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By Gary L. Hundley, D. N. Nilsen, and R. E. Siemens



UNITED STATES DEPARTMENT OF THE INTERIOR



**Report of Investigations 8977**

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UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

°C degree Celsius

mm millimeter

cm centimeter

pct percent

g gram

ppm part per million

h hour

# EXTRACTION OF CHROMIUM FROM DOMESTIC CHROMITES BY ALKALI FUSION

By Gary L. Hundley,<sup>1</sup> D. N. Nilsen,<sup>1</sup> and R. E. Siemens<sup>2</sup>

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## ABSTRACT

The Bureau of Mines has devised a procedure to recover chromium chemicals from low-grade domestic chromites, which contain silicon and aluminum impurity levels that are too high to permit processing by present industrial processes. The Bureau procedure consists of reacting chromite with molten sodium hydroxide (NaOH) under oxidizing conditions to form sodium chromate ( $\text{Na}_2\text{CrO}_4$ ). The reaction product is leached with methanol to remove the majority of the unreacted sodium hydroxide, then with water to remove the sodium chromate and the remainder of the sodium hydroxide. The sodium chromate product is recovered by evaporative crystallization from the aqueous solution.

This report presents results of laboratory tests to determine the optimum fusion conditions and the chromium extractions obtained from several domestic chromite concentrates. These concentrates are from a variety of sources, including the Stillwater Complex in Montana, Kanuti River-Caribou Mountain, Red Bluff Bay, Kenai Peninsula, and Kodiak Island areas in Alaska, deposits in northern California, and a nickel-cobalt laterite from southern Oregon. All of these concentrates were successfully treated by the Bureau procedure. The best chromium extractions obtained for each of these materials ranged from 69.5 to 98.9 pct.

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## INTRODUCTION

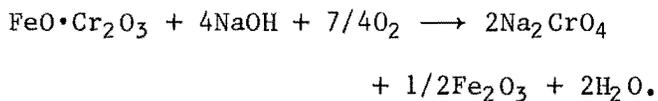
Chromium is a commodity that is essential to the Nation's metallurgical, chemical, and refractory industries. The United States has no domestic production or economic reserves of the only commercial ore of chromium, chromite, and must rely on imports to meet national needs. The chemical industry uses approximately 25 pct of the chromite consumed in the United States for the production of pigments, chromic acid for plating, and other chemicals for leather tanning, wood preservatives, catalysts, and corrosion inhibitors (1).<sup>3</sup>

Commercial processes presently used to chemically treat chromite concentrates include an oxidizing roast of the chromite with sodium carbonate and lime in a rotary kiln at a temperature of 1,100° to 1,150° C. The amount of reagents and a diluent is controlled so that the reaction mixture remains as a solid phase in the kiln (2). Concentrates that have been produced from domestic chromite deposits contain too much silicon to be processed by this method. The silicon forms molten, sticky reaction products with the sodium carbonate, which cause balls or rings of material to form in the kiln, hindering its operation. The aluminum content in domestic resources is also high, resulting in an excess consumption of reagents (3).

A simplified flowsheet for the Bureau of Mines procedure to recover chromium chemicals from low-grade domestic chromites is shown in figure 1. Briefly, the procedure consists of reacting the chromite at 550° to 650° C with an excess of molten sodium hydroxide under oxidizing conditions to produce sodium chromate. The product from the fusion reaction is solidified, crushed, and leached with methanol to remove the bulk of the unreacted sodium hydroxide. The residue from the methanol leach is leached with water to remove the remainder of the sodium hydroxide and the sodium chromate. The aqueous solution is purified by sparging

with carbon dioxide (CO<sub>2</sub>) to precipitate aluminum and silicon compounds, and then is treated with lime to remove the carbonate compounds formed during the carbon dioxide sparge. The final sodium chromate product is recovered from the aqueous solution by evaporative crystallization. The sodium chromate product from this procedure is a basic chemical used industrially, and it can be used to produce the other common chromium chemicals in commercial use.

This report describes the experimental results obtained in the first step of the Bureau process--the fusion reaction of the chromite with the sodium hydroxide. The general equation for the chemical reaction involved is shown below.



Previous work by Chandra (4) showed that an excess of sodium hydroxide must be used to maintain a fluid reaction mixture. A weight ratio of approximately 4:1 (22.4:1 mole ratio) of sodium hydroxide to chromite is typically necessary to maintain fluidity and to obtain good conversion of the chromium in the chromite to sodium chromate. Reaction products build up on the surface of the chromite particles, preventing further reaction, so the mixture must be kept well agitated to remove these surface products. Chandra used a small ball-mill-type reactor in his studies, but this type of reactor proved to be unworkable in larger sizes. A stirred-pot-type reactor was used in the present work. Studies are also being conducted in Japan on a similar procedure, using sodium nitrate (NaNO<sub>3</sub>) as the oxidizing media rather than air as used in the Bureau method (5-6).

