CHEMICAL COMPOSITION OF CHROMITES FROM PESHAWAR REGION

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Chemical analyses and study of the composition of chromites from Peshawar region are presented for the first time. Complete analyses of ten samples and partial analyses of seven samples have been given. The Qilla deposits are of metallurgical grade with Cr/Fe ratio exceeding 3:1. The samples from Landi Raud, Ospan Khare and Behram Dehri have low chromium content and may be exploited for chemical and refractory purposes. The chemical composition of these chromites is discussed on the basis of unit cell structure. All of these, excepting the two, are found in the fields of aluminian chromites.

Introduction

Economic deposits of chromites occur in the north of Peshawar. The deposits are found in Ospan Khare (near Tangi) and adjoining areas extending into Malakand Agency. Nothing can be said at present in regard to the extent of these deposits and their reserves, as the geological investigations of the area are in the preliminary stage. The Geological Section of the North Regional Laboratories, Peshawar, have recently undertaken the geological studies of the area.

M/S. Hyesons Steel Mills Ltd. have obtained the prospecting lease of a part of this area. They are engaged in the prospecting work at Badasar, Qilla, Landi Raud, Jamud Rang, Behram Dehri and Heroshah. These places approximately cover an area of 12 sq. miles. All the samples described have been collected from this area.

The present investigations were undertaken to determine the chemical composition of the chromites of Peshawar region and compare these with the chromites of Zhob Valley.

Chemical Analysis

Complete chemical analyses of ten samples of chromite from Peshawar area are given in Table 1. The chemical analysis was done by the method reported by Bilgrami and Ingamells.[1] The chromite samples were ground to pass through 200 mesh sieve (B. S.). 0.5 gm. of the powdered material was treated with 1-2 ml. of concentrated perchloric acid (70%). The solution was used for the estimation of Cr_2O_3, Al_2O_3, Fe_2O_3, MgO, CaO, and TiO_2, while SiO_2 was determined in the residue.

Ferrous iron was determined by the indirect method of Seil.[2]

Partial chemical analyses of seven samples of chromite from Peshawar region are given in Table 2.

Composition of Chromites

Chromite mineral could be represented by the general formula $R''O.R''_2O_3$ where R'' stands for a bivalent metal (mainly Fe^{2+} & Mg^{2+}) and R''' represents Cr^{3+}, Al^{3+} and Fe^{3+}. The formula may be written as (Fe, Mg) O. (Cr, Al, Fe)$_2O_3$.

Ionic Content of Chromite Unit Cells

Chromite is a member of the Spinel group of minerals with the unit cell content 8 $(R''O.R_2'''O_3)^3$. With this structure there should be a total number of 8 bivalent cations and 16 trivalent cations per unit cell in a chromite. Taking this as the unit cell content, the number of trivalent and bivalent metallic ions per unit cell in the chromites of Peshawar region were calculated. The method of calculation is as follows.

Molecular ratios of oxides (Table 3) were obtained by dividing the percentage of each oxide by its molecular weight. In the case of FeO correction was made for ilmenite by taking out from the molecular proportion of FeO the molecular ratio of TiO_2. Molecular ratios were converted to atoms per unit cell, assuming 8 bivalent and 16 trivalent atoms in each unit cell. The number of atoms per unit cell, thus calculated for these chromites are given in Table 4.

Composition in Terms of Molecular Percentage

By dividing the number of atoms per unit cell of each of the bivalent and trivalent metallic ions by 8 and 16, respectively and multiplying by 100, the molecular percentage of each metallic ion is obtaind in terms of RO and R_2O_3. The formulae for the ten complete analyses are given in Table 5.

It is seen that all the chromites show a high molecular percentage of magnesium.

