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Mineralogical characterization and evaluation of manganese ore from Bajaur Agency, Khyber Pakhtunkwa, Pakistan

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Abstract

Reconnaissance study of the Bajaur area had indicated the presence of manganese and afterwards in 2006 Directorate of minerals, FATA (Federally Administered Tribal Area) conducted a detailed investigation on the Takht area of the Agency and reported the presence of about 0.12 million tons of manganese ore in the area. In order to evaluate the Takht manganese ore, Bajaur Agency, different mineralogical and chemical studies were carried out at PCSIR (Pakistan Council of Scientific and Industrial Research) Laboratories. The mineralogical studies included the petrography, scanning electron microscope, microprobe and XRD to study manganese ore and its associated gangue minerals. It is concluded from these studies that the manganese ore is of complex nature, comprising of oxides and silicates. The manganese minerals are very fine grained and are inter-grown with gangue minerals, mainly calcite and quartz. Chemical analyses showed the $MnO_2$is 72 % on average. Various beneficiation techniques including flotation, heavy medium separation, gravity concentration and magnetic separation were used to upgrade the ore. Of these techniques, the only floatation could enhance the grade of MnO_2 to ~77.13%, while no notable success was achieved through other beneficiation methods.

Keywords: Mineralogy; Characterization; Manganese; Bajaur; Pakistan.

1. Introduction

In strategic importance manganese comes after iron and aluminum, copper. Important minerals of manganese are pyrolusite, manganite, and hausmannite (Roberts et al., 1990). In general, ores containing at least 35 % manganese are classified as manganese ores. Ores having 10-35 % manganese are known as ferruginous manganese ores, and those containing 5-10 % manganese are known as manganiferrous ores (Encyclopedia of Chemical Technology, 2004). While, ores containing less than 5% manganese with the balance mostly iron are classified as iron ores. Geologically, most manganese deposits are complex and all primary deposits are believed to have formed as carbonates or silicates (Jacoby, 1983). Sedimentary manganese deposits and the deposits formed by residual concentration have been the most productive (Jacoby, 1983). Manganese is the most important constituent of ferro-manganese alloy. It is necessary for making of high manganese steel. It is also an essential constituent in the manufacture of all kinds of carbon steels. About 6.5 kg of manganese ore is required for the production of one ton of steel. Its chief purpose in steel making is to remove oxygen and sulphur in order to produce a sound clean metal/steel. Most of the oxides, whether ore or others, are probably going into the manufacture of dry cells, with remainder going into other uses like glass making, metal treatment medium, pharmaceuticals, water and waste water treatment etc.

In Pakistan, manganese occurs are mostly associated with ophiolite thrust belt that extends from Bela through Zhob, and Waziristasn, to Parachinar (Kazmi and Abbas, 2001). Small deposits of manganese oxide minerals occur in Galdanian, Chura Gali, Tarnawai, and Thal in Abbottabad and Kohat, respectively. The deposit in Thal occurs as a ferruginous and cherty zone, underlying strongly folded limestone of Cretaceous (?) age. Probably, this deposit is similar to the Galdanian and Chura Gali deposits in origin (Ahmad and Siddiqi, 1993).

Bajaur Agency covers an area of 1354 km^2 (Fig. 1), out of which 1250 km^2 area had been explored geologically on reconnaissance scale (1:50,000) previously by the then FATA DC (Badshah, 1979), which has indicated favorable geological environments for occurrences of metallic minerals like manganese and chromite in the Agency. However, no attention was given to the detailed survey of manganese showings exposed around Takht area for determination of its economic viability in the past. In l 2006 the Directorate of minerals FATA undertook a detailed survey of the area and compiled their findings in a report (Haqqani and Ahmaduddin, 2006) showing an estimated reserves of 0.12 million tons and with MnO_2 content varying from 64 to 72%.

Main objective of the present study was to determine its mineralogy and its texture in order to understand the relationship of ore with the gangue minerals, which in turn would determine the possibilities of upgradation/beneficiation. The exploitation of this resource will save a substantial amount of foreign exchange presently being spent on the import of this commodity. All of the ferromanganese is being used by local iron and steel industries.

