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Caustic Leaching of Montana Chromite

Chester Freshour

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CAUSTIC LEACHING
OF MONTANA CHROMITE

by

Chester Freshour

A Thesis

Submitted to the Department of Metallurgy
in Partial Fulfillment of the
Requirements for the Degree of
Bachelor of Science in Metallurgical Engineering

MONTANA SCHOOL OF MINES
BUTTE, MONTANA
MAY 17, 1949

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INTRODUCTION

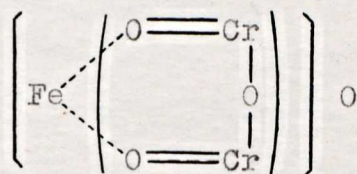
Chromite is the most important ore used for the production of chromium and chromium alloys. At present, the domestic production is insignificant as compared with the amount of chromite consumed in the United States. In 1948 the total domestic production was estimated at 3,500 tons of metallurgical-grade chromite--chromite having a chrome:iron ratio of 3:1--whereas, the total consumption was 380,000 tons. The imported ore, in decreasing order of receipts, came from the U.S.S.R., Turkey, Southern Rhodesia, South Africa, and New Caledonia.¹ Most of the domestic supply came from Shasta County, California; however, workable deposits have been found in Pennsylvania, Maryland, Montana, North Carolina, Oregon, Washington, and Wyoming.²

The large vein of chromite which runs through Stillwater and Sweetgrass Counties, Montana, is apparently the largest single deposit of chrome ore in the United States; however, it is of somewhat lower grade than that of other known domestic chromites.³ Although this ore is easy to mine and can be concentrated by gravity concentration methods, the low percentage of Cr_2O_3 and the low chrome to iron ratio, 1.47:1⁴, present

metallurgical problems which, as yet, have not been satisfactorily solved. If a solution of these problems can be found, the United States will be in a much better position to obtain a sufficient supply of chromite from domestic sources in the event that the foreign sources of high-grade chromite are again cut off as they were during the last war.

Chromite

Structure. Chromite is a member of the spinel group of minerals with an empirical formula of FeCr_2O_4 . It has an isometric crystalline form; although it is most commonly found in the massive, granular state.² The coordination theory of atomic bonding is used to explain the structure of chromite with the following graphic formula:⁵



Theory. Alfred Werner introduced his Coordination Theory in 1893. He said, "Even when, to judge by the valence number, the combining power of certain atoms is exhausted, they still possess in most cases the power of participating further in the construction of complex

molecules with the formation of very definite atomic linkages. The possibility of this action is to be traced back to the fact that, besides the affinity bonds designated as principal valences, still other bonds on the atoms, called auxiliary valences, may be called into action."⁶

Sidgwick noted the possession of at least one lone pair of electrons by each molecule or ion capable of coordination with a metallic atom. This atom acts as the acceptor of a pair of electrons donated by the coordinating group. These compounds are usually very stable. An explanation of their stability is that they either form an inert gas configuration or that the number of molecules or ions coordinated with a central metallic atom is, in general, a value which allows a symmetrical spatial arrangement of the coordinated groups about the central atom. This bond may be considered to be covalent in character; therefore, those groups coordinated with a metal ion are essentially nonionic in nature.⁶

Uses. A greater tonnage of chromite is used in the production of an alloy called ferrochromium than in the production of metallic chromium. This alloy is used for the production of many of the ferrous alloys.

Other uses of chromite are for the production of refractory materials and for the production of chemicals used by the chemical industries.

Montana Chromite

Geology and Development. The Montana chromite from the Stillwater and Sweetgrass deposits is of relatively low grade. The chromite-bearing material is composed of massive and disseminated ore occurring in juxtaposition with a differentiated igneous sheet of pre-Cambrian age.⁷ These deposits are continuous with an estimated 10,000,000 tons of possible ore. During the war they were developed by the Defense Plant Corporation. Three mills were built which produced 102,000 dry tons of chromite concentrates, but before the end of the war, imports of chromite from foreign countries were large enough so that work on the Montana deposits was discontinued.⁸

Future Uses. With the development of cheap power from the numerous dams which have been and are now being built in several Western States, the use of low-grade chromite to produce ferrochromium and stainless steel may turn the western deposits into profitable producers.³

Analysis. An analysis of a sample of the ore taken by the United States Bureau of Mines is shown in table 1.³

