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# Roasting and Leaching of Montana Chromite

Jerry D. Murphy

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ROASTING AND LEACHING  
OF MONTANA CHROMITE

by

JERRY D. MURPHY

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  
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## CHAPTER I

### INTRODUCTION

The United States, although the leading consumer of chromite, depends almost entirely on imports for its supply. Domestic production of chromite is limited, because high-grade imported ore is plentiful and inexpensive in normal times. There are several large deposits of chromite in the United States, representing millions of tons of low grade ore. These deposits form a strategic reserve that must be used in time of national emergency.

Montana chromite deposits are the largest in the United States and their exact size is unknown. The ore is easily mined and can be concentrated by tabling to produce a good grade of chromite. However, this requires further treatment to produce a marketable product, because the chromic oxide content, and chromium iron ratio are too low.

#### I. THE PROBLEM

Statement of the problem. The purpose of this investigation was to study the possibilities of treating a Montana chromite concentrate from the Benbow property by roasting and leaching, producing soluble chromate from which chromium or a chromium compound of high purity may be obtained.

## II. CHROMIUM

History. Louis Vauquelin<sup>1</sup> discovered chromium in 1798, but it was not produced in the pure state until 1859. After the discovery and development of the Goldschmidt process, in the early nineteen hundreds, the metal became important.

Properties. In the periodic system chromium is a member of the oxygen group, having the atomic number 24 and atomic weight of 52.01. The pure metal is hard and brittle with a metallic luster and light gray color. It ranks sixteenth among the elements in primary abundance, forming 0.5 per cent of the lithosphere, but it is never found in the native state.

Chromium is one of the nineteen industrial nonferrous metals used essentially as an alloying constituent. No substitute can be found for chromium as an alloying agent. Chromium alloys can be welded to steel forming either a hard surface or a core that is impenetrable to the finest drilling tools.

The pure metal can be cold-rolled or drawn. It is resistant to corrosion and will not oxidize at temperatures below 1200 degrees C.

Production. Chromium metal can be produced by any



one of three methods:

1. The electric furnace method produces pure chromium that can be converted into the high-chromium alloy known as ferrochromium.
2. The thermite process produces pure chromium and it is easily converted to a very low carbon ferrochromium.
3. The electrolytic deposition of chromium is satisfactory but expensive, because of the extremely low current efficiency.

Uses. The largest use of chromium is in steel making because it gives high-strength and resistance to abrasion as well as corrosion. When added to steel, it increases hardness, toughness, susceptibility to magnetism and resistance to acids. Ferrochrome and not the pure metal is added to steel as the alloying agent.

Chromium steels are used in projectiles, armor plates, cutting tools and for transmission parts of aircraft, tanks and motor vehicles; also for exhaust valves, turbine blades, pump rods, rollers for bearings, electric heating stoves, and cooking utensiles. Chromium alloyed with cobalt, tungsten or molybdenum and added to tool steel given a greater hardness and a better cutting edge which is retained at high temperatures.

The second largest use of the metal is for refractories for furnace linings. Chromite bricks retain their shape under high furnace temperatures, and are therefore widely used in the metallurgical industry.

Chromium is also used for tanning leather, for yellow, green and red pigments, and for the production of many chemicals.

### III. SOURCE OF CHROMIUM

Ore. Chromite<sup>2</sup>, the only important mineral of chromium, has the chemical formula  $\text{FeO} \cdot \text{Cr}_2\text{O}_3$ . It is assigned to one of three divisions of the spinel group and occurs principally in massive form in such basic rocks as peridotite and serpentine. The mineral has a metallic luster and black color, but gives a brown streak.

Foreign Supply. The foreign supply of chromite comes from Turkey, South Africa, South Rhodesia, Yugoslavia, Greece and New Caledonia. Imported high-grade chromite must contain at least 48 per cent  $\text{Cr}_2\text{O}_3$  (chromic oxide) and chrome iron ratio of 3:1. Ore of this quality demands about \$40.00 per ton with premiums being paid for higher percentages of chromic oxide and for higher chrome iron ratios. At the start of World War II the foreign supply of chromite was cut off and domestic ores had to be substituted.

Domestic Chromite. The principal sources of domestic chromite are Montana, California, Oregon and Alaska. Small and widely scattered deposits are located in another dozen states. Without exception these deposits are low grade, require beneficiation to produce a commercial product, and are not competitive with imported high-grade ore, because the additional treatments increases the cost and makes the ore more expensive.

Production and Consumption. Table I gives a brief survey of chromite production and consumption for the years of 1944, 1945, 1946 and for the first quarter of 1947. The values are listed in short tons.

TABLE I

Year	Domestic Production	Imported	Total Supply	Consumption
1944	45,629	848,390	894,019	848,449
1945	13,973	914,765	914,765	808,120
1946	3,920	754,308	758,228	734,759
1947	None	188,247	188,247	217,838

Prices. The price of metal containing 97 per cent chromium was 89 cents a pound on September 30, 1946. The E. & M. J. quoted the following prices;

Indian and African chromite \$43.50 a ton with a chrome iron ratio of 3:1 and 48 per cent  $\text{Cr}_2\text{O}_3$ ; \$41.00 a ton with a ratio of 2.8:1.

