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Autoclave Leaching of Montana Chromite

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AUTOCLAVE LEACHING OF MONTANA CHROMITE

A Thesis
Presented to
the Department of Metallurgy

In Partial Fulfillment
of the Requirements for the Degree
of Bachelor of Science in Metallurgical Engineering

by
Leonard S. Greely
Montana School of Mines
Butte, Montana
February, 1960

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ACKNOWLEDGMENTS

The writer wishes to express his appreciation to Professor Ralph I. Smith for his encouragement and many helpful suggestions throughout this investigation. Acknowledgment is also given Professor Harry J. Christoffers for his suggestions, and Mrs. Loretta B. Peck for her assistance in the background portion of the investigation.

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AUTOCLAVE LEACHING OF MONTANA CHROMITE

I. INTRODUCTION

The United States is the world's largest consumer of chromium and yet, domestic chromium production is so small compared to world production that we have always been dependent on foreign sources for the greater percentage of our chromium consumption. In times of peace and prosperity, we do not worry about this dependence; indeed, it may be considered advantageous as a stimulant to free world trade. In times of international stress, this situation may be reversed. World War I is an excellent example of what can develop when provisions are not made for emergency supplies of a strategic mineral like chromium. At the outbreak of war, we needed large supplies of chromium for chromium-alloy steels in armament. The world production of chrome ore was less than 150,000 tons and domestic production was practically nil. The United States developed a number of small, high cost deposits, but the price of all chromium products soared to fantastic heights. Domestic prices rose from 15 dollars per ton to 100 dollars per ton of ore, and ocean freight costs alone rose as high as 65 dollars per ton. Even at these prices, adequate shipping was not available, and there was a chromium shortage throughout the war period.

Two courses of action can be taken to prevent a recurrence of what has happened in past World Wars. The government can stockpile enough ore to last until domestic production can reach a level where imports are no longer necessary and it can promote research in the

development of low-grade deposits, so that if it becomes necessary, the country can produce 100% of its own consumption.

The largest known domestic deposit of chromite is located in the Stillwater and Sweetgrass counties in Montana. This ore can be concentrated by gravity separation to meet chromic oxide requirements, but the chrome iron ratio is too low to meet present standards for direct use in the manufacture of steel.

History of Chromium

Chromium was discovered by the French chemist, Louis Nicolaus Vauquelin, in about the year 1797; however, a hundred years elapsed before any great use was made of chromium. P. Berthier published a paper on "Chromium in Iron and Steel" as early as 1821, and E. Fremy published his paper on "Crystallized Chromium and Its Alloys" in 1857; however, very little attention was paid to these developments. In 1905, Goldschmidt developed the aluminothermic process for producing chromium metal. This development aroused the first real interest in chromium metal and led to the use of chromium in electrical-resistance alloys. F. M. Becket and E. F. Price developed a cheap process for the production of ferrochromium in 1908, based on a carbon and silicon reduction, and by 1915, chromium steels were quite common. From that time until the present, chromium has been playing an ever-increasing role in the metallurgical field and it is only reasonable to assume that chromium has a permanent and growing place in the metal industry.

Mineralogy and Geology

Chromite is a spinel whose composition can be expressed by the formula $(\text{Mg,Fe})(\text{Cr,Al,Fe})_2\text{O}_4$. The magnesium replaces the divalent iron and the aluminum replaces the chromium and/or the trivalent iron. Although the degree of replacement varies, minerals of this general formula are usually given the broad mineralogical name "chromite". When the replacement has been extensive, the ore is named "chrompicotite".

The spinel group is divided into three series based on the dominant trivalent element:

- (1) Spinel Series - Al as Al_2O_3
- (2) Magnetite Series - Fe as Fe_2O_3
- (3) Chromite Series - Cr as Cr_2O_3

From numerous analyses, it appears that natural chromites are essentially solid solutions of various spinel. The bivalent FeO of pure chromite may be replaced by Mg, Zn, Mn or Ni. Mg is the normal replacement element. Zn, Mn and Ni replace Fe so rarely that they are usually disregarded. The trichromium may be replaced by trivalent Al or Fe. Both are normally present in small amounts in natural chromites.