TABLE 1

Constituent	Per Cent
Cr_2O_3	26.41
FeO	17.23
MnO	1.02
SiO_2	17.24
Al_2O_3	12.72
CaO	1.16
MgO	23.76
P	0.070
S	0.124

The analysis of the concentrate used for this investigation is shown in table 2.⁴

TABLE 2

Constituent	Per Cent
Cr_2O_3	43.15
FeO	25.70
Al_2O_3	12.20
MgO	1.60
SiO_2	3.35

Statement of Problem

The purpose of this investigation was an attempt to find a method by which a concentrate of Montana chromite from the Benbow mine could be leached with a caustic solution to obtain either a soluble chromite or chromate of commercial value.

CHEMICAL ANALYSIS

The procedure for analysis of the ore was obtained from the Analytical Edition of Industrial and Engineering Chemistry, Volume 9, 1937, as developed by G. Frederick Smith and C. A. Getz of the University of Illinois.⁹

The analysis for the solutions was a modification of the above procedure as developed by J. D. Murphy.¹⁰ The solutions and materials necessary for this analysis are as follows:

Chromite Solvent: 8 parts of 95 per cent sulfuric acid and 3 parts of 85 per cent phosphoric acid.

Oxidation Solution: 2 parts of 72 per cent perchloric acid and 1 part of distilled water.

Standard Solutions: 0.05 N. ferrous sulfate and 0.10 N. ceric sulfate.

Indicator: 0.025 M. solution of Ferroin.

Other Materials: Finely ground crystals of potassium permanganate, dilute (1 to 3) HCl, and dilute (1 to 1) H₂SO₄.

Special Apparatus: Digestion flask still head.

Ore Analysis

Detailed Procedure. "Grind the sample to pass a 100-mesh screen and dry for 2 hours at 105° to 110° C. Carefully weigh out from 100 to 150 milligrams of the sample and transfer to a dry 500-milliliter Erlenmeyer flask. Add 10 milliliters of chromite solvent and

immediately swirl the flask vigorously to get the sample in suspension and to prevent a strong tendency to form a cake which will stick to the bottom of the flask. Adjust the refluxing still head in the neck of the flask and heat to a gentle boiling temperature, continuing the swirling motion for 5 to 15 minutes or until the sample is seen to be entirely dissolved. Leave the flask on the burner without swirling for 5 minutes longer. Samples which are not all dissolved in the time given should be ground finer. The solution at this point is grayish green in color, and only a very small amount of insoluble silica is found suspended in the solution. In swirling the hot flask, a laboratory metal clamp is conveniently employed.

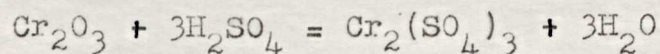
"Allow the contents of the flask to cool for a minute and add, through the still head, 12 milliliters of the oxidizing solution. Place a small Anschutz thermometer, suspended from a small platinum wire, within the solution in the flask, and heat to 215° C. during a time interval of 5 minutes. The droplets of condensed acid on the flask walls should all be undergoing rapid reflux down the flask walls at the end of this period. Remove the flask from the burner, cool the contents to 210° C., add 60 to 70 milligrams of powdered potassium permanganate, and swirl the flask

to disperse the permanganate. With continued swirling, dip the flask into cold water, and, after 8 to 10 seconds, add 125 milliliters of distilled water cautiously through the refluxing still head. Remove and rinse the still head and thermometer. Rinse the flask walls and add 25 milliliters of dilute (1 to 3) hydrochloric acid and a Filter-Cel boiling chip.

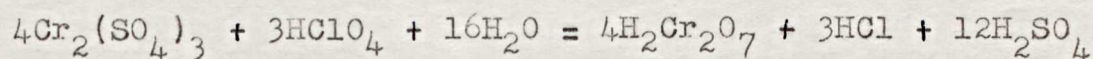
"Heat to a gentle boil and continue to boil for 5 minutes after the disappearance of potassium permanganate and manganese dioxide to remove the chlorine. Cool to ordinary temperature and add 40 milliliters of dilute (1 to 1) sulfuric acid. Titrate, using a standard solution of approximately 0.05 N. ferrous sulfate, until the greater part of the hexavalent chromium is reduced. Add 3 drops of ferroin indicator and titrate to complete reduction of the chromium as indicated by the appearance of a definite pink coloration. About 0.05 milliliters of the ferrous sulfate is required after the first appearance of an orange color in the blue-green reduced solution. From the measured volume of standard ferrous sulfate required, the per cent of chromic oxide may be calculated. The potassium permanganate is used in this procedure to eliminate the effect of hydrogen peroxide which is known to form during oxidations using perchloric acid at or near 200° C."⁹