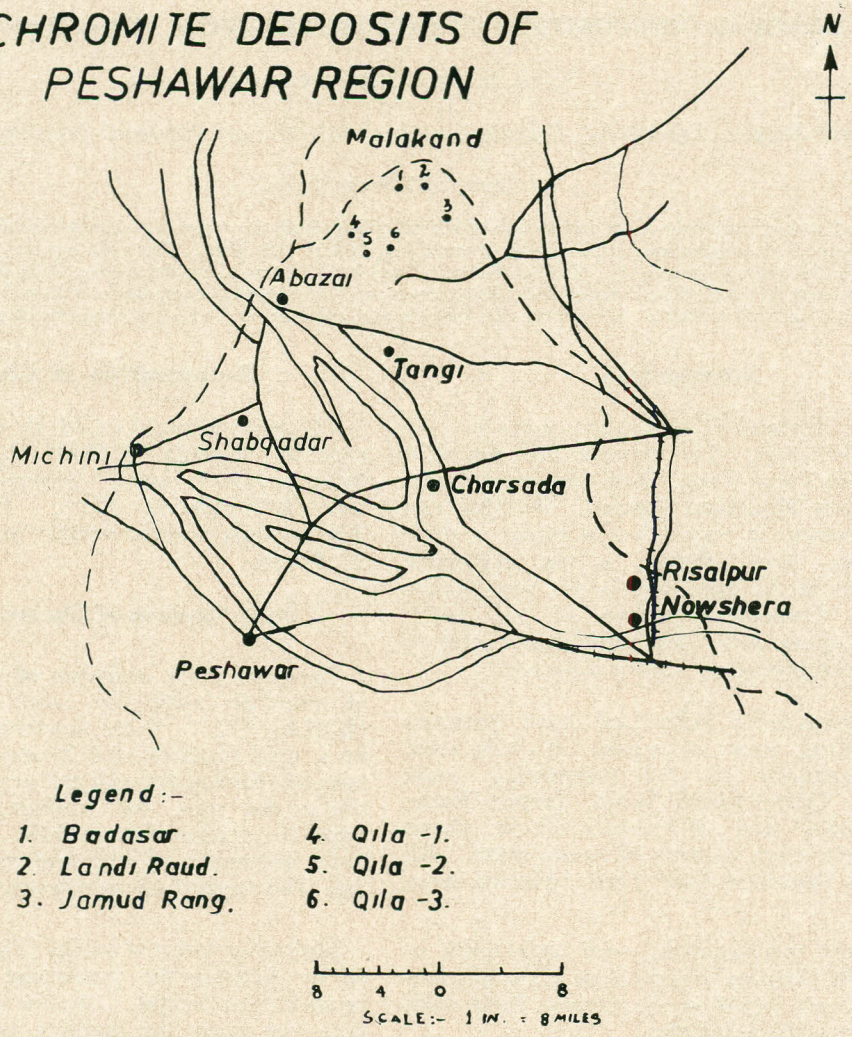

Table 1.—Chemical Analyses of the Chromites from Peshawar Region.

	Mine I	Mine IIA	Mine IIB	Mine 96	Mine 99A	Mine 99B	Mine 100A	Mine 100B	Mine L.R/3	Mine 105
Cr_2O_3	54.50	50.95	49.20	45.40	50.45	34.42	42.70	42.64	30.50	41.50
Al_2O_3	5.23	12.24	8.52	8.20	8.75	9.40	11.44	5.60	12.80	10.00
Fe_2O_3	6.02	5.02	7.20	11.28	3.20	11.41	8.36	13.92	8.41	11.48
TiO_2	0.15	Trace	0.15	0.22	0.20	0.23	0.12	0.20	0.15	0.10
FeO	10.98	8.55	8.20	10.70	12.60	9.40	10.60	11.48	10.64	12.43
MgO	16.75	17.99	17.60	19.90	18.83	18.62	18.36	18.82	22.00	12.00
CaO	Trace	Trace	Trace	Trace	Trace	Trace	Trace	Trace	Trace	Trace
SiO_2	3.16	3.19	6.11	4.00	4.10	13.56	6.20	7.10	12.10	12.50
Loss on ignition	1.34	1.51	1.06	0.94	1.10	2.66	1.21	0.56	3.92	1.30
Total:-	98.13	99.45	98.04	100.64	99.23	98.70	98.99	100.32	100.52	99.31
Cr	37.30	34.85	33.61	31.70	34.68	24.48	28.66	29.00	20.81	28.40
Fe	11.90	9.48	10.85	15.38	11.20	13.89	12.27	17.92	13.44	15.32
Cr/Fe	3.11	3.67	3.10	2.06	3.10	1.76	2.33	1.61	1.54	1.20
RO/R_2O_3	1.26	1.16	1.21	1.58	1.46	1.48	1.35	1.47	1.83	0.99

