MINERALOGY OF SOME ASBESTOS FROM NORTH-WEST PAKISTAN

M. A. QAISER, M. K. ALI and A. H. KHAN

North Regional Laboratories, Pakistan Council of Scientific and Industrial Research, Peshawar

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Chemical, X-ray, differential thermal analysis and thermogravimetric data are presented for asbestos from Charsadda Tehsil, Khyber and Mohmand Agencies. Asbestos from Charsadda area was identified to be chrysotile, Khyber and Mohmand minerals were tentatively grouped with tremolite-anthophyllite asbestos. Poor strength of fibres limits their commercial utilisation.

The critical shortage of asbestos fibre in Pakistan today brings to the foreground the question of locating and developing new deposits. Sporadic reports have appeared as to the occurrence of asbestos. Data on the physical and chemical characteristics of the indigenous asbestos are scarce.

The object of the present paper is to report the chemical, X-ray and thermal properties of asbestos from Charsadda Tehsil, and Mohamand and Khyber Agencies.

Materials and Experimental Procedure

In Charsadda area deposits of asbestos are sporadically developed near the Qilla village $(34^{\circ}26',$ $71^{\circ}46')$ about 8 miles from Tangi. The slip fibre asbestos veins are located between lameller antigorite of serpentine rock mass, and are sometimes 10 inch thick. The country rock was most probably formed by the serpentization of dunite. Lenses of chrome ores are also found in the serpentine rocks.

Since 1964 the people of the nearby villages have been selling the asbestos to dealers in Peshawar. Mining methods are primitive. About 20 tons of asbestos is produced every month. The pits' mouth value of Qilla asbestos is about Rs. 120 per ton.

The occurrence of asbestos in the Khyber Agency was first described by A.L. Coulson. He noted small veins of slip fibre asbestos in limestone near the junction with an intrusive epidiorite on the side of the road from Char Bagh Fort (34°07', 71°07') to the Kafir Kot piquet post, but found it uneconomical. In spite of its uneconomic nature it has been used in Peshawar as a substitute of imported asbestos.

The sample from Mohmand Agency was collected by a tribesman. Its geology and extent is not known. The three samples examined were Chrystotile from Qilla, and tremolite- anthophyllite from Khyber and Mohamand Agencies (Table 1).

Chemical Analyses.—All the three samples were analysed by classical methods. Structural water of sample K_1 was estimated by the Penifield tube method. This method gave low results for K_2 and K_3 samples. As the amount of carbonate mineral in K_2 is low and is absent in K_3 the loss on ignition minus absorbed water and carbon

C	C 1	T .		Feel	
Source	Colour	Lusture	Bulk	Fibre	Identification
Qilla, Charsadda area	Greenish white	High silky	Soft	Silky fibres, flexible weak threads	Chrysotile
Char Bagh Fort, Khyber Agency	Light brown	Silky	Waxy	Thread-like, flexible, weak	Tremolite- anthophyllite
New Dehrai Mohmand Agency	White	Silky	Waxy	Thread-like, very weak	Tremolite- anthophyllite
	Source Qilla, Charsadda area Char Bagh Fort, Khyber Agency New Dehrai Mohmand Agency	SourceColourQilla, Charsadda areaGreenish whiteChar Bagh Fort, Khyber AgencyLight brown WhiteNew Dehrai Mohmand AgencyWhite	SourceColourLustureQilla, Charsadda areaGreenish whiteHigh silkyChar Bagh Fort, Khyber AgencyLight brownSilkyNew Dehrai Mohmand AgencyWhiteSilky	SourceColourLustureQilla, Charsadda areaGreenish whiteHigh silkySoftChar Bagh Fort, Khyber AgencyLight brownSilkyWaxyNew Dehrai Mohmand AgencyWhiteSilkyWaxy	SourceColourLustureFeelQilla, Charsadda areaGreenish whiteHigh silkySoftSilky fibres, flexible weak threadsChar Bagh Fort, Khyber AgencyLight brownSilkyWaxyThread-like, flexible, weakNew Dehrai Mohmand AgencyWhiteSilkyWaxyThread-like, very weak

TABLE I.—DESCRIPTION OF SAMPLES.

dioxide was regarded as equivalent to structural water.