Rhodesian ore 45 to 48 per cent  $\text{Cr}_2\text{O}_3$  \$31.00 to \$43.50 per ton depending upon the Cr:Fe ratio.

Domestic ore containing 48 per cent  $\text{Cr}_2\text{O}_3$  and a chrome iron ratio of 3:1, \$43.50 per ton minus \$7.00 freight allowance.

Ferrochrome containing 65-70 per cent Cr, 13 to 14.5 cents a pound according to crushed size.

Low carbon ferrochrome 19.5 to 54 cents a pound.

Chrome bricks \$54.00 per thousand at point of manufacture.

During the war a premium of \$1.10 a ton was paid for each one per cent of chromic oxide above 48 per cent and a premium of \$1.50 a ton for each tenth increase in chromium-iron ratio. Penalties were charged at the same rate for grades down to a minimum of 42 per cent chromic oxide and a chrome iron ratio of 2:1.

Montana Chromite. The most extensive deposit of domestic chromite is located in Stillwater and Sweetgrass counties, Montana. The ore occurs in the Stillwater complex, a belt of ultramafic rocks some thirty miles long and one to five miles wide. Over five million tons of ore

containing more than 20 per cent chromic oxide have been developed. This ore can be concentrated to meet the requirements of the chromic oxide, but the chrome iron ratio is too low. Montana chromite can be used in the manufacture of low-chromium alloy steels, but high freight rates to the eastern markets prohibit its use.

During the war the Benbow and Mouat-Sampson chromite mines at Columbus, Montana, were operated by the Anaconda Copper Mining Company as agent for the Metals Reserve Company. Work started in 1941 and was suspended in 1943 when shipping was resumed from some foreign countries.

It is obvious that Montana may have a prosperous chromium industry when the quality of imported chromite can not meet the necessary requirements. However if cheap electrical power becomes available, through the Missouri Valley Authority, large quantities of electrolytic chromium could be produced within the state of Montana.

Review of Previous Literature. The United States Bureau of Mines, recognizing the possibilities of domestic chromite production, has undertaken investigations to develop methods of utilizing these ore. The problem has been approached from three angles:

1. Mechanical methods of concentration.
2. Beneficiation by chemical or metalurgical methods.
3. Production of metallic chromium by electrolysis of solutions prepared from ore or concentrates.

In general, previous work used combinations of the above steps. A few of the most common methods of treating chromite ore are:

1. Selective reduction by roasting with carbon and leaching to increase the chromium iron ratio<sup>3</sup>.
2. Matte Smelting to improve the chromium-iron ratio<sup>4</sup>.
3. Roasting with an alkali, and leaching with water, producing soluble chromites<sup>5</sup>.
4. Chlorination roasting producing  $\text{CrCl}_3$  which may be treated to produce chromates<sup>6</sup>.
5. Fused electrolite for the production of pure chromium<sup>7</sup>.

Other process have been tried, but with a lesser degree of success. The Bureau of Mines and private industry are working on new methods, incorporating new ideas, for the treatment of domestic chromite. However, there is no

information available on these methods at the present time.

#### IV. OUTLINE OF PROBLEM

Processing chromite. Mr. George W. Gleeson\* Dean of the School of Engineering at Oregon State College, suggested that this investigation follow the procedure found satisfactory for treating Oregon chromite. Major problems involved in this process are:

1. Furnace roasting the ore with an alkali to produce a leachable fusion mass from which the sodium chromate may be recovered.
2. Leaching of the mass to produce a highly concentrated chromate solution with purification of the solution to eliminate silica and alumina.
3. Splitting of the chromite liquor into an acid and alkali fractions with subsequent recovery of the alkali for further furnace use.
4. Reduction of the acid chromate to chromic oxide or to metallic chromium.

Time available for this investigation did not allow the completion of all of these problems. Therefore, this

\* Private communication to author.

investigation was limited to the study of time, temperature and composition required for roasting and leaching. Interpretation of results can only be made by accurate analytical work. The analytical method, roasting and leaching procedures and recommendations for future studies, will be discussed in the following chapters.



## CHAPTER II

### ANALYTICAL METHOD

At the outset of this investigation, it was realized that a large number of analyses for chromium would have to be made. The standard procedure for the quantitative determination of chromium in chromite requires a considerable amount of time, and certain factors introduce the possibility of error. A long analytical method would consume so much time that the number of roasting and leaching experiments would be limited.

Dr. Edwin G. Kock, Professor of Chemistry at Montana School of Mines, recommended the use of an analytical method developed by G. Fredrick Smith and C. A. Getz<sup>8</sup> at the University of Illinois, for the determination of chromium in any chromite ore. This method of analysis was very rapid and accurate, and was used for all of the analysis of the chromite concentrate and calcine in this investigation. Examination of this procedure revealed the fact that special equipment and reagents were needed. Since all of the items were not obtainable, modifications had to be made and used; these proved to be successful.

It was obvious that analyses of both solids and solutions would be necessary. This method of analysis can be used for both solids and solutions. However a very rapid

and accurate method for the analysis of solutions was discovered in this investigation. Consideration of these two analytical methods, one for solids and one for solutions, will be given separately in the following discussions.