The Montana chromite deposits in the Stillwater and Sweetgrass counties constitute about 75% of the domestic chromite resources. The average grade of this ore is low (between 35 and 40 per cent Cr_2O_3) and the Cr:Fe ratio is low (about 1.6:1). The other domestic deposits are located in California, Oregon, and Alaska.

The major foreign sources of chromite are India, Africa, Rhodesia, and Turkey. These countries have larger deposits than the United States

with a higher chromite content and a more favorable chrome iron ratio. The African and Indian chromites have a chrome iron ratio of 3:1 and 48% Cr_2O_3 . The Rhodesian chromite averages about 46% Cr_2O_3 with a chrome iron ratio of 2.7:1. The grade and chrome iron ratio of the Turkish chromite is reported to be quite high, but no actual figures are available.

Properties

Chromium's atomic number is 24 and its atomic weight is 52.01.

Contrary to popular belief, chromium is not hard and brittle, but quite ductile at room temperature when pure. However, small traces of oxygen and nitrogen tend to make chromium very brittle. This is a common characteristic of all body-centered cubic metals. Other physical properties of chromium include: melting point - 1930°C ; boiling point - 2480°C ; magnetic properties - paramagnetic.

Chromium readily forms three series of compounds:

- (1) Chromous compounds, CrX_2 , containing divalent chromium, moderately basic.
- (2) Chromic compounds, CrX_3 , containing trivalent chromium, weakly basic.
- (3) Chromate compounds, CrX_6 , containing hexavalent chromium, strongly acid.

In addition to these more well-known compounds, univalent and pentavalent compounds of chromium have been produced under controlled conditions.

Uses

The major part of the world's chrome production is consumed by

the steel industry. Chromium, when added to steel, makes the steel much stronger, harder, resistant to acid corrosion, and more susceptible to magnetism. Ferro-chrome, rather than pure chrome, is used as the alloying agent because it is much cheaper to produce.

Aside from the steel industry, chromium chemicals have many important industrial uses. The four major consumers of chromium chemicals are:

- (1) Pigment industry
- (2) Leather and textile industry
- (3) Chemical industry
- (4) Surface treatment of metals

In addition to these major users of chromium chemicals, the oil and gas industries use them in corrosion control and the preparation of catalysts; the food and beverage industries use them in refrigerating brines and cleansing compounds, the pyrochemical industry uses them in matches and fireworks, and they are essential to the photographic industries in lithography and engraving.

II. STATEMENT OF PROBLEM

The purpose of this investigation was to determine the feasibility of caustic autoclaving of Montana chromite in order to recover the chromium in a relatively pure solution of sodium chromate. It was amply demonstrated by Jerry D. Murphy in 1948 that this concentrate could be treated by means of a caustic roast and water leach to produce sodium chromate. However, Chester Freshour attempted direct caustic leaching with negative results in 1949. It was felt that leaching at high temperatures and pressures might produce a sodium chromate solution and at a lower cost than that of the roasting and leaching operation.

Analysis of Ore

A sample of this concentrate (the mineral chrompicotite as determined by X-ray diffraction; Appendix, Figure I) was taken by the United States Bureau of Mines for assay and test work. The assays of the ore and the table concentrate are listed in Table I.

TABLE I

<u>Component</u>	<u>Ore</u>	<u>Per Cent</u> <u>Concentrate</u>
Cr ₂ O ₃	26.41	43.15
FeO	17.23	25.70
MnO	1.02	---
Al ₂ O ₃	12.72	12.20
MgO	23.76	1.60
SiO ₂	17.24	---

III. LABORATORY PROCEDURE

The direct caustic autoclaving of a chromite concentrate has apparently never been investigated. Chester Freshour, at the Montana School of Mines and the United States Bureau of Mines in Boulder City, Nevada, attempted caustic leaching at atmospheric pressures. Chester Freshour was unsuccessful in obtaining any positive results, but he felt at the time that leaching might have been successful if it had been done at high temperatures and pressures; however, he was not equipped with the necessary autoclave. The Bureau of Mines did not publish their results, so it is assumed that they were negative.