The other major steps of the process (methanol and water leaching, solution purification, and evaporative crystallization) are currently being studied at the Bureau, and the results will be presented in a future publication.

<sup>3</sup>Underlined numbers in parentheses refer to items in the list of references at the end of this report.

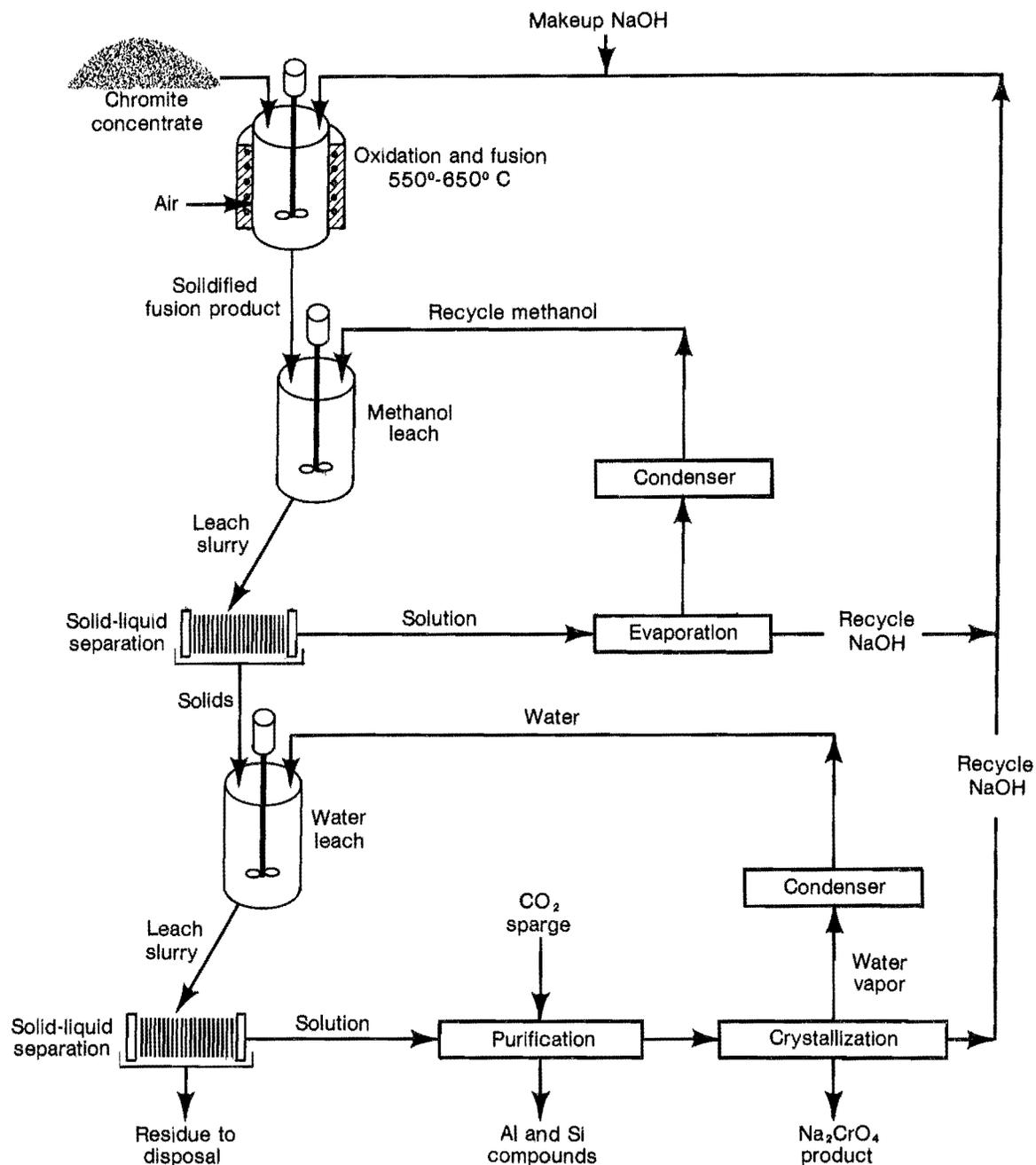


FIGURE 1. - Flowsheet for chemical processing of chromite.

#### RAW MATERIALS

The chromite concentrates tested in this study were obtained from a variety of sources in Alaska, California, Montana, and Oregon. They were categorized in one of the following groups:

1. High-chromium (metallurgical-grade) chromite that contained a minimum of 46 pct Cr<sub>2</sub>O<sub>3</sub> with a Cr:Fe ratio greater than 2.0:1.

2. High-iron (chemical grade) chromite that contained 40 to 46 pct Cr<sub>2</sub>O<sub>3</sub> with a Cr:Fe ratio of 1.5:1 to 2.0:1.

3. Marginal chromite that met either the grade or Cr:Fe ratio requirements for one of the classifications above and very nearly met the other.

4. Submarginal chromite that failed to meet the above classifications.

These classifications were obtained from Dahlin (7). All of the concentrates tested are listed in table 1 with their origin, composition, and classification of quality.

