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The Extraction of Chromate Salts from Montana Chromite

Server Tasdemiroglu

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THE EXTRACTION OF CHROMATE SALTS FROM MONTANA CHROMITE

By

Server Tasdemiroglu

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 15, 1941
THE EXTRACTION OF CHROMATE SALTS FROM MONTANA CHROMITE

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MONTANA SCHOOL OF MINES
BUTTE, MONTANA
May 15, 1941
## CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>INTRODUCTION</td>
<td>1</td>
</tr>
<tr>
<td>CHROME ORE AND ITS PROPERTIES</td>
<td>2</td>
</tr>
<tr>
<td>USES OF CHROMITE</td>
<td>3</td>
</tr>
<tr>
<td>SOME CHEMICAL SALTS AND THEIR USES</td>
<td>6</td>
</tr>
<tr>
<td>SOME CHROME PIGMENTS</td>
<td>7</td>
</tr>
<tr>
<td>WORLD PRODUCTION OF CRUDE CHROMITE</td>
<td>9</td>
</tr>
<tr>
<td>PRICES IN THE UNITED STATES</td>
<td>12</td>
</tr>
<tr>
<td>EXTRACTION PROCESS OF CHROMATE AND DICHROMATE FROM THE CHROMITE ORE</td>
<td>13</td>
</tr>
<tr>
<td>INVESTIGATIONS</td>
<td>22</td>
</tr>
<tr>
<td>QUANTITATIVE ANALYSIS OF CHROMITE ORE</td>
<td>25</td>
</tr>
<tr>
<td>SOLUBILITIES OF SOME SALTS</td>
<td>30</td>
</tr>
<tr>
<td><strong>I. ROASTING TESTS</strong></td>
<td></td>
</tr>
<tr>
<td>A. Vary Temperature</td>
<td>31</td>
</tr>
<tr>
<td>B. Vary Time</td>
<td>33</td>
</tr>
<tr>
<td>C. Vary Soda Ash</td>
<td>34</td>
</tr>
<tr>
<td>D. Vary Lime</td>
<td>34</td>
</tr>
<tr>
<td><strong>II. LEACHING TESTS</strong></td>
<td>35</td>
</tr>
<tr>
<td><strong>III. PURIFICATION TESTS</strong></td>
<td>36</td>
</tr>
<tr>
<td>CONCLUSIONS</td>
<td>40</td>
</tr>
<tr>
<td>REFERENCES</td>
<td>43</td>
</tr>
</tbody>
</table>
INTRODUCTION

This thesis, which was chosen for me by Dr. Curtis L. Wilson, Professor of the Metallurgical Department at the Montana School of Mines, contains some metallurgical researches on the Stillwater County chromite for the conversion of chromite to chromate salts.

In this thesis I have tried to determine the suitable temperature, time and the amount of soda ash and lime needed for the calcining process. The leaching and purification tests were studied experimentally too.

The first chromate was prepared from chromite in 1817. Richard Tilghman used potassium feldspar for alkali in 1847. The earlier process for making chromate from chromite was not the same as is used today. Therefore I have found useful to put into this thesis the newest method for making chromate salts and their important uses.

Some information about chromite ore and chrome chemicals was summarized in this thesis with the thought that it would help to understand the experimental work.
Chrome is the single ore of chromium. It consists of ferrous chromite: FeO.Cr₂O₃. Pure chromite contains 68% Cr₂O₃ and 32% FeO.

Chromite ore may contain MgO.Al₂O₃ as a proportion to FeO.Cr₂O₃. The usual impurities in chromite ore are:

- 2MgO.SiO₂
- 3MgO.2SiO₂
- (MgO.FeO).SiO₂

Enstatite
Serpentine
Hypersthene

Serpentine is the most common gangue rock.

Chromite ore is a hard mineral; it is brittle and tends to slime badly when crushed. Chromite is black to brownish, sometimes yellow, red, in color, it has a brown streak and has a submetallic to metallic luster. It is sometimes feebly magnetic, practically infusible. Hardness 5.5 and sp.gr 4.32-4.53. Chromite is a magnetic segregation.
USES OF CHROMITE

(1) Metallurgical; for extraction of metallic chromium and alloys.

(2) Chemical; for extraction of chromate salts, etc.

(3) Refractory; for making furnace hearths, etc.

Metallurgical ore should have low grade impurities such as Magnesia, alumina and lime, because they increase the slag volume in smelting which increases the cost of smelting operation. SiO₂ and Al₂O₃ are readily removed by gravity concentration. A moderate replacement of FeO by MgO is an advantage rather than a disadvantage, since it improves the Cr:Fe ratio of the ore and makes it possible to produce a higher grade of ferrochromium. Since the Cr:Fe ratio desired in the ferrochromium is 2:1 or better, and since there is some loss of chromium in the smelting operation, the ore for metallurgical use should have a Cr:Fe ratio of about 2.5:1. As the Cr:Fe ratio in pure chromite is 1.9:1, an ore with some FeO replaced is required for the best grade of metallurgical ore.

Metallurgical ore is reduced by carbon in the electric
furnace and produced ferrochromium alloy. The reaction is as follows:

$$\text{Fe}_2\text{O}_3 \cdot \text{Cr}_2\text{O}_3 + 4\text{C} \rightarrow 4\text{CO} + \text{Fe}_2\text{Cr}$$

This alloy contains carbon about 6 to 8%. If no carbon is desired, one reduces the ore with Mg or Al by the Thermite process.

Power consumption per ton of ferrochromium alloy made:

<table>
<thead>
<tr>
<th>Containing</th>
<th>kwhr/ton</th>
<th>Recovery</th>
</tr>
</thead>
<tbody>
<tr>
<td>S-10% C</td>
<td>55000-6000</td>
<td>90-95%</td>
</tr>
<tr>
<td>.7% C</td>
<td>7000-7500</td>
<td>75%</td>
</tr>
</tbody>
</table>

One uses the metallic chromium for making chromium steels and other alloys. Chromium makes strength, toughness, hardness, resistance to abrasion and wear, resistance to chemical and atmospheric corrosion, resistance to oxidation and mechanical weakness at high temperatures, and electrical resistance.