Chemical Equations. The chemical reactions for this analysis are as follows:

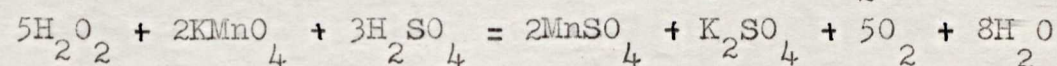
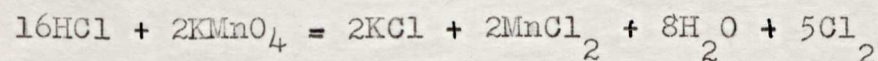
Solvent:



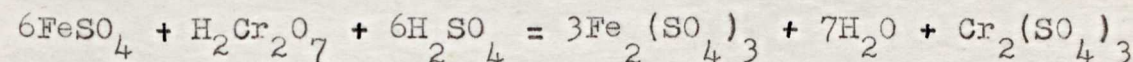
Oxidation:



Permanganate:



Titration:



Standardization of Ferrous Sulfate. The ferrous sulfate was standardized against 0.10 N. ceric sulfate. An approximate normality of 0.05 was required for titration; therefore, 13.901 grams of ferrous sulfate were used per liter of solution (13.901 = molecular weight of ferrous sulfate x 0.05). In order to stabilize the ferrous sulfate solution, it was necessary to add 20 milliliters of concentrated sulfuric acid¹⁰ in each liter of solution.

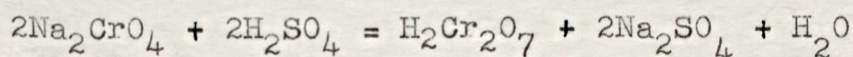
Solution Analysis

The Smith and Getz method of analysis as modified by J. D. Murphy¹⁰ was used for analysis of all solutions.

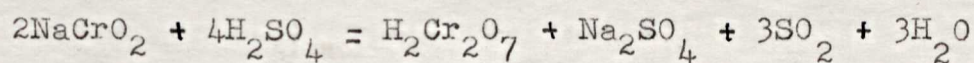
Detailed Procedure. "Accurately measure two milliliters of the solution containing sodium chromate or sodium chromite and transfer to a clean 500 milliliter beaker. Add 10 milliliters of chromite solvent, and stir until the solution is orange in color. This will be only a matter of seconds. Dilute with 100 milliliters of distilled water, and add three drops of ferrion as an indicator. Titrate with ferrous sulfate solution, approximately 0.05 normal, until the chromium is completely reduced as indicated by the appearance of a definite pink coloration."¹⁰

Chemical Equations. The chemical reactions for this analysis are as follows:

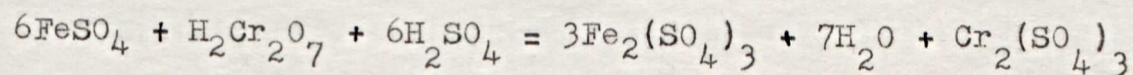
Chromate:



Chromite:



Titration:



LABORATORY PROCEDURE

The leaching of chromite concentrates which have not been previously roasted or otherwise treated has not been investigated to any great extent. However, the United States Bureau of Mines has a pilot plant at Hoover Dam for the caustic leaching of chromite, but no written report has been made on the results at this date. Since no published reports could be found on any past investigations that may have been made on this, or a similar, problem, the laboratory experiments had to be based on the trial and error procedure.

Preliminary Work

Before any tests could be made in the laboratory, a basis for a leach solution had to be found. Most of the leach solutions used in this investigation were based on the following references made by J. W. Mellor¹¹:

"C. Fricke and O. Windhausen determined the solubility of hydrated chromic oxide in a solution of sodium hydroxide. A 9.89 normal solution of sodium hydroxide with an agitation time of 3 days gave the best results."

"Billwater digested the chromite with sodium hydroxide in an iron vessel at 500°--600° C. through which was passed a current of air; an oxidizing agent was also added to the mixture."

