

SOME ASPECTS OF CHROMITE WITH REGARD TO
POSSIBLE USES OF NORTH CAROLINA MATERIAL

Minerals Research Laboratory
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Lab Nos. 3460, 3461, 3464, 3468,
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by
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Abstract

An investigation was undertaken to review and examine the uses of chromite, and determine if North Carolina chromite could meet any of the present industrial requirements. Samples from six of the largest deposits were concentrated and thoroughly cleaned to remove all gangue constituents. These concentrates were then analysed to determine the composition of the chrome spinel constituents in each sample.

This report contains a general review of the uses of chromite. It also explains why North Carolina chromite has been disregarded in the past, and why it should be considered in the future.

Chromite Chemistry

Chromite is the major mineralogical constituent of chrome ores. It has been described as follows: isometric in octahedrons, commonly massive, fracture uneven, brittle, H. = 5.5, G. = 4.1 - 4.9, luster submetallic to metallic, color between iron black and brown black, streak brown, and sometimes feebly magnetic.⁽¹⁾ Chromite is a double oxide of the spinel group fitting the general formula $RO \cdot R'2O_3$ (like spinel, $MgO \cdot Al_2O_3$; magnesioferrite, $MgO \cdot Fe_2O_3$; magnetite, $FeO \cdot Fe_2O_3$; and hercynite, $FeO \cdot Al_2O_3$). The basic formula for chromite is

FeO . Cr₂O₃, 68.0 percent chromium sesquioxide and 32.0 percent iron protoxide, (1.88 : 1 Cr to Fe ratio). But in the chromite of commercial chrome ores, a substantial part of the FeO is replaced by MgO and part of the Cr₂O₃ by Al₂O₃.

Thus, the principal mineral species in chrome ores might be described as a solid solution of the spinel type containing the oxides FeO, MgO, Cr₂O₃ and Al₂O₃ in varying proportions. Other accessory materials found in chromite include; TiO₂, 0.1 to 1.0 percent; NiO, 0.1 to 0.5 percent; MnO, 0.1 to 0.5 percent; and 0.1 to 0.2 percent V.

The gangue minerals in chrome ores are important technologically and interesting scientifically, but have received little attention. The most common gangue minerals are serpentine, chlorite, talc and bronzite. Others commonly found include olivine, amphibole, and calcic plagioclase. Minerals such as quartz, tourmaline, dolomite, etc. are secondary hydrothermal replacements or fillings.

Uses of Chromite

Chromite consumed in industry is classified into three groups, metallurgical, refractory and chemical. These groups, or grades, are based on physical and chemical properties, but advances in technology are allowing interchangeability among the three industrial fields. In the United States, over the last twenty years, the metallurgical industry has accounted for about 57 percent of all chromite consumed, with refractories consuming 30 percent and the remaining 13 percent going to chemical uses.

Metallurgical Grade Chromite - This variety depends on the steel industry for its markets. Its largest outlet is in the manufacture of chrome ferroalloys used in the production of stainless and heat resisting steels. Chromium is usually added to ferrous alloys as ferrochromium (66-72 percent Cr), and it is for the purpose of making the 70-72 percent ferrochromium that the Cr:Fe ratio must be in the order of 3:1, after smelting losses are taken into account. In many European countries, where 60 percent ferrochromium is acceptable, ores with higher percentage of iron can be used. This is particularly true in the manufacture of high-carbon ferrochromium. In the production of 70 percent ferrochromium, the Cr and Fe content of the ore used is determined by economics in both the production of ferrochromium and its use in making steel. Ores with a chromium-to-iron ratio lower than 3:1 can be blended with ores of higher than 3:1 ratio; in this manner lower-ratio ores are used. The development of exothermic alloys has allowed the industry to use ores as low as 1.6:1 in ratio. (2)

Metallurgical grade chromite ores are described in the following way.

- I. Lumpy: Natural chromite ore being hard, dense, non-friable, with no more than 25 percent passing a one inch screen when originally received.
- II. Fines: Material essentially comparable in character to Type I material above, but having more than 25 percent passing a one inch screen.
- III. Concentrates: Product of a physical process whereby the chromite content has been enriched, with practically all material being less than 1/8 inch in particle size.