The Alaskan samples were obtained by the Bureau's Alaska Field Operations Center in a separate study to characterize potential chromite resources in Alaska. These samples were then beneficiated at the Albany Research Center, and the results are reported in the work of Dahlin (7-8). Samples of the Alaskan concentrates were selected that ranged from high-chromium, low-iron materials having a Cr:Fe ratio greater than 2.0:1 to a submarginal material with a relatively low chromium content and a Cr:Fe ratio of 0.6:1. The silicon impurity levels ranged from 1.4 to 8.0 pct SiO<sub>2</sub>.

Several samples from northern California and southern Oregon were tested. The samples from northern California were a high-chromium concentrate containing 3.0 pct SiO<sub>2</sub> and two high-iron concentrates containing 2.7 to 3.5 pct SiO<sub>2</sub>. A concentrate from southern Oregon was derived from a nickel-cobalt laterite leach residue. This material was the residue remaining after processing in the Bureau's roast-leach procedure for recovering nickel and cobalt. Beneficiation of this residue resulted in a high-iron chromite

concentrate containing 41.5 pct Cr<sub>2</sub>O<sub>3</sub> with a Cr:Fe ratio of 1.8:1 (9). The silica content of this concentrate was 1.7 pct. An additional sample from the southern Oregon area was obtained from the black sand deposits along the coast. This was a relatively low-grade high-iron concentrate with a Cr:Fe ratio of 1.2:1. The silica content of this material was low, however, at 0.75 pct.

A concentrate from the Mouat mine in the Stillwater complex in Montana was also tested. This was also a low-grade high-iron material with a Cr:Fe ratio of 1.5:1 and a high silicon content of 8.5 pct SiO<sub>2</sub>.

The impurity content of the chromites is generally of two types: gangue components associated with the chromite grains or lattice impurities in the chromite mineral itself. The silicon impurity is generally in the form of silicate minerals such as olivine (iron-magnesium silicate) and serpentine (magnesium silicate). Silicon is not present in significant quantities in the form of silica minerals such as quartz.

The chromite mineral is a spinel structure represented by the formula FeO·Cr<sub>2</sub>O<sub>3</sub>. Magnesium can substitute for the Fe<sup>2+</sup>, and Al<sup>3+</sup> and Fe<sup>3+</sup> can substitute for the Cr<sup>3+</sup> in the crystal lattice, giving a more general formula: (Mg,Fe)O

TABLE 1. - Head analyses of chromite concentrates

Location	Sample	Analysis, pct					Cr:Fe ratio	Quality classification
		Cr <sub>2</sub> O <sub>3</sub>	Fe	Mgo	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>		
Alaska:								
Baranof Island...	Red Bluff Bay.	41.7	14.3	16.9	9.2	8.0	2.0	High-Fe.
Central.....	Kanutu River..	49.5	20.4	10.7	7.4	2.6	1.7	Do.
Do.....	..do.....	46.3	14.6	16.6	10.4	5.9	2.2	High-Cr.
Kenai Peninsula..	Red Mountain..	56.4	13.7	15.2	8.8	1.4	2.8	Do.
Kodiak Island....	Halibut Bay...	53.5	11.6	17.8	8.6	4.3	3.2	Do.
Do.....	..do.....	31.4	23.8	13.6	15.8	5.0	.9	Submarginal.
Tonsina area.....	Dust Mountain.	25.1	30.4	11.1	21.8	2.2	.6	Do.
Northern California	Bar-Ric 1466..	44.6	14.9	16.7	13.8	2.7	2.0	High-Fe.
Do.....	Bar-Ric 1467..	45.6	16.7	15.5	11.5	3.5	1.9	Do.
Do.....	Wild Finn.....	57.7	13.2	17.5	7.2	3.0	3.0	High-Cr.
Southern Oregon....	Eight Dollar Mt. laterite.	41.5	16.1	12.4	22.3	1.7	1.8	High-Fe.
Southern Oregon coast.	Shepard Mine beach sands.	40.9	24.2	8.8	9.9	.75	1.2	Marginal.
Montana, Stillwater Complex.	Mouat.....	36.1	16.7	16.3	15.0	8.5	1.5	Do.

•(Al,Fe,Cr)<sub>2</sub>O<sub>3</sub>. In addition to the lattice impurities, additional iron in the form of magnetite (Fe<sub>3</sub>O<sub>4</sub>) is also

commonly associated with the chromite grains.

#### EQUIPMENT AND EXPERIMENTAL PROCEDURES

Most of the testing was conducted in a small stainless steel open-top reactor measuring 9 cm in diam by 15 cm deep. The reaction mixture was stirred with an attritioner-type mixer, and air was sparged into the mixture through two stainless steel tubes. The reactor was suspended in an electric furnace, and the contents were emptied by removing the reactor from the furnace and pouring the contents into a tray.