X-ray Diffraction.—Clean materials from each of the representative samples were examined by X-ray fibre and powder methods. Copper radiation with a nickel filter was used in these experiments. Fibre photographs were taken with a fibre camera, the distance between the fibre and the film being 4 cm. Powder photographs were taken with a 114.6 mm diameter Debye-Scherrer camera. Exposure time for fibre and powder patterns were 2.50 and 7.0 hour respectively, with X-ray unit running at 40 kV and 21 mamp.

Differential Thermal Analysis.—D. T. A. was carried out with a uniform rise of temperature of the furnace (10°C per min) controlled by a Variac transformer. DTA curve was recorded on a Cambridge Recorder with a range of +1 to -1 mV.

Thermobalance —Brabender thermobalance was used in the present investigation.

Results and Discussion

1. Oxide Composition of Minerals

The results of the chemical analysis of absestos are given in Table 2. The relationship of the ions in octahedral and tetrahedral coordination as calculated from the checmial analyses of the specimens are shown in Table 3. The method of calculation is similar to that given by Hendricks and Ross.⁵ The structural formula for the samples may be written as :

$$\begin{array}{cccccc} \mathrm{K_{1}} & \mathrm{Mg_{5.51}} \ \mathrm{Fe_{0.03}^{+2}} \ \mathrm{Fe_{0.15}^{3+}} \ \mathrm{Al_{0.16}} \ (\mathrm{Si_{3.97}} \ \mathrm{O_{10}}) (\mathrm{OH})_{8} \\ \mathrm{K_{2}} & \mathrm{Ca_{1.121}} \ \mathrm{Mg_{6.117}} \ \mathrm{Fe_{0.017}} \ \mathrm{Fe_{0.451}} \ \mathrm{Mn_{0.033}} \\ & \mathrm{(Si_{7.456.22})} \ (\mathrm{OH})_{2} \\ \mathrm{K_{3}} \ \mathrm{Ca_{1.887}} \ \mathrm{Mg_{4.71}} \ \mathrm{Fe_{0.123}} \ \mathrm{Fe_{0.181}} \ \mathrm{Mn_{0.025}} \\ & \mathrm{(Si_{7.95}O_{22})} \ (\mathrm{OH})_{2} \end{array}$$

2. X-ray Diffraction Studies

Chrysotile.—The X-ray diffraction data of sample K_1 is given in Table 4. Pattern as a whole is diffuse though the reflections at d=7.36, 4.52, 3.66 and 1.53A are quite well defined. Fibre pattern is also diffuse but comparable to the Canadian chrysotile in d values. Treatment with 1N hydrochloric acid on water bath for 1 hr. as well as heating the fibre to 400° C for 30 min resulted in a marked decrease in the intensity of the pattern. When the fibre was heated to 600° C no pattern was observed on the film, most probably due to the collapse of chrysotile structure.

Tremolite-anthophyllite Asbestos.—The X-ray diffraction data of K_2 and K_3 (Table 5) are rather complex. The well-defined lines having similar

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		K1%	K2%	K ₃ %
010 ₂	••	41.33	50.90	58.05
A1203		1.46	0.12	0.00
e ₂ O ₃		2.00	1.60	I.20
feO		0.39	3.67	2.46
MnO		0.00	0.27	0.22
MgO		38.45	27.88	23.10
CaO		0.00	7.12	12.88
Na ₂ O		0.29	0.35	0.14
K ₂ Ō		0.06	0.10	0.02
H_2O+		12.36	6.68*	2.20*
$H_{2}O^{-}$		3.50	0.57	0.00
ſiŌ,		0.00	0.00	00.00
CO,		0.00	0.55	0.00
$P_{2}O_{5}$		0.52	0.35	0.12
2 -				0.14
Total		100.36	100.16	100.39
Sp. gr.		2.10	2.10	2.84

* Caclulated from loss on ignitition.

TABLE 3.—RELATION OF THE IONS IN OCTAHEDRAL AND TETRAHEDRAL COORDINATION AS CALCULATED FROM THE CHEMICAL ANALYSES OF THE SPECIMENS STUDIED.