Present geological studies are therefore, attributed to the Takht area, which of course has the potential to become a viable mining venture for manganese and if developed, can also serve as a model elsewhere in Mohmand and Bajaur Agencies (Fig. 1). The study area is located about 16 km south of Khar, the agency Headquarter It lies in the survey of Pakistan Topo sheet No. 38N/10. Manganese showings are located in the area in the form of lenticular bodies, where the largest body as determined on the ground is 230×2 meters.

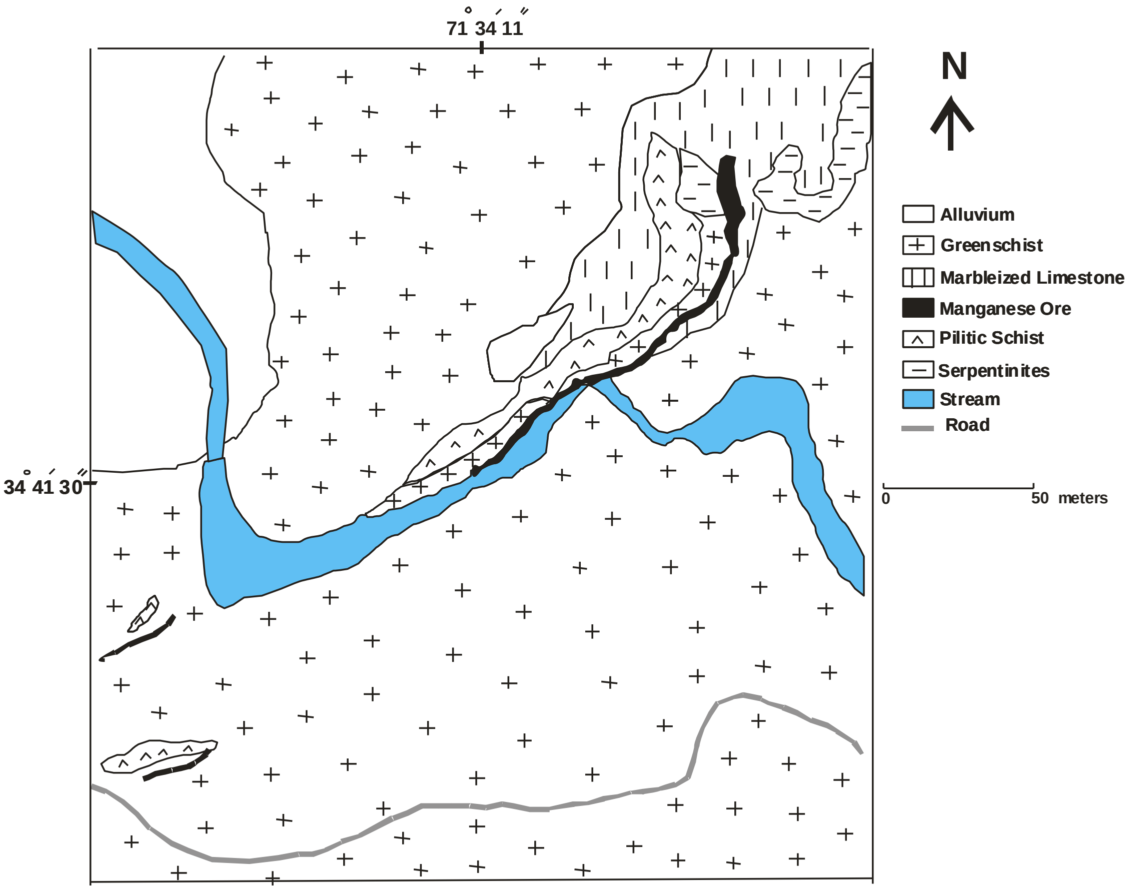


Fig. 1. Map showing lithological configuration of Takht Manganese prospects of Bajaur Agency (After Haqqani and Ahmaduddin, 2006).

1.1. Regional and local geological setting of Bajaur area

The area lies in the upper extremity of Indian Plate in typical ophiolites mélange zone of ocean floor slicing indicated by the presence of green schist as remnant of the pre-existing basalts and tholeiite and subordinate serpentinites of the ocean lithosphere (Haqqani and Ahmaduddin, 2006). Main southern suture zone (MMT) encircles the area immediately east of Precambrian to early Paleozoic metamorphic rocks i.e. various kinds of schist, marble, gneisses and granite rocks are thrusted over by the rocks of the Kohistan Island Arc from the north (Haqqani and Ahmaduddin, 2006).

