

STUDIES ON CHERAT VOLCANIC ASH NWFP PAKISTAN

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The volcanic ash deposits of Garhi Chandan near Peshawar have been studied for the first time. Geology, chemistry, swelling properties, bleaching property, x-ray diffraction, DTA, DTG and TG results have been presented in the paper. These studies reveal that volcanic ash contains montmorillonite, illite, feldspar, quartz and calcite. Acid activation tests show that the bleaching property of volcanic ash is sixty per cent active as compared to that of imported fuller's earth. Volcanic ash after beneficiation may be exploited commercially as a filler in soaps, paper, plastics and other products and as a decoloriser of vegetable oil.

Key words: Volcanic ash, Cherat, NWFP - Pakistan.

Introduction

Activated bentonites are extensively employed in refining and bleaching mineral and vegetable oil. Bentonite formed by the alteration of volcanic ash [1] is composed of montmorillonite ($\text{Al}_{1.67} \text{Mg}_{0.33}^{\text{Ca}_{0.33}} \text{Si}_4\text{O}_{10}(\text{OH})_2$ with substitution of magnesium for part of aluminum and minor beidellite (hydrous AlSiO_2) with traces of constituents like feldspar, gypsum, quartz, calcite and other minerals. Bentonite may be of varying colour like white, gray, pink or brown, yellowish, green or olive green.

This paper presents a preliminary characterization and resource evaluation of Cherat olive gray volcanic ash which is altered to montmorillonite with subordinate amounts of illite, feldspar, calcite and quartz.

Materials and Methods

Geology of the area. The volcanic ash deposits are located along Spin Khak-Matanni road near Garhi Chandan village and Irish bridge at a distance of 25 and 28 km respectively south-east of Peshawar (Fig 1).

The ash is found within lacustrine sediments unconformably overlying Murree formation of early miocene age. The ash bearing sediments are tilted and cut by the ENE trending Irish bridge fault with the northern side upthrown [2]. In Garhi Chandan area, three volcanic ash horizons upper, middle and lower are found having thicknesses of 2.00 meters, 1.30 meters and 1.50 meters respectively and they can be traced for about one kilometer. Burbank and Tahirkheli [3] dated the lower ash horizon by the fission-track method at 2.4 ± 0.2 million years. The ash is olive gray, massive, friable and coarse grained. The upper portion of the ash outcrop is highly weathered and contaminated with sandy and clayey material. The lower 0.50 meters of ash horizon has a distinct

dark gray colour and contains rich concentrations of biotite flakes. The Irish bridge locality contains only one ash horizon which is 1.50 meters thick and exposed intermittently for nearly one kilometer. The physical characters of this locality are similar to the Garhi Chandan ash horizon.

Chemical analyses. 100g of each sample of the volcanic ash were ground to a fine powder (-100 ± 120 mesh) and analyzed using standard method of chemical analysis [4]. The constituents determined were SiO_2 , Al_2O_3 , Fe_2O_3 , FeO , CaO , MgO , TiO_2 , MnO , P_2O_5 , Na_2O , K_2O and L.O.I. The results are given in Table 1.

Benzidine test. Benzidine or Benzidine hydrochloride produces a blue coloration [5] in contact with clay minerals

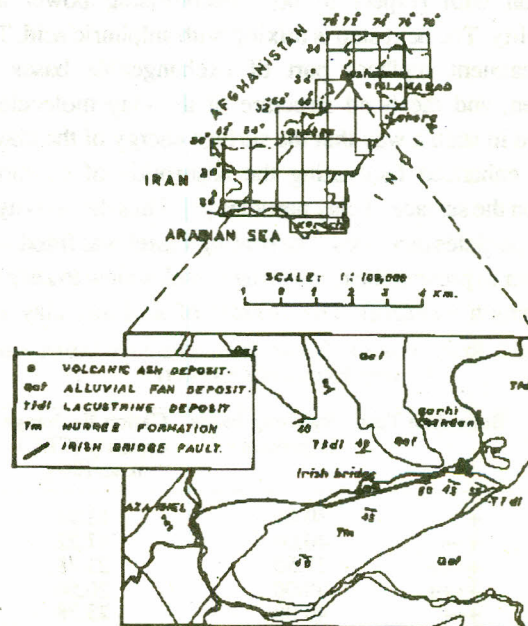


Fig 1. Location map showing the volcanic ash deposits in Cherat Area, N.W.F.P., Pakistan.