Type I and II metallurgical grade ores are generally used for production of high-carbon ferrochrome, medium carbon ferrochrome and chrome silicide. Type III is used for production of low carbon ferrochrome. The general range of chemical analyses of chromite ores used in ferroalloys is as follows:

	<u>Type I and II</u>	<u>Type III</u>
Cr ₂ O ₃	46-52%	52-56%
Cr	32-36%	36-38%
Fe	9-12%	10-16%
SiO ₂	4-6%	2-4%
MgO	14-20%	9-13%
Al ₂ O ₃	10-12%	10-13%

Rhodesia, long a major Free World source of high grade metallurgical lump, was banned from delivering ore and chrome ferroalloys to the U. S. by President Johnson's Executive Order of January 5, 1967. Since that time the U.S.S.R. has set the pace for ore markets and is now the leading U. S. source of high-grade lump.

Refractory Grade Chromite - Specifications for refractory grade chromite are not so rigid as those for metallurgical grade. However, refractory grade ore must be physically as well as chemically acceptable. Chrome ores, not too many years ago, assumed considerable importance as raw materials for basic refractories, particularly in various combinations with magnesite.

At one time chrome refractories were used in furnace construction primarily because they were considered to be "chemically neutral". Chrome brick resists both basic and acid slags quite well and is the

only common refractory with this property. For this reason it is used in furnace construction to separate basic and acid refractories; for example, it is placed between magnesite and fire clay brick because they tend to react and flux each other at operating temperatures, if laid in direct contact. Except for the fact that chrome refractories do not withstand the destructive action of iron oxides,⁽³⁾ they are used in much the same way as magnesite, that is, as general-purpose basic refractories. In such use they have the advantages, compared with magnesite, of slightly lower cost, better resistance to fluxing with silica, moderate thermal expansion, stability of crystalline form at high temperatures, and lower thermal conductivities.

While chromite is a true refractory, the associated gangue has a relatively low softening point, ranging from 1,260° to 1,427°C, whereas chromite as a whole has a softening point in the order of 2,100°C. This lower softening temperature, combined with the amount and fluidity of the silicates and their physical distribution, determines the suitability of chromium ore for refractory purposes.

Since it is desirable to keep the silica content of refractory chromite as low as possible and because refractoriness is inversely proportional to, and reactivity directly proportional to, the iron content, the chromic oxide plus the alumina content should not be less than 60 percent. The FeO and SiO₂ contents, which cause shrinking on heating, should not be more than ten percent and five percent respectively.

The various chrome ores used for refractories throughout the world range from 30 to 46 percent Cr₂O₃, nine to 23 percent total Fe,

ten to 32 percent Al_2O_3 , eight to 20 percent MgO , and two to 15 percent SiO_2 . Although all are considered "refractory grade" because they are used for refractories, there is a wide range in ore compositions. (4)

The above ore types fall into three groups; the Cuban and Philippine ores which have an analysis of 30 to 32 percent Cr_2O_3 , a Cr_2O_3 plus Al_2O_3 of 60 percent minimum, and a maximum of 5.5 percent SiO_2 ; the Turkish and Rhodesian ores which have an analysis of 40 to 44 percent Cr_2O_3 , 15 to 20 percent Al_2O_3 and three to five percent SiO_2 ; and the high grade Turkish, Iran, and Greek ores which run 48 to 52 percent Cr_2O_3 , 15 to 20 percent Al_2O_3 and 1.5 to 3.0 percent SiO_2 . While some ores are hard and lumpy, others are soft and friable. And there is a wide range of plasticity, from sandy to sticky. All of these characteristics are considered when ores are combined to arrive at the desired final properties.

The majority of the chromite ores used for refractory purposes are made into bricks and molded shapes. There are many varieties based on composition, and they further vary as to being fired, unfired or electrocast. Besides molded shapes, many other chromium refractories are marketed. Large quantities are used in patching mixtures, which are bonded into monolithic structures, in place, in the furnace.

There has been a constant increase, over the past 20 years, in the use of various combinations of chrome ores and dead-burned magnesite. The most common compositions of commercial chromium bricks are: 100 percent chromite, 75 percent chromite and 25 percent magnesite, 60 percent chromite and 40 percent magnesite, and 25 percent chromite and 75 percent magnesite.