Nos. 1 to 3 from Qilla
Nos. 4 to 9 surface lode samples from Landi Raud
No. 10 from Heroshah

Composition in Terms of Triangular Diagram

Variations in the chemical composition of chromites can be shown by plotting the unit cell composition in a triangular diagram.[4] Plots of Peshawar region chromites are shown in Fig. 1.

It is seen from the figure that all of the chromites from Peshawar region excepting chromites from Landi Raud (Nos. 96 & 100 B) are within the field of aluminian and chromites No. 96 and 100 B are ferrian chromite. In this respect the chromites from Peshawar region differ from the Zhob Valley Chromites, where all the chromites are aluminian chromites.[1]

Expression in Terms of End Members

The chemical analyses of Peshawar region chromites may also be expressed in terms of end member formula and weight percentages devised by Stevens.[4] By this method the percentage proportion of spinel, Magnesio-chromite, Ferrochromite and magnetite in chromites are obtained. The end member formulae per unit cell have been obtained by the following method :—

Spinel	=	$Al/2$
Magnesiochromite	=	$Mg-Al/2$
Ferrochromite	=	$Cr + Al/2-Mg$
Magnetite	=	$Fe''/2$

Where Al, Mg, Cr, Fe'' represent the number of atoms per unit cell of the respective element.