TABLE 1. CHEMICAL COMPOSITION OF CHERAT VOLCANIC ASH

Weight %	Samples							
	1	2	3	4	5	6	7	8
SiO ₂	58.01	58.10	58.80	57.80	56.82	63.60	60.20	61.23
Fe ₂ O ₃	3.22	3.13	3.38	3.76	3.54	2.87	2.88	4.47
FeO	0.81	0.76	0.67	0.90	1.08	1.34	1.40	0.56
Al ₂ O ₃	14.02	15.04	14.47	15.92	16.39	16.90	14.05	13.80
TiO ₂	1.40	0.90	0.60	1.01	1.02	1.03	0.90	1.02
MnO								
P ₂ O ₅	0.50	0.18	Trace	0.10	0.34	0.10	Trace	0.10
CaO	7.17	7.18	6.49	4.72	4.02	3.36	4.70	4.56
MgO	0.59	0.54	1.15	1.01	1.59	0.86	1.15	4.86
Na ₂ O	3.75	4.10	2.75	3.15	3.01	3.20	2.25	2.50
K ₂ O	1.75	1.10	1.75	1.65	1.70	2.74	2.02	2.00
L.O.I.	8.80	8.80	10.10	10.40	10.40	4.50	9.61	8.80
Total	100.02	99.83	100.16	99.42	99.91	100.50	99.16	99.90

of the montmorillonite group. A saturated water solution of Benzidine hydrochloride was mixed with Bentonite and formation of blue colour was studied. The results are given in Table 2.

Acid activation. The aim of the activation test is to find a suitable use of the extensive deposits. Activated clays are used for bleaching of oils-vegetable as well as petroleum products. In order to assess the suitability of volcanic ash, a composite sample was used. The initial step in this process is crushing the raw sample. Though bentonite particles of finer size offer a greater surface area for activation, the material passing through 100 mesh is found to be satisfactory for activation with respect to both decolorising power and filterability. The next step is mixing with sulphuric acid. The acid treatment replaces part of exchangeable bases by hydrogen, and the bond structure of the clay molecule is modified in such a way that the surface energy of the clay is sharply enhanced facilitating the adsorption of colouring matter on the surface of clay particles [6]. Thus the activity of the clay particles increases. The heating vessel was fitted with condenser to prevent the loss of water (with a view to keep the acid strength constant). The mixture of acid and clay was

TABLE 2. RESULT OF BENZIDINE TEST, SWELLING INDEX AND CATION EXCHANGE CAPACITY

Sample	Benzidine Test	Swelling Index in percent	Cation Exchange capacity (CEC) m.eq/100 g
1.	+	30.00	13.94
2.	+++	40.00	17.22
3.	++++	27.50	23.78
4.	++++	30.00	20.50
5.	+++	40.00	23.78
6.	++	10.00	7.32
7.	+	32.50	18.32
8.	-	32.00	17.22

heated for a pre-determined optimum period when maximum base exchange takes place between clay and acid. Incomplete reaction means the occurrence of less than maximum base exchange between the reactants resulting in low adsorption capacity. The treated mixture was washed on a Buchner filtering funnel or by decantation until substantially free from excess acids and salts. The filter cake was dried at 110°, ground to pass through 300 mesh and kept in air tight bottles. Acid activation test was performed on the composite sample prepared by mixing equal quantity of each sample.

Decolorising property. The test for decolorising property of activated volcanic ash was done with standard methylene blue dye solution. (1 ml = 1 mg) 1 gm of activated sample was placed in a beaker and standard methylene blue was added in small quantity at a time. Imported activated clay (Fuller's earth, BDH) was treated likewise and bleaching values compared with the samples prepared in the laboratory. The results are given in Table 3.

