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Study of the structural modification on heat treatment of Bijoypur white clay (BWC) of Bangladesh

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Abstract : Different samples were prepared from as collected, washed and heat treated Bijoypur White Clay (BWC) of Bangladesh. The X-ray diffractometric analysis of BWC reveals that it is possible to remove a major part of silica by washing the as-collected clay. On heat treatment of washed BWC at 1273 K, it is observed that kaolinitic BWC transforms to a compound containing mullitic phase. The infrared (IR) spectroscopic analysis indicates the presence of OH stretching (hydroxyl absorption of kaolinite) in washed BWC. Moreover, IR spectra indicate that the clay mineral in this study is mostly kaolinitic in nature. The OH stretching is not observed in heat treated (773 and 1273 K) BWC. From the Differential Thermal Analysis (DTA) it is evident that metakaolinite is formed after evolution of water of crystallization at 853 K. A high temperature phase (mullite) transformation is observed at about 1273 K for BWC The photomicrographs manifest the formation of clusters of different sizes on heat treatment. It is also seen that the porosity is inversely proportional to the pressure of pellet preparation.

Keywords : White clay, XRD, DTA

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1. Introduction

The engineering properties of clay depend on the compositional and environmental factors. It is important to know the different types of clay minerals for designing and analyzing different geotechnical problems. In Bangladesh, BWC is being utilized for the manufacture of various ceramic products, low tension insulators and in processing rubber by many industrial units. The mottel variety of white clay (kaolin) which is slightly sandy is used for making fire bricks. Structure, lithology, mode of occurrence and texture of the BWC indicate that it has been transported and deposited and its source is not far away [1]. And it seems that the source materials of BWC are in the Indian side and that is of sedimentary origin. BWC is light gray to gray and turns pale white on exposure to Sun. Near the surface it is pinkies with yellow patches. It is mostly soapy to feel but at places gritty.

The IR study on as-collected BWC was made by M A Biswas *et al* [2]. M Q I Khuda *et al* [3] have done the quantitative chemical analysis of raw and washed BWC. The X-ray diffractometric (XRD) study of the as-collected BWC was done by M N Islam [4]. The result of the above investigations identified the main mineral of BWC as kaolinite. So far, no detailed work has yet been appeared in the literature on the effect of heat treatment on BWC.

In this paper, the results of XRD, IR, DTA and optical investigations of BWC are presented. The clay mineral composition of the raw BWC, washed BWC and heat treated (773 K and 1273 K) BWC was studied qualitatively by XRD. IR has widely been used in both qualitative and quantitative characterizations of clay minerals, coals *etc.* In this investigation, qualitative identification of different characteristic groups in washed and heat treated BWC was carried out. Under heat treatment, a substance may undergo structural changes, *e.g.*, physical as well as chemical. This changes occurring due to dehydration, transition from one crystalline variety to another, destruction of crystalline lattice, oxidation and decomposition *etc.* DTA is used to see the phase changes of BWC on heat treatment. Microphotographs of different pellets prepared at different pressures and heat treated were also studied to see the changes of surface structure.

2. Experimental details

2.1. Method of BWC washing and sample preparation :

The BWC was collected in the form of hard lumps from the mine at Bijoypur area in the district of Netrokona, Bangladesh. The method of washing of as-collected BWC as adopted in the laboratory scale is based on the principle of washing in a slow stream of water as describe in a previous literature [5].

The washed BWC was dried in an electric oven at 378 K for 24 hours. The dried BWC sample was then ground and was allowed to pass through 200 mesh sieve Then pellets (dia. 0.005 m) were obtained by a die punch at 2000, 3000 and 3500 psi by using a hydraulic pressure unit. The thickness of the pellet sample depends on the applied pressure and amount of BWC. After removing the sample from die punch its edges were then polished by a metallographic polisher (MSP-2 of Shimadzu Scientific Instrument Company Ltd., Japan) and using CAMBIMENT special silicon carbide grinding paper with grit number 320, 400 and 420. Finally, the samples are heat treated at 773 and 1273 K for 5 hours. These samples are used for polarizing microscopy. For the other investigations, the washed BWC powder and washed BWC powder heat treated at 773 and 1273 K are used These samples are represented as follows :

Sample A : As-collected BWC,
Sample B : Washed BWC,
Sample C : Washed BWC heat treated at 773 K and
Sample D : Washed BWC heat treated at 1273 K.