A little work has been done on pure chromite. C. Fricke and O. Windhausen determined the solubility of pure chromite in a solution of 10 normal sodium hydroxide. An agitation time of three 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. Chromite and chrompicotite may not have identical bonding so these two sources of information were only indirect indications to what might be used in this experimental work.

The variables present in this operation are time, temperature, pressure, reagents, fineness of sample, and pulp dilution. Fineness of sample and pulp dilution were held constant because of the limited scope of the investigation. The concentrate was ground in a pulverizer to pass a 150-mesh screen. The pulp dilution was maintained at 7.5% solids.

During each experiment, the conditions in the autoclave were changed from two to five times, each set of conditions representing one test. The reagents added were the only variables that could not be changed after the experiment had started; therefore, the reagent was varied only at the beginning of each experiment, a total of fifteen times. Although the pressure was variable, it was dependent on the temperature and should be considered a dependent variable. The only independent variables were time and temperature.

Laboratory Tests

The autoclave used for this work is illustrated on page 3 of the appendix. It is a product of Autoclaving Engineers, Inc. and was designed especially for laboratory work. It has a one-gallon capacity and can contain pressures up to 1200 psig. A safety valve is set at 1200 psig to release the pressure when this maximum valve is exceeded. The construction is of 18-8 stainless steel to minimize corrosion. The temperature is controlled by a Honeywell heating control unit.

The initial test was a one-hour leach with sodium carbonate solution at 212^oF. The results were negative so the temperature was increased to 380^oF. (195 psig). Again, the results were negative, so the temperature was increased to 500^oF. (680 psig). The results of this experiment were all negative, and the first signs of difficulty in autoclave leaching of chromite were becoming apparent.

The second experiment was also a sodium carbonate leach, but with an oxidizing agent present. The oxidizing atmosphere was based

on the roasting of this concentrate in an oxidizing atmosphere by Jerry D. Murphy. Seventy-five grams of sodium nitrate were added to the solution, but again the results were negative.

Experiments 3 and 4 were run with a sodium hydroxide leach solution in the expectation that sodium hydroxide might prove to be a stronger reagent, but again the results were negative. Ten normal sodium hydroxide was used in Experiment 3, and a mixture of sodium hydroxide, sodium carbonate, and sodium nitrate was used in Experiment 4.

At this point, it was decided that sodium nitrate was an unfortunate choice for an oxidizing agent because nitrates are relatively ineffective oxidizers in basic solutions. Therefore, sodium peroxide was used as the oxident in Experiment 5. The results were good, but when the experiment was repeated, the results were negative. The positive results, first obtained, were due to an error in the assaying procedure and the experiment had to be discarded.

Experiment 6 was a sodium carbonate leach with sodium peroxide as an oxident. Twenty-five psig of oxygen were added to give the reaction an oxidizing atmosphere. Oxygen gas is relatively stable, but it was hoped that the sodium peroxide would act as a catalyst for the oxidation by O_2 . The results of this experiment were negative.

It seemed advisable at this point to examine the bonding in the mineral itself. Experiment 9 was run with this purpose in mind. Samples of concentrate, before and after leaching, were analyzed with the X-ray. Figure II shows that the peaks are different in magnitude,

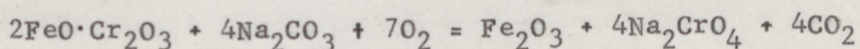
but not in position. The fact that the peak positions were unchanged, proved that the bonding had not been touched by the sodium carbonate. The change in peak magnitude only indicates that one sample was finer than the other. The denser sample produces the higher peak.

Experiments 10 through 15 were based on the work of C. Fricke, C. Windhausen, and Billwater. The time of leaching was greatly increased to try to break the bonding in the mineral. Experiments 10 through 11 were run for seventy-two hours with ten normal sodium hydroxide. Experiments 12 and 14 were also run for seventy-two hours, but with the addition of sodium peroxide as an oxident. Experiment 15 was run for ninety-six hours with potassium permanganate as the oxident. The results were negative in all cases.

