

**STUDY OF PROPERTIES AND MINERALOGY OF A SALT RANGE HALOTRICHITE**

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A naturally occurring alum from Karuli area (Choa Saidan Shah) District Jhelum has been studied for its physical characteristics and chemical composition. It has been identified as Halotrichite by DTA, Spectroscopy, and X-ray diffraction analysis. The assemblage in which it occurs consists of mainly halotrichite, pickeringite and small amounts of free aluminium sulphate, and rock fragments. The genesis of the deposit has also been discussed.

**Introduction**

The occurrence of natural alums in the Salt Range has long been known.<sup>1</sup> Recent work in the Glass and Ceramics Division of West Regional Laboratories has revealed the presence of aluminite ( $\text{Al}_2\text{SO}_4(\text{OH})_4 \cdot 7\text{H}_2\text{O}$ ) alunite [ $(\text{KAl}_3(\text{SO}_4)_2(\text{OH})_6)$ ] and boehmite [ $(\text{AlO} \cdot (\text{OH}))$ ] in association with kaolinite in a deposit in the Southern Salt Range.<sup>2</sup>

This communication deals with a new deposit occurring in village Karuli near Choa Saidan Shah, District Jhelum in the Eastern Salt Range. No detailed geological survey of this deposit has so far been carried out. The senior author visited the site, and collected the representative sample for the study. Although it is difficult to comment on the exact extent of the deposit, the authors are of the view that it occurs in economically exploitable quantities.

**Experimental**

Physical properties like refractive index, specific gravity, texture etc., chemical analysis differential thermal analysis and spectroscopic and x-ray diffraction analyses were done by the usual methods. Thermogravimetric analysis (T.G.A.) was done after A.B. Carpenter.<sup>3</sup>

**Results and Discussion**

The mineral is transparent and fibrous in texture, greenish brown in colour, brittle and has strong astringent taste. In addition small parts of fibrous white and greenish white inclusions and coal fragments were also observed. For a detailed study the rock and coal fragments were eliminated from the representative sample and selective hand picking was done to separate the three constituents of the mineral namely white, greenish white and brownish white.

*Chemical Analysis.*—The chemical analysis of the representative sample and the three fractions is given in Table I which shows that the major constituents of this mineral are  $\text{Al}_2\text{O}_3$  and  $\text{FeO}$ . It was found that all the iron present was in the ferrous state and as such iron oxide is reported as  $\text{FeO}$ . The three samples contain 37.00–38.80% and 45.30–46.72%  $\text{SO}_3$  and water respectively. This accounts for the very high loss on ignition and also indicates the presence of hydrated sulphates of ferrous iron and aluminium. The other components like  $\text{CaO}$ ,  $\text{MgO}$  and  $\text{SiO}_2$  are also present in small quantities. The  $\text{SiO}_2$  present in the sample appears to be due to inclusion of rock fragments.

TABLE I.

Minerals %	White portion	Greenish white	Brownish white	General	Sicilian halotrichite
L/I	80.02	79.34	78.78	78.08	80.05
SiO	00.63	00.55	00.64	1.46	—
$\text{Al}_2\text{O}_3$	13.20	13.05	13.21	12.85	10.54
FeO	5.22	5.91	6.69	6.28	6.86
CaO	00.59	00.62	00.47	00.85	—
MgO	00.23	00.38	00.21	00.25	0.85
Water	45.30	46.67	46.72	45.82	43.63
Sulphur trioxide	37.00	37.95	38.80	36.40	36.42

*Spectrographic Analysis and Circular Thin Layer Chromatographic Analysis*

The spectrographic analysis of representative samples also generally confirms the results of chemical analysis with the exception of manganese which was not detected in the course of chemical analysis. Al, 10–100; Fe, 3–30; Si, 0.1–1; Mg, 1–10; Mn, 0.3–3%. The general sample was then subjected to an examination by the thin layer circular chromatographic technique of Hashmi *et al.*<sup>5</sup> and traces of Au, V, Cu Mo, K and Na were also detected.

*Physical and Optical Properties*

The results of physical and optical properties are: colour, yellow white; taste, strongly astringent; tenacity, brittle; lustre, silky; aggregate, fibrous; sp. gravity, 2.05; refractive index, 1.482. A microscopic examination of the sample indicated that it consists of magnesium halotrichite and a fine grained iron magnesium sulphate possibly pickeringite.

