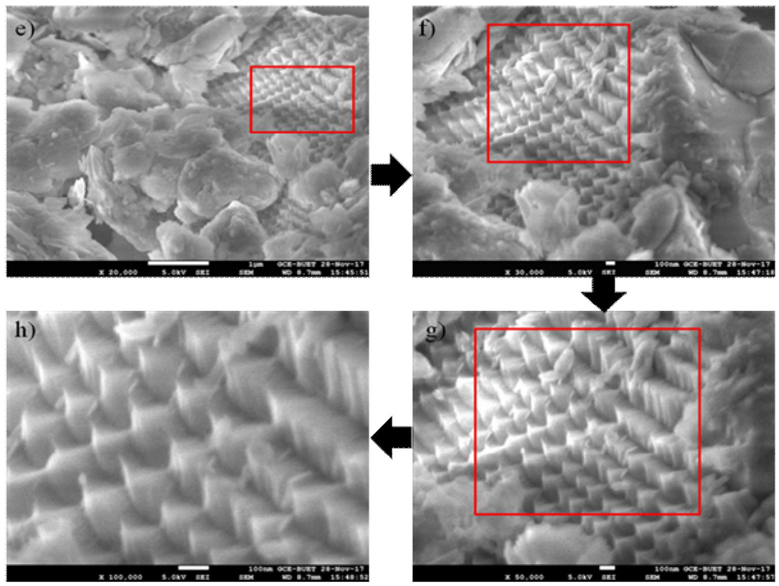

Figure 5. High magnification of FESEM micrograph of Hobiganj clay

Furthermore, EDX is used for *qualitative* (the type of elements) as well as *quantitative* (the percentage of the concentration of each element of the sample) analysis. Most SEM-EDX has dedicated software enabling auto-identification of the peaks and calculation of the atomic percentage of each element. One more advantage of the EDX technique is that it is a non-destructive characterization technique, which requires little or no sample preparation [13].

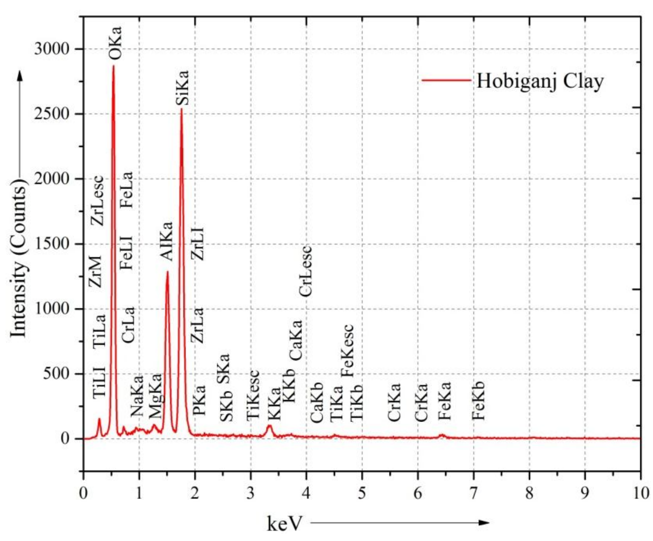

Figure 6. SEM-EDX spectra of Hobiganj clay

The Figure 6 shows the EDX curve with atomic % and mass % of different element into Hobiganj clay materials. In this analysis result Al and Si content is high like other clay minerals shown in Table 2. In Hobiganj clay the ratio of Al and Si is lower around half value. Table 2 shows that Ti, Ca, Fe, K, Fe and Zr are present in this clay sample.

Table 2: EDX-Analysis result of Hobiganj Clay

Element	(keV)	Hobiganj Clay	
		Element in Mass%	Element in Atom%
O(K)	0.525	37.77	52.31
Na(K)	1.041	0.30	0.29
Mg(K)	1.253	0.69	0.63
Al(K)	1.486	16.09	13.21
Si(K)	1.739	38.31	30.22
Ti(K)	4.508	0.81	0.37
K(K)	3.312	2.78	1.58
Ca(K)	3.690	0.52	0.29
S(K)	2.307	0.10	0.07
Fe(K)	6.398	2.55	1.00
P(K)	2.013	0.04	0.07
Zr(L)	1.480	0.07	0.02
Total		100.00	100.00

3.4. DSC-TG Characterization

DSC-TG analysis measures both heat flow and weight changes in a material as a function of temperature or time in a controlled atmosphere. The complementary information obtained allows investigating the exothermic and endothermic effects of reactions, such as carbon oxidation and dehydroxylation respectively [14]. Figure 7 shows the effect of energy changes (endothermic or exothermic reactions) in a sample.

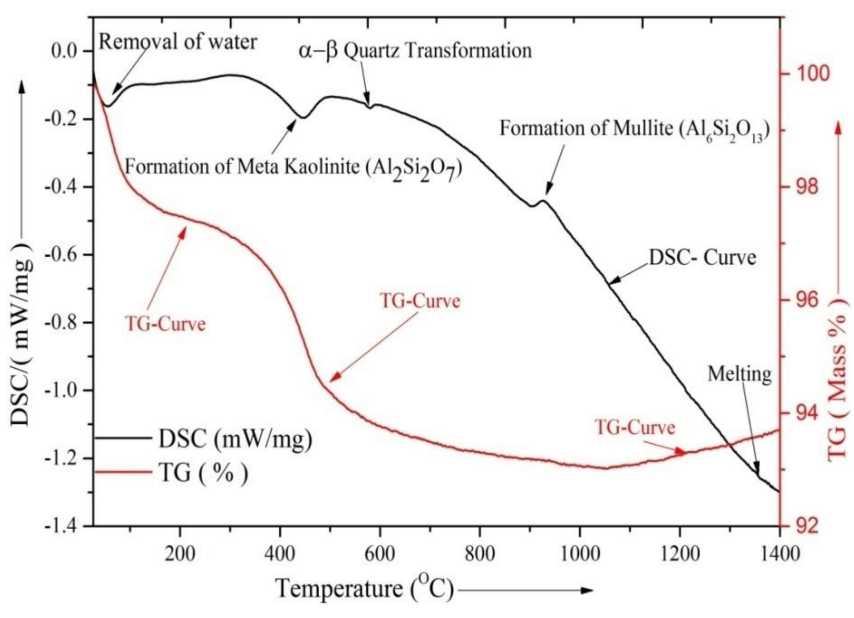

Figure 7. DSC and TG analysis curve of Hobiganj clay

For clays, endothermic reactions involve desorption of surface H_2O (e.g. H_2O on exterior surfaces) and dehydration (e.g. interlayer H_2O) at low temperatures (100^0C), dehydration and dehydroxylation at more elevated temperatures and eventually melting. At high temperature metakaolinite phase formation occurs at around 456^0C and α-β quartz transformation takes place at 573^0C. Exothermic reactions are related to recrystallization at high temperatures that may be nearly concurrent with or after dehydroxylation and melting [15-17]. From the thermal behaviour of this clay, it is evident that Hobiganj clay is ball clay.

4. CONCLUSIONS

From chemical composition, SEM-EDX, XRD and DSC analysis of Hobiganj clay, it is concluded that Hobiganj clay contains silica and alumina as major constituents and iron, calcium, potassium and magnesium oxide are present as minor quantities. High amount of free silica causes crack into the brick and tiles. As well as high alumina content improve the refractory properties of clay related product. From above various properties of clay, it is apparent that Hobiganj clay may be used as an impotent raw material in brick and tiles industries in Bangladesh to produce various structural ceramic related products and has the prospect to lower the dependency of imported structural ceramic materials.

5. ACKNOWLEDGEMENTS

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