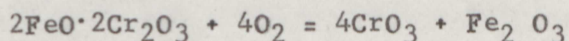
Test data are tabulated on pages 3 and 4 of the appendix.

IV. CONCLUSION

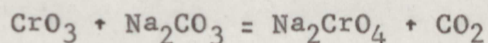
The reason for the negative results in this experiment should be explainable on the basis of the thermodynamics involved; however, a literary search failed to uncover any thermodynamic data pertaining to these tests. In the absence of the necessary data, the conclusion can only be a matter of conjecture. At first glance, it would seem that if 85% chromium recovery is possible with a caustic roast and water leach, a caustic leach at high temperature and pressure would produce similar results. The fact that these results were not produced indicates that a reaction takes place in the roast that is unobtainable in the autoclave. Jerry D. Murphy wrote one equation for the roasting reaction:



This equation is chemically sound; however, it does not tell the complete theory. To get from $\text{FeO}\cdot\text{Cr}_2\text{O}_3$ to Na_2CrO_4 , the chromium must first be oxidized to break the spinel bonds after which the Cr can be oxidized. Since sodium carbonate is not an oxidizing agent, the first reaction must be between the oxygen and the chromite to break the bond and to produce chromic acid and ferric oxide.



Chromic acid is very reactive and will react with the sodium carbonate to produce sodium chromate which is quite soluble in cold water.



If this theory is correct, the reason for the failure of the autoclaving operation lies in the fact that extremely high temperatures are needed to break the bond and to oxidize the Cr_2O_3 to CrO_3 and these temperatures were not obtainable in the autoclave.

Recommendations

I would recommend that any further research in the autoclaving of chrompicotite be done in conjunction with a roasting operation. If the mineral is first roasted to break the bond and oxidize the Cr_2O_3 to CrO_3 , the autoclave might prove to be very effective in the subsequent leaching operation.

This experimental work was initiated with the idea of finding a cheap method of producing sodium chromate by eliminating the roasting operation. The elimination of the roasting operation now seems infeasible in the light of these experimental results.