Regionally, igneous and meta-sedimentary rocks cover the area. Metasediments include amphibolites, epidote chlorite schist, pillitic schist, talc-carbonate schist, graphitic schist and slates. The igneous masses comprise granites, diorites, ultra-basic and volcanic rocks. The intrusion of diorites commenced sometimes in the late Cretaceous, while the whole magmatism ended with the last phase of granitic stocks and dykes in Middle Eocene (Badshah, 1979). The late upper Cretaceous to Eocene-Oligocene ultra-basic phases of serpentinites, peridotite and pyroxenite/hornblendite lie interbedded with the metasediments. Eocene to Oligocene volcanic rocks of andesitic, rhyolitic and tuffaceous compositions are also present. Poor mineralization of copper but promising mineralization of manganese, soapstone and chromite along with large deposits of marble are the primary resources of the area.

Field observations show that mineralization is mostly in the form of lenses/pockets of various dimensions associated with a peculiar environment in close proximity of marbleized limestone. The main body is hosted in green schist part of the horizons having partial development of pelagic chert along the contact zones with limestone.

In Bajaur Agency, manganese mineralization is reported from Charmang and Takht areas. In Takht area, manganese occurrences are recorded in metamorphic sequence of green schist (meta-volcanics) and metapellites along linear extension mostly confined to the contact or marbleized horizons. The length of manganese bed is 230m with an average thickness of 2 meters. The average weighted grade of MnO_2 is 42.2 %, Fe_2O_3 is 4 % while SiO_2 is 40 %.

1.2. Manganese mineralization

Manganese ore body is located at a distance of about 2 km. north of Sagi Bala village, in the moderate to high terrain. The manganese body is highly jointed and fractured, filled with argillaceous and calcareous materials. It has gradational contact with marbleized limestone on either side. The body is mostly covered with vegetation; therefore, its exact dimensions could not be established. Its dimensions are roughly are 230m× 2m. Detailed investigations about the estimate of the ore body will be carried out by FATA DA in future, however probable estimated reserves are to be 0.12 million tons (Haqqani and Ahmaduddin, 2006).

2. Materials and methods

Rock samples were collect from the Takht area of Bajaur, Agency. The samples were divided into two fractions; one for powdering and another for making thin sections (petrographic and SEM studies). Powdered material was used for XRD and chemical analysis. Mineralogical studies have been carried out on various instruments like SEM, XRD, Microprobe and Polarizing Microscope, and the results obtained from all these techniques were compared.

3. Experimental

3.1. Mineralogical studies

3.1.1. Petrography

As most of the rock is composed of manganese minerals, therefore, reflected light was used to study the ore's character.

The manganese minerals constitute about 70 % of the rock, while calcite and quartz are the secondary minerals. Manganese occurs as anhedral, rounded to sub rounded grains, where most of the grains vary from 0.02mm to 0.3 mm in size. The margins of the grains are curved in most of the cases, where the grains are distinguished from one another. Hausmannite occurs as brownish grey grains with strong anisotropy and blood-red internal reflection (James and David, 1994). Besides Hausmannite, Braunite occurs in these samples and can be distinguished from the former by the presence of birefringence and pleochroism. Bixbyite occurs in small proportions, in creamy-grey color and is isotropic with no internal reflection. Psilomelane and Braunite also occurs as minor manganese phases.

Calcite occurs as groundmass and seems to be secondary in origin because it occurs as micrite which is a fine-grained recrystallized calcite. Only very few medium-sized calcite grains are found within micritic groundmass. The percentage of manganese minerals is high. Calcite is found sparsely disseminated in the rock generally and also is found in veins. Secondary calcite forms thin rims around some of the manganese grains. Quartz is generally found in minor amounts and occurs as small grains of subhedral shape.

3.1.2. SEM studies

SEM, 6380 (LA) was used to analyze the manganese ore samples with the energy range of 0-20 keV. Various spots (areas on the sample chosen for scanning) were analyzed on different thin sections of the ore. Most of the spots showed the presence of Hausmannite, and Braunite (Figs. 2 and 3, respectively).