*X-Ray Diffraction.*—The 'd' values and the relative intensities observed from the x-ray powder diffraction data of the sample along with the standard ASTM data for halotrichite and some of the other possible minerals is shown in Table 2. It will be observed that there is considerable overlapping and close approximation in the standard 'd' values specially between halotrichite and pickeringite. The data obtained on the sample generally agrees well with the standard values for halotrichite but there are some values which lie between the reported values of halotrichite and pickeringite. As an example the 4.80°A value for the sample lies between 4.77°A for halotrichite and 4.82°A for pickeringite and 4.79°A for Al(OH)<sub>3</sub>. This appears to indicate that the mineral sample rather than being a mixture of well defined phases of halotrichite and pickeringite in particular is substituted magnesium halotrichite as suggested by the microscopic examination. This interpretation would account for the median 'd' values of the sample. Some of the characteristic values for pickeringite uncommon to halotrichite are also observed in the sample under study. For example 4.69°A for pickeringite agrees well with 4.70°A value for the sample which further complicates the picture.

It is also observed that the main characteristic values for Al(OH)<sub>3</sub> alunogenite, and nordstrandite also agree closely with the corresponding values of the sample although generally the intensities of these values in the sample are comparatively much less indicating their presence in small quantities.

It may be mentioned that the 'd' values 3.90°A, 3.56°A, 2.72°A and 2.52°A and also 2.27°A etc. observed in the sample find no corresponding values in literature for the sulphate minerals.

*Mineralogical Composition.*—The presence of halotrichite and pickeringite having been already confirmed the mineralogical content of these two minerals was calculated. As already stated, in all cases the Al<sub>2</sub>O<sub>3</sub> content of the samples on the FeO equivalent requirement basis for halotrichite was in excess. For the purpose of these calculations it was assumed that all the FeO was present as halotrichite. Also it was assumed that all the MgO estimated in the samples was present in the form of pickeringite. The calculation of halotrichite and pickeringite on these premises is shown in Table 3.

The crystal structure of the halotrichite group which includes halotrichite, pickeringite, apjohnite (MnAl<sub>2</sub>(SO<sub>4</sub>)<sub>4</sub>.22H<sub>2</sub>O, dietrichite (Zn Al<sub>2</sub>(SO<sub>4</sub>)<sub>4</sub>.22H<sub>2</sub>O, bilinite Fe (Fe<sub>2</sub>(SO<sub>4</sub>)<sub>4</sub>.22H<sub>2</sub>O, and redingtonite (Fe Mg Ni) (Cr Al)<sub>2</sub>(SO<sub>4</sub>)<sub>4</sub>.22H<sub>2</sub>O are not known. A complete series by mutual substitution of the divalent cation extends between halotrichite and pickeringite and at least a partial series extends from these species to apjohnite. Because of the absence of Zn, Ni, Cr and ferric iron, the possibility of the last three above named minerals is ruled out. However, because of the presence of Mn, the presence of apjohnite in small quantities is indicated. The balance of Al<sub>2</sub>O<sub>3</sub> is assumed to be present as aluminium sulphate (Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>.18H<sub>2</sub>O), this assumption being further supported by the material balance as far as the sulphate and water content are concerned.

*Differential Thermal Analysis.*—The published work on the DTA of halotrichite and the related minerals is rather scanty and at the same time in considerable disagreement where more than one set of data are available on the mineral. The published DTA data on the mineral likely to be present is shown in Table 4. Hydrated sulphates decompose on heating in two stages. In the first stage the water of hydration is decomposed beginning at about 600°C. Both these decomposition processes are endothermic and the peaks observed on DTA are characteristic of the system.

Figure 1 shows the thermogram of the general sample. A very small endothermic peak at 90°C probably corresponds to the expulsion of absorbed water. A shallow complex peak is observed between 120° and 410°C corresponding to the stage where all the water of hydration is expelled. Gruver<sup>6</sup> observed a similar complex peak with

TABLE 2.—X-RAY POWDER DATA OF SAMPLE AND ASTM VALUES.