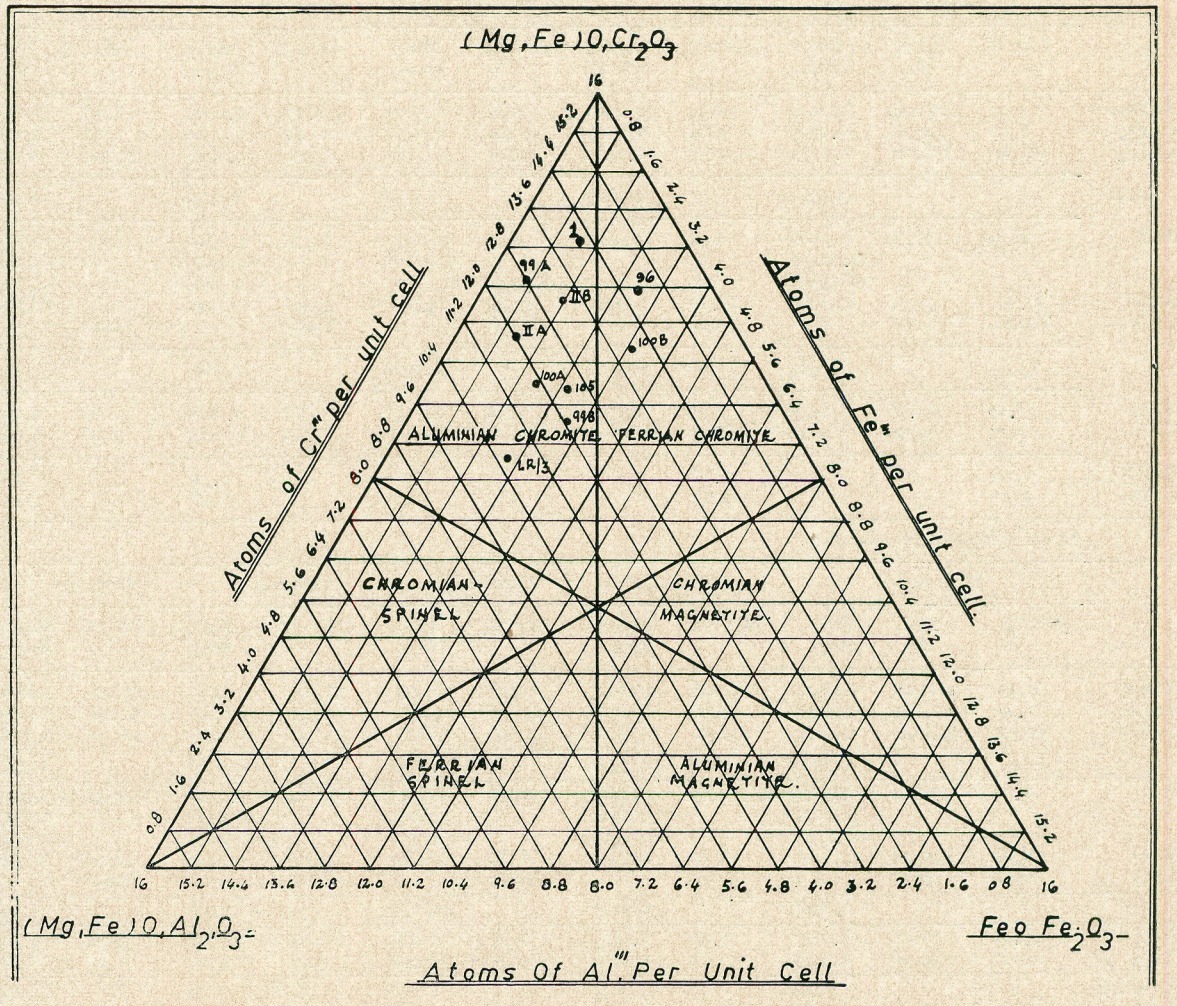

Fig. 1.—Triangular diagram showing composition of chromites from Peshawar Region.

Table 2.—Partial Chemical Analyses of Chromites from Peshawar Region.

Mine Nos.	Cr_2O_3 (%)	Total iron as FeO (%)	Cr	Fe	Cr/Fe
I	50.8	20.18	34.68	15.79	2.1:1
IIA	39.0	14.68	26.01	11.20	2.3:1
IIB	35.0	15.30	24.50	11.90	2.0:1
IIIA	39.0	17.10	26.01	13.30	1.9:1
IIBD	48.7	17.56	33.29	13.66	2.4:1
IIIBD	34.0	20.70	23.24	16.10	1.4:1
IVBD	39.0	15.84	26.70	12.32	2.1:1

Nos. 1 to 4 surface lode samples from Ospan Khare.
Nos. 5 to 7 surface lode samples from Behram Dehri.

Table 3.—Molecular Ratios of the Chromites from Peshawar Region.

	Mine I			Mine IIA		Mine IIB		Mine 96		Mine 99A	
	(Wt. %	Mol. Wt.	Mol.) Prop.	(Wt. %	Mol.) Prop.	(Wt. %	Mol.) Prop	(Wt. %	Mol.) Prop.	(Wt. %	Mol. Prop.
Al_2O_3	5.23	101.94	0.0513	12.24	0.1200	8.52	0.0835	8.20	0.0344	8.75	0.0858
Fe_2O_3	6.02	159.68	0.0377	5.02	0.0314	7.20	0.0450	11.28	0.0706	3.20	0.0200
Cr_2O_3	54.50	152.02	0.3585	50.95	0.3351	49.20	0.3236	45.40	0.2986	50.45	0.3318
Total			0.4475		0.4865		0.4521		0.4036		0.4376
FeO	10.98	71.84	0.1528— 0.0018* =0.1510	8.55	0.1190	8.20	0.1141— 0.0018* =0.1123	10.70	0.1489— 0.0029* =0.1460	12.60	0.1753— 0.0025* =0.1728
MgO	16.75	40.32	0.4154	17.99	0.4461	17.60	0.4365	19.90	0.4835	18.83	0.4670
CaO	Trace	56.08	—	Trace	—	Trace	—	Trace	—	Trace	—
			0.5664		0.5651		0.5488		0.6395		0.6398
SiO_2	3.16	60.06	0.0526	3.19	0.0531	6.11	0.1017	4.00	0.0666	4.10	0.0699
TiO_2	0.15	79.90	0.0018	Trace	—	0.15	0.0018	0.22	0.0029	0.20	0.0025
RO/R_2O_3	1.26			1.16			1.21		1.58		1.46
Cr/Fe	3.11			3.67			3.10		2.06		3.10

*After substracting for ilmenite.