These steels are used in the axles, crankshafts, etc. (Cr-steels) containing 1% Cr used in gears, in crushers. 18-8 stainless steels (18% Cr--8% Ni) used in restaurant equipment, automobile parts, chemical equipment.

Chrome plating is important for three reasons:

1. the brilliant luster.
2. the resistance to corrosion.
3. its hardness and resistance to rubbing wear.

The chromium layer is usually 0.000002--0.0005 inches thin. Chromium plate is analyzed by x-ray diffraction.

For chemical uses SiO₂ should be in ore less than 8% because SiO₂ makes more consumption of reagents. For this purpose chromite is converted to chromate by roasting the chromite with soda ash and lime. It is then leached with water in which converted chromate is dissolved and this extracted by crystallization from the mother liquor.
SOME CHEMICAL SALTS AND THEIR USES:

\( \text{Na}_2\text{CrO}_4 \) (sodium chromate)  
used in treating feed water for the prevention of boiler scale,  
and effects on the purification of sewage treatment in bacterial filters.

\( \text{Na}_2\text{Cr}_2\text{O}_7 \) (sodium dichromate)  
used extensively in chrome tanning.  
as a mordant in the dyeing industry,  
as a discharge in bleaching oils and fats,  
as an oxidation agent, and  
in the manufacture of other Cr salts and pigments.

\( \text{CrO}_3 \) (chromic anhydride)  
used as a powerful oxidizing agent.

\( \text{CrO}_3 \) and \( \text{Cr}_2(\text{SO}_4)_3 \)  
are used in making chromium plating baths.

Basic Cr-Sulphate  
used in tanning industry.

\( \text{CrCl}_3 \) and \( (\text{CH}_3\text{COO})_2\text{Cr} \)  
are good mordants.

\( \text{Cr}_2(\text{SO}_4)_3 \)  
is an excellent mordant used in dyeing industry.
SOME CHROME PIGMENTS

<table>
<thead>
<tr>
<th>Pigment</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>PbCrO₄</td>
<td>Chrome yellow from deep orange to light yellow.</td>
</tr>
<tr>
<td>ZnCrO₄ and BaCrO₄</td>
<td>Yellow color. ZnCrO₄ soluble in water, therefore used in interior paints.</td>
</tr>
<tr>
<td>Chrome greens</td>
<td>are a mixture of Prussian blue and PbCrO₄, but not very durable.</td>
</tr>
<tr>
<td>Chrome oxide green</td>
<td>is Cr₂O₃ (Chromic sesqui oxide) a permanent dull color, but expensive.</td>
</tr>
<tr>
<td>Zinc green</td>
<td>is a mixture of ZnCrO₂ and Prussian blue.</td>
</tr>
<tr>
<td>Chrome red</td>
<td>is basic chromate of lead. It is a brilliant scarlet. Used extensively as a protective pigment in paints for iron and steel. It equals or excels red lead, but is expensive.</td>
</tr>
</tbody>
</table>

Chromite can not be reduced by Co and it is neutral and almost insoluble in slags and fluxes, has high thermal conductivity, low electric resistivity, high melting point and stability. Therefore it is used for refractory purposes mostly in metallurgical plants, especially in kilns as lining for drying sulphate paper pulp and in reverberatories and furnace hearths. Too much iron may reduce the normal fusibility to a point where the chromite is of no value as a refractory. The Cr₂Fe
ratio in refractory ores varies within wide limits, depending upon the temperature to be withstood and the particular combination of impurities in the ore, but roughly 2:1 may be set as the upper limit and 1:1 as the lower limit, although the latter is greatly influenced by the fusibility of the impurities present.
WORLD PRODUCTION OF CRUDE CHROMITE

<table>
<thead>
<tr>
<th>name of country</th>
<th>1939 in metric tons</th>
<th>per cent of total</th>
</tr>
</thead>
<tbody>
<tr>
<td>Turkey</td>
<td>210,000</td>
<td>22.1</td>
</tr>
<tr>
<td>South Africa</td>
<td>160,014</td>
<td>16.8</td>
</tr>
<tr>
<td>Southern Rhodesia</td>
<td>139,083</td>
<td>14.7</td>
</tr>
<tr>
<td>Philippines</td>
<td>126,748</td>
<td>13.5</td>
</tr>
<tr>
<td>Cuba</td>
<td>66,926</td>
<td>7.0</td>
</tr>
<tr>
<td>Greece</td>
<td>55,000</td>
<td>5.8</td>
</tr>
<tr>
<td>New Caledonia</td>
<td>52,000</td>
<td>5.5</td>
</tr>
<tr>
<td>Yugoslavia</td>
<td>44,097</td>
<td>4.6</td>
</tr>
<tr>
<td>United States</td>
<td>3,099</td>
<td>.3</td>
</tr>
<tr>
<td>Russia and others</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>950,000</td>
<td>100.0</td>
</tr>
<tr>
<td>Country</td>
<td>Metric Tons</td>
<td>Per Cent of Total</td>
</tr>
<tr>
<td>------------</td>
<td>-------------</td>
<td>-------------------</td>
</tr>
<tr>
<td>Germany</td>
<td>104,156</td>
<td>54.0</td>
</tr>
<tr>
<td>United States</td>
<td>19,438</td>
<td>10.1</td>
</tr>
<tr>
<td>France</td>
<td>18,825</td>
<td>9.7</td>
</tr>
<tr>
<td>Sweden</td>
<td>15,980</td>
<td>8.1</td>
</tr>
<tr>
<td>Italy</td>
<td>15,736</td>
<td>8.2</td>
</tr>
<tr>
<td>Norway</td>
<td>17,122</td>
<td>8.9</td>
</tr>
<tr>
<td>Poland</td>
<td>1,885</td>
<td>1.0</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>192,842</strong></td>
<td><strong>100.0</strong></td>
</tr>
</tbody>
</table>
Chromite imports to the United States mainly come from Turkey, Southern Rhodesia and Transvaal, and New Caledonia.