2.2. *Experimental techniques :*

An X-ray difractometer (model JDX-8P) of JEOL LTD., Tokyo, Japan was used. The target is CuK_α and the wavelength of X-ray radiation is 1.5418 Å. Fine BWC powder, sieved through 200 mesh, was used. XRD patterns were recorded for 2θ from 5° to 81° for samples A, B, C and D.

The IR spectra of samples B, C and D were recorded at room temperature using an IR spectrophotometer (IR-470 Shimadzu Corporation, Japan).

A Shimadzu Micro DTA system (model DT-30) manufactured by Shimadzu Corporation, Kyoto, Japan is used in the present investigation.

A Reichert Metavert reflected polarized light microscope of C. Reichert Optische Werke AG, Austria was used. Different areas are chosen to see the variation of the surface structures.

3. Results and Discussion

3.1. *XRD analysis :*

The XRD patterns of samples A, B, C and D are presented in Figure 1. The XRD patterns are represented respectively by diffractograms 1, 2, 3 and 4. The 2θ, d_{hkl} and the possible constituent compounds identified, are depicted in Tables 1, 2, 3 and 4 for samples A, B, C and D respectively. The XRD analysis of sample A (diffractogram 1) shows the presence of kaolinite (7.03, 3.56 and 1.49 Å), silicon oxide (4.15, 3.32 and 1.82 Å), aluminium oxide (4.44, 2.44 and 1.45 Å), iron oxide (1.67, 1.38 and 1.28 Å), potassium aluminium silicate hydroxide (4.93, 3.56, 2.53 and 2.37 Å), aluminium silicate (9.61 and 4.44 Å) *etc*. Very small amount of oxides of potassium, calcium, sodium *etc*. may also be present as reported by Alim Biswas and Basak [2]. In diffractogram 2 (washed BWC) it is seen that the percentage composition of the main ingredient, *i.e.*, kaolinite increases and that of silicon oxide decreases due to washing of as-collected BWC. There is not much change in other compositional compounds in the washed clay. The XRD pattern of sample C

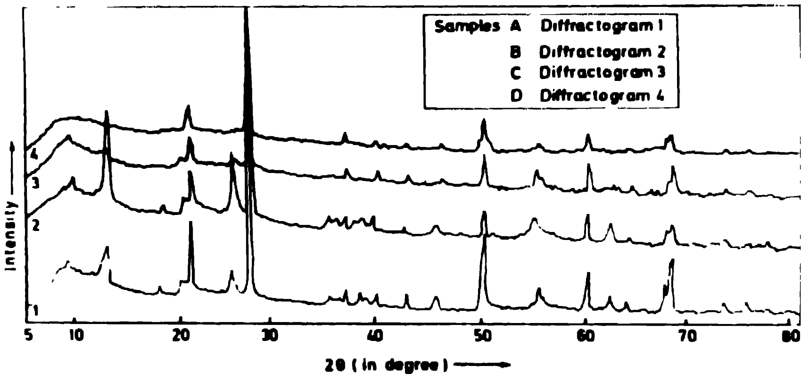

Figure 1. XRD patterns of different samples of BWC

(diffractogram 3), gives the signature of the presence of all the constituent compounds those are present in the washed BWC with some variations. It is observed that there is much

Table 1. 2θ, d_{hkl} and the plane of reflections of different constituents of sample A (diffractogram 1).

2θ in degree	d_{hkl} in Å	Kaolinite	Silicon oxide	Aluminium oxide	Aluminium silicate	Potassium aluminium silicate hydroxide	Iron oxide
9.2	9.61				001		
12.6	7.03	001					
18.0	4 93					004	
20.0	4.44	110		$20\bar{1}$	$\bar{1}10$	$11\bar{1}$	
21.2	4.15		100		012		
25.0	3 56	002			$\bar{1}\bar{1}2$	$113, 20\bar{4}$	
26.8	3.32		101		022	006	
35.2	2.53	130		$11\bar{1}$	$\bar{1}31$	311, 116	
36.8	2.44		110	111	$\bar{2}10$	$11\bar{7}$	
38.0	2.37	003				$117, 20\bar{8}$	400
40.0	2.26		102		220		
40.3	2.24		111	$40\bar{2}$			
42.8	2.11		200		$\bar{1}\bar{3}3$	208	
46.0	1.96	221	201	601	$\bar{2}31$	$22\bar{5}, 11\bar{9}$	332
50.2	1.82		112	510	$\bar{1}15$		431
55.0	1.67	$\bar{2}04$	202	601	105		440
60.0	1.54	114	211	313			611
62.4	1.49	060		113, 801			
64.2	1.45	330	113	020			622
67.8	1.38	062	212	712			631
68.4	1.36		301				
73.6	1.28	$\bar{4}02$	104				721
75.8	1.24		220				

Table 2. 2θ, d_{hkl} and the plane of reflections of different constituents of sample B (diffractogram 2).

