High Intensity Magnetic Separation Studies of Low Grade Chromium Ore

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Summary: Studies were undertaken to beneficiate a low grade indigenous chromium ore of Muslim Bagh, Balochistan, Pakistan using high intensity dry magnetic separation (HIDMS) technique. The different parameters of magnetic separation such as intensity of the magnetic field, particle size of the feed, feed rate and number of operations were optimized to obtain maximum grade and recovery of chromium. The ore containing 28% Cr$_2$O$_3$ was upgraded to a concentrate assaying more than 40% Cr$_2$O$_3$ with 90% recovery. The final concentrate produced met all the specifications of the chemical grade chromium concentrate.

Introduction

Chromite is the main mineral of chromium whose composition may be represented by the formula (Fe, Mg) O. (Cr, Al, Fe) _2O$_3$. Other, commercially less important mineral is crocoite PbCrO$_4$. The natural mineral of chromite is rarely a pure chromite (FeO.Cr$_2$O$_3$) and contains various amounts of magnesium (Mg) and aluminum (Al) in addition to iron (Fe). FeO is being replaced by MgO and Cr$_2$O$_3$ by Al$_2$O$_3$ or Fe$_2$O$_3$. But the components FeO and MgO form ferrochromite FeO.Cr$_2$O$_3$ and magnesiochromite MgO.Cr$_2$O$_3$, spinels respectively. Chromite mineral containing Al$_2$O$_3$ in addition to Cr$_2$O$_3$ is called aluminian chromite FeO.(Cr,Al)$_2$O$_3$ whereas Fe$_2$O$_3$ containing mineral is called ferrarian chromite FeO.(Cr, Fe)$_2$O$_3$. These spinels are susceptible to substitutions which account for the change in chrome to iron ratio in chromite mineral. There is a substitution of Cr$_2$O$_3$ by Al$_2$O$_3$ or Fe$_2$O$_3$ in case of chromite with low chrome to iron ratio [1].

Chromite concentrates made out of low grade ore are classified as metallurgical, refractory and chemical grade concentrates. Metallurgical grade chromite concentrates have a Cr : Fe ratio of 3:1 or better with more than 48% Cr$_2$O$_3$ and negligible amount of SiO$_2$ (< 3%). Chemical grade chromite concentrates generally contain 40-48% Cr$_2$O$_3$ with a Cr : Fe ratio of ~1.5:1 and less than 8% SiO$_2$. Refractory grade chromite concentrates contain 30-40% Cr$_2$O$_3$ with 20-30% Al$_2$O$_3$ and between 12% Fe$_2$O$_3$. Over 50% of the world’s requirement is for the metallurgical grade concentrate. About 30% of chromite concentrate is used for the preparation of refractory materials while remaining is used in chemical industry [2]. Metallurgical grade chromite concentrates are used in the production of chromium metal, ferrochrome, nichrome, stainless steel, tool and alloy steel. Refractory grade chromite concentrates are used in the manufacture of chrome bricks and crucibles. Chemical grade chromite concentrates are used in the preparation of chromium compounds such as sodium chromate, sodium dichromate, potassium chromate, potassium dichromate, barium chromate, lead chromate, chromic acid and basic chromium sulphate. These chemicals are extensively used as oxidizing agents, in paint pigments, tanning and dying of leather, textile processing, electroplating and medicines [3].

Chromite deposits of Pakistan occur in ultramafic complexes of magmatic origin which intrude along the axial belt lying on the western borders of the country from Waziristan, Malakand and Mahmard in the north through Zhob Valley to Jhlanwan in the south. But the most extensive deposits occur around Muslim Bagh in Zhob Valley. These deposits are located at Khanozai, Jungtohar, Saplaigorh, Nasai and Fort Sandeman. The Zhob Valley igneous complex is spread over an area of more than 5000 sq. Km. and contains deposits which are quite variable in size, shape, grade and disposition of the ore bodies. The reserves of chromite ore of Zhob Valley are estimated to be more than 6 million tonnes [4]. In these deposits, there are limited reserves of high grade ore, which are being depleting due to export.
The processing of chromite ore is generally accomplished by gravity concentration, froth flotation or by high intensity magnetic separation [2]. The selection of the beneficiation technique depends upon the mineralogical composition and the texture of the ore. Gravity concentration by tabling and spiral is generally employed for chromite ores which are coarsely associated with low specific gravity gangue minerals, whereas, for finely disseminated ores, which require fine grinding for the liberation of chromite mineral, it is technically important to recover the mineral by froth flotation. The ores containing gangue minerals possessing densities closer to the chromite are treated by high intensity magnetic separation technique [5-7].