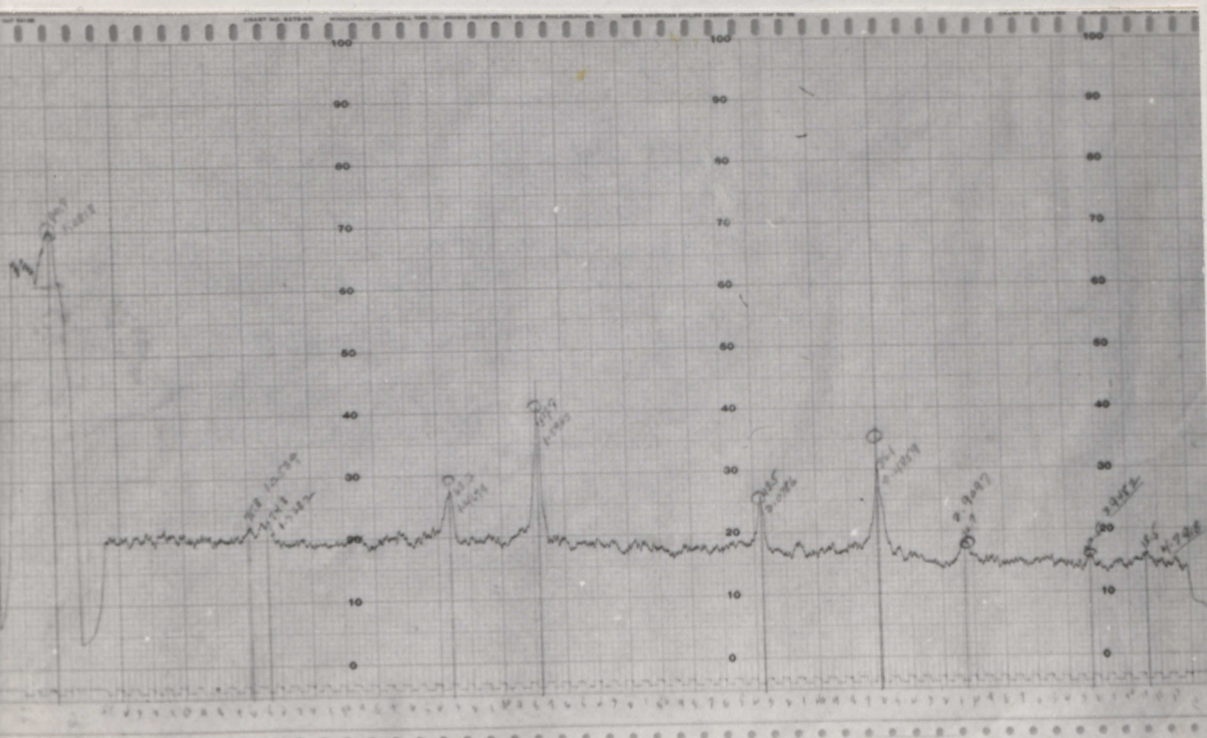
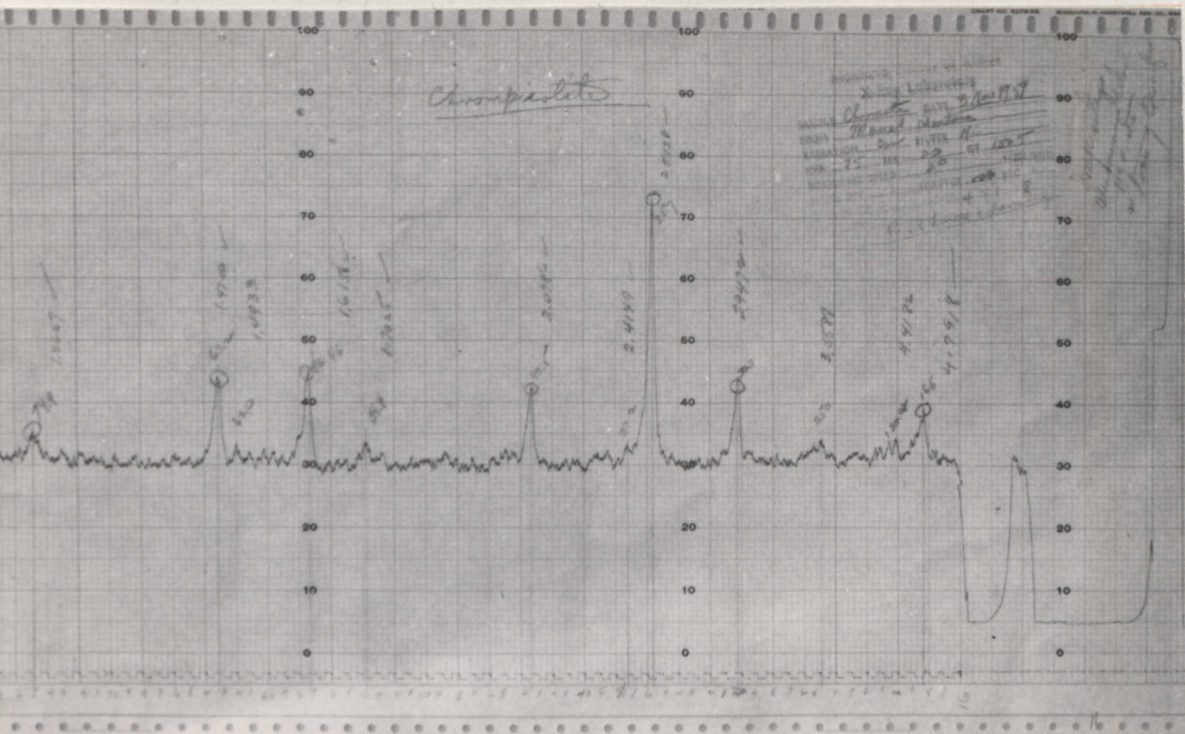
V. BIBLIOGRAPHY