Some of the advantages of adding magnesite to chrome can be seen when reviewed with the chemistry of chromite and chromite ores. Magnesia combines with the relatively nonrefractory magnesium silicates, present as impurities in chrome ores, to form forsterite in the bonding mass surrounding the grains of chrome spinel. This gives a more heat-resistant product with better load-bearing capacity. Magnesia added to chrome ores also tends to replace FeO in the spinel structure. It also combines with the Fe₂O₃ in a stable solid solution. These actions are beneficial if the material is exposed to iron oxides or if the brick is exposed to oxidation-reduction processes that would oxidize the FeO in the spinel. (5)

According to Thayer: (6)

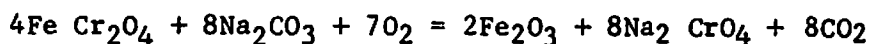
"Depletion of the podiform deposits will entail major changes in the quality of ore, and presumably prices. The podiform deposits are the principal source of high-chromium ores (Cr₂O₃ more than 45 percent, Cr:Fe more than 2:1) and the only source of high-alumina ore (Al₂O₃ more than 20 percent); excepting parts of the Great Dyke, all stratiform chromites are the high-iron variety (Cr₂O₃ more than 40 percent, Cr:Fe less than 2:1). The high-chromium and high-alumina ores will be seriously depleted by 1975, and at a premium. If, for any reason, normal supplies from Southern Rhodesia and the Union of South Africa are interrupted, the Free World would soon face a severe crisis. Unless someone finds a substitute for chromium in stainless steel, the experts all agree that consumption of chrome ores will continue to increase steadily, and 10 or 15 years hence the major problem is more likely to be supply than marketing."

Chemical Grade Chromite - Ideally, these ores contain a low gangue or impurity level with respect to the percentage of chromic oxide. The Cr₂O₃ in ores of this grade varies between 44 and 46 percent, with SiO₂ and FeO rising up to 11 percent and 20 percent respectively. Cr:Fe ratios

are normally low and in the range of 1.5 or 1.6 to one. Some consumers require even stricter specifications of 2.5 percent SiO₂ maximum content, with 1.5 percent or less preferred. The Al₂O₃ content should be less than 15 percent, MgO contents around ten percent, and the sulphur content must be low. Fines are preferred because the ore must be ground for processing into sodium and potassium chromates and dichromates.

The primary chromium chemical, from which nearly all the others are derived, is sodium bichromate (Na₂ Cr₂O₇ . 2H₂O). Although other principal chemicals include sodium chromate, potassium dichromate, potassium chromate, and chromic acid; total chemical production and usage is quoted in terms of sodium bichromate equivalent.

The manufacture of sodium chromate, the first stage in the production of the other principal chromium chemicals, is carried out by roasting a mixture of pulverized chrome ore, soda ash, and lime in an oxidizing atmosphere in accordance with the following reaction:



The lime serves to prevent fusion of the mix. The calcine is leached with hot water and the liquor concentrated. The sodium chromate may be separated directly by crystallization, however, the solution is usually treated with H₂SO₄ and, after separation of the sodium sulphate, is further concentrated to obtain sodium bichromate. Other methods using carbon dioxide are also employed.

Principal uses of chromium chemicals are: pigments for paints, inks, dyes, etc.; leather tanning; textile mordants ; corrosion control of metals; chromium plating; wood preservation; photography; lithography; and chemical processes. (7)

In the United States virtually only one type of chrome ore, Transvaal friable, with about 44 percent Cr_2O_3 and a Cr:Fe ratio of 1.5 - 1.6, is used for chemicals. Other types of ore, such as high-chromium Turkish and New Caledonian, could be used for chemical manufacture but the choice of ore for this purpose is dictated by the cost per unit of Cr_2O_3 recovered from the ore which rules out the expensive high-Cr-low-Fe ores.

Chromite in North Carolina

The history of chromite in North Carolina has at best been spotty. Several references have been made through the years by journals, books, and professional papers. Perhaps the best, and most admirable, condensation of the history is given by Stuckey.⁽⁸⁾ In an effort to save space and conserve detail it is presented here in its entirety.

"Chromite has been known to occur in North Carolina since 1870 and sporadic attempts have been made to mine it since about 1871 or 1872. The first systematic attempt to mine corundum in North Carolina, according to Pratt and Lewis (1905), was made at Corundum Hill in the fall of 1871; where the presence of chromite in peridotite, with which the corundum was associated, led to a search for commercial deposits of chromite. Systematic prospecting for chromite began about 1880 and continued for the next twenty years. Detailed information on the various prospects opened and the amount of chromite produced is, unfortunately, not available. There was little interest in chromite in North Carolina between 1900 and the beginning of World War I in 1917. During 1918, operations were carried on at five localities in Buncombe, Jackson and Yancey Counties. Production amounted to 339 tons of ore with a chromic oxide content of 45 percent or more, but total shipments amounted to only 124 tons. Between 1918 and 1940 there was little or no interest in chromite in North Carolina. However, about 1940 there was renewed interest in chromite in this State that resulted in some exploratory work. Prospecting was carried out at Webster, Jackson County, but no production was made. During the summer and fall of 1941, Southern Minerals Company of Asheville made a small production from chromite sands along Ivey River near Democrat, Buncombe County, by means of a small portable hydraulicking plant.