Samples		Ions in octahedral co-ordination						Ions in tetrahedral co-ordination					
bampies	Mg	Fe ²⁺	Fe ³⁺	Al	Mn	Ca	Na	K	Σ' oct.	Si	Al	Fe ³⁺	Σ tet.
K ₁ *	5.51	0.03	0.15	0.16	<u> </u>	—	0.05	0.007	5.907	3.97	_		3.97
K ₂ **	6.12	0.45	0.018	0.021	0.033	I.121	0.099	0.018	7.88	7.45	_		7.45
K ₃ **	4·71	0.181	0.025		0.025	1.887	0.037	0.003	6.868	7.95	-	—	7.95

* Calculated on the basis of 18 (O, OH). ** Calculated on the basis of 24 (O, OH).

d values (7.93, 3.06, 2.66, 2.29, 2.14, 1.99, 1.64, 1.57, 1.49, 1.43, 1.36A) are present in both the samples. When the d values are compared with the d values of anthophyllite ¹,³ there is a marked similarity except that 3.24A reflection is very

TABLE 4.-X-RAY DIFFRACTION DATA FOR K1.

	K ₁ (F	ibre)	K ₁ (Por	wder)	Chrysotil	le ⁸	
~	d(A)	I	d(A)	Ι	$\overline{d(A)}$	Ι	
	7.37	VS	7.36	S	7.36	10	
	4.59	S	4.52	S	4.58	6	
	3.72	VS	3.66	S	3.66	10	
	2.68	vw			2.66	4	
			2.56	w	2.549	6	
	2.48	S	2.44	S	2.456	8	
	-		2.08	vw	2.096	6	
			1.72	vw	1.748	6	
			1.53	vs	1.536	8	
			1.31	w	1.317	4	

weak in both K_2 and K_3 ; these lines have been reported to be strong in anthophyllite. Presence of the strong reflection d=7.93A together with weak line d=3.31A is suggestive of the tremolite structure ³,⁶ have shown that tremolite could be distinguished from anthophyllite by the presence of a strong reflection d=2.71A. Absence of this reflection in both K_2 and K_3 does not support the tremolite structure. As both the tremolite and anthophyllite are the members of the amphibole series it is very likely that K_2 and K_3 have structures in between tremolite and anthophyllite. Thus K_2 and K_3 may be regarded tentatively as tremolite—anthophyllite asbestos.

3. Differential Thermal Analysis

Chrysotile.—The DTA of K_1 is compared with the Canadian chrystoile in Fig. 1. The similarity is very obvious. K_1 is characterised by a small endothermic peak between room temperature and 140°C which corresponds to the removal of absorbed water. Another peak appears between 590° and 690°C with the peak position at 687°C. The endothermic trough is

TABLE 5.-X-RAY POWDER DATA FOR K2 AND K3.

K ₂		K	-3	Anthophy	llite ¹	Tremolite ³		
d(A)	I	d(A)	I	d(A)	I	$d(\mathbf{I})\mathbf{A}$	Ī	
7.93	VS	7.93	vs			7.92	s	
4.37	VW			-	-	-	-	
3.308	VW	3.31	vw	3.36	7	3.32	vvw	
3.20	W	3.23	vw	3.23	5	3.22	vw	
3.068	VS	3.06	VS	3.05	26	3.07	ms	
2.88	w	2.89	w	2.87	5		_	
2.66	VS	2.66	VS	2.688	7			
2.55	W	2.55	W	2.54	10	<u> </u>		
2.48	w	2.48	W	2.43	3	2.49	w	
2.29	S	2.29	- S	2.29	5	2.31	ms	
2.13	S	2.14	S	2.142	7			
1.99	S	1.99	S	1.99	4			
1.87	W	1.87	w	1.875	2.5	1		
1.79	vw	1.79	vw	I.734	7			
_		1.67	vw	1.693	3		<u> </u>	
1.64	VS	1.64	VS	1.639	2	1.65	vvw	
1.56	w	1.57	S	1.583	5	and the second s		
1.52	w	1.52	vw	1.530	2	1 - Carl		
1.49	S	1.49	S	1.503	7		- S.	
1.42	VS	1.43	VS	I.45	ms	I.45	- S	
1.36	S	1.36	S	1.364	3	1.35	vvw	
1.33	S	1.33	w	1.33	5			
		1.30	w	1.308	2	_		
1.20	w	1.29	W	1.294	1.5			
1.28	w		—		— °	1.28	w	

the record of the heat effect on destruction of crystal structure due to the loss of hydroxyl ions. The exotherm begins at 830°C, sharply reaches the peak at 833°C and ends at 870°C. The exothermic peak corresponds to the heat effect accompanying the recrystalization of the dehydrated chrysotile into a new phase-assemblage.⁴