## I. CHEMICAL ANALYSIS OF SOLIDS

The procedure developed by Smith and Getz for the analysis of chromium in all types of chromite eliminates the usual peroxide fusion. In this method, the chromite is dissolved in a mixture of phosphoric and sulfuric acids. The conditions for subsequent oxidation of chromium, in the mixed acid solution, and the final titration follow in the detailed procedure. The resulting method is very rapid, accurate and economical. For the best results the following directions must be followed carefully.

Detailed Procedure. Grind the sample to pass minus 100 mesh and dry for two hours at 105 degrees to 110 degrees C., weigh between 100 and 150 milligrams of the sample accurately, and transfer to a dry 500 milliliter Erlenmeyer flask. Add 10 milliliters of chromite solvent and swirl flask vigorously at once to get the sample in suspension and overcome the strong tendency to form a cake and stick to the bottom of the flask. Adjust the refluxing still head in the neck of the flask and heat to gentle boiling temperature, continuing the swirling

motion five to fifteen minutes, or until the sample is entirely dissolved. Leave the flask on the burner without swirling five 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 will be 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 oxidizing solution. The solution in the flask turns immediately to a darker green color. Place a small Anschutz thermometer, suspended from a platinum wire, within the solution in the flask and heat to about 210 degrees C. during a five minute interval of time. The droplets of condensed acid on the flask walls should be undergoing rapid refluxing down the flask walls. The solution gradually changes from a green to an orange color during the latter part of this period.

Remove the flask from the source of heat, cool for a minute, add about 70 milligrams of potassium permanganate, and swirl the flask contents to disperse the permanganate. With continued swirling, carefully dip the flask into cold water. After eight to ten seconds,

add 125 milliliters of distilled water. The water must be added cautiously, pouring it through the refluxing still head. The solution will have a cherry color at this point.

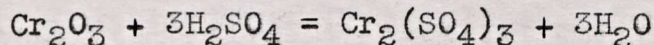
Remove and rinse the still head and thermometer and rinse the flask walls. Add about 25 milliliters of dilute ( 1:3 ) hydrochloric acid, heat to a gentle boil and boil five minutes after the disappearance of the permanganate. The solution now will be light yellow in color.

Cool the solution to room temperature (either fast or slow cooling) and add 40 milliliters of (1:1) sulfuric acid. The solution is now ready for titration with ferrous sulfate solution of approximately 0.05 normal. Add three drops of ferrion indicator and titrate to the complete reduction of chromium as indicated by an appearance of a definite pink coloration. One drop of the ferrous sulfate is required after the appearance of an orange color in the blue-green reduced solution. From the measured volume of ferrous sulfate required, the percent of chromium or chromic oxide present may be calculated.

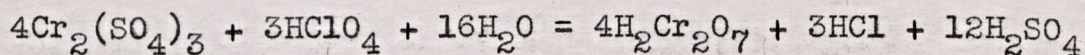
This procedure is easily accomplished in about one-half hour. After a few practice analyses by this method, one will be able to do about four analyses at one time,

having each sample at a different point in the procedure.

Chemical Equations. This procedure is based upon the following chemical reactions:

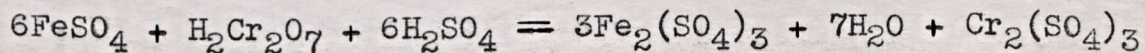


Chromic Sulfate,  $\text{Cr}_2(\text{SO}_4)_3$  is a green solution.

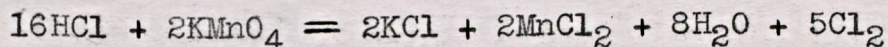
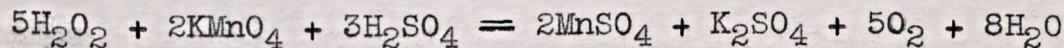


Dichromic acid,  $\text{H}_2\text{Cr}_2\text{O}_7$  is an orange solution.

Equation for titration,



Side reactions,



Method of Calculating. Either the amount of chromium or chromic oxide may be calculated.

1. To find the grams of  $\text{Cr}_2\text{O}_3$  in the sample:

$$\text{Grams } \text{Cr}_2\text{O}_3 = \text{cc FeSO}_4 \times \text{N FeSO}_4 \times \frac{\text{Cr}_2\text{O}_3}{6000}$$

$$\text{Per cent of } \text{Cr}_2\text{O}_3 = \frac{\text{Grams } \text{Cr}_2\text{O}_3}{\text{Weight of Sample}} \times 100$$

2. To find the grams of Cr in the sample:

$$\text{Grams Cr} = \text{cc FeSO}_4 \times N \text{ FeSO}_4 \times \frac{\text{Cr}}{3000}$$

$$\text{Per cent Cr} = \frac{\text{Grams Cr}}{\text{Weight of Sample}} \times 100$$

If several samples are to be analyzed with the same ferrous sulfate solution, it is convenient to make one calculation and find a factor that simplifies this operation. This is done by multiplying  $N \text{ FeSO}_4$  by  $\frac{\text{Cr}_2\text{O}_3}{6000}$ . Obviously, this factor will be different for each normality of the ferrous sulfate.