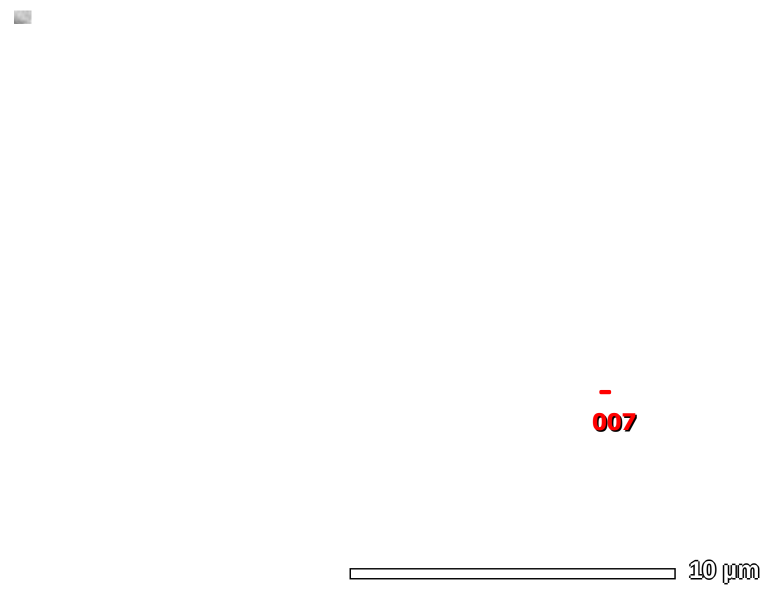
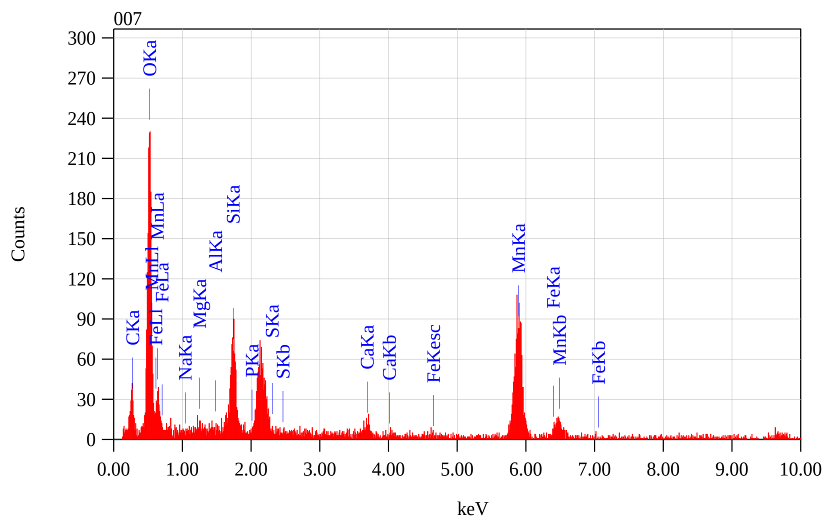


Fig. 2. Data from SEM analyses of the manganese ore from Bajaur Agency showing the analysis of Hausmannite mineral.