"R. von Wagner used a mixture of sodium hydroxide and potassium ferricyanide."

Laboratory Tests

Agitation Tests. Three agitation tests were made on the laboratory rolls as shown in table 3.

TABLE 3

Test No.	Wt. of Sample	Leach Solution	Agitation Time	Recovery
1	5 gm.	500 ml 10 N. NaOH	48 hr.	----
2	10 gm.	500 ml 10 N. NaOH	48 hr.	----
*3	2 gm.	200 ml Sat. Na ₂ CO ₃	24 hr.	----

*50 ml H₂O₂ used as an oxidizing agent.

The solution from test number 3, Na₂CO₃ and H₂O₂, was faintly colored; however, no solution of chromite was obtained in any of the three tests. Since sodium carbonate is used to form a soluble chromate in the roasting of chromite ore¹⁰, a saturated solution of sodium carbonate was used in test number 3 to determine whether or not it would have any effect as a leaching agent on chromite. This, and subsequent tests, indicated that it did not.

The chromite samples used in tests number 1 and 2 were taken from the concentrate as it was received

from the mill, but all subsequent tests were made on minus-100 mesh samples.

Boiling Tests. The agitation tests were made in solutions at room temperature. All other tests were made in boiling solutions as listed in table 4.

Tests from number 1 to 8 inclusive and tests number 15 and 16 were made with different combinations of leaching solutions and oxidizing agents. No satisfactory results were obtained from any of these tests.

The characteristic green color of a chromite was obtained in the solution from test number 2, sodium hydroxide and chromic acid; however, when the solution was analyzed for chromium, the only chromium recovered was that which had been added as an oxidizing agent in the form of chromic acid.

The solution in test number 6, sodium hydroxide and potassium permanganate, turned dark green in color. This color persisted when a sample was taken for analysis; so the procedure as described under Solution Analysis could not be used. Before trying a different analytical method for the determination of chromium, a qualitative analysis was made with the spectrograph. Although chromium lines were visible on the spectrograph, the lines were so faint that only a trace of chromium could

have been present; therefore, no further analysis was made. The dark green color of the solution was probably caused by the formation of sodium manganate or the manganate ion.

Solution 8, sodium hydroxide and potassium ferricyanide, turned pale green in color. When the solution was analyzed for chromium, the end point turned a blue-green color instead of pink. The analysis on the spectrograph showed even less distinct lines than were obtained from test number 6; so it was concluded that only a slight trace of chromium was in solution. It is believed that the blue-green end point was caused by the formation of ferric ferrocyanide--Prussian blue--from the potassium ferricyanide used as an oxidizing agent.

Tests number 9 to 14 inclusive were made with mixtures of different leach solutions without the addition of oxidization agents. No positive results were obtained from any of these tests.

Sodium fluoride was tried in tests 10 to 13 as a leaching solution because fluorine has a strong tendency to form complex coordination compounds with iron. The fluorine ion is one of the most active of the anions; therefore, it seemed that some reaction should have taken place. However, the only apparent reaction was

between the fluorine and glass as indicated by the etch lines on the beaker.

Autoclave Test. Test number 17 was made in an autoclave under a pressure of 28 lb/sq in. The solution, sodium hydroxide and sodium peroxide, turned bright yellow in color, but no test for chromium was obtained. The yellow color was probably caused by a reaction between the sodium hydroxide and the melted grease from inside the pressure gage which ran into the autoclave.

Only one test was made with the autoclave because of the shortage of time. A mercury retort made of cast iron was used for the autoclave. A thirty-pound gage attached to the cover of the retort with a short pipe completed the apparatus. The autoclave was mounted on a ring stand, and a Fisher burner was used as the source of heat. A sketch of the autoclave is on page 18.