Materials Used. The chromite solvent consisted of a mixture of eight parts of 95 per cent sulfuric acid and three parts of 85 per cent phosphoric acid. The oxidizing solution is made up with two parts of 72 per cent perchloric acid and one part of distilled water. Dilute (1:3) hydrochloric acid, dilute (1:1) sulfuric acid, and finely ground crystals of potassium permanganate must also be provided.

Ferrion, a trade name for "ortho phenanthroline ferrous complex", is used as the indicator. A 0.025 molar solution of ferrion may be obtained from the G. Fredrick Smith Chemical Company. This indicator gives a very sharp end point and is a definite asset in the ferrous sulfate titration.

Ferrous sulfate should be made approximately 0.05 normal, and with the addition of about 20 milliliters of concentrated sulfuric acid the solution becomes stable. It is conveniently made up and stored in a liter measuring flask. The solution must remain clear, but if it becomes cloudy, it must be discarded. When properly made and stored in an air-tight container, the solution should remain stable for as long as two weeks, varying only a few thousandths in normality.

Ceric sulfate is a stable compound, and a solution of a definite normality may also be obtained from the G. Fredrick Smith Chemical Company. This is used in the standardization of the ferrous sulfate. For convenience, 5 milliliters of  $\text{CeSO}_4$  should be used in this operation. Using ferrion as the indicator, 5 milliliters of 0.10 normal ceric sulfate will require 10 milliliters of 0.05 normal ferrous sulfate for standardization.

FIGURE I



Figure I illustrates the method employed for storing the chemical reagents. The four brown bottles on the left side of the photograph contained the chromite solvent, oxidizing solution, dilute sulfuric and hydrochloric acids. This size reagent bottle was very satisfactory, because it held enough solution for about thirty analyses. The liter measuring flask held the ferrous sulfate, and this solution should be made in this container without transferring to any other unit. The large brown bottle on the right contained ceric sulfate, and the small bottle contained the ferrion indicator.



Apparatus and Equipment. The rather high temperatures used in this method will cause the heavy acids to volatilize and leave the Erlenmeyer flask as a vapor, thus causing losses of the dissolved chromium. For this reason, a refluxing still head is required. This still head is nothing more than a piece of glass tubing placed in the neck of the flask which will allow the vapors to condense and run back down into the hot solution.

Still heads of the proper design are difficult to make, unless one is experienced in the art of forming and shaping glass. The type still head used in the analyses for this investigation was modified from the recommended design. The reason for this modification was due to the fact that only long thermometers were available at the beginning of this study, and these could not be used in conjunction with the recommended type still head. Therefore, glass tubing approximately one inch in diameter and ten inches long was formed so that only two inches of the tubing would fit in the neck of the flask, and the remaining portion was above the flask, allowing ample surface for condensation to take place. Still heads of this design proved very satisfactory, and no great difference was found with still heads made of either glass or pyrex tubing.

It would be well to mention here that the best and

most rapid method of making still heads is to bring the glass tubing to a local neon sign company and have their glass blowers do the job. Their experience and skill will save time and, needless to say, glass tubing.

The still head should fit snugly in a 500 milliliter Erlenmeyer flask. A good supply of these flasks should be available, because they are easily broken as a result of thermal shock. Only a pyrex flask should be used.

A Bunsen burner is the most satisfactory source of heat for the gentle boiling of the chromite solvent. The flask can be held over the burner flame by the use of a laboratory clamp, and, at the same time, the contents may be swirled.

It is imperative that a constant temperature of 210 degrees, plus or minus one degree, be maintained. This was accomplished in this investigation by the use of a gas-fired hot plate, fortunately set at 210 degrees C. Either an electric hot plate or a modified Rodgers ring burner with accurate temperature control may be used. The hot plate has an advantage that several analyses may be conducted at the same time because of the large surface area at a constant temperature.

Thermometers with external calibration marking are not satisfactory, as their etched markings are generally darkened by use of chromic oxide which is soon dissolved off the instrument, introducing error and leaving the

thermometer difficult to read. Only an Anschutz type thermometer should be used. A convenient size thermometer is 6.25 inches long calibrated over the range 198 to 250 degrees C. in single degree intervals. No trouble was encountered in the use of this type thermometer, and the markings can be easily read, even in contact with fumes from perchloric acid and sulfuric acid because the calibrations are protected by a glass tube covering the instrument.

FIGURE II

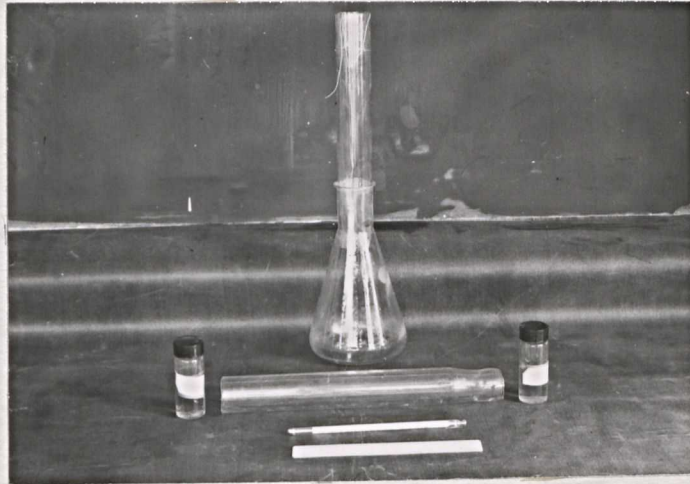


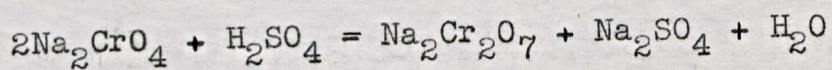
Figure II shows a 500 millileter Erlenmeyer flask with a refluxing still head in position. Directly in front of the flask, a refluxing still head is shown between two small thirty-millileter assay solution bottles. The small thermometer, placed next to the six-inch ruler, is an Anchutz type thermometer.