A larger reactor was also constructed to use in preparing larger samples for subsequent leaching studies and to compare the chromium extractions obtained in the two different-sized reactors. The larger reactor measured 15 cm in diam by 31 cm deep. This equipment contained integral heating elements around the reactor and was fitted with a bottom drain valve to empty the contents. In addition, the entire furnace could be tipped to pour the contents from the top of the reactor if desired. This reactor also used an attritioner-style mixer and contained four sparge tubes to introduce air into the reactor.

With both reactors, the desired amount of sodium hydroxide was placed in the reactor and then heated to the reaction temperature. After the desired temperature was reached, the chromite concentrate was added. The typical charge size was 100 to 150 g concentrate and 200 to 300 g NaOH in the small reactor and 10 times these amounts in the large reactor. After the reaction time had elapsed, the contents of the reactor were emptied into a pan and allowed to solidify. The product was kept in a drying oven to prevent the absorption of moisture until further processing.

The analytical procedure used to determine metal extractions is described below. The metal extractions are defined as the amount of the various metals in the chromite converted to a water-soluble form by the fusion reaction. The reactor product was crushed in a jaw crusher to

minus 3 mm and then leached with water at 15 pct solids for 2 h to determine the soluble metal content. The entire reaction product from the small reactor was leached; in the case of the large reactor, a 200-g sample was split from the crushed product and leached. The resulting leach solutions were analyzed for chromium, aluminum, silicon, sodium, and sodium hydroxide. The residue from the leach step was analyzed for chromium. The chromium extraction was determined by a material balance between the chromium in the feed material, the chromium in the leach solution, and the chromium in the insoluble residue remaining after water leaching. Silicon and aluminum extractions were determined by comparing their amount in solution with the amount in the chromite feed. A small amount of ferrous iron was also found in solution, but this oxidized to ferric iron on exposure to air and precipitated from solution. The chromium extraction values represent the amount of chromium in the chromite converted to soluble sodium chromate and are not necessarily the overall recovery that could be attained in a process.

The variables studied in this work were reaction time, temperature, sodium hydroxide-to-chromite ratio, and additives in the reaction mixtures. The sodium hydroxide-to-chromite ratio was based on the chromite content of the concentrate, not on the total weight of concentrate. Such variables as stirring rate, particle size of the chromite, and airflow rate were not studied. The agitation rate and airflow were kept the same for all tests. Early testing showed that as long as the product was well stirred and sufficient airflow was maintained, these variables did not affect the results. The concentrates were generally minus 65 mesh, although the laterite concentrate was minus 200 mesh. The particle size of the concentrates was the size necessary for liberation of the chromite mineral in the beneficiation

studies. No additional grinding or sizing of the chromite particles was performed.

Many of the concentrates tested were prepared by laboratory-scale beneficiation studies, which resulted in a limited

amount of material available for testing. Larger quantities of material were available for the Mouat, Eight Dollar Mountain, Red Mountain, and Red Bluff Bay concentrates, so these concentrates were studied more thoroughly.

## EXPERIMENTAL RESULTS AND DISCUSSION

### CHROMIUM EXTRACTION

The Mouat concentrate from Montana was tested under a variety of conditions. Reaction times from 1 to 4 h were used at temperatures of 650° and 550° C, and the sodium hydroxide-to-chromite ratio was varied from 2:1 to 6:1. The minimum sodium hydroxide-to-chromite ratio that could successfully be used with this material was 4:1. At ratios lower than this, the reaction mixture became too viscous to stir. As indicated in table 2 and figure 2, the best extractions obtained with this material averaged 92.4 pct at a 4:1 sodium hydroxide-to-chromite ratio and 91.7 pct at a 6:1 ratio. The reaction mixture was quite viscous, however, at a 4:1 ratio and would not pour out of the reactor. Consequently, a sodium hydroxide-to-chromite ratio of 6:1 would be necessary in a large-scale operation to obtain a product that will flow out of a reactor. Even at this ratio, the mixture is fairly thick and does not flow readily. The data also indicate that a reaction time greater than 2 h does not greatly increase the chromium extraction at 650° C but has a greater effect at 550° C (fig. 3).

Most of the early testing with the Mouat concentrate was conducted with sodium carbonate ( $\text{Na}_2\text{CO}_3$ ) added to the reaction mixture to reduce viscosity. This reagent is less expensive than sodium hydroxide and is the reagent used industrially to process chromites. To reduce the viscosity to an acceptable level, the amount of sodium carbonate added was equal to the weight of concentrate in the reaction mixture. Sodium hydroxide-to-chromite ratios varying from 2:1 to 4:1 were tested with this additive. Results indicated that this additive hindered the chromium extraction slightly (table 2) even though it reduced the viscosity of the reaction mixture. If the reaction mixture was too viscous at a

given sodium hydroxide-to-chromite ratio, it was found to be more beneficial to add extra sodium hydroxide to reduce the viscosity rather than adding sodium carbonate. This extra sodium hydroxide should not significantly affect the economics of the process because the unreacted sodium hydroxide is recycled back to the fusion step.