- Bichowsky, "Thermochemistry of Chemical Substances," New York: Reinhold Publishing Corp., 1936.
- Bray, John L., "Nonferrous Production Metallurgy," New York: John Wiley and Sons, Inc., 1947.
- Brown, Lester C., "A Preliminary Investigation of Chromite," Thesis, Montana School of Mines, 1947.
- Burns, L. R., "Ductile Chromium," Chemical Engineer, Nov., 1959.
- Conraw, John M., "Factors Affecting Chromite Production in Montana," De Re Metallica, Feb., 1945.
- Dean, R. S., U. S. Bureau of Mines Report of Investigation 3480, "Selective Reduction of Chromite Ores," 1939.
- Doerner, H. A., U. S. Bureau of Mines Report of Investigation 2999, "Roasting of Chromite Ores to Produce Chromate," 1930.
- Freshour, Chester, "Caustic Leaching of Montana Chromite," Thesis, Montana School of Mines, 1949.
- Hayward, Carle R., "Metallurgical Practice," New York: D. Van Nostrand Corp., Inc., 1955.
- Koster, J., U. S. Bureau of Mines Report of Investigation 3322, "Studies of Treatment of Domestic Chromite," 1936.
- Murphy, Jerry D., "Roasting and Leaching of Montana Chromite," Thesis Montana School of Mines, 1948.
- Rieman, Neuss, and Naiman, "Quantitative Analysis," New York: McGraw Hill Book Co., 1942.
- Sully, A. H., "Chromium," New York: Academic Press Inc., 1954.
- Udy, Marvin J., "Chromium," Vol. I, New York: Reinhold Publishing Corp., 1956.
- Udy, Marvin J., "Chromium," Vol. II, New York: Reinhold Publishing Corp., 1956.

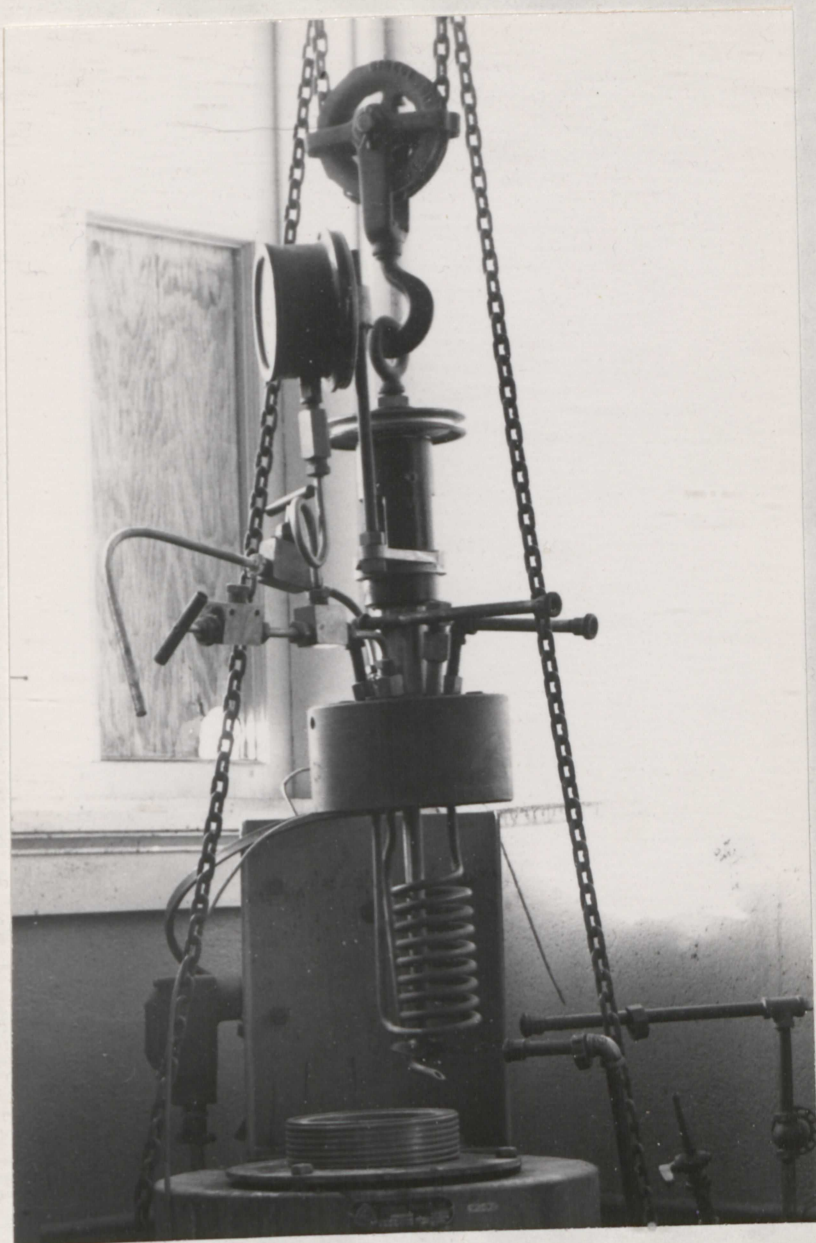
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X-RAY