Sample		Halotrichite		Pickeringite		Alunogenite		Al(OH) <sub>3</sub>		Nordstrandite	
"d" A	I (Rel)	"d" A	I (Rel)	"d" A	I (Rel)	"d" A	I (Rel)	"d" A	I (Rel)	"d" A	I (Rel)
15.9	8										
10.5	6	10.4	15	10.6	5						
9.50	15	9.5	13	9.7	18						
7.90	14	7.82	10	8.0	12						
6.70	3			7.12	4						
6.30	5										
6.02	29	6.02	30	6.08	20						
5.80	8			5.87	10						
5.30	14	5.24	15	5.31	14						
4.99	34			4.97	14						
4.80	100	4.77	100	4.82	20						
4.70	11			4.69	100			4.79	100		
4.53	21	4.62	30	4.62	10						
4.40	20			4.40	14	4.42	100			4.49	100
4.29	55	4.29	55	4.32	35			4.33	20		
4.20	43			4.18	20			4.20	15		
4.12	43	4.09	45	4.122	30						
3.99	25	3.95	35	3.97	20	3.95	60				
3.90	5										
3.79	39	3.75	40	3.791	30						
3.69	10										
3.56	5			3.67	6						
3.50	100	3.48	100	3.510	90						
3.35	13										
3.29	13	3.30	20								
3.19	13	3.16	15								
3.09	10	3.05	15								
2.98	13	2.96	20								
2.90	19	2.86	30								
2.82	11										
2.79	11										
2.77	10	2.76	20								
2.72	5										
2.69	22	2.67	25								
2.61	15	2.61	20								
2.55	14	2.55	20								
2.52	5										
2.44	5	2.447	10			2.48	20				
2.39	8	2.390	6							2.39	70
2.29	6	2.79	12								
2.27	9									2.26	70
2.25	4										
2.23	5	2.231	6								

Plus 14 lines to 1.66 Plus 5 lines to 1.66

TABLE 3.—CALCULATED MINERALOGICAL COMPOSITION.

	White portion	Greenish white portion	Brownish white portion	General	Sicilian sample <sup>4</sup>
Halotrichite $\text{FeAl}(\text{SO}_4)_4 \cdot 24\text{H}_2\text{O}$	64.08%	72.98%	82.77%	77.43%	84.65%
Pickeringite $\text{MgAl}_2(\text{SO}_4)_4 \cdot 22\text{H}_2\text{O}$	4.29%	7.72%	4.29%	5.14%	18.01%
Aluminium sulphate $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$	31.63%	19.30%	12.94%	17.43%	Nil

aluminium sulphate. However no such complex peak is reported in any of the other sulphates under discussion. The earlier conclusion based on the mineral analysis of the sample indicating the presence of aluminium sulphate ( $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ ) is therefore confirmed. The small exothermic peaks

at 410/442°C and 920°C are likely to be due to impurities.

The very small exothermic peak at 540°C does however, coincide with the reported value of Ivanova<sup>7</sup> for halotrichite. It may be mentioned

that Cocco<sup>8</sup> does not report any exothermic peak for halotrichite. It seems likely that this small peak both in the present case and in the Ivanova sample are due to impurities.

The very large endothermic peak with a maximum between 805°C and 840°C is in, fairly good agreement with Cocco (805°C) as far as the value is concerned but not in magnitude. The peak in the general sample is very large compared to the medium large peak reported by Cocco.

In addition to the very small exothermic peak at 540°C, Invanova also reports a very small endothermic peak at 900°C. Both these peaks are not observed either in Cocco's data or in the present sample. It seems therefore, reasonable to conclude that the impurity level of Cocco's sample is lower.

The thermograms of the three selected hand-picked fractions of the deposit are shown in Figure 1-A. In the light of the discussion for the general

TABLE 4.—PUBLISHED DATA ON DIFFERENTIAL THERMAL ANALYSIS OF HALOTRICHITE AND RELATED SULPHATES.

No.	Name	T(—)*	S.**	T(—)	S.	T(—)	S.	T(—)	S.	T(+)	S.	Reference
(I)	(i) Halotrichite	100 } 150 }	Medium	330	Small	680 } 755 }	Medium large	900	Very small	540	Very small	7
	(ii) Halotrichite Fe Al <sub>2</sub> (SO <sub>4</sub> ) <sub>4</sub> ·24H <sub>2</sub> O	120 } 150 }	Very large	320	Medium	805	Medium large					8
(II)	(i) Pickeringite	70 } 140 } 170 }	Medium large	365	Very small	830	Medium small					9
	(ii) Pickeringite Mg Al <sub>2</sub> (SO <sub>4</sub> ) <sub>4</sub> ·22H <sub>2</sub> O	70	Very small	150 } 180 }	Large	390	Medium large					8
(III)	(i) Aluminum sulphate Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	830 } 930 }	Very large	350	Medium small	900	Medium					13
	(ii) Aluminium sulphate Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> ·18H <sub>2</sub> O	100	Very small	350	Medium small	900	Medium					14
	(iii) Aluminium sulphate Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> ·18H <sub>2</sub> O	250 } 235 }	Very large (complex peak)	350	Medium small	860	Medium					

\*Maximum temperature of the peaks. \*\* Size of the peaks.