2θ in degree	d_{hkl} in Å	Kaolinite	Silicon oxide	Potassium aluminium silicate hydroxide	Aluminium silicate	Aluminium oxide	Iron oxide
9.2	9.61				001		
12.6	7.03	001					
18.0	4.93			004			
20.0	4.44	110		$11\bar{1}$	$\bar{1}10$	$20\bar{1}$	
21.2	4.15		100		012		
25.0	3.56	002		$113, 20\bar{4}$	$\bar{1}\bar{1}2$		
26.8	3.32		101	006	022		
35.2	2.53	130		311, 116	$\bar{1}31$	$11\bar{1}$	
36.8	2.44		110	$11\bar{7}$	$\bar{2}10$	111	

Table 2. *(Cont'd.).*

2θ in degree	d_{hkl} in Å	Kaolinite	Silicon oxide	Potassium aluminium silicate hydroxide	Aluminium silicate	Aluminium oxide	Iron oxide
38.0	2.37	003		117, $20\bar{8}$			400
40.0	2.26		102		220		
40.3	2.24		111			$40\bar{2}$	
42 8	2.11		200	208	$\bar{1}33$		
46 0	1 96	221	201	$22\bar{5}$, $11\bar{9}$	$\bar{2}31$	601	332
50.2	1 82		112		$\bar{1}15$	510	431
55.0	1.67	$\bar{2}04$	202		105	601	440
60.0	1.54	114	211			313	611
62 4	1.49	060				113, 801	
64.2	1.45	330	113			020	622
67 8	1.38	062	212			712	631
68.4	1.36		301				
73.6	1.28	$\bar{4}02$	104				721
75.8	1.20					400	

Table 3. 2θ, d_{hkl} and the plane of reflections of different constituents of sample C (diffractogram 3).

2θ in degree	d_{hkl} in Å	Kaolinite	Silicon oxide	Aluminium oxide	Aluminium silicate	Iron oxide
9.2	9.61				001	
12.6	7.03	001				
20.0	4.44	110		$20\bar{1}$	$\bar{1}10$	
21.2	4 15		100		012	
26.8	3 32		101		022	
35 2	2.53	130		$11\bar{1}$	$\bar{1}31$	
36.8	2.44		110	111	$\bar{2}10$	
40.0	2.26		102		220	
40.3	2.24		111	$40\bar{2}$		
42.8	2 11		200		$\overline{133}$	
46.0	1 96	221	201	601	$\bar{2}31$	332
50.2	1.82		112	510	$\bar{1}15$	431
55.0	1.67	$\bar{2}04$	202	601	105	440
60.0	1.54	114	211	313		611
64.2	1 45	330	113	020		622
67.8	1 38	062	212	712		631
68.4	1.36		301*			
73.6	1.28	$\bar{4}02$	104			721
75 8	1.24		220			

decrease of peak intensities of kaolinite whereas the peak of potassium silicate hydroxide is not present in the sample C. This may be due to the transformation of kaolinite to metakaolinite state and removal of hydroxyl group from potassium silicate hydroxide. The XRD patterns of sample D, diffractogram 4, reveals the appearance of a new phase (possibly mullite) corresponding to 2.24, 2.22 and 1.84 Å reflections [6]. XRD reflections for silicon oxide persist whereas the XRD reflections for kaolinite are absent in sample D thereby indicating a major transformation of kaolinite in the BWC to its high temperature phase mullite. These kind of transformations around this temperature region have been reported by several authors [7–10].

Table 4. 2θ, d_{hkl} and the plane of reflections of different constituents of sample D (diffractogram 4).