TABLE 2. - Results of chromite fusion tests, Mouat concentrate

(Small reactor unless otherwise indicated)

NaOH-chromite, wt ratio	Temp, °C	Time, h	Extraction, pct		
			Cr	Al	Si
$\text{Na}_2\text{CO}_3$ ADDITION EQUAL TO CONCENTRATE WEIGHT					
4:1.....	650	4	87.5	58.0	44.1
	650	4	87.5	56.7	46.9
	650	4	86.0	43.9	41.1
3:1.....	650	4	85.7	50.6	26.6
	550	4	67.9	33.8	46.7
2:1.....	650	4	78.9	32.4	11.2
	550	4	56.2	13.8	26.4
NO $\text{Na}_2\text{CO}_3$ ADDITION					
6:1.....	650	4	92.6	69.9	64.9
	650	4	92.4	67.8	72.9
	650	4	90.0	61.7	50.1
	650	2	88.9	67.1	81.0
	550	4	85.2	64.8	92.2
	550	4	77.9	62.6	83.0
	550	2	82.2	55.1	86.5
6:1 <sup>1</sup> .....	650	4	95.4	70.6	77.9
	650	4	94.3	81.5	80.5
5:1.....	650	4	91.7	61.3	57.6
	550	4	81.3	49.2	71.2
4:1.....	650	4	94.3	61.5	38.6
	650	4	90.5	52.0	45.2
	650	3	88.0	51.8	53.3
	650	2	85.1	50.8	54.3
	650	1	80.9	50.8	54.8
	550	4	87.0	48.1	48.5
	550	2	63.3	34.6	73.8
3:1.....	550	.5	8.3	.1	89.7

<sup>1</sup>Large reactor.

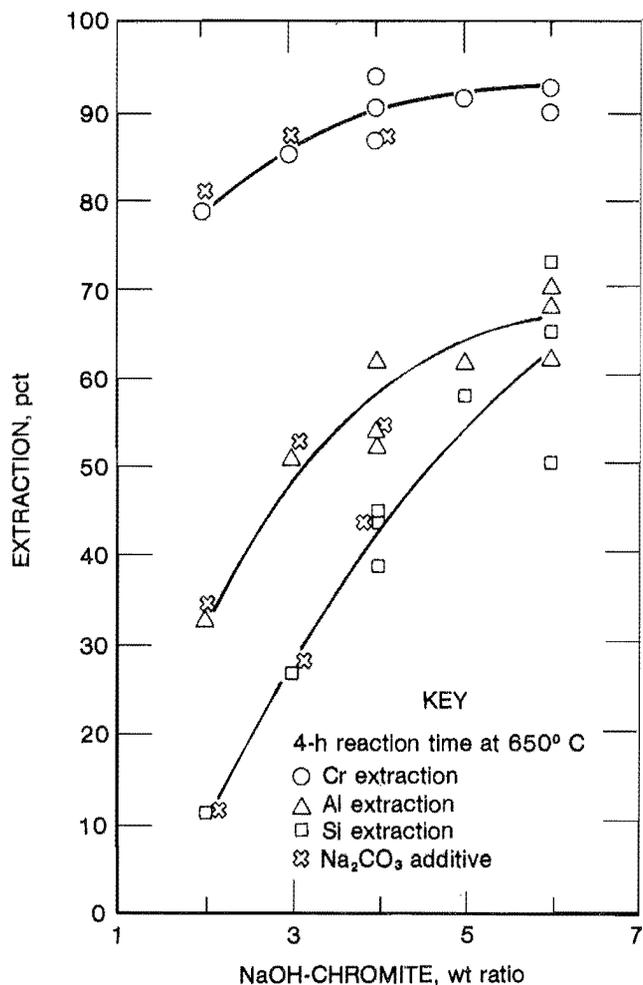


FIGURE 2. - Effect of sodium hydroxide-to-chromite weight ratio on metal extraction, Mouat chromite.

The chromite concentrate obtained from the Eight Dollar Mountain laterite leach residue is a high-iron chromite containing only 1.7 pct SiO<sub>2</sub>. The maximum chromium extraction obtained from this material in the small reactor was 93.5 pct at a sodium hydroxide-to-chromite ratio of 4:1, a temperature of 650° C, and a reaction time of 4 h. The sodium hydroxide-to-chromite ratio had very little effect on the chromium extraction (fig. 4, table 3), and the reaction mixture remained very fluid under all conditions tested. The effect of time and temperature on chromium extraction was more pronounced for the laterite leach residue than for the Mouat concentrate, as shown in figure 5 and table 3. The chromium extraction increased from 71.4 to 93.5 pct as the