TABLE 3. DECOLORISATION PROPERTY

Volume of methylene blue Decolorized by one gram activated volcanic ash	Volume of methylene blue decolorized by one gram fuller's earth (BDH)
70 ml	115 ml

Base exchange capacity. For the determination of cation exchange capacity [7] exactly the above method (decolorising test) was applied, except that the crystalline dye was dried at 105° (to remove any absorbed water due to hygroscopicity of the dye) before dissolving 3 g/litre in distilled water. The weight loss at 105° being 12.34 per cent.

As the equivalent weight of the anhydrous dye is 319.9, the normality of the methylene blue solution is $3/319.9 \times 100.00 - 12.34/100 = 0.0082$ N.

The CEC in milliequivalent per 100 g dried clay is calculated from the formula:

$$\text{CEC} = \frac{100 \times \text{volume of methylene blue decolorized}}{\text{weight of dried sample (at } 105^\circ) \text{ taken}} \times 0.0028$$

The cation exchange capacity of the samples expressed as m.eq/100 g is given in Table 2.

Swelling characteristics. Swelling index is the relative expansion in volume with respect to dry clay material. Bentonite or montmorillonite clays are characterized by their ability to swell when immersed in water [5] and show swelling properties 15 times the volume of the dry material. When saturated they form a gelatinous mass and remain in suspension for weeks before settling. This property is one of the few reliable tests to identify bentonite; no other clay material will remain in suspension more than a few hours. Chemical

analyses of the swelling bentonites show them to be high in alkalis (up to 5.70% Na₂O) earths with sodium predominating [8]. These constituents are mostly in the form of replaceable ions.

Swelling characteristics of the samples were determined by taking 10 cm of dry material (-30 + 52 mesh; the coarse material is usually preferred for this test to facilitate the trapped air bubble to escape during the process) to a 100 cubic centimeter graduated cylinder and adding water up to mark of 100 cubic centimeter. The sample was left to stand for 68 hours and apparent volume of the settled clay was noted. The swelling index of the samples expressed as m.eq/100 g is given in Table 2.

X-ray diffraction (XRD) analyses. The X-ray powder diffraction data of the samples of volcanic ash are given in Table 5. Seifert X-ray unit with Debye-Scherrer Camera (dia = 11.4 cm) was used. Paste of the sample was made with a drop of collodion and molded to a cylinder 0.5 cm in diameter and 1 cm in length. The samples were irradiated to Ni-filter Cu K α radiation for 6 hours at 35 kV and 20 mA. X-ray powder data is in Table 4.

Thermal analysis. MOM Derivatograph (Paulik-Erdey Hungary) [9] was used for simultaneous Differential Thermal Analysis (DTA). Thermogravimetry (TG) and Derivative Thermogravimetry (DTG) for all the samples. The experiments

were carried out using platinum crucibles and static air atmosphere over a temperature range 20-1000°. Heating rate was 10°C/min. Alumina (Al₂O₃) heated previously at 1000° was used as reference material. The derivatogram (DTA, TG and DTG curves) was recorded on a photographic chart. Derivatograms of the samples are shown in Fig 2.

Results and Discussion

XRD reflections (Table 4) for plagioclase feldspars (3.18, 4.04, 3.34 Å) and quartz (3.36, 4.26, 1.82 Å) are present in all the samples. Reflections for calcite (3.03, 2.09, 2.82 Å) are present in sample 1 and 2 and of very low intensity in 7 and 8. Reflections of calcite are often overlapped by the reflections of feldspar. However, reflections at 2.03 Å in all the samples could not be identified. All the samples have been analyzed before and after ethyl glycol treatment. Samples 2,3,4,5 and 7 seem to contain montmorillonite giving reflection at about 14.7 Å with very low intensity. Reflections for illite (4.46, 3.36, and 2.57 Å) with very low intensity are also present in all the samples except sample 6. Sample 6,7 and 8 also contain hematite (2.69, 1.69, 2.51 Å).