50 per cent of chromite used in the United States is for metallurgical purposes. (Ore content is high in $\text{Cr}_2\text{O}_3$.)

40 per cent is used for refractory purposes. (Ore content is high in $\text{Al}_2\text{O}_3$.)

10 per cent is used for chemical purposes. (High in iron.)
<table>
<thead>
<tr>
<th>Product</th>
<th>Price and Details</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Turkish chromite</strong></td>
<td></td>
</tr>
<tr>
<td>50 per cent concentrate</td>
<td>$24-30/ton at Atlantic sea port.</td>
</tr>
<tr>
<td>40 per cent lump</td>
<td>$16-22/ton at Atlantic sea port.</td>
</tr>
<tr>
<td><strong>Rhodesia, Southern chromite</strong></td>
<td></td>
</tr>
<tr>
<td>48 per cent lump</td>
<td>$23-28/ton at Atlantic sea port.</td>
</tr>
<tr>
<td><strong>Transvaal chromite</strong></td>
<td></td>
</tr>
<tr>
<td>44 per cent lump</td>
<td>$15-18/ton at Atlantic sea port.</td>
</tr>
<tr>
<td><strong>Chrome brick</strong></td>
<td></td>
</tr>
<tr>
<td>$47.00/short ton</td>
<td>at Atlantic seaport.</td>
</tr>
<tr>
<td>Ferrochrome alloy (Fe.2Cr)</td>
<td></td>
</tr>
<tr>
<td>with 4-6% C</td>
<td>11 cents/lb Cr</td>
</tr>
<tr>
<td>with .1-.06% C</td>
<td>20 cents/lb Cr</td>
</tr>
<tr>
<td>with (8-10% C)</td>
<td>$101.85/ton of Cr content</td>
</tr>
<tr>
<td>with (.7% C)</td>
<td>$203.70/ton of Cr content</td>
</tr>
<tr>
<td>97 per cent metallic chrome</td>
<td>80 cents/lb.</td>
</tr>
<tr>
<td>Pottassium chromate or</td>
<td></td>
</tr>
<tr>
<td>dichromate</td>
<td>2½ cents per lb.</td>
</tr>
<tr>
<td>Sodium Chromate or dichromate</td>
<td>1 3/4 cents per lb.</td>
</tr>
</tbody>
</table>
EXTRACTION PROCESS OF CHROMATE AND DICHROMATE FROM THE CHROMITE ORE

The process shortly consists of calcining chromite with soda ash and lime; and then leaching the calcine with hot water. Chromate obtained from the leaching solution by crystallization.

High on the Army's list of strategic materials are chrome chemicals. Chromium is very important for the National Defense. Chrome steel, on account of its hardness and toughness is used in the production of armor plate and armor-piercing projectiles and the stainless steel is used in naval construction. Chromium is important in the tanning of leather for shoes and other items of military equipment. Also important from a military standpoint is its use as a dye for olive drab cloth.

A complete plant for the extraction of chromate and dichromate from the chromite ore has been worked out and described by H. A. Doerner at the State College of Washington. (6) According to him a plant with a capacity of 20 tons of ore per day shall work as follows:
First the chromite ore (roughly 50 per cent \( \text{Cr}_2\text{O}_3 \)) and limestone must be reduced to -150 mesh particles. They are pulverized most efficiently in separate units, each consisting of a ball mill and air separator in closed circuit. It is recommended that a 42x72 inch ball mill be used for each. After this, two parts chromite ore, three parts limestone and 1.4 parts soda ash will be mixed. Mixing is accomplished in a long conveyor by rotating blades which discharges into the Rabble Furnace. The Rabble Furnace is the Edwards type with a single hearth about 2000 sq. ft. area, fired with oil or gas mechanically, temperature 1000°C. The charge is carried across the hearth by heat-resistant alloy rabbles mounted on water-cooled arms. Chromite reacts with soda ash and oxygen from the air to form sodium chromate and carbon dioxide.

\[
\text{Cr}_2\text{O}_3 + 2\text{Na}_2\text{CO}_3 + \frac{3}{2} \text{O}_2 \xrightarrow{850-1070^\circ\text{C}} 2\text{Na}_2\text{CrO}_4 + 2\text{CO}_2
\]

Soda ash used, because its salt is more soluble in water than kalium's. Limestone is used to prevent fusion and keep the mass porous, which facilitates oxidation. The discharge of the rabble furnace is a more or less fused and lumpy sinter. The chromate does not dissolve in

-14-
water completely, therefore it is necessary to grind it. It is done by wet grinding. According to the flow-sheet
No. 1 ball mill 5'x36" (90 hp.). No. 2 ball mill 5'x22"
(20 hp.). Two bowl or counter-current classifiers. One
tray Dorr Type thickener. The thickener receives hourly
1350 lbs.-150 mesh solids in a 42 degree Be' liquor con-
taining 2780 lb. Na_2CrO_4 dissolved in 5170 lb. water.
Clear liquor overflow weight 4870 lb. of which 1700 is
salt. Underflow from the last tray of the thickener
containing 42 per cent solids is filtered and washed
on a continuous rotary vacuum filter (8'x12'). Clear
liquor overflow contains except Na_2CrO_4, sodium aluminate
and silicate. To obtain a satisfactory product these must
be eliminated, since pH of liquor should be kept down
to 8.04 of pure solution of Na_2CrO_4.