Some prospecting was done on the Plyler property northeast of Statesville, Iredell County, but no production was reported. The Department of Conservation and Development and the Tennessee Valley Authority carried out a cooperative study of chromite in North Carolina in 1941 during which six holes varying in depth from 84.8 feet to 131.6 feet were drilled at Webster. The results of this study were published by the Department of Conservation and Development as Bulletin 42, 'Chromite Deposits of North Carolina', by Hunter, Murdock and MacCarthy (1942). The only prospecting for chromite in North Carolina since the close of World War II in 1945 consisted of two drill holes, one near Adam Mountain, Wake County, and the other near Wilton, Granville County, both of which were drilled about 1950. The chromite recovered averaged less than 30 percent Cr₂O₃ in most cases and no attempt at mining was made."

Searching back to the beginning, Pratt and Lewis (9) show analyses on chromite from Price Creek, six miles southwest of Burnsville, Yancey County; Webster, Jackson County; Corundum Hill, Macon County; and Mine Hill, five miles north of Burnsville, Yancey County as follows:

	<u>Price Creek</u>	<u>Corundum Hill</u>	<u>Webster</u>	<u>Mine Hill</u>
Cr ₂ O ₃	59.20	57.20	39.95	58.00
Al ₂ O ₃	7.15	7.82	29.28	15.52
FeO	25.02	25.68	13.90	14.45
MgO	4.42	5.22	17.31	8.26
SiO ₂	3.20	2.80	-	3.20
MnO	<u>0.92</u>	<u>0.69</u>	<u>-</u>	<u>0.70</u>
Total	99.91	99.41	100.44	100.13

These analyses were reported in Economic Survey Papers "The Mining Industry in North Carolina from 1904 to 1936." The only additions or changes made were two new analyses. The first appeared in the 1913-1917 edition showing a report of work done near Democrat, Buncombe County, along the Ivey River, There concentrated sand assayed 54.09 percent Cr₂O₃ and a hand cobbled sample ran 48.78 percent Cr₂O₃. The next appearance of a new analysis was in the report covering 1927-1928,

where a sample from Dark Ridge, near Balsam Gap, Jackson County, ran 49 percent Cr_2O_3 . Then in the 1937 - 1945 publication emphasis was shifted to analyses reported in Bulletin No. 42, North Carolina Department of Conservation and Development, by C. E. Hunter, T. G. Murdock and G. R. MacCarthy. These analyses showed the following:

	<u>Day Book (Mine Hill)</u>	<u>Democrat</u>	<u>Webster</u>	<u>Dark Ridge</u>	<u>Addie.</u>
Cr_2O_3	44.20	55.52	22.61	39.66	29.46
Al_2O_3	21.30	-	16.70	26.80	24.00
Fe_2O_3	20.05	28.50	18.91	14.18	19.89
MgO	14.48	-	24.62	12.34	15.74
SiO_2	<u>0.30</u>	<u>0.80*</u>	<u>16.90</u>	<u>7.20</u>	<u>11.40</u>
Total	100.33	84.82	99.74	100.18	100.49

*Si analysis.

These analyses have appeared in all subsequent publications concerning North Carolina mineral industries. However, it is a serious mistake to assume that these analyses represent clean, pure, chromite.

Chromite, as a crystal, has no room or space in its structure for silica. Any SiO_2 reported in a chemical analysis must be present in the sample as a gangue constituent. An examination of a report on the forsterite olivine deposits hosting the chromite⁽¹¹⁾ reveals that the olivine "gangue" contains about 40 percent SiO_2 .

If we assume that all the SiO_2 reported in the previous analyses to be present as olivine, we can calculate the percent gangue diluent in each analysis. Using this method, it appears that the Dark Ridge sample had 18.0 percent gangue, the Addie sample had 28.5 percent gangue, and

the Webster sample had 42.2 percent gangue diluent in the analysed sample.

In Division of Mineral Resources Bulletin No. 42, the following statement is found to precede each analysis, "A chipped sample of the chromite including some matrix... has the following analysis". It is unfortunate that when others attempted to quote Mr. Hunter, they actually misquoted him by failing to mention the analyses were of ores and not chromite minerals.