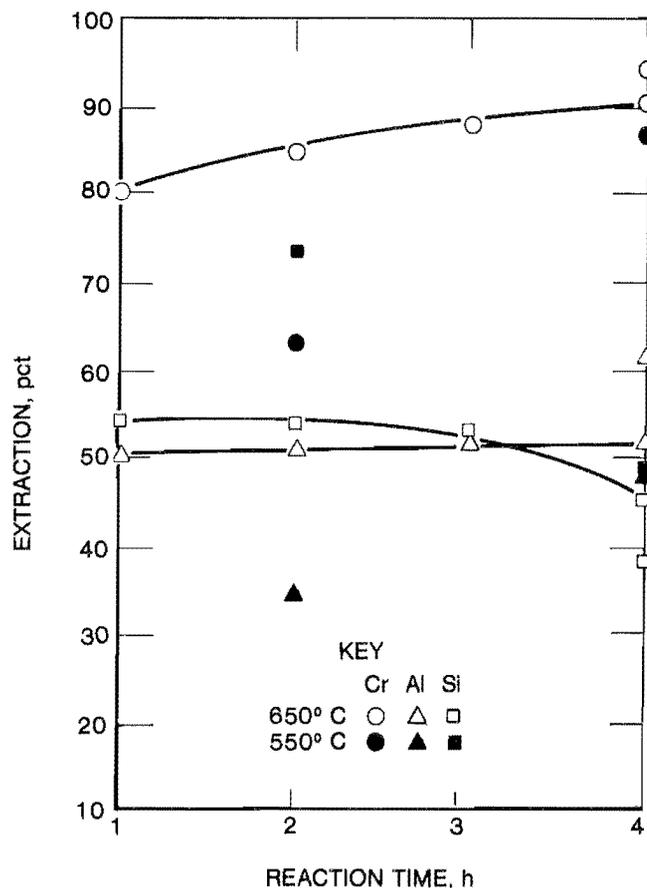


FIGURE 3. - Effect of reaction time on metal extraction, Mouat chromite. (Curves are not shown for the 550° C results because only two data points are available for each metal. The data are shown for comparison purposes.)

reaction time was increased from 1 to 4 h at 650° C. At 550° C, the chromium extraction increased from 51.2 pct to 80.1 pct as the reaction time was increased from 1 to 4 h.

The Red Bluff Bay chromite is another high-iron chromite, which contains 8.0 pct SiO<sub>2</sub>. In contrast to the effects found with the previous material, the effect of time on the chromium extraction was not very significant with this chromite, while the sodium hydroxide-to-chromite ratio was much more important (figs. 6-7, table 4). This material reacted quite rapidly, with a chromium extraction of 91.7 pct obtained after 1 h and a 94.4-pct extraction obtained after a 4-h reaction time in the small reactor. Changing the sodium hydroxide-to-chromite

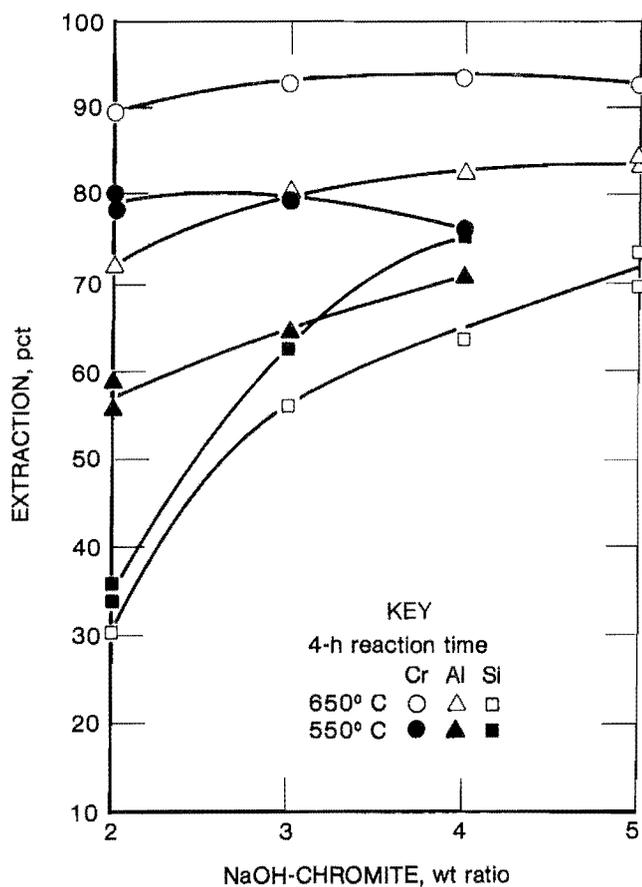


FIGURE 4. - Effect of sodium hydroxide-to-chromite weight ratio on metal extraction, Eight Dollar Mountain laterite.