Alumina and silica are precipitated by passing flue
gas through the liquor with mechanical agitation. This
is done in two 54" Turbo-Mixers, with 18" duplex im-
pellers, operated in series. About 400 gallons of liquor
per hour is neutralized by 1250 cu. ft. of flue gas.
About 10 lb. per hour (dry weight) of hydrated alumina
and silica are thus precipitated and removed by an 18"
plate and frame filter press. The filtrate is poured into the 5000 gallon Na$_2$CrO$_4$ storage tanks. The liquor is evaporated in a forced circulation type steel evaporator with an 18" steam chest and 300 sq. ft. of heating surface. It should be operated at 140° F and 1.2 lb. abs. pressure. Sodium crystallizes in an attached settler and is separated from its mother liquid in a 24" Bird Continuous centrifugal. Total daily production is 60,000 lbs. of yellow crystals of (Na$_2$CrO$_4$·4H$_2$O) when operating sodium chromate only. The finishing of the sodium dichromate is a bit more complicated. Sulphuric acid is added to the 5,000 gallons of sodium chromate storage tanks until the pH comes down to 4.7, then the liquor is ready for evaporation.

Reaction by adding H$_2$SO$_4$:

\[
\begin{align*}
\text{Na}_2\text{CrO}_4 + \text{H}_2\text{SO}_4 & \rightarrow \text{Na}_2\text{SO}_4 + \text{H}_2\text{CrO}_4 \\
\text{Na}_2\text{CrO}_4 + \text{H}_2\text{CrO}_4 & \rightarrow \text{H}_2\text{O} + \text{Na}_2\text{Cr}_2\text{O}_7
\end{align*}
\]

or

\[
2\text{CrO}_4^{--} + 2\text{H}^+ \rightarrow \text{H}_2\text{O} + \text{Cr}_2\text{O}_7^{--}
\]

Yellow or crystals less soluble than Na$_2$CrO$_4$ orange red
The evaporator must be operated at $176^\circ$ F. and 2.79 lb. abs. pressure. At this temperature the Na$_2$SO$_4$ crystalizes and it is removed by centrifugal. A water cooled crystallizer is required however, to drop out the hydrated (Na$_2$Cr$_2$O$_7$$\cdot$2H$_2$O) crystals at $70^\circ$ F. and even then only 70% of the salt will be crystallized. The liquor is returned to the evaporator. This unit produces 38,000 lb. of Na$_2$Cr$_2$O$_7$ and 18,000 lb. Na$_2$SO$_4$, when operating for these products.

**THE COST FOR SUCH A PLANT**

The cost of equipment for the 20 tons capacity plant is approximately $125,000.

- Minor items, such as small pumps, motors, conveyors, pipe lines, etc.: $25,000.
- Freight charges to Washington: $15,000.
- A building: $30,000.
- Installation: $20,000.

**TOTAL** $215,000.

At least $60,000 is needed for working capital. A total investment should be approximately $300,000.
Product of 60,000 lb. Na₂CrO₄ per day makes a total of 60,000 x $0.021 = $1,260.00.

or

Product of 38,000 lbs. Na₂Cr₂O₇ per day makes a total of 38,000 x $0.0391 = $1,487.00.
ESTIMATES OF OPERATING COSTS PER DAY

(1) 20 tons 50 per cent ore at $20.00 = $400.00
(2) 30 tons limestone at 3.40 = 102.00
(3) 14 tons soda ash at 17.90 = 250.00
(4) 6.5 tons fuel oil at 9.40 = 61.10
(5) 10 tons H₂SO₄, 66° Bé at 22.50 = 225.00
(6) Power, 8500 kwh at 0.05 = 42.50
(7) Labor = 100.00
(8) Supervision = 30.00
(9) Laboratory = 30.00
(10) Supplies = 75.00
(11) Interest and depreciation (20%) = 137.00
      \[
      \frac{25000 \times 0.20}{365} =
      \]
(12) Overhead, taxes, etc. = 30.00

TOTAL = $1483.20

These figures show that such a plant can make a profit.
THE FLOW-SHEET OF CHROMIUM EXTRACTION BY ELECTROLYSIS CELLS

Lime Chromite Soda Ash
Calcining Furnace
Leaching tanks
Filter
washed water
Leach solution
evaporation
Cake
To dump
Fe$_2$O$_3$
Fe$_2$O$_3$
Al$_2$O$_3$
MgO
CaO
CaCrO$_3$
1% Cr discard

Concentrated Solution
H$_2$SO$_4$
Agitators
Crystallizing pans
Centrifugal
Na$_2$SO$_4$
.1% discard

CrO$_3$ + HNO$_3$
Melting
CrO$_3$
electrolyte
Metallic Chromium
As plating.

Na$_2$Cr$_2$O$_7$ solution
H$_2$SO$_4$
Agitator
Crystallizing pan
HNO$_3$
Centrifugal
HNO$_3$, H$_2$SO$_4$, NaHSO$_4$
Still
HNO$_3$
CrO$_3$
Dryer
HNO$_3$
Addition of concentrated $\text{H}_2\text{SO}_4$ to the $\text{Na}_2\text{Cr}_2\text{O}_7$ solution reacts as follows:

$$\text{Na}_2\text{Cr}_2\text{O}_7 + 2\text{H}_2\text{SO}_4 \rightarrow 2\text{NaHSO}_4 + \text{H}_2\text{O} + 2\text{CrO}_3$$

and $\text{CrO}_3$ crystallizes. $\text{HNO}_3$ is added to prevent the following reaction to go right instead of left and reduces the solubility of $\text{CrO}_3$ in water.

$$2\text{CrO}_3 \xleftrightarrow{\text{add HNO}_3} \text{Cr}_2\text{O}_3 + \frac{3}{2} \text{O}_2$$

*This flow-sheet was taken from the O'Connor's Master Thesis.* (5)
I experimentally worked out in the laboratory according to the following sketch, which was given to me by Professor Curtis L. Wilson, of the Metallurgical Department of the Montana School of Mines.