## II. CHEMICAL ANALYSIS OF SOLUTIONS

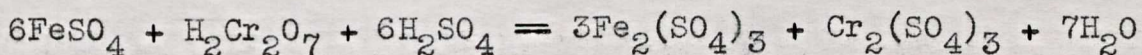
During the roasting operations conducted in this investigation, it was disclosed that sodium chromate ( $\text{Na}_2\text{CrO}_4$ ) was formed. This compound is very soluble in water, and after the roasted material was leached in water, the mass was filtered and the first part of the solution saved for assay.

The method of analysis previously described was at first used for these solutions. It was discovered that this leached solution would become orange colored with the addition of the chromite solvent. This solution proved to be dichromic acid, and with ferrion indicator, could be titrated directly with the ferrous sulfate. Several check analyses were made between the method developed by Smith and Getz and this shorter method. There were no appreciable differences in the check samples, and for this reason, the short method was adopted and used for all analyses of solutions.

Chemical Equation. This short method of solution analysis is based on the following equations:



The dichromic acid ( $\text{H}_2\text{Cr}_2\text{O}_7$ ) formed was titrated in the same manner as previously described.



Details of Procedure. Accurately measure two milliliters of the solution containing sodium chromate 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 indicator. Titrate with ferrous sulfate solution, approximately 0.05 normal, until the chromium is completely reduced as indicated by the appearance of definite pink coloration.

The method of calculating is the same as used for the analysis of solids. Each milliliters of solution will represent a definite amount of chromium. To illustrate this, assume two grams of a soluble chromate salt were dissolved in twenty milliliters of water. Each milliliter would represent 0.1 grams of the chromate salt.

This procedure is extremely rapid and accurate but careful work must be preformed. The volume of ferrous sulfate used should check by one-tenth of one milliliter. The measured volume of chromate solution must be accurate, because a small variation causes considerable error. Each

analysis requires about three minutes and fifty analyses may be easily made in one afternoon. The author suggests that for best results three analyses be made for each solution.

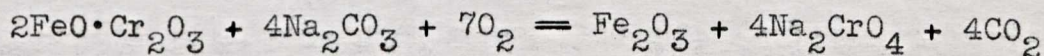
It may be possible to use concentrated sulfuric acid in place of the chromite solvent, but if a large volume of the latter solution is prepared, the author can see no reason why it should not be used, thus eliminating one extra reagent bottle.

## CHAPTER III

### LABORATORY PROCEDURE

The roasting of chromite concentrates with sodium carbonate to produce sodium chromate, and the leaching of the calcined mass with water forming highly concentrated solutions of soluble chromate is an old art. This method of treating Montana chromite ore has never been thoroughly investigated. Therefore, this investigation was undertaken to study the feasibility of roasting and leaching a Montana chromite ore.

This procedure consists of roasting chromite ore or concentrate with sodium carbonate and lime at relatively high temperatures and dissolving the sodium chromates formed with water. The principal reaction during the roast may be written:



The furnace gases furnish the oxygen necessary for this reaction. The lime is added to the charge to keep it in a porous condition so that the reaction may take place.

Seventy-five pounds of chromite concentrate was available for this investigation, and was obtained from the Anaconda Copper Mining Company. This organization, acting



as agent for the United States Government during World War II, operated the chromium mines near Columbus, Montana.

The material was thoroughly mixed and sampled. Four analyses were made to determine the amount of chromic oxide present, and results of these analyses averaged 43.18 per cent. This checked closely with the results obtained by Brown<sup>10</sup>, and according to him, the chromium-iron ratio was 1.47:1. Table II shows analysis of the balance of the concentrates.

TABLE II

Compound	Wt. per cent
FeO	25.7
Al <sub>2</sub> O <sub>3</sub>	12.2
MgO	1.6
SiO <sub>2</sub>	3.35

In this investigation, all calcined material was analyzed for chromium and then leached and filtered. The first portion of the filtrate was saved and assayed. The amount of chromium in the leached solution, divided by the amount of chromium in the calcine, gave the percentage of chromium converted to the soluble state. The amount of chromium in the solution and in the calcine were calculated

to represent equal unit weights. Obviously, roasting and leaching experiments were done together, one dependent upon the other for the interpretation of the results.

## I. PRELIMINARY INVESTIGATIONS

Suitable working time, temperature, and furnace charge had to be established. This was accomplished by conducting a series of small-scale test covering a wide range of various conditions.