2θ in degree	d_{hkl} in Å	Mullite	Silicon oxide	Aluminium oxide	Iron oxide
21.2	4.15		100		
26 8	3.32	210	101		
36.8	2 44	111	110	111	
40.0	2 26		102		
40.3	2.24	201	111	402	
40.6	2.22	121			
42.8	2.11		200		
46 0	1.96	320	201	601	332
49.5	1 84	311			
50.2	1.82	321	112	510	431
60.0	1 54	331	211	313	611
67.8	1.38	112	212	712	631
68.4	1 36	341	301		
73.6	1.28		104		721
75.8	1.24		220		

3.2. *DTA :*

The DTA trace of washed BWC is shown in the Figure 2. The DTA curve shows a small initial endothermic reaction which may be due to poorly crystalline kaolinite containing

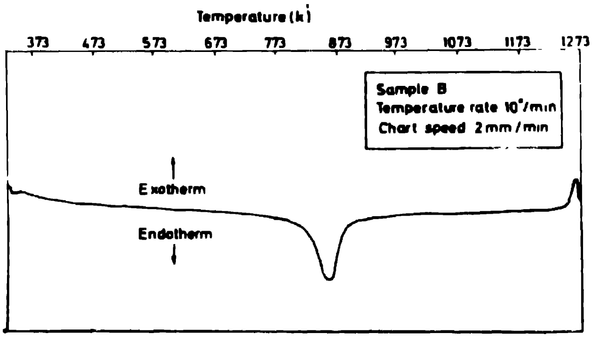

Figure 2. DTA of washed BWC.

BWC [11]. The curve has an intense endothermic reaction at 853 K corresponding to the evolution of the water of crystallization, *i.e.*, the expulsion of water from mineral lattice and thereby forming metakaolinite. This endothermic peak is about 30 K lower than that for well crystallized kaolinite [12]. The exothermic peak at 1266 K is characteristic of the clay mineral kaolinite. This exothermic peak is also considered to be resulted from mullite formation [11].

3.3. IR spectrometric analysis :

IR absorption spectra for samples B, C and D are given in Figure 3. The major absorption bands for these three spectra are summarized in Table 5. The spectrum 1, for sample B, shows a close similarity to a standard kaolinite [13,14] along with other absorption bands.

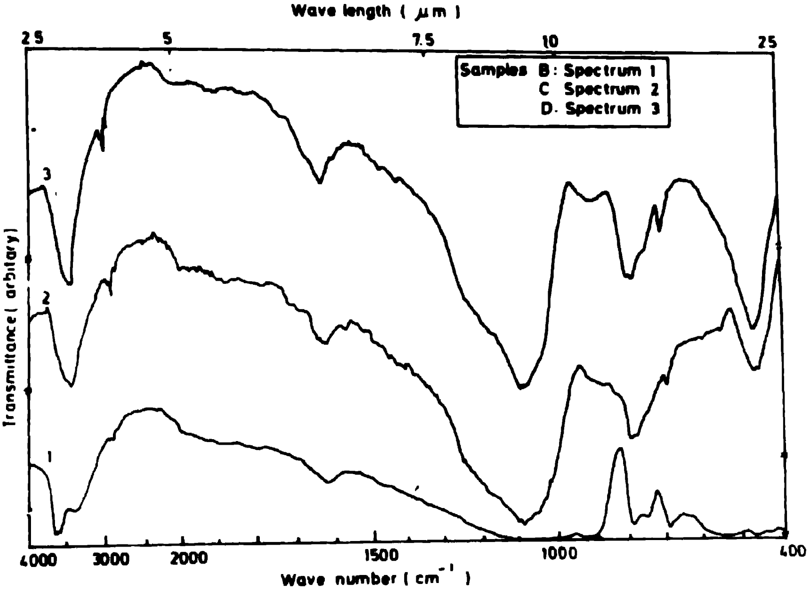

Figure 3. IR spectra of various samples of BWC.

The minor departure in the absorption features of this clay with that of standard kaolinite may be attributed to the variation of kaolinitic content, degree of crystallinity, presence of other constituents *etc*. In spectrum 2, for sample C, it is seen that the absorption of kaolinitic OH stretch at 3600–3700 cm^{-1} disappears which agrees well with the result of XRD of sample C (diffractogram : 3, Figure 1). In spectrum 3, for sample D, the absorptions at 3600–3700 cm^{-1} is also absent which again agrees with the result of XRD of sample D (diffractogram : 4, Figure 1). And the kaolinitic absorptions decrease further and only 780, 690 and 460 cm^{-1} are observed. Which indicates the transformation of kaolinite to its high temperature mullite phase. This fact corroborates with the result of XRD analysis. The number of IR bands for silicon oxide [15], those are found in spectrum 1 are reduced in spectrum 2 and 3 (samples C and D).

Table 5. Comparison of the absorption bands for washed and heat treated BWC samples of major constituents.