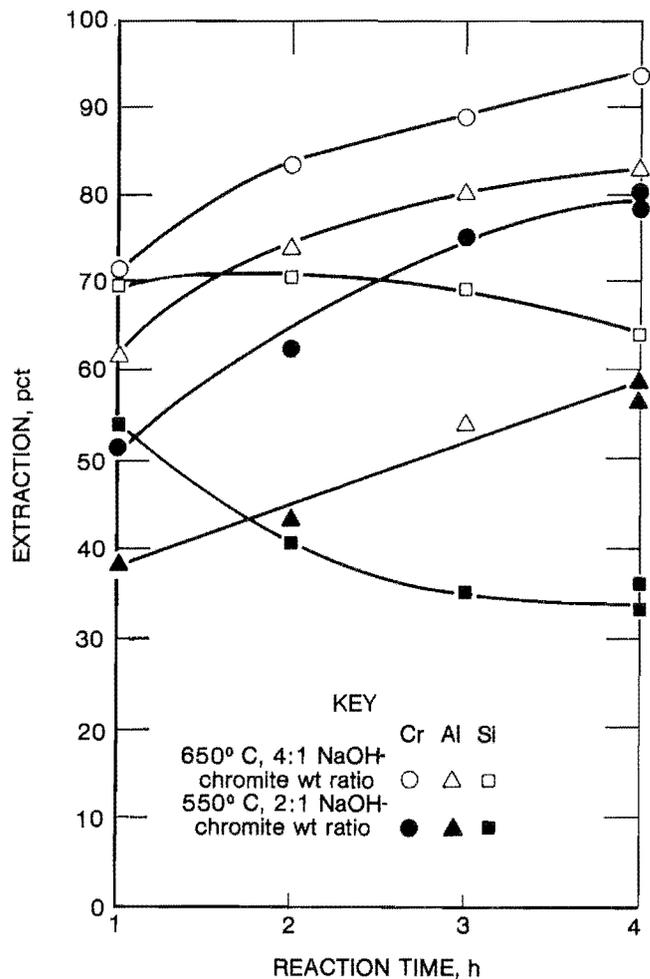


FIGURE 5. - Effect of reaction time on metal extraction, Eight Dollar Mountain laterite.

TABLE 3. - Results of chromite fusion tests, Eight Dollar Mountain laterite

(Small reactor unless otherwise indicated)

NaOH-chromite, wt ratio	Temp, °C	Time, h	Extraction, pct			NaOH-chromite, wt ratio	Temp, °C	Time, h	Extraction, pct		
			Cr	Al	Si				Cr	Al	Si
5:1.....	650	4	92.6	82.7	69.7	3:1.....	650	4	93.0	80.5	56.3
	650	4	91.8	84.5	73.4		550	4	80.0	64.7	62.5
4:1.....	650	4	93.5	82.8	63.9	3:1 <sup>2</sup> .....	550	4	69.5	54.7	67.6
	650	3	88.9	80.1	69.0	2:1.....	650	4	89.4	72.2	30.4
	650	2	83.5	73.9	70.3		550	4	80.1	56.2	35.9
	650	1	71.4	61.9	69.6		550	4	78.5	58.8	32.9
550	4	76.3	70.8	76.0	550		3	75.0	53.9	34.8	
4:1 <sup>1</sup> .....	650	4	94.7	86.6	73.9	550	2	62.2	43.1	40.5	
		550	1	51.2	38.1	53.8					

<sup>1</sup>Large reactor.

<sup>2</sup>Na<sub>2</sub>CO<sub>3</sub> added, 50 pct of concentrate weight.

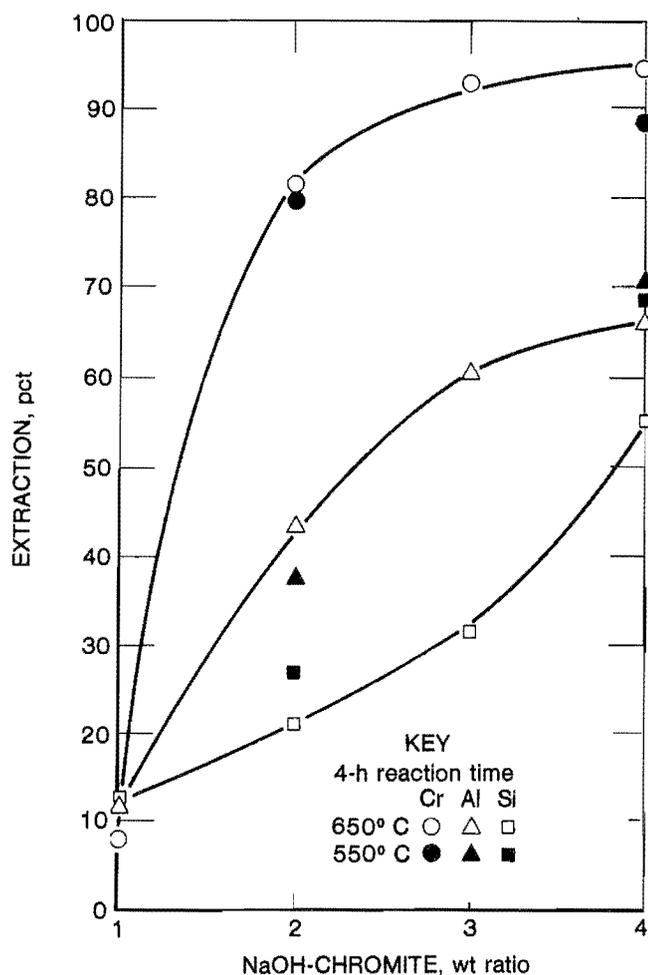


FIGURE 6. - Effect of sodium hydroxide-to-chromite weight ratio on metal extraction, Red Bluff Bay chromite. (Data points are shown for a temperature of 550°C for comparison purposes.)