The thermal curves of all the samples are similar. Endothermic peaks in DTA curves due to moisture are at 120° in all the samples. Montmorillonite loses inter-layer water in the range 100-120° giving a collapsed structure.

TABLE 4. X-RAY POWDER DIFFRACTION DATA OF CHERAT VOLCANIC ASH

Sample-1		Sample-2		Sample-3		Sample-4	
a	b	a	b	a	b	a	b
d Å	I*	d Å	I*	d Å	I*	d Å	I*
4.23	10	9.82	1	14.70	1	15.75	1
4.40	5	6.32	2	9.82	10	6.55	2
3.63	5	4.23	20	4.23	1	4.23	5
3.36	95	4.04	25	4.04	1	4.04	10
3.18	80	3.90	1	3.70	1	3.70	1
3.02	60	3.73	10	3.35	30	3.36	70
2.93	1	3.64	1	3.18	30	3.18	60
2.80	5	3.36	95	3.02	15	3.02	60
2.42	1	3.18	90	2.93	5	2.93	5
2.39	1	3.02	50	2.84	1	2.82	1
2.28	20	2.93	10	2.28	2	2.52	5
2.12	1	2.84	10	2.12	1	2.28	10
2.10	1	2.52	20	1.98	1	2.10	1
1.97	2	2.45	1	1.89	1	1.91	1
1.90	3	2.28	20	1.82	1	1.87	1
1.86	3	2.12	5	1.66	5	1.82	2
1.82	10	2.03	1	1.54	1	1.66	1
1.77	2	1.99	1	1.37	1	1.54	5
1.66	5	1.91	5	1.18	1	1.37	1
1.54	10	1.87	5	1.16	1	1.54	10
1.37	10	1.82	10			1.37	2
		1.54	10				
		1.37	10				
		1.35	1				

Contd. Table 4

Contd. Table

Sample-5		Sample-6				Sample-7				Sample-8			
a	b	a	b	a	b	a	b	a	b	a	b	a	b
d Å	I*	d Å	I*	d Å	I*	d Å	I*	d Å	I*	d Å	I*	d Å	I*
13.50	1	14.00	1	4.23	30	4.23	10	14.73	1	15.00	1	11.05	2
4.46	2	4.23	5	4.04	25	4.04	10	9.82	2	3.70	2	4.43	1
4.23	1	4.04	30	3.76	15	3.73	10	3.36	95	3.36	95	4.25	2
3.73	1	3.73	1	3.63	2	3.36	95	3.18	90	3.18	90	4.04	10
3.36	50	3.36	50	3.36	95	3.18	80	3.02	10	3.02	10	3.78	5
3.18	50	3.18	50	3.18	85	2.93	5	2.67	2	2.67	2	3.64	1
3.02	1	3.02	1	2.93	2	2.28	5	2.28	5	2.28	5	3.36	50
2.93	1	2.93	1	2.63	5			2.12	2	2.12	2	3.18	50
2.84	1	2.84	1	2.52	4			2.01	2	2.01	2	3.02	10
2.52	1	2.28	2	2.42	5							2.93	5
2.28	2	2.03	1	2.28	10							2.84	1
2.03	1			2.12	5							2.63	1
1.54	2			2.03	5							2.52	1
1.48	1			1.82	20							2.46	1
1.41	1			1.66	10							2.30	5
1.37	1			1.54	30							2.11	1
				1.51	1							2.03	1
				1.37	10							1.84	2
				1.29	2							1.80	2
												1.54	5
												1.38	2