AUTOCLAVE



LABORATORY TESTS

<u>Experiment</u>	<u>Test</u>	<u>Reagent</u>	<u>Time</u>	<u>Temp. F.</u>	<u>Pressure</u>	<u>Rec.</u>	
1	1	150 gms Na_2CO_3	1 hr.	212	0	0	
	2		1 hr.	380	195	0	
	3		1.5 hr.	500	680	0	
2	1	150 gms Na_2CO_3	1 hr.	300	100	0	
	2	75 gms NaNO_3	1 hr.	400	250	0	
	3		2 hr.	400	250	0	
	4		4 hr.	400	250	0	
	5		6 hr.	400	250	0	
3	1	10 N. NaOH	1 hr.	300	67	0	
	2		1 hr.	360	150	0	
	3		4 hr.	440	380	0	
4	1	200 gms NaOH	4 hr.	300	67	0	
	2	100 gms Na_2CO_3 30 gms NaNO_3	12 hr.	360	150	0	
	3		17 hr.	400	320	0	
5	1	150 gms Na_2CO_3 10 gms Na_2O_2	-----Discarded-----				
6	1	150 gms Na_2CO_3 2 gms Na_2O_2	4 hr.	250	70	0	
	2	25 psi O_2	1.5 hr.	350	200	0	
7	1	150 gms Na_2CO_3	4.5 hr.	250	30	0	
	2		1.5 hr.	350	130	0	
8	1	150 Na_2CO_3 20 gms NaOH	4 hr.	250	30	0	
	2	20 gms Na_2O_2	3 hr.	350	130	0	

<u>Experiment</u>	<u>Test</u>	<u>Reagent</u>	<u>Time</u>	<u>Temp. °F.</u>	<u>Pressure</u>	<u>Rec.</u>
9*	1	200 gms Na ₂ CO ₃ 20 gms Na ₂ O ₂	6 hr.	350	130	0
10	1	10 N. NaOH	24 hr.	300	67	0
	2		48 hr.	300	67	0
	3		72 hr.	300	67	0
11	1	10 N. NaOH	24 hr.	360	150	0
	2		48 hr.	360	150	0
	3		72 hr.	360	150	0
12	1	10 N. NaOH 20 gms Na ₂ O ₂	24 hr.	300	67	0
	2		48 hr.	300	67	0
	3		72 hr.	300	67	0
13	1	10 N. NaOH	24 hr.	500	680	0
	2		36 hr.	500	680	0
	3		72 hr.	500	680	0
14	1	10 N. NaOH 30 gms Na ₂ O ₂	24 hr.	360	150	0
	2		48 hr.	360	150	0
	3		74 hr.	360	150	0
15	1	10 N. NaOH 20 gms KMnO ₄	36 hr.	500	680	0
	2		72 hr.	500	680	0
	3		96 hr.	500	680	0

* X-Ray analysis was run on the sample before and after leaching.

ANALYTICAL PROCEDURE

The standard analytical method for determining chromium in chromite required too much time for its use in this series of experiments. Therefore, a simplified method developed by G. Fredrick Smith and C. A. Getz, was adapted as the standard analytical procedure. Jerry D. Murphy used this same procedure and also developed a method for assaying solutions for chromium. Murphy's method for solution analysis proved quite accurate and was used throughout this work.