Huiatt, [8] studied the beneficiation of chromite ore from low grade deposits of USA, containing 16-24 % Cr₂O₃ and prepared concentrates of 43-45 % Cr₂O₃ with 85-87 % recovery by conventional and column flotation using cationic collector (amine) and found that grade and recovery of chromium (Cr) is lower when conventional flotation is used while Tagirov et al. [9] used the technology of gravity concentration for the beneficiation of the fine grade of chromium ores and recovered Cr from tailings by high intensity magnetic separation to improve the recovery. Abdel Khalek, [10] performed anionic flotation of low grade chromite ore of Egypt using oleic acid as anionic collector and sodium fluorsilicate as depressant. Mati, et al. [11] had to replace the gravity concentration method with high intensity magnetic separation technique due to increase in the %age of olivine (sp.gr. = 3.3) in deeper seated ore bodies of a chromite ore in Albania. Guney, et al. [12] used high intensity wet magnetic separation (HIWMS) and column flotation for the recovery of the chromite fines from the tailings of a chromium plant in Turkey and prepared a concentrate of 47% Cr₂O₃ with 37% recovery. Zverev, et al. [13] applied the technology of gravity and magnetic separation for the beneficiation of lean chromium ores (30-38% Cr₂O₃) of Russia and prepared a concentrate with 50% Cr₂O₃. Nermin, [14], prepared a chromite concentrate of more than 52% Cr₂O₃ with 70% recovery from a chromite ore, in Turkey, by multi gravity separators. Kalmukhev, et al. [7] used magnetic and gravity beneficiation for preparing chromite concentrates from a lean complex ore of disseminated type. They used low power magnetic field for the separation of magnetite and high strength magnetic field for the concentration of residual ore. Concentrate obtained was subjected to gravity concentration for the removal of silicates and quartz.

The differing magnetic properties of minerals are widely exploited in large scale separation of valuable minerals from gangue materials. Magnetic susceptibility is the characteristic of the minerals containing parallel electron spins. Certain minerals are strongly paramagnetic and are attracted by even low intensity magnetic separator, whereas weakly magnetic minerals needs high intensity magnetic separator for their separation. Chromite is a weakly paramagnetic mineral, which provides a basis for its separation from the associated gangue minerals by high intensity magnetic separation [15].

Due to the scarcity of high grade ore and availability of large reserves of low grade chromium ore in Pakistan, it is important to utilize these ore reserves, present in considerable quantity, to meet the future chrome requirement of the country. Therefore, the main objective of the present investigation is the development of a suitable technology for the utilization of indigenous sources of low grade chromite ore. High intensity dry magnetic separation (HIDMS) was applied for the beneficiation of a low grade chromium ore of Muslim Bagh area from Zhob Valley (Balochistan) and test work was carried out at Material Science Research Centre (MSRC), PCSIR Laboratories Complex Lahore.

Results and Discussion

Table-1 shows that the percentage of Cr₂O₃ in ore is 28.05 %. This grade is sufficient to exploit the ore. However, the presence of siliceous gangue minerals appears to be the main impurities. As chromite is a weakly paramagnetic mineral, while the other minerals present in the Muslim Bagh ore are non-magnetic in nature. It was decided, in this perspective, to involve the high intensity dry magnetic separation technique which has the potential to reduce these siliceous gangue minerals effectively.

Table-2 reveals that after beneficiation, Cr₂O₃ content has been increased significantly from
Table-1: Chemical Analysis of Chromite Ore.

<table>
<thead>
<tr>
<th>Constituents</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr₂O₃</td>
<td>28.60</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>12.15</td>
</tr>
<tr>
<td>SiO₂</td>
<td>14.30</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>15.85</td>
</tr>
<tr>
<td>CaO</td>
<td>0.20</td>
</tr>
<tr>
<td>MgO</td>
<td>21.20</td>
</tr>
<tr>
<td>LOI</td>
<td>7.65</td>
</tr>
</tbody>
</table>

Table-2: Chemical Analysis of Chromite Concentrate.