All roasting tests were conducted in a small gas-fired, muffle furnace, originally installed for high-temperature laboratory work. The temperature desired in this furnace was obtained by carefully adjusting the gas and air valves, and was accurately read in degrees F. by the use of a chromel alumel thermocouple connected to a Bristol instrument. Three different furnace charges were considered. Previous investigators<sup>5,11</sup> indicated that a charge of one part of concentrate, one part of sodium carbonate and one part of lime gave good results, but the amounts of the reagents used were not in the correct proportions. For this reason charges containing lesser amounts of sodium carbonate and lime were prepared. The three furnace charges used are tabulated in Table III.

TABLE III

	Concentrate	Sodium Carbonate	Lime
Charge I	1	1	1
Charge II	2	1	1
Charge III	2	1½	1½

Henceforth, these will be referred to as Charge I, II, III. Since the sodium chromate formed during roasting has a solubility of 87.3 grams in 100 milliliters of water at zero degree C., no difficulties were expected during the leaching operation.

Roasting. The first preliminary roasting was done in clay scorifying dishes with Charge I placed on the dish in stratified beds. For test 1, the sodium carbonate was placed on the bottom, covered with chromite and capped with lime. In test 2, the positions of the lime and sodium carbonate were reversed. The chromite was placed on top of a mixture of sodium carbonate and lime in test 3. These tests gave unsatisfactory conversion percentages, as can be seen in Table IV. All other tests were performed with a mixed charge.

TABLE IV

Test	Charge	Time of Roasting	Temp.	Leaching Time	Pulp Dilution	Conversion Percentage
1	I	2 hrs.	1800°F.	20 min.	10:1	37.2
2	I	" "	"	" "	"	41.6
3	I	" "	"	" "	"	47.8

The material for Charges I, II and III was ground to a minus 100 mesh, and then each charge was intimately mixed. In determining the influence of the different charges and time, seven small crucibles were filled with Charge I and placed in the furnace for intervals of one-half, three-quarters, one, two, three, four, and five hours, at an average temperature of 1950 degrees F. This procedure was repeated using Charge II and III.

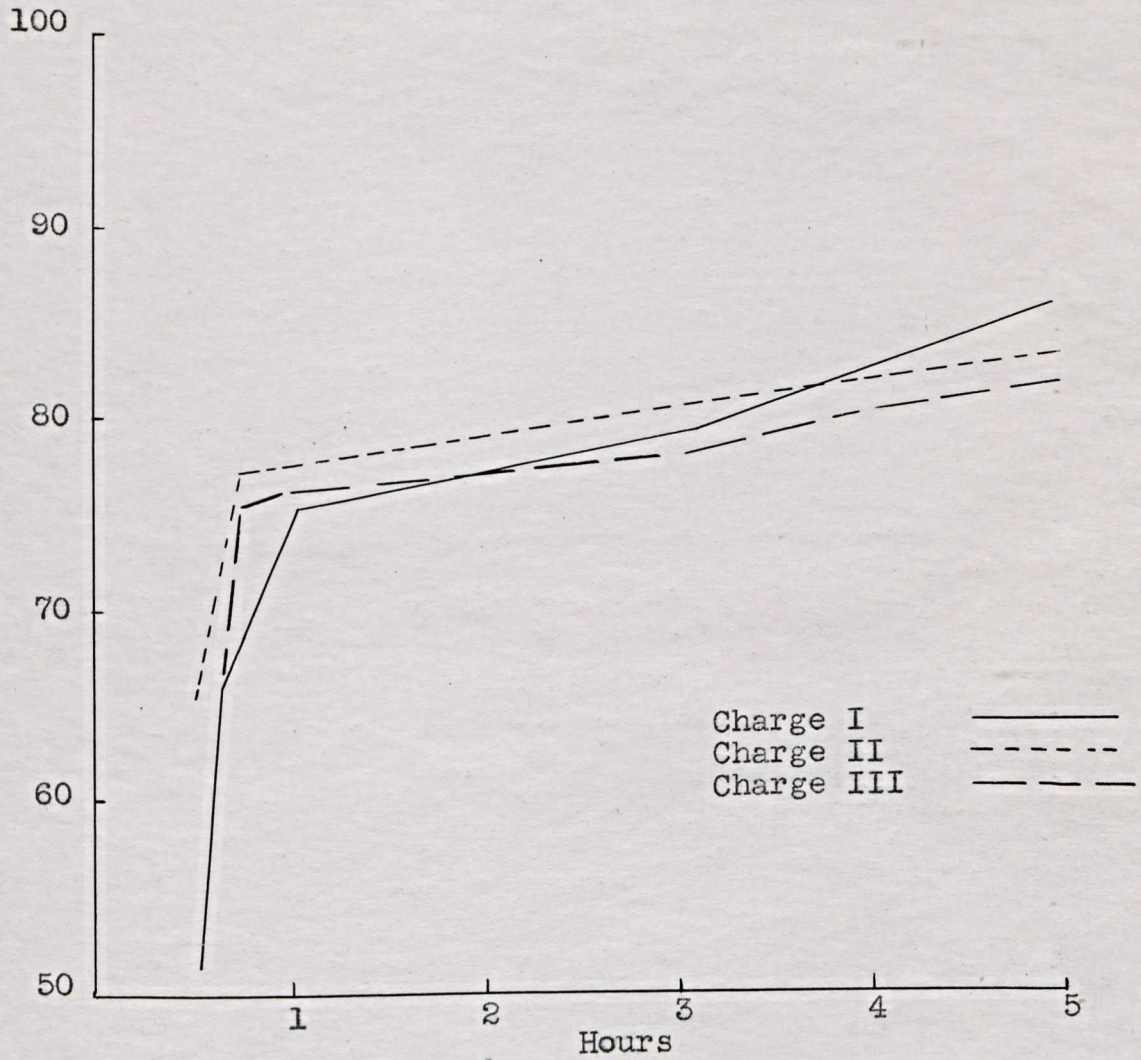
The results of the small crucible tests are tabulated in Table V and plotted on Graph I.