Sample absorption	B wave no. cm^{-1}	C wave no. cm^{-1}	D wave no. cm^{-1}
Kaolinite	3700, 3660, 1108, 1025, 1000, 910, 782, 749, 690, 530 and 422	782, 690 and 460 (weak)	782, 690 and 460 (very weak)
Silicon oxide	1160, 1055, 790, 690 and 450	1108, 782, 690, 460 and 440	790, 770 and 460

3.4. Optical analysis :

Microphotographs of different samples are presented in Figure 4. It is obvious that the surface structure changes significantly on heat treatment and pressure of pellet preparation. It is found that porosity in the pellets decreases with the increase of pellet preparation pressure. It is clearly seen that cluster results due to heat treatment at higher temperature. This may be an indication of decomposition and structural change that might have taken place in the BWC owing to heat treatment.

4. Conclusions

The XRD analysis of BWC reveals that it is possible to remove a major part of silica by washing. The DTA experiment reveals that metakaolinite is formed after evolution of water of crystallization at 853 K. And a high temperature mullite phase at about 1273 K is also observed. On heat treatment, as has been seen from the XRD and DTA, in the temperature around 1273 K, the washed BWC transforms to possible mullite phase. From the IR bands it is seen that the BWC samples under examination are identical with those of the clay mineral, kaolinite. It is also seen that the OH stretching is not present in heat treated (773–1273 K) BWC. The photomicrographs manifest the formation of clusters of different sizes on heat treatment.

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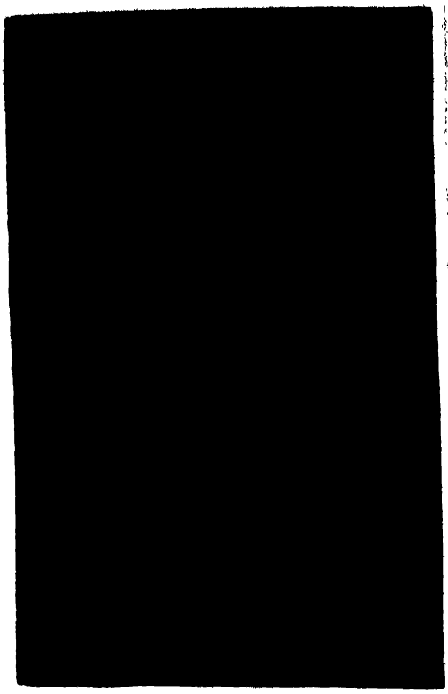
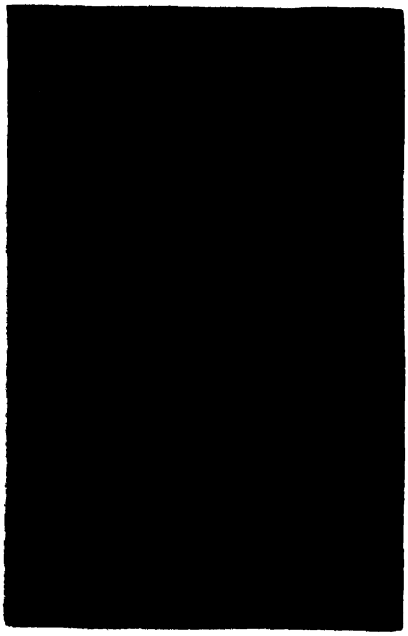
Plate I

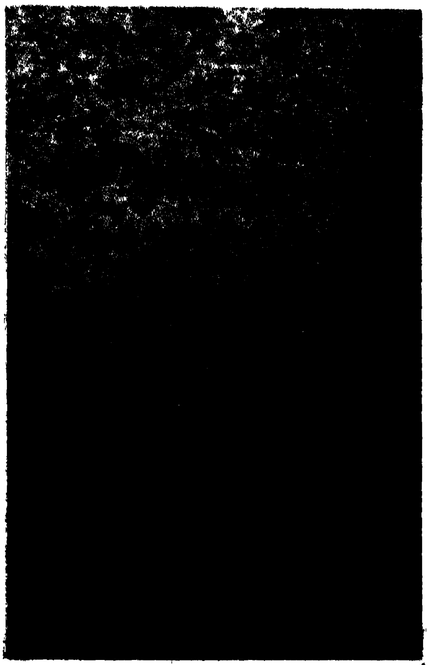


Sample A1

Sample A3



Sample D1



Sample D3

Figure 4. Photomicrographs (250x) of samples

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