TABLE 4

General Data:

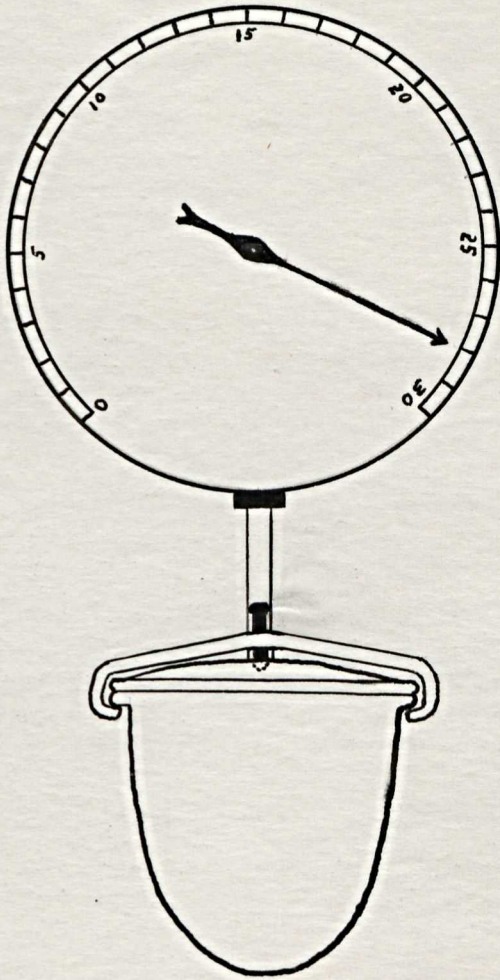
Sample Wts.--Tests 1 to 8, 2 gm.; Tests 9 to 17, 0.5 gm.
Boiling Time--Tests 1 to 16, 2 hr.; Test 17, 1 hr.

Test No.	Leach Solution	Oxidizing Agent	Recovery
1	250 ml 10 N. NaOH	1 gm Na_2O_2	----
2	200 ml 10 N. NaOH	.5 gm CrO_3	----
3	200 ml 10 N. NaOH	50 ml H_2O_2	----
*4	200 ml 10 N. NaOH	50 ml H_2O_2	----
*5	200 ml Sat. Na_2CO_3	50 ml H_2O_2	----
6	200 ml 10 N. NaOH	1 gm KMnO_4	Trace
7	200 ml 10 N. NaOH	.5 gm NaClO_4	----
8	200 ml 10 N. NaOH	.5 gm $\text{K}_3\text{Fe}(\text{CN})_6$	Trace
9	50 ml 10 N. NaOH 50 ml Sat. Na_2CO_3	----	----
10	50 ml 10 N. NaOH 50 ml 1 N. NaF	----	----
11	50 ml Sat. Na_2CO_3 50 ml 1 N. NaF	----	----
12	100 ml 10 N. NaOH 2.1 gm NaF (Solid)	----	----
13	100 ml 1 N. NaF Increased to 2 N.	----	----
14	50 ml 10 N. NaOH 50 ml 10 N. NaOH	----	----
15	50 ml 10 N. NaOH	50 ml 2 N. NaNO_3	----
16	50 ml Sat. Na_2CO_3	50 ml 2 N. NaNO_3	----
#17	200 ml 10 N. NaOH	.5 gm Na_2O_2	----

* Al_2O_3 used as a catalyst.

#Made in an autoclave; pressure 28 lb/sq in.

AUTOCLAVE



CONCLUSIONS AND RECOMMENDATIONS

Conclusions

The object of this investigation was an attempt to find a suitable caustic leaching solution which could be used to leach a Montana chromite ore to form a soluble chromite or chromate of commercial value.

No solution to this problem was found; however, the following conclusions can be drawn from results obtained from the laboratory tests completed:

1. Although Montana chromite ore cannot be leached with the caustic solutions listed in tables 3 and 4, the relatively small number of tests made in this investigation is far from being conclusive that chromite cannot be leached in a caustic solution.
2. Since a trace of chromium was found in two solutions, future work on this problem may be successful.
3. Organic substances should not be present in any piece of equipment used in conducting experiments with strong caustic solutions.

4. Chromite is chemically inactive in ordinary caustic solutions.

Recommendations

It is recommended that the following points be taken into consideration in future investigations on this problem:

1. The use of an autoclave capable of withstanding pressures up to 100 pounds per square inch.
2. A more detailed investigation on the chemical bonding of chromite.
3. Catalysts other than aluminum oxide should be tried.

ACKNOWLEDGMENTS

The writer wishes to express his appreciation to Mr. Ralph I. Smith for his assistance and criticisms during this investigation. Acknowledgment is also given to Professor J. P. Spielman, Dr. E. G. Koch, and Mr. C. L. Graversen for their helpful suggestions and encouragement.

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