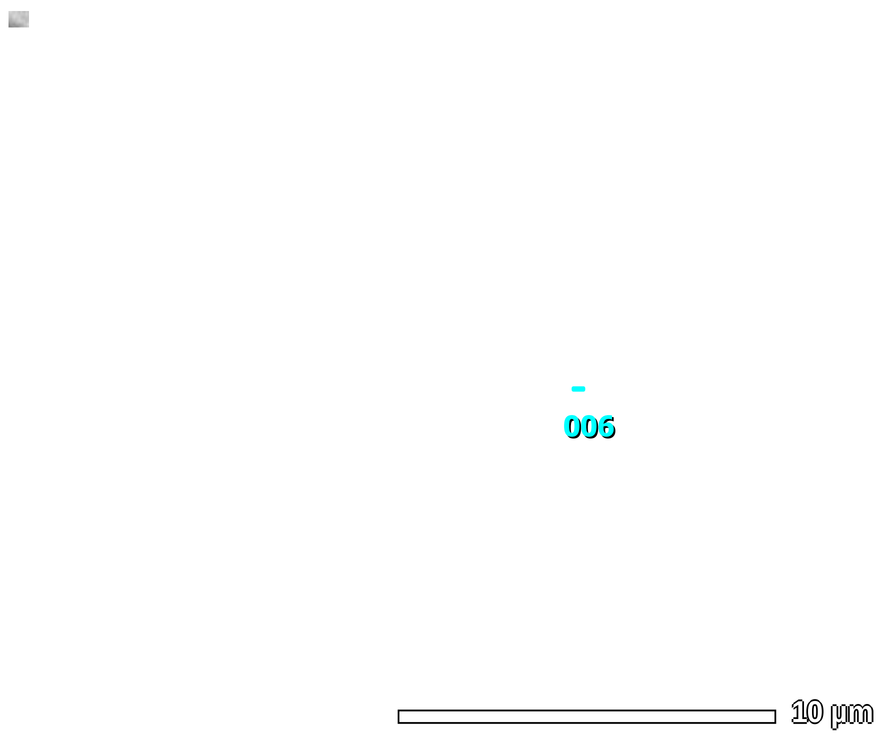
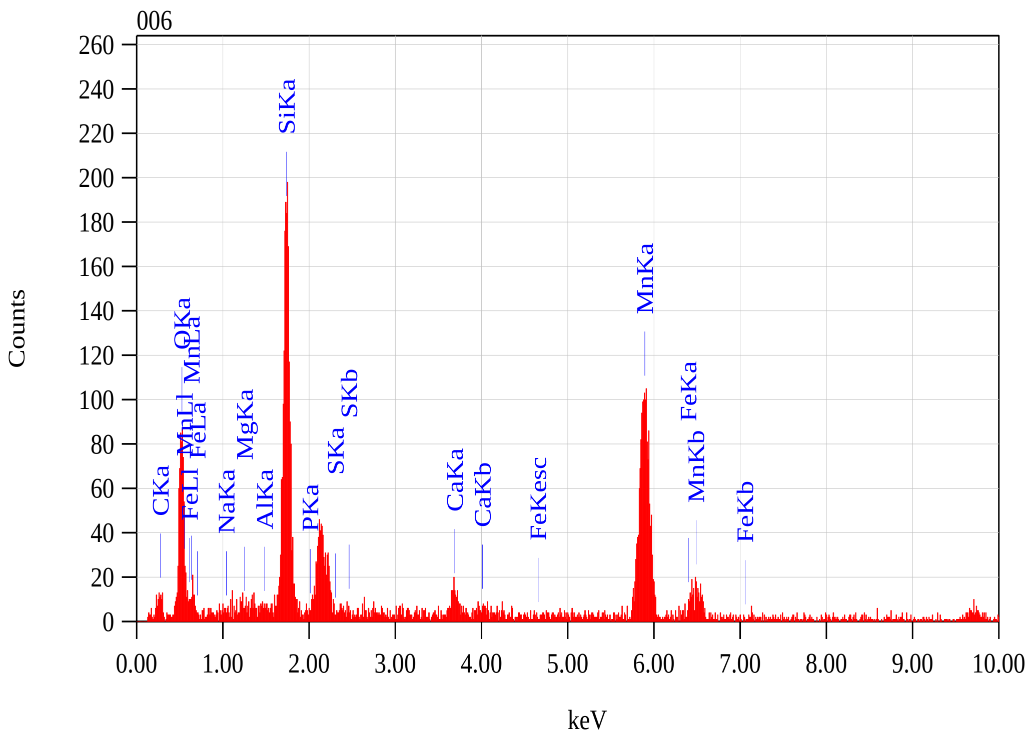


Fig. 3. Data from SEM analyses of the manganese ore from Bajaur Agency showing the analysis of Braunite.



3.1.3. Microprobe analyses

Various manganese minerals were analyzed on microprobe JEOL Super (Probe 733). These studies revealed the composition of Hausmannite and Braunite as major manganese minerals (Table-1).