TABLE V

Test	Charge	Time of Roast	Furnace Temp. Degrees F.	Leaching Time	Pulp Dilution	Conversion Percentage
4	I	0.5 hrs.	1980	20 min.	10:1	51.0
5	I	0.75 "	"	"	"	71.3
6	I	1 "	"	"	"	76.6
7	I	2 "	"	"	"	77.2
8	I	3 "	"	"	"	79.0
9	I	4 "	"	"	"	82.5
10	I	5 "	"	"	"	85.6
11	II	0.5 hrs.	1935	"	"	63.5
12	II	0.75 "	"	"	"	76.0
13	II	1 "	"	"	"	77.2
14	II	2 "	"	"	"	77.3
15	II	3 "	"	"	"	78.7
16	II	4 "	"	"	"	80.3
17	II	5 "	"	"	"	82.6
18	III	0.5 hrs.	2000	"	"	57.1
19	III	0.75 "	"	"	"	77.4
20	III	1 "	"	"	"	78.2
21	III	2 "	"	"	"	79.7
22	III	3 "	"	"	"	80.3
23	III	4 "	"	"	"	81.7
24	III	5 "	"	"	"	83.7

GRAPH I

conversion %



Graph I shows the curves resulting from the roasting and leaching test of Table V. The curve for Charge I indicates the most favorable results for the longer roasting periods.

FIGURE III



The picture shown above illustrates the type of furnaces used for all roasting tests. A chromel alumel thermocouple is shown at the right inserted in the furnace. This unit is connected to a Bristol instrument from which the temperature was read directly in degrees F. Two dishes are shown in the center of the picture. The charge was placed in these and roasted. The dish on the left contains calcine as it appeared after roast while the dish on the right contains calcine ground to a minus 100 mesh.

It can be seen that roasting Charge I for five hours at 1950 degrees F. gave the best results. It is evident that a longer roasting time should be used to obtain a higher percentage conversion of the chromite to the chromate form.

Leaching. The calcined product from the foregoing tests supplied the material for leaching operations. Preliminary leaching was done with cold water at a pulp dilution of 10:1. Two grams of the calcine were added to 20 milliliters of distilled water and agitated in a 50 milliliter beaker. The agitation was supplied by a glass stirring rod connected to a motor-driven stirring mechanism. Each sample was agitated for twenty minutes, immediately filtered and the first portion of the filtrate saved and analyzed for chromium. The results shown in Table V were obtained in this manner.

The leaching procedure appeared to be satisfactory, but it was discovered that vaporization took place, leaving the solution more concentrated with chromates, and giving slightly higher results.

It was decided that leaching could be done in 100 milliliter bottles sealed with rubber stoppers to prevent vaporization. All other tests were performed in these bottles and agitated on the laboratory rolls.



Preliminary leaching experiments did not establish favorable conditions. Several hundred grams of calcine made from Charge I, roasted for five hours at 1900 degrees F., were used to determine the most suitable time and temperature for leaching.

Roasting was performed in a glazed porcelain dish, four inches in diameter and one inch deep. The resulting mass was very coarse and was ground to a minus 100 mesh. This green-colored material was highly soluble in water and produced a bright yellow solution.

Five grams of calcine and fifty milliliters of water were placed in bottles and immediately agitated. The time of agitation varied from five, ten, fifteen, twenty, twenty-five and thirty minutes. The results of these tests are tabulated in Table VI. Leaching for fifteen minutes gave the maximum conversion percentage.

TABLE VI

Test	Pulp Dilution	Time	Temp.	Solvent	Conversion Percentage
25	10:1	5 min.	20°C	Water	84.0
26	"	10 "	"	"	85.6
27	"	15 "	"	"	86.0
28	"	20 "	"	"	85.7
29	"	25 "	"	"	84.9
30	"	30 "	"	"	85.8

The same leaching procedure was repeated using boiling water as the solvent. These tests did not show improved results, but were slightly lower than those obtained when cold water was used. Table VII contains the results of these tests.

TABLE VII

Test	Pulp Dilution	Time	Temp.	Solvent	Conversion Percentage
31	10:1	5 min.	90°C.	Water	85.2
32	"	10 "	"	"	85.6
33	"	15 "	"	"	86.0
34	"	20 "	"	"	85.3
35	"	25 "	"	"	85.6
36	"	30 "	"	"	85.1

The remaining portion of the calcine was leached with dilute (5:1) sulfuric acid, and the results were not as desirable as those obtained with cold water. The acid leach tended to dissolve other compounds besides the sodium chromate. This was indicated by a difference in the color of the leach solutions. It is probable that aluminum, magnesium and iron were dissolved in varying amounts. The results of these tests are listed in Table VIII.