I Roasting tests

A. Vary temperature
   1. 700° C.
   2. 800° C.
   3. 1000° C.

B. Vary time
   1. ½ hour
   2. 1 hour
   3. 2 hours
   4. 3 hours

   1 hour

B. Vary time

   1. ½ hour
   2. 1 hour
   3. 2 hours
   4. 3 hours

   at best temperature

C. Vary soda ash.
   3 different

D. Vary lime
   3 different

II Leaching tests

A. Cold water

B. Hot water

C. Dilute H₂SO₄

III Purification tests.
The ore, which I have worked with, was from Stillwater County, Montana. It was already concentrated by tabling.

A complete chemical analysis shows the composition of the ore from the ground and the concentrate.

<table>
<thead>
<tr>
<th></th>
<th>Chromite ore</th>
<th>Concentrated Chromite</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{Cr}_2\text{O}_3)</td>
<td>30.5 % (20.8 Cr)</td>
<td>43.5 % (29.7 Cr)</td>
</tr>
<tr>
<td>(\text{FeO})</td>
<td>19.6 % (15.23 Fe)</td>
<td>28.9 % (22.49 Cr)</td>
</tr>
<tr>
<td>(\text{Al}_2\text{O}_3)</td>
<td>17.0 %</td>
<td>12.2 %</td>
</tr>
<tr>
<td>(\text{MgO})</td>
<td>16.7 %</td>
<td>9.1 %</td>
</tr>
<tr>
<td>(\text{SiO}_2)</td>
<td>11.7 %</td>
<td>3.3 %</td>
</tr>
<tr>
<td>moisture</td>
<td>4.5 % (by diff.)</td>
<td>3.0 % (by diff.)</td>
</tr>
<tr>
<td>(\text{C}r:\text{Fe}) equals 1.36:1</td>
<td>(\text{C}r:\text{Fe}) equals 1.32:1</td>
<td></td>
</tr>
<tr>
<td>100.0 %</td>
<td>100.0 %</td>
<td></td>
</tr>
</tbody>
</table>
For my experiments I have ground the concentrate chromite in the grinding machine and the soda ash on the iron plate to -150 mesh. The lime was already -150 mesh and very pure.

The calcining was done on clay scorifying dishes in a large gas fired assay muffle. Temperature determined by a radiation type pyrometer. I ground the calcine to -80 mesh for leaching purposes.
Quantitative analysis of chromite ore is very difficult. It is generally treated with Na$_2$CO$_3$ and Na$_2$O$_2$. According to the new method treating less than 150 mg. sample with three parts of 80% phosphoric acid and eight parts of 95% H$_2$SO$_4$ is applicable.

Cr$_2$O$_3$ determination: the sodium peroxide fusion boiled with water acidified with H$_2$SO$_4$. The solution is completely reduced by ferrous ammonium sulphate and titrated with standard potassium permanganate.

SiO$_2$ determination: Peroxide fusion is boiled with water, acidified with perchloric acid, and evaporated to perchloric acid fumes. H$_2$O and HCl are added and boiled to remove impurities from the silica. This is filtered and the filtrate is evaporated to perchloric acid fumes a second time in order to obtain all the silica.

FeO determination: Peroxide fusion made in a silver crucible, is boiled with water and diluted to 500 c.c. in a volumetric flask. The solution is filtered and the residue is dissolved in dilute nitric acid. The
silver is precipitated with hydrochloric acid. The solution is boiled to coagulate the silver chloride, and the latter is filtered off. The iron is determined in the filtrate.

$\text{Al}_2\text{O}_3$ determination: peroxide solution with water diluted to 500 c.c. The residue is allowed to settle then is filtered. C. P. Na$_4$Cl is then added to a 200 c.c. aliquot of the clear filtrate, and the solution is boiled. The resulting precipitate is SiO$_2$ and Al$_2$O$_3$ determine Al$_2$O$_3$.

MgO determination is difficult. Peroxide fusion is boiled with water. The solution acidified with acetic acid just sufficiently. The solution is boiled, diluted 500 c.c., and filtered. MgO or CaO determined in aliquots of the filtrate.

I took 0.3 grams of -200 mesh concentrated ore and mixed thoroughly with about 2 grams of Na$_2$ CO$_3$ and 3 grams Na$_2$O$_2$. Fused at low red heat for about 10 minutes in a nickel crucible. I dissolved the cooled melt in hot water in which H$_2$O$_2$ was added to insure complete oxidation. After 10 minutes boiling I diluted the solution to 250 c.c. with cold water and filtered on a
suction filter. I washed the cake with hot water thoroughly. I neutralized the filtrate with $\text{H}_2\text{SO}_4$ and boiled one-half hour to decompose peroxides. After cooling, added 10 c.c. of 1:1 $\text{H}_2\text{SO}_4$ and diluted to 700 c.c. with cold water. Two grams of crystallized c.p. ferrous sulphate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) weighed out and dissolved in the 700 c.c. solution, which changes it from brown yellow to a fine blue. A green tinge indicates insufficient ferrous salt. I titrated the excess ferrous salt with $\frac{1}{10}$ $\text{KMnO}_4$ solution, and calculated the percentage of $\text{Cr}_2\text{O}_3$ in the chromite ore as follows:

**ROASTING REACTION**

$$\frac{\text{Cr}_2\text{O}_3}{152.02} + \frac{2\text{Na}_2\text{CO}_3}{2 \times 105.99} + 3 \frac{\text{O}_2}{2} \rightarrow \frac{2\text{Na}_2\text{Cr}_2\text{O}_7}{2 \times 162} + \frac{2\text{CO}_2}{272.02}$$

**REACTIONS WITH $\text{H}_2\text{SO}_4$**

$$\frac{2\text{Na}_2\text{Cr}_2\text{O}_7}{2 \times 162} + \frac{\text{H}_2\text{SO}_4}{98.08} = \frac{\text{Na}_2\text{Cr}_2\text{O}_7}{262.01} + \frac{\text{Na}_2\text{SO}_4}{142.08} + \frac{\text{H}_2\text{O}}{18.02}$$