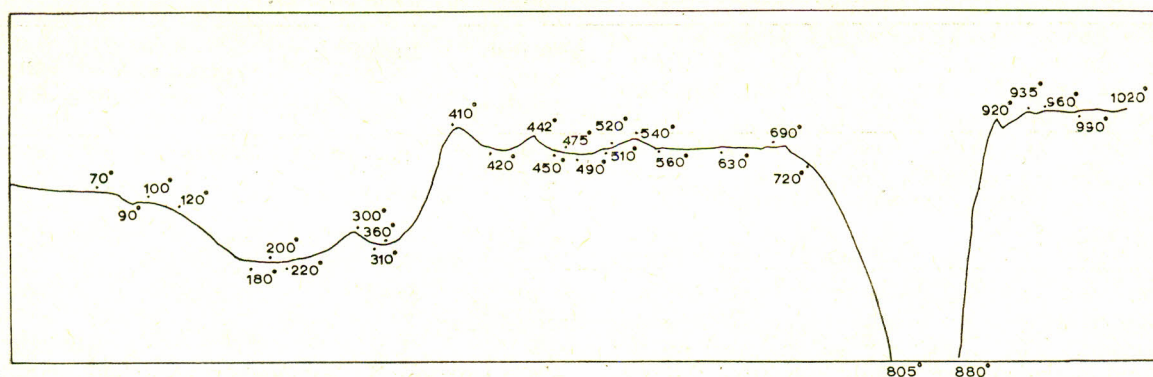


Fig. 1.—DTA curve halotrichite.

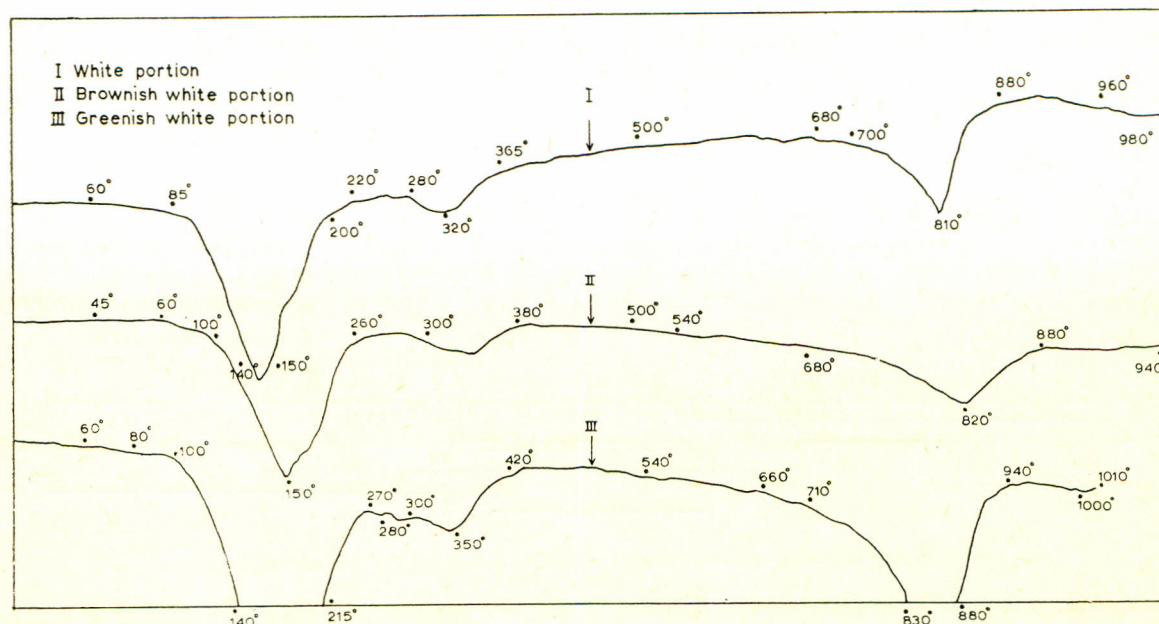
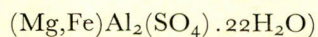


Fig. 1-A.

sample the presence of aluminium sulphate in all these sample is confirmed. The characteristic peaks reported for halotrichite are observed in all these samples. The water peak in all cases is more sharply defined. The water as well as the sulphate decomposition peaks in the case of the greenish white sample, however, are very large. The maxima of sulphate decomposition peak lies between 830°C and 880°C at a temperature somewhat higher than that reported for halotrichite. Dunbansky<sup>9</sup> reports a medium small endothermic peak for pickeringite at 830°C. A reference to Table 4 shows that this sample contains the largest amount of pickeringite (7.72%) on a calculation basis as compared to 4.29% each for the other two samples. Dana<sup>10</sup> mentions the substitution of  $Mg^{++}$  for  $Fe^{++}$  in a complete series of



The names of pickeringite and halotrichite, are here applied to the halves of the series where  $Mg > Fe$  iron  $Fe > Mg$  respectively. Mn also substitutes for Mg and Fe in a partial series toward apjohnite. The large peaks in case of greenish white portion, indicate the presence of larger quantity of magnesium halotrichite with a very small amount of substituted Mn and the large sulphate decomposition peak is therefore the cumulative effect of two successive decomposition peaks.