3.2. Chemical characterization/sieve analyses

Roll-crushed sample was used for sieve analysis by passing a known weight of material through fine sieves to determine the percentage weight of each fraction. All the sieve fractions were then analyzed chemically (for Si, Mg, Al), on atomic absorption spectrometer model Z-8000, Hitachi Japan. The Mn and Fe were analyzed on flame photometer model PFP 7 JENWAY UK and Ca, Na, K on UV double beam spectrophotometer model Hitachi Japan (P) to determine metal distribution pattern (tables 2 and 3).

Table 1. Microprobe Analyses of Manganese Minerals in Ore

Mineral	**Hausmannite**		**Braunite**	
Oxide	**Oxide (wt. %)**	**Error (%)**	**Oxide (wt. %)**	**Error %**
MnO_2	96.14	2.4	63.16	1.5
Fe_2O_3	0.4	0.4	0.21	0.1
Al_2O_3	0.56	0.1	0.61	0.2
SiO_2	0.57	0.2	27.24	0.6
CaO	0.12	0.1	4.23	0.3
Cr_2O_3	0.07	0.1	0.23	0.1
K_2O	0.04	0.0	0.20	0.1
TiO_2	0.04	0.0	0.08	0.1
Na_2O	0.03	0.0	0.50	0.2
NiO	0.00	0.0	0.12	0.1
MgO	0.0	0.0	1.62	0.1
ZnO	-	-	1.80	0.8

Table 2. Chemical Analysis of bulk and sieve fractions of Manganese ore from Takht area, Bajuar Agency.

Size, μ m	**MnO_2**	**Fe_2O_3**	**SiO_2**	**Al_2O_3**	**CaO**	**MgO**	**L.O.I.**	**P_2O_5**	**Na_2O**	**K_2O**	**Total**
Bulk	72.09	1.09	9.37	0.78	5.85	0.04	10.01	0.02	0.21	0.19	99.65
+500	74.61	1.51	9.36	0,95	5.02	0.01	7.48	0.01	0.20	0.16	99.31
-500+180	72.20	1.80	9.56	0.77	5.62	0.05	8.70	0.02	0.21	0.18	99.11
-180+105	71.72	1.12	9.43	0.65	6.22	0.03	10.13	0.02	0.22	0.19	99.73
-105+75	69.74	1.08	9.66	0.62	7.50	0.04	10.50	0.02	0.20	0.19	99.55
-75+63	72.24	0.89	9.31	0.69	5.96	0.06	9.90	0.01	0.17	0.19	99.42
-63	72.24	0.86	9.08	0.80	6.02	0.06	10.02	0.06	0.27	0.22	99.63

3.3. Beneficiation studies

After detailed mineralogical characterization, various beneficiation techniques were used for the up gradation of this ore (Riaz et al., 2010), which is very briefly described here:

Heavy Media Studies are used for the determination of potential gravity application. Various size fractions of the roll-crushed material were subjected to sink and float tests, using an organic liquid, tetrabromoethane of specific gravity 2.96. The material was stirred in this heavy liquid and then allowed to settle until complete separation of float and sink took place.

A number of gravity separation tests were performed by varying speed of water and slope of the shaking table deck in order to achieve maximum recovery of the concentrate. Magnetic separation was carried out by both the Drum and Disc Types techniques. Flotation studies of manganese ore samples were carried out by Denver Flotation Machine.

4. Results and discussion

The mineralogical studies of Bajaur Agency manganese deposits revealed the presence of Mn oxide and Mn silicate minerals comprising of Hausmannite and Braunite, respectively. Gangue minerals are calcite and silicates. The manganese minerals are very fine grained and are intergrown with each other and gangue minerals. The chemical analyses show that these meet the specifications laid down by the ferro-manganese industry. Beside the high Mn/Fe ratio, phosphorous and silica contents are very much in the tolerable limits for the utilizations of ore in the ferro-manganese production.

The manganese ore was tested for its susceptibility to beneficiation through gravity concentration, magnetic separation and flotation techniques. The gravity concentration, and magnetic separation studies revealed the marginal increase in Mn concentration against the theoretical possibility of substantial enrichment by rejecting the ~ 20% gangue minerals. However, the flotation technique gave comparatively the better grade and recovery, enhancing its grade from 72% MnO_2 to 77%. It is concluded from these studies that the separation of the manganese minerals from associated gangue is difficult, partly because of the mineralogical complexity and mainly due to the extreme fineness of texture.

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