	Mine 99B			Mine 100A		Mine 100B		Mine L.R/3		Mine 105	
	(Wt. %	Mol. Wt.	Mol.) Prop.	(Wt. %	Mol.) Prop.	(Wt. %	Mol.) Prop.	(Wt. %	Mol.) Prop.	(Wt. %	Mol.) Prop.
Al_2O_3	9.40	101.94	0.0922	11.44	0.1122	5.60	0.0549	12.80	0.1255	10.00	0.0981
Fe_2O_3	11.41	159.68	0.0713	8.36	0.0523	13.92	0.3871	8.41	0.0526	11.48	0.0718
Cr_2O_3	34.42	152.02	0.2264	42.70	0.2809	42.64	0.2811	30.50	0.2006	41.50	0.2729
			0.3399		0.4454		0.4231		0.3787		0.4428
FeO	8.04	71.84	0.1169— 0.0029* =0.1140	10.60	0.1489— 0.0014* =0.1475	11.48	0.1597— 0.0025* =0.1572	10.64	0.1481— 0.0018* =0.1463	10.43	0.1453— 0.0013* =0.1440
MgO	18.62	40.32	0.4643	18.36	0.4553	18.82	0.4667	22.00	0.5456	12.00	0.2976
Ca O	Trace	56.08	—	Trace	—	Trace	—	Trace	—	Trace	—
			0.5783		0.6028		0.6238		0.6919		0.4416
SiO_2	13.56	60.06	0.2257	6.20	0.1032	7.10	0.1182	12.10	0.2014	12.50	0.2081
TiO_2	0.23	79.90	0.0029	0.12	0.0014	0.20	0.0025	0.15	0.0118	0.10	0.0013
RO/R_2O_3			1.48		1.35		1.47		1.83		0.99
Cr/Fe			1.76		2.33		1.61		1.54		1.20

*After subtracting for ilmenite.

TABLE 4.—THE NUMBER OF BIVALENT AND TRIVALENT METALLIC IONS PER UNIT CELL OF THE CHROMITES.

No.	Mine No.	Cr	Al	Fe″	Fe″	Mg
1	I	12.82	1.83	1.35	2.13	5.87
2	IIA	11.02	3.95	1.03	1.68	6.32
3	IIB	11.45	2.50	1.60	1.64	6.36
4	96	11.84	1.36	2.80	1.83	6.17
5	99A	12.13	3.14	0.73	2.16	5.84
6	99B	9.29	3.79	2.92	1.58	6.42
7	100A	10.10	4.03	1.87	1.96	6.04
8	100B	10.62	2.08	3.30	2.02	5.98
9	LR/3	8.48	5.30	2.22	1.69	6.31
10	105	9.86	3.54	2.60	2.61	5.39

The formula per unit cell were then multiplied by 100 and divided by 8 to get the formula percentage of chromites.

The weight percentages of the end members were obtained by multiplying the formula per unit cell by molecular weight and recalculating them to a total of 100. Table 6 shows formula percentages and weight percentages of the end members for the chromites from Peshawar region.

It is evident from the Table 6 that the chromites from Peshawar region show great variations in composition. The variations are in individual constituents as well as in total chromite content. Spinel varies from 9.43 to 33.12%, and variations in the magnesio chromite, ferrochromite, and total chromite are 45.22 to 67.35%, 1.4 to 22.43% and 53 to 80.11%, respectively.

TABLE 5.—COMPOSITION IN TERMS OF MOLECULAR PERCENTAGE.

Mine No.	RO	R_2O_3
I	$(Mg_{73}Fe_{27})$	$(Cr_{80}Al_{12}Fe_8)$
IIA	$(Mg_{79}Fe_{21})$	$(Cr_{72}Al_{18}Fe_{10})$
IIB	$(Mg_{79}Fe_{21})$	$(Cr_{69}Al_{25}Fe_6)$
96	$(Mg_{77}Fe_{23})$	$(Cr_{74}Al_9Fe_{17})$
99A	$(Mg_{63}Fe_{27})$	$(Cr_{76}Al_{20}Fe_4)$
99B	$(Mg_{80}Fe_{20})$	$(Cr_{58}Al_{24}Fe_{18})$
100A	$(Mg_{75}Fe_{25})$	$(Cr_{63}Al_{25}Fe_{12})$
100B	$(Mg_{74}Fe_{26})$	$(Cr_{66}Al_{13}Fe_{21})$
L.R/3	$(Mg_{79}Fe_{21})$	$(Cr_{53}Al_{33}Fe_{14})$
105	$(Mg_{67}Fe_{33})$	$(Cr_{59}Al_{25}Fe_{16})$