**REACTION WITH FERROUS SALT**

$$\text{Na}_2\text{Cr}_2\text{O}_7 + 6\text{FeSO}_4 + 8\text{H}_2\text{SO}_4 \rightarrow \text{Cr}_2(\text{SO}_4)_3 + 3\text{Fe}_2(\text{SO}_4)_3 + 2\text{NaHSO}_4 + 7\text{H}_2\text{O}$$
or
\[
\frac{2\text{Cr}^{3+} + 6\text{Fe}^{2+}}{2\times 52.01} \rightarrow \frac{6\text{Fe}^{3+} + 2\text{Cr}^{3+}}{6\times 55.84}
\]

REACTION OF EXCESS FERROUS SALT WITH PERMANGANATE

\[
10\text{FeSO}_4 + 2\text{KMnO}_4 + 8\text{H}_2\text{SO}_4 \rightarrow 5\text{Fe}_2(\text{SO}_4)_3 + 2\text{MnSO}_4
\]

or
\[
\frac{10\text{Fe}^{2+} + 2\text{Mn}^{2+} + \text{H}_2\text{O}}{10\times 55.84} \rightarrow \frac{10\text{Fe}^{3+} + 2\text{Mn}^{2+}}{2\times 59.93}
\]

1 c.c. of \(\frac{1}{10}\) n \(\text{KMnO}_4\) solution corresponds to 27.801 mg. of \(\text{FeSO}_4 \cdot 7\text{H}_2\text{O}\) which equals to \(\frac{15.202}{6} = 2.5337\) mg. of \(\text{Cr}_2\text{O}_3\).

I used 20.5 c.c. of \(\frac{1}{10}\) n \(\text{KMnO}_4\) solution for filtration of excess ferrous salt, therefore:

2000 ——— 20.5 x 27.801 = 1430 mg. ferrous used for reduction of \(\text{Cr}^{3+}\) to \(\text{Cr}^{2+}\) thus, our 300 mg. chromite ore contains:

\[
1430 \times \frac{2.5337}{27.801} = 1430 \times 0.0913 = 130.5\text{ mg }\text{Cr}_2\text{O}_3
\]

or chromite contains:

\[
\frac{130.5}{300} \times 100 = 43.5\text{ per cent }\text{Cr}_2\text{O}_3
\]
For the preparation of $\frac{1}{10}$ $\text{K}_2\text{MnO}_4$ solution I took $3.1605$ grams of c.p. $\text{K}_2\text{MnO}_4$ and dissolved in one liter of water and for the $\frac{1}{10}$ $\text{ferrous}$ solution I dissolved $27.801$ grams of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ in one liter of water. Whenever I had to titrate, first I standardized the $\frac{1}{10}$ $\text{K}_2\text{MnO}_4$ solution with ferrous salt.
THE SOLUBILITIES OF SOME SALTS

Solubility in 100 parts of:

<table>
<thead>
<tr>
<th></th>
<th>Cold water</th>
<th>Hot water</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaSO₄</td>
<td>1.1759 (at 0°C)</td>
<td>1.1619 (at 100°C)</td>
</tr>
<tr>
<td>Cr₂(SO₄)₃</td>
<td>soluble</td>
<td></td>
</tr>
<tr>
<td>CrO₃</td>
<td>163.4 (at 0°C)</td>
<td></td>
</tr>
<tr>
<td>Fe₂(SO₄)₂</td>
<td>slightly soluble</td>
<td></td>
</tr>
<tr>
<td>FeSO₄•7H₂O</td>
<td>15.65 (at 0°C)</td>
<td>206.7 (at 100°C)</td>
</tr>
<tr>
<td>Na₂SO₄ (Rhombish)</td>
<td>5.0 (at 0°C)</td>
<td>48.6 (at 50°C)</td>
</tr>
<tr>
<td>Na₂SO₄ (monochline)</td>
<td>49.8 (at 40°C)</td>
<td>42.5 (at 100°C)</td>
</tr>
<tr>
<td>CaCrO₄</td>
<td>.52</td>
<td>.05</td>
</tr>
</tbody>
</table>
I. Roasting tests.
A. Vary temperature.

<table>
<thead>
<tr>
<th>Sample no.</th>
<th>Cr₂O₃</th>
<th>CaO</th>
<th>Na₂CO₃</th>
<th>Time (hr.)</th>
<th>Temp. (°C)</th>
<th>Recovery per cent</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>1.93</td>
<td>1.61</td>
<td>1</td>
<td>650°</td>
<td>25.0 %</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>1.93</td>
<td>1.61</td>
<td>1</td>
<td>750°</td>
<td>40.7 %</td>
</tr>
<tr>
<td>3</td>
<td>1</td>
<td>1.93</td>
<td>1.61</td>
<td>1</td>
<td>850°</td>
<td>68.5 %</td>
</tr>
</tbody>
</table>

For this experiment there was used -150 mesh of 50 gr. chromite ore, 92 gr. lime and 35 grm. soda ash.
10 grm. calcine of each sample was leached with hot water, then acidified and filtered. The dichromate solution was filled into a 1000 c.c. volumetric flask and for titration, 25 c.c. of the dichromate solution and 10 c.c. of \( \frac{1}{10} \) ferrous solution were used. For the base of calculations of the per cent extractions, sample No. 3 is illustrated as an example:

For standardization of \( \frac{1}{10} \) KMnO₄ solution with \( \frac{1}{10} \) FeSO₄ solution: It was taken 10 c.c. of the \( \frac{1}{10} \) FeSO₄ solution for titration. There was used:
39.70 - 39.50 = 10.20 c.c. of permanganate solution.
so

1 c.c. of KMnO₄ Solution = \frac{10}{10.2} = 0.98 c.c. of FeSO₄ Solution.