It was in an effort to correct the misconceptions about North Carolina chromites that this present work was undertaken. In May of 1969 samples of chromite ores were collected with the help of the personnel of the Division of Mineral Resources and the Minerals Research Laboratory. These samples were then treated in the following manner;

1. Jaw crushed to minus $\frac{1}{2}$ inch.
2. Stage ground by a disc mill to minus 28 mesh.
3. Scrubbed at 80 percent solids for ten minutes.
4. Deslimed on a 150 mesh screen.
5. Separated in heavy liquid at Sp. Gr. = 2.96.
6. Separated on a Frantz Isodynamic Magnetic Separator.
7. Leached with hot concentrated hydrochloric acid.
8. Separated in heavy liquid at Sp. Gr. = 2.96.
9. Separated on a Frantz Isodynamic Magnetic Separator.
10. Chemically analysed for composition.

The deposits sampled represent the larger of the chromite - olivine deposits, some of which have been mined in the past for chromite.

In the case of one sample, No. 3461, Holcombe Branch, the material sampled was a stream accumulation; therefore, the first four steps were shortened to screening and tabling.

The chemical analyses shown in Table 1, "Analyses of the Chrome Spinel Constituents of Certain Chromite Samples," therefore, are not analyses of ore samples. Neither can one expect to produce material of this grade with simple ore dressing methods. They only represent what they are - chrome spinel constituents of certain chromite samples.

Comparison of the analyses with the general requirements of industry seems to place the chromites into certain possible end-product uses. Three of the chromites, Democrat, Day Book, and Addie, would fit into any of the classifications if Cr:Fe ratios are disregarded. One chromite would fit into metallurgical and chemical uses, and one into refractory uses. Only one sample, Holcombe Branch, would seem to be left out of all use classifications.

These statements are not meant to say that any, or all, of these deposits could produce chromite of suitable economical, chemical, and physical properties to actively compete with other world sources of chromite. It is highly doubtful that any of the mentioned deposits could replace present sources of chromite if produced as a primary product. However, if chromite were produced as by-product, or co-product, of olivine mining these chances would be greatly improved.

Conclusion

In closing, certain facts and recommendations can be related to this work.

1. In the first ten months of 1968, the Communist countries exported to the United States about 33 percent of our entire imports. This makes the metallurgical chromite industry in the U. S. relatively dependent on the Communist countries.
2. North Carolina chromite appears to be suitable as a supplement to imported chromite.
3. The olivine deposits of Western North Carolina contain tremendous reserves of disseminated chromite. (See Table 2, "Indicated Reserves of Disseminated Chromite")
4. Approximately twenty more locations of chromite should be checked for chemical composition.
5. The Minerals Research Laboratory should prepare itself to accommodate industry in its search for ore deposits of chromite in the State.

Under suitable sponsorship, pilot plant production of chromite should be undertaken in order to produce tonnage quantities of beneficiated product to be suitably tested by industries. It is possible that the United States may then again place itself on the list of chromite producing countries.

Table 1

Analyses of Chrome Spinel Constituents of Certain
Chromite Samples

<u>Laboratory No. and Location</u>	<u>Analysis in Percent</u>					<u>Ratio Cr:Fe</u>	<u>Sp. Gr. gr/cc</u>
	<u>Cr₂O₃</u>	<u>FeO*</u>	<u>Al₂O₃</u>	<u>MgO</u>	<u>SiO₂</u>		
#3460 Democrat	48.5	23.9	12.0	10.7	3.0	1.8	4.53
#3461 Holcombe Branch	52.9	27.5	9.1	6.5	1.6	1.7	4.70
#3464 Day Book	56.5	18.9	10.4	12.5	0.2	2.6	4.56
#3468 Dark Ridge	50.8	17.6	16.1	12.8	0.4	2.6	4.43
#3469 Webster	46.7	25.2	12.0	11.0	1.4	1.6	4.42
#3470 Addie	53.0	24.7	10.7	9.4	0.2	1.9	4.60

* Total iron reported as FeO.

Table 2

Indicated Reserves of Disseminated Chromite*

<u>Deposit Name</u>	<u>Olivine, Millions of Tons</u>		<u>Indicated Chromite Millions</u>	
	<u>Fresh</u>	<u>Altered</u>	<u>Percent</u>	<u>of Tons</u>
Democrat	2.0	25.0	1.0	0.27
Holcombe Branch	3.5	17.5	2.0	0.40
Day Book	3.2	6.7	1.5	0.15
Dark Ridge	16.6	24.5	2.5	1.03
Webster	58.2	167.9	1.0	2.26
Addie	28.4	102.5	2.0	2.62

*Reconstructed from Division of Mineral Resources Bulletin No. 41,
C. E. Hunter.

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