Discussion

The chromites from Qilla deposits show high chromium content and high Cr/Fe ratio. All the three samples show a Cr/Fe ratio of more than 3:1; Mine No. I, 3.1:1, Mine No.-IIA 3.67:1 and Mine No.-IIB 3.1:1. In terms of end members, the magnesio chromite content (54.32 to 61.99) is higher than ferrochromite. Thus the amount of magnesium exceeds iron.

Analysis of the surface lode sample from Hero-shah (Mine No. 105) shows low Cr/Fe ratio, 1.2:1. Molecular composition of the mineral is $(Mg_{67}Fe_{33})$ $(Cr_{62}Al_{22}Fe_{16})$. Its end member composition shows that magnesiochromite is more than ferrochromite. For Landi Raud six complete analyses are presented. All of them excepting one, show a Cr/Fe ratio lower than 3:1 ranging from 1.54:1 to 2.33%.

In the case of Mine No. 99A, Cr/Fe ratio is 3.1:1. In the end member composition, all of them, excepting L.R/3, are rich in magnesiochromite. In the case of L. R/3 the spinel content is appreciably high (33.12%) and the amount of total magnesium is more than iron, $(Mg_{79}Fe_{21})$ $(Cr_{53}Al_{33}Fe_{14})$.

Chromites from Ospan Khare and Behram Dehri are represented by the partial analyses, with a low Cr/Fe ratio varying from 1.4-2.3%.

It will be seen from the foregoing discussion that the chromites of Peshawar region are rich in magnesium and low in iron. This suggests that this mineral might be of earlier magmatic differentiation. However, as nothing is known about the geology of this area, no definite inference can be drawn as regards the origin of the chromites of Peshawar region. Research work on

Table 6.—End Members Formula Percentages of Chromites.

	Mine	Mine IIA	Mine IIB	Mine 96	Mine 99A	Mine 99E	Mine 100A	Mine 100A	Mine LR./3	105
Spinel	11.43	42.68	18.47	9.77	19.61	23.65	25.20	13.00	£3.12	2015
Magnesiochromite	61.91	54.32	61.00	67.35	53.35	53.39	50.31	61.75	45.78	4522
Ferrochromite	18.20	14.60	10.54	5.38	22.43	1.46	12.70	4.63	7.25	1641
Magnetite	8.44	6.40	10.00	17.50	4.57	18.29	11.74	20.62	13.88	1622
				END MEMBERS WEIGHT PERCENTAGES						
Spinel	8·32	18.61	13·68	7·1	14·76	17·91	19·03	9·46	25·7	10·88
Magnesiochromite	60·87	55·43	61·99	66·1	54·29	57·93	51·37	60·77	47·90	46·51
Ferrochromite	20,83	18·06	12·28	6·13	25·35	1·74	15·15	5·33	82·84	21·05
Magnetite	9·99	7·90	12·05	20·67	5·60	22·42	14·45	24·44	17·50	21·55

this aspect of the problem has been undertaken by the geologists of the North Regional Laboratories, Peshawar, and the results of their findings will be presented in a separate paper.

The chromites of Qilla area, with high Cr/Fe ratio are of metallurgical grade and can be compared with the chromites of Juntogarh group of the Zhob valley.[1]

The chromites from Landi Raud, Ospan Khare and Bearam Dehri are low grade. Some of these low grade chromites could be used for the purpose of refractory materials[5] and also for the preparation of much needed chemicals like sodium chromate and sodium dichromate for the leather tanning industry of Pakistan. The work is in progress on the preparation of chemicals and pigments from the low grade chromites of this region and the results will be published later.

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