The solutions and apparatus required for this analysis are:

Chromite Solvent - 8 parts of 95% sulfuric acid and 3 parts of 85% phosphoric acid.

Oxidation Solution - 2 parts of 72% perchloric acid and 1 part of distilled water.

Standard Titrating Solution - 0.05 N. ferrous sulfate and 0.10 N. ceric sulfate.

Indicator - 0.025 M. solution of ferrion.

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

Special Apparatus - Digestion flask still head.

Detailed Procedure for a Mineral

Grind the sample to pass minus 100 mesh and dry for two hours at 105° C., take between 100 and 150 milligrams of the sample and put in a dry 500 milliliter Erlenmyer flask. Add 10 milliliters of chromite solvent and swirl vigorously at once to get the sample in suspension and overcome the strong tendency of the material to form a cake and stick to the flask. Adjust the refluxing still head in the neck of the flask and heat to gentle boiling, 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 solution. In swirling the hot flask, a laboratory metal clamp can be 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 anchutz thermometer, suspended from a platinum wire, in the solution in the flask and heat until the solution temperature has reached 210° C., and hold for five minutes. 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, and at the end of five minutes should be totally orange. If not all orange, continue until the orange color is attained.

Remove the flask from the source of heat, cool for a minute, add about 70 milligrams of potassium permanganate, and swirl the flask 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 through the still head. The solution will have a cherry red color at this point.

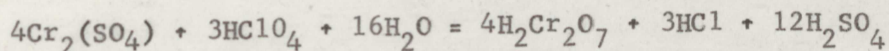
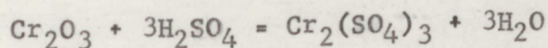
Remove and rinse the still head and thermometer and rinse the flask walls. Add about twenty-five milliliters of dilute hydrochloric acid (1 to 3), heat to a gentle boil and boil five minutes after the disappearance of the permanganate. The solution now will be light yellow in color.

Cool the solution to room temperature (either fast or slow cooling) and add 40 milliliters of dilute sulfuric acid (1 to 1). The solution is now ready for titration with ferrous sulfate solution of approximately 0.05 N. strength. Add three drops of ferrion indicator and titrate to the complete reduction of chromium as indicated by the appearance of a definite pink coloration.

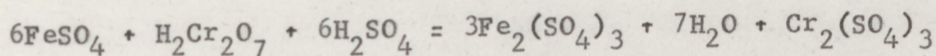
An orange color appears towards the end of the titration. One or two drops of the titrating solution is required to reach the end of the titration from this point. From the measured volume of ferrous sulfate required, the per cent of chromium or chromic oxide present may be calculated.

Using this method, a sample can be assayed in less than twenty minutes after it has been ground and dried.

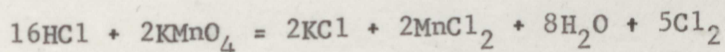
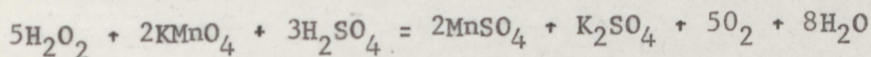
Chemical Equations: This analytical procedure is based on the following chemical reactions:



Titration



Side Reactions



Calculations

Cr₂O₃

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

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

Cr

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

$$\text{Percent Cr} = \frac{\text{Grams Cr}}{\text{Sample Weight}} \times 100$$

Modified Procedure for Solution Obtaining Leaching

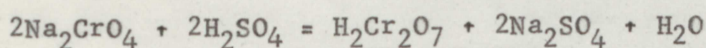
A method for analyzing solutions was developed by J. D. Murphy and this method proved very useful for analytical work throughout this research.

Detailed Procedure

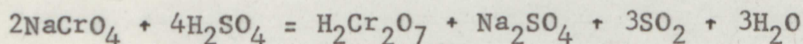
"Accurately measure two milliliters of the solution containing sodium chromate or sodium chromite into a clean 500 milliliter beaker. Add 10 milliliters of chromate solvent, and stir until the solution is orange in color. This will be only a matter of seconds. Dilute with 100 milliliters of distilled 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."

Chemical Equations.

Chromate



Chromite



Titration