Tremolite Anthophyllite Asbestos.—The DTA curve of Khyber asbestos (K_2 , Fig. 2) is marked by an endotherm and an exotherm. The curve is almost parallel to the base line upto 633°C. The endotherm reaches the peak at 644°C and ends at 690°C. The exotherm is very sharp, begins at 825°C reaches the peak at 838° and ends at 865°C. The DTA curve of Mohmand asbestos (K_3 , Fig. 2) is almost parallel to the base line upto 1000°C.

The great contrast between the DTA curves of K_2 and K_3 and similitude between K_1 and K_2 are inexplicable, especially when the X-ray diffraction of K_2 and K_3 have common strong lines.

4. Thermogravimetric Investigations

Chrysotile.—The dehydration curve of Qilla Chrysotile (K_1) is shown in Fig. 3. There is a rapid loss of absorbed water between 40° and 150° C. Another big loss (about 10.6%) occurs between 590° and 800° C. This loss corresponds with the endothermic reaction as shown by the DTA curve. The loss in weight is only 0.3% between 800° and 1000° C. The dehydration curve of Qilla chrysotile is very similar to those of kaolinite and halloystie.

Tremolite-Anthophyllite Asbestos.—There is a continuous loss in weight between 40° and 570° C on heating the Khyber asbestos (K₂, Fig. 4). Between 570° C, and 630° C, loss is about 3.3%. The specimen also shows a small inflection between 740° and 910° C approximately. This



Fig. 1.—DTA curves [a, Canadian chrysotile; b, Qilla asbestos (K_1)].

suggests that a portion of the water is held somewhat more strongly than that given off at the lower temperature. Such a two-step dehydration is not observed for Mohmand asbestos (K_3 , Fig. 5). There is a small continuous loss in weight between 150° and 350°C. Beyond 350°C



Fg. 2.—DTA curves [(a, Khyber Agency asbestos (K₂); b, Mohmand Agency asbestos (K₃)].



Fig. 3.—Thermogravimetric curve of K1.



Fig. 5.—Thermogravimetric curve of K_3 .

monotonic character is demonstrated upto 880° C. Most of the water is removed between 880° and 950° C. The total loss in weight approximates about 2.2%. Posnjak and Bowen⁷ demonstrated the role of water in tremolite by static-loss experiment. They showed that the theoretical water content (2.22%) is driven off, and the following reaction takes place in the sloid state.

$$\begin{array}{rl} \mathrm{Ca_2Mg_5Si_8O_{22}} & (\mathrm{OH})_2 + \bigtriangleup H = 2 & \mathrm{CaSiO_3.} \\ & 5\mathrm{Mg}\,\mathrm{SiO_3} + \mathrm{SiO_2} + \mathrm{H_2O} \end{array}$$

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A similar reaction is suggested for K_3 taking into account the correspondence in the temperature of dissociation and the amount of water lost.

Conclusions

Chemical compositions X-ray diffraction data, DTA, dehydration curve and specific gravity of Qilla asbestos clearly indicate chrysotile structure. Poor tensile strength seems to be the only disadvantage for the commercial utilisation of this asbestos.

The great similarity in the X-ray diffraction data, but variations in chemical composition, DTA, dehydration curve and specific gravity of Khyber and Mohmand asbestos complicate correct identification. The two minerals have been tentatively grouped with tremolite-anthophyllite asbestos. Poor strength of these limits the utilisation. Acknowledgement.—The authors are thankful to Dr. S. A. Warsi, Director, North Regional Laboratories, Peshawar, for encouragement throughout the work. Thanks are also due to members of the staff of Geochemistry and Mineral Exploration Section for their help during the progress of the work.

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