<table>
<thead>
<tr>
<th>Constituents</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr₂O₃</td>
<td>40.18</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>16.96</td>
</tr>
<tr>
<td>SiO₂</td>
<td>7.26</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>20.75</td>
</tr>
<tr>
<td>CaO</td>
<td>0.12</td>
</tr>
<tr>
<td>MgO</td>
<td>12.73</td>
</tr>
<tr>
<td>LOI</td>
<td>1.52</td>
</tr>
</tbody>
</table>

28.05% to 40.15% with decrease in amount of silica from 14.30% to 7.26% and magnesia from 21.20% to 12.73% respectively. Concentrates having Cr₂O₃ and SiO₂ in this range are considered suitable for the preparation of chromium based chemicals. Even, the concentrate containing 35% Cr₂O₃ can also be used provided it has relatively less amount of SiO₂ [16].

Table-3 presents the results of mesh of liberation studies regarding chromite mineral. Microscopic examination of various sieve fractions shows that about 80% chromite particles are liberated around 50 mesh and can be recovered by high intensity magnetic separation. The size analysis of roll crusher product also shows that crushing produces considerable quantity of fines. This is due to the fact that ore is brittle and friable in nature. To avoid difficulties in magnetic separation, controlled grinding in rod mill is recommended in order to reduce the generation of excessive slimes. Due to this reason, the chromium ore of Muslim Bagh was crushed in a rod mill (Denver, USA) to prepare a feed of 50 mesh size.

Table-4: XRD of Chromite.

<table>
<thead>
<tr>
<th>2θ (°)</th>
<th>d (Å)</th>
<th>Intensity</th>
</tr>
</thead>
<tbody>
<tr>
<td>18.406</td>
<td>4.8173</td>
<td>17.23</td>
</tr>
<tr>
<td>30.331</td>
<td>2.9451</td>
<td>6.14</td>
</tr>
<tr>
<td>35.827</td>
<td>2.5048</td>
<td>100.00</td>
</tr>
<tr>
<td>43.573</td>
<td>2.0758</td>
<td>43.93</td>
</tr>
<tr>
<td>56.203</td>
<td>1.6357</td>
<td>7.98</td>
</tr>
<tr>
<td>66.621</td>
<td>1.4029</td>
<td>12.12</td>
</tr>
<tr>
<td>74.914</td>
<td>1.2668</td>
<td>17.15</td>
</tr>
</tbody>
</table>

talc as gangue minerals. JCP.CAT search/ match X-ray Diffractometer D-5000 (Siemens, Germany) programme contains d/l values of about 60,000 Standards for material identification. Ore microscopy shows that chromium ore of Muslim Bagh area is composed of chromite mineral associated with various silicate minerals. This ore is medium to fine grained, massive and disseminated in texture. The grain size of chromite ranges from 0.2-0.5 mm. The colour of chromite looks to be brownish to black with sub metallic to metallic luster. The density of the ore was found to be 2.67 indicating the presence of light weight gangue minerals in the ore. The fracture of the ore was observed to be uneven.

The results obtained at different field intensities (Fig. 1) show that there is a gradual increase in grade with increase in field intensity up to 4000 gauss, but after further increase in field intensity, the grade decreases with slight increase in recovery. This is due to the fact that, as field intensity increases, some of middling particles are also attracted by magnet and falls in the magnetic portion which results a decrease in grade with little improvement in recovery of chromium [17]. At field intensity of 4000 gauss, a concentrate with optimum grade and recovery was achieved.

The tests carried out at various particle sizes (Fig. 2) show that grade increases with
Feed Size = 90 % - 50 mesh, Feed Rate = 15 kg/hr, No. of Passes = 2

Fig. 1 Effect of Field Intensity on the Grade and Recovery of Chromite.

Field Intensity = 4000 Gauss, Feed Rate = 15 kg/hr, No. of Passes = 2

Fig. 2 Effect of Feed Size on the Grade and Recovery of Chromite.

decrease in particle size up to the value of 95% passing 50 mesh sieve and further grinding does not improve the grade and recovery. It is due to the reason that, the ore produces more slimes on excessive grinding that reduce the selectivity [18] and hence decrease the grade and recovery of concentrate. The best result was attained at the feed size of 95% passing 50 mesh size.