a = Sample as such, b = Sample after ethyl glycol treatment

* Intensities were measured visually

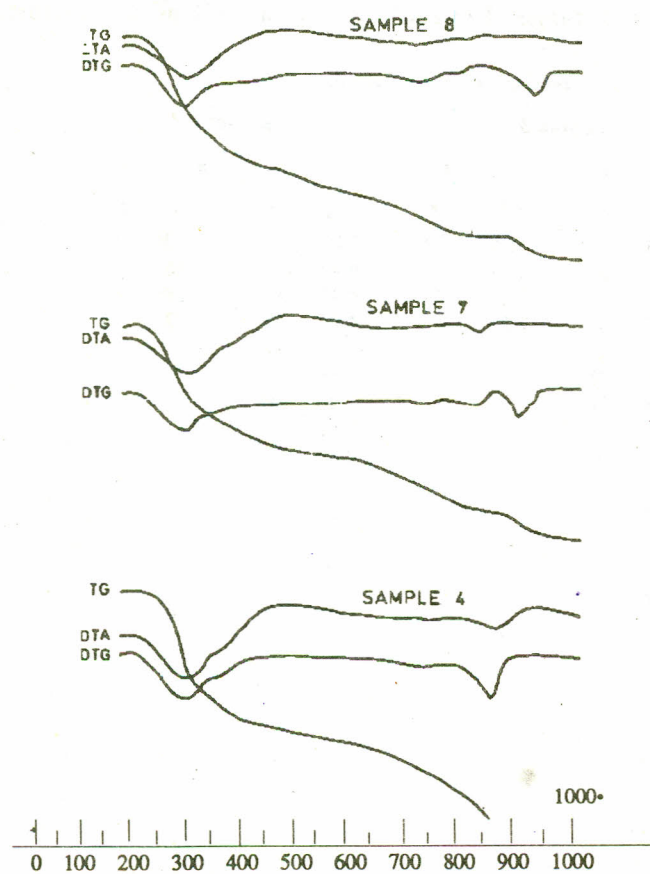


Fig 2. Derivatograms of sample No. 4, 7 and 8

Montmorillonite on heating at 500-700° loses water of constitution from the hydroxyl group. At about 850° montmorillonite gives an endothermic peak. Mixed layer illite-montmorillonite clay gives a small hump in the endothermic peak at about 200°. The absence of an endothermic peak in DTA curve caused by the decomposition of calcite ($\text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2$) indicates the presence of calcite in very low quantity.

Cherat volcanic ash is characterized by a high silica content ranging from 57.08 to 63.60%, moderate lime content 3.36 to 7.18% and high iron content Fe_2O_3 2.87 to 4.47%; FeO 0.56 to 1.40%. All the samples contain high alkali content Na_2O 2.25 to 4.10% K_2O 1.10 to 2.74% which conforms to their swelling character. All the samples under study do not exhibit any marked difference in their chemical composition.

Chemical analyses alone, however, are of little value in determining the quantity of any particular clay mineral in a mixture. This is due to similarities in chemical composition of certain minerals of various groups. It is, therefore, difficult to say which material chemically analyzed should be classed as bentonite.

However, X-ray diffraction analyses indicate the presence of montmorillonite, illite, feldspar and calcite in Cherat ash samples. The high TiO_2 contents in all the samples are due to illite. Alkalis may be partially attributed to the presence of

feldspar. However, presence of calcite in very low quantity is indicated.

Sample 3,4 and 5 show cation exchange capacity in the range of 20.50 to 23.78 m.eq/100 g whereas CEC of sample 1,2,6,7 and 8 is in the range of 7.32 to 18.32 m.eq/100 g. Therefore, samples 3,4 and 5 have more bentonite than other samples.

Acid activation imparts bleaching property to the volcanic ash samples and bleaches 70 ml of methylene blue dye solution (1 ml=1 mg) as compared to 115 ml methylene blue solution bleached by imported fuller's earth. The low result may be attributed to the impurities (grit) present in the sample (nearly 44%). If the gritty matter is removed by elutriation the activity will greatly enhance. The economics of the activation process, however, involves consideration of the cost of filtration, removal of the acid employed for activation, elimination of wastage of bentonite in the separation of gritty matter and the drying of the activated clay at optimum temperature.

The preliminary studies on cherat ash show that the ash has been altered to bentonite approximately to the same degree, but in its original form has no commercial use. The ash, after beneficiation by elutriation, may be utilized commercially as a filler in soaps, paper, plastics and other products and as decoloriser of vegetable oil and petroleum products.

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samples.

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