TABLE VIII

Test	Pulp Dilution	Time	Temp.	Solvent	Conversion Percentage
37	10:1	5 min.	20°C.	(5:1)H <sub>2</sub> SO <sub>4</sub>	84.3
38	"	10 "	"	"	85.7
39	"	15 "	"	"	83.6
40	"	20 "	"	"	85.3

An examination of the results obtained from the leaching tests, indicated that the most satisfactory conditions were produced in cold water for fifteen minutes.

## II. STUDY OF THE EFFECT OF TIME FOR ROASTING

A considerable quantity of Charge I was prepared, thoroughly mixed, and 200 grams were placed in glazed porcelain dishes for the roasting operations.

The first series of tests were performed at a temperature of 2000 degrees F. for six, eight, ten and twelve hours. At the end of each time interval the dishes were removed from the furnace and the calcined material examined. This roasting procedure produced a coarse, dark brown calcine which was fused to the dishes, making it difficult to remove. The calcine was reduced

to a minus 100 mesh for subsequent testing.

After leaching this material in water and filtering, the analysis showed that less than fifty per cent of the chromite was converted to the soluble chromate. These unsatisfactory results were due to the high temperature of the roasting operation. Evidently, a surge in the furnace temperature caused the mass to fuse, and insoluble calcium chromates were formed along with the soluble sodium chromates.

Another series of tests were conducted in the same manner but at a temperature of 1700 degrees F. The calcine did not fuse to the dishes but was coarse and had to be reduced to minus 100 mesh. Roasting at this temperature produced a green-colored calcine which was leached with cold water. The material was agitated for fifteen minutes at a pulp dilution of 10:1.

The results of this series of tests are tabulated in Table IX. The conversion percentage obtained increased with time of roasting, and ranged from 77.4 per cent for the six-hour period to a maximum of 92.5 per cent for the twelve hour period.

TABLE IX

Test	Charge	Time of Roasting	Temp.	Leaching Time	Pulp Dilution	Conversion Percentage
41	I	6 Hrs.	1700 <sup>o</sup> F.	15 min.	10:1	77.4
42	I	8 "	"	"	"	79.5
43	I	10 "	"	"	"	88.5
44	I	12 "	"	"	"	92.5

## CHAPTER IV

### CONCLUSIONS, AND RECOMENDATIONS

#### I. CONCLUSIONS

The object of this investigation was an attempt to correlate the effects of furnace charge, time and temperature upon roasting and leaching a Montana chromite concentrate. Optimum conditions were not attained but the fields in which they will be found were bracketed.

Success of the operation depended upon a selective reduction of chromium, to render it soluble in water, leaving the iron, aluminum and magnesium insoluble. Small scale laboratory tests were conducted under ideal conditions and these served as a guide for which conclusions are drawn.

The time available for this study did not allow the completion of the problems involved. However, the conclusions that are drawn are as follows:

1. The roasting of chromite concentrate, sodium carbonate and lime produced sodium chromate which was soluble in water.
2. The amount of sodium chromate formed during roasting depended upon the composition of the charge, time and temperature.

3. The time of roasting was directly dependant upon temperature.
4. At a constant temperature, the percentage of soluble chromates formed increased with longer roasting periods.
5. The charge had to be thoroughly mixed, reduced to minus 100 mesh and roasted below the fusion temperature before a high conversion of the chromite was attained.
6. Roasting at 2000 degrees F. fused the material and produced insoluble calcium chromates.
7. Roasting at 1700 degrees F. converted 92.5 per cent of the chromite to the soluble chromate form.
8. A charge composed of one part of chromite concentrate, one part of sodium carbonate and one part of lime was more satisfactory than the other charges used.
9. Leaching was done in hot and cold water and in dilute sulfuric acid. Sodium chromate was more soluble in cold water than in the other solvents.
10. The mixture of calcine and water had to be agitated to obtain all of the soluble chromate in solution.

11. Agitating the pulp in corked bottles minimized volatilization and simplified the analytical procedure.
12. The time required to complete leaching was fifteen minutes. Longer periods did not improve leaching results.
13. This process, for treating Montana chromite ore, was not developed but problems of roasting and leaching were investigated and definite results were obtained.
14. The analytical methods employed for the quantitative determination of chromium in both solutions and solids save time and produced excellent results.

## II. RECOMENDATIONS

It is recommended that future investigators consider the following specific points:

1. A charge of equal parts of chromite concentrate, sodium carbonate and lime should be roasted at 1850 degrees F. for six, eight, ten, twelve, fourteen, and sixteen hours. The twelve hour roast at this temperature should show a high conversion of the chromite and the longer roasting periods will serve as a comparison to definitely establish the proper roasting time.



2. Other charges containing both sodium carbonate and lime in larger quantities should be roasted at the same temperature and for the same time periods. These tests should indicate a more favorable conversion than the (1:1:1:) charge used in this investigation. The stoichiometric quantity will undoubtedly give the best results.
3. After a feasible charge is discovered a large quantity of it should be roasted and leached. A study should be made of methods for extracting the chromium from solution, either as a chromate salt or electrolytic chromium.
4. A complete cost study should be made after the method is developed. This should include the expected cost of each operation and the final cost per pound of the finished product.

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