DATA:
Ore roasted was 50 grams.
Calcine obtained = 98 grams.
Calcine leached = 10 grams.
Leach solution obtained = 1000 c.c.
Leach solution titrated = 25 c.c.
FeSO₄ solution used = 25 c.c.

For the excess FeSO₄ solution there was used:
50.05 - 39.80 = 10.25 c.c. of permanganate solution.

CALCULATIONS:

Ferrous solution used by dichromate = \frac{10.04}{25 - 10.25 \times 0.98} = 0.04 g.

14.96 c.c. according to these data:

50 gram chromite contains = \frac{2.5337 \times 14.96 \times 1000}{25} \times \frac{98}{10} = 14.96 \text{ grams of } Cr₂O₃.

or

\frac{14.9}{50} \times 100 = 29.8 \text{ per cent } Cr₂O₃.
Chemical analysis shows that ore contains 43.5 per cent $\text{Cr}_2\text{O}_3$, therefore, the extraction $= \frac{29.8}{43.5} \times 100 = 68.5$ per cent.

B. Vary time.

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>The proportion of $\text{Cr}_2\text{O}_3$, CaO, Na$_2$CO$_3$</th>
<th>Time (hr)</th>
<th>Temp. ($^\circ$C)</th>
<th>Recovery per cent.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>$\frac{1}{2}$</td>
<td>950</td>
<td>57%</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>1</td>
<td>950</td>
<td>70%</td>
</tr>
<tr>
<td>3</td>
<td>1</td>
<td>2</td>
<td>950</td>
<td>84.1%</td>
</tr>
<tr>
<td>4</td>
<td>1</td>
<td>3</td>
<td>950</td>
<td>92.7%</td>
</tr>
</tbody>
</table>

The same amount of substances were used as in the preceding experiment. 5 g. calcine was leached from each sample. 25 c.c. of 1000 c.c. dichromate solution and 10 c.c. of $\frac{1}{10}$ m ferrous solution was titrated. During the roasting of the first sample the temperature may correct 860$^\circ$ and for the following samples, 940$^\circ$-960$^\circ$. 
### C. Vary Soda Ash.

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>The proportion of Cr$_2$O$_3$, CaO, Na$_2$CO$_3$</th>
<th>Time (hr)</th>
<th>Temp ($^\circ$C)</th>
<th>Recovery per cent</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>1.93</td>
<td>1.55</td>
<td>1</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>1.93</td>
<td>1.78</td>
<td>1</td>
</tr>
<tr>
<td>3</td>
<td>1</td>
<td>1.93</td>
<td>2.00</td>
<td>1</td>
</tr>
</tbody>
</table>

The soda ash used, 33.6-38.6-43.4 grm. 2 g. of calcine was leached in each case.

### D. Vary Lime.

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>The proportion of Cr$_2$O$_3$, CaO, Na$_2$CO$_3$</th>
<th>Time (hr)</th>
<th>Temp ($^\circ$C)</th>
<th>Recovery per cent</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>1.0</td>
<td>2.00</td>
<td>1</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>2.0</td>
<td>2.00</td>
<td>1</td>
</tr>
<tr>
<td>3</td>
<td>1</td>
<td>3.0</td>
<td>2.00</td>
<td>1</td>
</tr>
</tbody>
</table>

Lime was used: 21.7-43.5-65.2 grams. 1 gram of calcine was leached.
II. Leaching tests.

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>The proportion of</th>
<th>Time (hr)</th>
<th>Temp. (°C)</th>
<th>Leached with</th>
<th>Recovery per cent</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Cr₂O₃ 1</td>
<td>CaO 1.93</td>
<td>Na₂CO₃ 1.61</td>
<td>1</td>
<td>900°C cold water</td>
</tr>
<tr>
<td>B</td>
<td>Cr₂O₃ 1</td>
<td>CaO 1.93</td>
<td>Na₂CO₃ 1.61</td>
<td>1</td>
<td>900°C hot water</td>
</tr>
<tr>
<td>C</td>
<td>Cr₂O₃ 1</td>
<td>CaO 1.93</td>
<td>Na₂CO₃ 1.61</td>
<td>1</td>
<td>900°C dilute H₂SO₄</td>
</tr>
</tbody>
</table>

In each case 25 grams of calcine was leached in 500 c.c. of liquid by one hour agitation.
III. Purification Tests.

When some samples leached with hot water containing sulphuric acid, the following contaminants were dissolved in a maximum amount.

From A, Sample No. 1.

<table>
<thead>
<tr>
<th>Contaminants</th>
<th>Percentage of the ore.</th>
</tr>
</thead>
<tbody>
<tr>
<td>desirable</td>
<td></td>
</tr>
<tr>
<td>Cr$_2$O$_3$</td>
<td>10.8%</td>
</tr>
<tr>
<td>FeO</td>
<td>13.50%</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>5.65%</td>
</tr>
<tr>
<td>MgO</td>
<td>4.18%</td>
</tr>
<tr>
<td>TOTAL</td>
<td>33.90%</td>
</tr>
</tbody>
</table>
From A, Sample No. 2.

<table>
<thead>
<tr>
<th>Contaminants</th>
<th>Dissolved as percentage of ore.</th>
</tr>
</thead>
<tbody>
<tr>
<td>desirable</td>
<td></td>
</tr>
<tr>
<td>Cr$_2$O$_3$</td>
<td>17.7%</td>
</tr>
<tr>
<td>FeO</td>
<td>10.54%</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>4.44%</td>
</tr>
<tr>
<td>MgO</td>
<td>3.32%</td>
</tr>
<tr>
<td>TOTAL</td>
<td>36.00%</td>
</tr>
<tr>
<td>undesirable</td>
<td></td>
</tr>
<tr>
<td>Cr$_2$O$_3$</td>
<td></td>
</tr>
<tr>
<td>FeO</td>
<td></td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td></td>
</tr>
<tr>
<td>MgO</td>
<td></td>
</tr>
</tbody>
</table>

From A, Sample No. 3.