*Thermo Gravimetric Analysis.*—Fig. (2) shows the T.G.A. curves of the general sample and the individual fractions. The data confirms the information obtained from DTA.

No weight loss is observed up to 70°C after which there is a sharp rise up to about 400°C corresponding to the expulsion of water of crystallization. A small fraction of water of crystallization is however retained in the system and is gradually expelled by 600°C. The value of weight loss at this stage agrees with the estimated water content.

The sulphate decomposition seems to occur quite rapidly between 650°C and 700°C and then some what more gradually to completion by about 900°C. These values also agree closely with the estimated sulphate content of the samples.

#### Genesis

Naturally occurring alums are known to be formed by the product of pyritic and aluminous and other rocks and are accumulated as fluorescences in sheltered places. The oxidation of sulphides lead to the formation of sulphuric acid which attacks the aluminous minerals forming aluminium sulphate for alums. The oxidation of pyrites would also lead to the formation of sulphate of iron.<sup>11</sup>

The present deposit is found at the bottom of the fireclay horizon sandwiched between two coal horizons. Although no coal or fire clay samples were analysed in this case it is a common knowledge that a large number of the coal and fire clay deposits of the Salt Range are pyritic in nature. Gypsum is also abundantly available in the area and could also be a possible source of sulphates.<sup>12</sup>

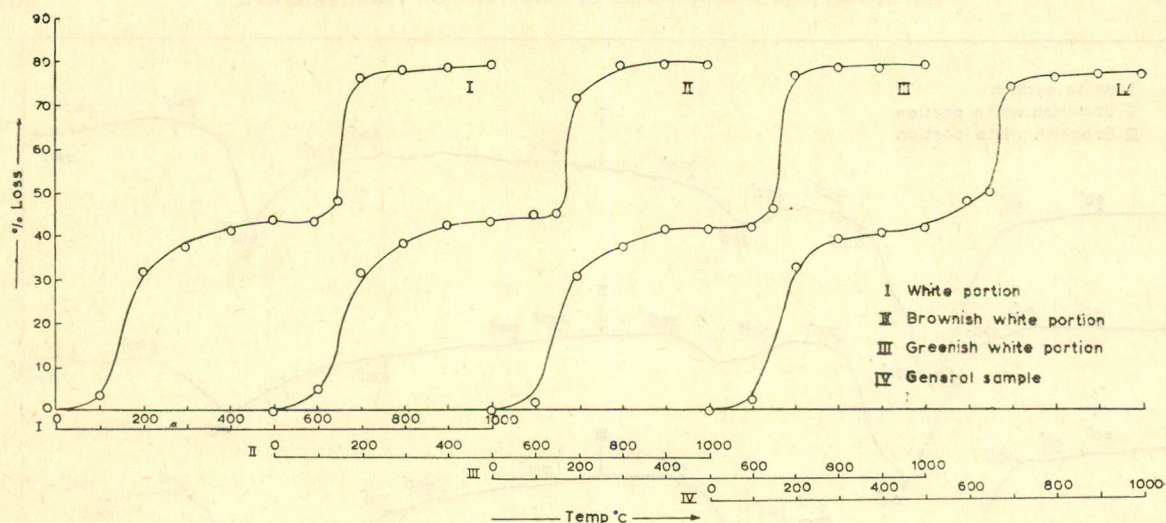


Fig. 2.—Thermogravimetric analysis of different fractions of halotrichite.

In the present case it appears likely that the pyrites in the upper coal horizon oxidized in the presence of seeping water and the solution containing ferrous sulphate and sulphuric acid on permeating through the fire clay bed dissolved sufficient quantities of alumina to form aluminium sulphate. Most of the resulting mixture of ferrous and aluminium sulphate appears to have crystallized out at the bottom of the fire clay horizon and the top of the lower coal horizon which served mainly as an impermeable bed. It may be mentioned here that a rain-fed stream at a lower level in the vicinity also contains measurable quantities of ferrous and aluminium sulphate. It is however, not clear as to whether this is due to the permeation of newly formed material or due to the solution of the main deposit.

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