The effect of feed rate on the efficiency of separation is evident from Figure-3, as there is a gradual decrease in the grade of the concentrate with increase in feed rate. It was observed that the effect of feed rate was directly related to the height of layer particles. With increase in the feed rate, the collection of magnetic particles got disturbed. The magnetic particles under the surface of non magnetic particles were not attracted and passed through along with non magnetic particles. Therefore, by reducing the rate of passage of particles (feed rate) it is possible to affect the less susceptible mineral particles [19]. It is clear from the results that the feed rate of 20 Kg/hr is suitable for optimum grade and recovery of concentrate.

Fig. 4 indicates that with the increase in number of operation, a gradual improvement in grade of concentrate has been resulted. This is due
Field Intensity = 4000 Gauss, Feed Size=95%-50 mesh, No. of Passes = 2

Fig. 3 Effect of Feed Rate on the Grade and Recovery of Chromite.

Field Intensity = 4000 Gauss, Feed Size = 95%-50 mesh, Feed Rate = 20kg/hr

Fig. 4 Effect of No. of Operations on the Grade and Recovery of Chromite.

to the fact that, in second and third stage operation, feed contain higher chromite content after removal of gangue minerals in first and second stage operation. It is clear from this Figure that multiple pass operation produces a higher grade concentrate by removing more gangue minerals and consequently increases the grade of concentrate with little decrease in recovery. In multiple pass operations, better results are achieved as compared to single pass operation [20]. Fourth stage operation seems to be less effective because the gangues were almost removed in three stages at that field intensity. It is obvious from these results that the optimum condition for the magnetic separation of chromite is achieved with three stage operation.

Experimental

Sample Preparation

The ore was crushed in laboratory jaw crusher (set at 20 mm) and roll crusher (set at 5 mm). In order to obtain the representative sample of the ore for further processing, sampling by coning and quartering was done, while riffling was used to prepare the head sample for chemical
analysis and mineralogical studies. The head sample was pulverized to 100 % minus 200 mesh (74μm) in disc pulverizer (Denver, USA).

Chemical Analysis

Pulverized ore was fused with sodium peroxide in nickel crucible and fused mass was leached in hot water. Solution marked as “A” containing soluble salts of Cr, Al, and Si was obtained after filtration and making the volume up to 250 ml while residue containing insoluble salts of Fe, Ca and Mg was dissolved in dilute HCl and made the volume up to 250 ml to obtain solution marked as “B”. Silica and alumina were determined from solution “A” by gravimetric methods, chromium from solution “A” and iron from solution “B”, by oxidation reduction titration while calcium and magnesium were estimated from solution “B” by complexometric titration using standard solution of EDTA. Loss on ignition (LOI) was determined at 1000 °C till constant weight was achieved.

Mineralogy

Ore microscope (Nikon, Japan) was used to study the nature of ore. The ore pieces were initially cut to about 0.1 mm in thickness by means of Thin Section Cut-off Saw and then ground to the thickness of 0.02-0.03 mm with decreasing grit sizes (Nos. 240, 400 and 600) followed by diamond polishing on cloth laps using 7 micron diamond paste. The thin sections of ore were placed on glass slide, covered with cover slip and examined under the microscope, using different magnification. Pulverized ore sample was run on X-ray Diffractometer (Model: D-5000 Siemens, Germany) to identify the type of minerals present in ore. Scan angle was varied to get main peaks. By the measurement of a series of scan angles (2θ) and intensity readings, matching with standard data, unknown minerals were identified.

Degree of Liberation

The roll crushed ore was subjected to sieve shaker (International Combustion, England) for size analysis using different sieves. The fraction of each sieve was weighed and analyzed for liberation of chromite grains. The % age of chromite liberation in various size fractions was determined using microscope particle counting method

Magnetic Separation Tests

The feed was subjected to dry high intensity magnetic separator (Davies, Model: 51V, Davies Magnetic Works Limited, Hertz, England) and a number of tests were conducted to study the effects of various parameters on the grade and recovery of chromium. The intensity of magnetic field was varied from 2000-5000 gauss, particle size of the feed from 80-100 % -50mesh, feed rate from10-25Kg/hr, and number of operations (passes) from 1-4. The magnetic and non magnetic portions were collected and chemically analyzed.

Conclusions

The results reported show that it is possible to upgrade low grade chromite ore of Muslim Bagh area by high intensity dry magnetic separation (HIDMS) technique to produce chromite concentrates of chemical grade with high recovery. The concentrate can be directly used for the production of chromium based chemicals. The advantage of this technique is that it produces a concentrate with high recovery, it is easy to operate, less expensive and environment friendly.

Acknowledgement

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References