<table>
<thead>
<tr>
<th>Contaminants</th>
<th>Dissolved as percentage of ore.</th>
</tr>
</thead>
<tbody>
<tr>
<td>desirable</td>
<td></td>
</tr>
<tr>
<td>Cr$_2$O$_3$</td>
<td>29.8%</td>
</tr>
<tr>
<td>FeO</td>
<td>12.2%</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>5.15%</td>
</tr>
<tr>
<td>MgO</td>
<td>3.85%</td>
</tr>
<tr>
<td>TOTAL</td>
<td>51.00%</td>
</tr>
<tr>
<td>undesirable</td>
<td></td>
</tr>
<tr>
<td>Cr$_2$O$_3$</td>
<td></td>
</tr>
<tr>
<td>FeO</td>
<td></td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td></td>
</tr>
<tr>
<td>MgO</td>
<td></td>
</tr>
</tbody>
</table>
From B, Sample No. 3.

<table>
<thead>
<tr>
<th>Contaminants</th>
<th>Dissolved as percentage of ore.</th>
</tr>
</thead>
<tbody>
<tr>
<td>desirable</td>
<td></td>
</tr>
<tr>
<td>Cr$_2$O$_3$</td>
<td>36.6%</td>
</tr>
<tr>
<td>FeO</td>
<td>7.14%</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>3.02% 12.40%</td>
</tr>
<tr>
<td>MgO</td>
<td>2.24%</td>
</tr>
<tr>
<td>TOTAL</td>
<td>49.00%</td>
</tr>
</tbody>
</table>

From B, Sample No. 4.

<table>
<thead>
<tr>
<th>Contaminants</th>
<th>Dissolved as percentage of ore.</th>
</tr>
</thead>
<tbody>
<tr>
<td>desirable</td>
<td></td>
</tr>
<tr>
<td>Cr$_2$O$_3$</td>
<td>40.3%</td>
</tr>
<tr>
<td>FeO</td>
<td>12.55%</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>5.30% 21.8%</td>
</tr>
<tr>
<td>MgO</td>
<td>3.95%</td>
</tr>
<tr>
<td>TOTAL</td>
<td>62.10%</td>
</tr>
</tbody>
</table>
These figures are true if we leach with hot water 
\( \text{H}_2\text{SO}_4 \). But if it is leached only with water, Fe, Al 
and Mg will not dissolve in large quantities. They may 
be dissolved but in such small amounts that it is difficult 
to measure them. In high pH solution only Al and Si will 
dissolve as sodium aluminate and sodium silicate. The 
experiments show that an average of 0.0115 lbs. of \( \text{Al}_2\text{O}_3 \) 
and \( \text{SiO}_2 \) may be dissolved per lb. of chromium extracted. 
\( \text{SiO}_2 \) and \( \text{Al}_2\text{O}_3 \) will be precipitated from the solution 
by lowering pH with acid or direct with passing \( \text{CO}_2 \) gas.
CONCLUSIONS

The best temperature for the roasting was 950° C. At this temperature, one hour roasting gave 70 per cent and three hours, 93 per cent extractions.

The soda ash consumption was a little high. When the ratio of Cr$_2$O$_3$:Na$_2$CO$_3$ was 1:2, there was obtained 76.1 per cent extraction in one hour roasting at 950° C.

It seems that when the amount of lime as as much as soda ash used, the extraction was higher.

The excess or less amount of lime did not give good results. Excess lime forms above 800° C calcium chromite. The latter is readily oxidized by the air to CaCrO$_4$, which in turn partly decomposes into acid-soluble calcium chromic-chromates of uncertain and perhaps variable composition. Under similar conditions Mg reacts to form a brown insoluble chromite, only a small portion of which oxidizes to a water-soluble chromate. No acid-soluble decomposition products were found.

The color of a good calcine should be dark yellowish
green and half sintered which can be ground easier.
A good calcine should not contain more than 1 per cent
unoxidized chrome ore. A complete conversion of chro-
mite to chromate requires more than three hours roast-
ing time, maybe six hours is sufficient. It is advis-
able to add a small amount of soda ash to the hot leach
solution to convert \( \text{CaCrO}_4 \) present to \( \text{Na}_2\text{CrO}_4 \). This
reaction is completed at \( 100^\circ \text{C} \). The concentration of
the liquor should be at the range of 30-40° Bome. The
temperature of the leach solution was not an important
factor for the dissolving of chromate from calcine.
Agitation reduces leaching time and gives more recovery.
Dilute \( \text{H}_2\text{SO}_4 \) solution has the disadvantage of dissolving
too much Fe, Al and Mg as impurities. The purification
tests has not been worked thoroughly, since there was
not enough time for the laboratory work. The amount
of impurities in the ore has little bearing upon the
problem of obtaining a pure liquor. In general, the
amount of contaminations depends upon the following factors:

1. Quantity and kind of roasting reagents.

2. Temperature and duration of roast.
3. Fusibility, rabbling, quenching, etc.
4. Temperature and duration of leaching.
5. Concentration of leached liquor.
6. Leaching reagents.

It seems to me that the Stillwater County Chromite, due to its high iron content, is not good for the metallurgical purposes unless the iron content can be reduced by some method. The gravity concentration does not even improve the ratio of Cr:Fe. However, the ore can be economically worked for the production of chromium compounds. The gravity concentration reduces the $\text{SiO}_2$ content to 3 per cent. $\text{Al}_2\text{O}_3$ and $\text{FeO}$ are a little high but they will not seriously reduce recovery of chromate. The Stillwater County chromite is best suited for refractory purposes.
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(7) Doerner, H. A., Producing Chromate salts from Domestic Ores, Chemistry and Metallurgy Journal, October 1940.
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ACKNOWLEDGEMENT

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