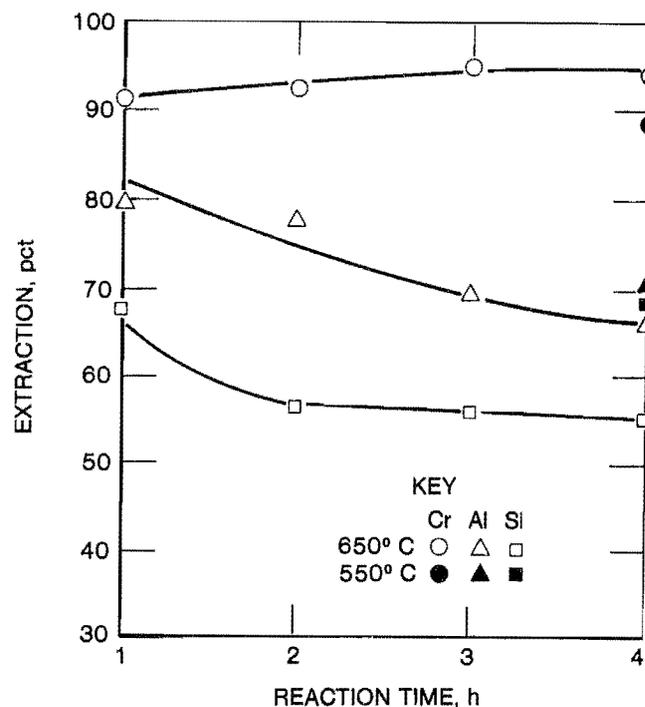


FIGURE 7. - Effect of reaction time on metal extraction, Red Bluff Bay chromite. (Data points are shown for a temperature of 550°C for comparison purposes.)

ratio from 2:1 to 4:1 increased the chromium extraction from 81.7 to 94.4 pct. This material also became less viscous as the sodium hydroxide content was increased. A ratio of 3:1 was the minimum practical amount with this concentrate because at a 2:1 ratio the reaction

TABLE 4. - Results of chromite fusion tests, Red Bluff Bay concentrate

(Small reactor unless otherwise indicated)

NaOH-chromite, wt ratio	Temp, °C	Time, h	Extraction, pct			NaOH-chromite, wt ratio	Temp, °C	Time, h	Extraction, pct		
			Cr	Al	Si				Cr	Al	Si
4:1.....	650	4	94.4	65.9	55.0	4:1 <sup>3</sup> .....	650	4	96.9	90.8	63.3
	650	3	95.0	69.5	55.9		650	4	93.0	60.7	31.6
	650	2	92.8	77.9	56.4		650	2	81.7	43.5	20.9
	650	1	91.7	80.0	67.8		550	4	79.8	37.7	26.8
	550	4	88.6	70.8	68.4		650	4	73.0	43.3	35.8
4:1 <sup>1</sup> .....	650	4	91.2	63.0	59.6	550	4	62.6	28.9	48.9	
	550	4	84.4	54.9	72.3	1:1.....	650	0.1	7.9	11.3	11.8
4:1 <sup>2</sup> .....	650	4	87.7	64.9	69.2						
	550	4	80.6	65.7	65.0						

<sup>1</sup>Na<sub>2</sub>CO<sub>3</sub> added, 50 pct of concentrate weight.

<sup>2</sup>Na<sub>2</sub>CO<sub>3</sub> added, 100 pct of concentrate weight.

<sup>3</sup>Large reactor.

mixture was very viscous and would not pour out of the reactor.

The Red Mountain concentrate is a high-grade, high-chromium material containing 1.4 pct  $\text{SiO}_2$ . A limited amount of this concentrate was available, so extensive testing was not performed. However, all conditions tested with this material resulted in chromium extractions in excess of 90 pct. Relatively mild reaction conditions (2-h fusion time at  $550^\circ\text{C}$  with a sodium hydroxide-to-chromite ratio of 2:1) resulted in a chromium extraction of 94.9 pct. More severe conditions (4 h fusion time at  $650^\circ\text{C}$  with a 4:1 ratio of sodium hydroxide-to-chromite) resulted in extractions as high as 98.8 pct (table 5). This material also stayed very fluid under all reaction conditions.

The other chromite concentrates listed in table 1 were tested under a narrow range of conditions, and the results are presented in table 5. These chromites cover the range from submarginal concentrates to high-grade, high-chromium concentrates. Chromium extractions were typically in the 50 to 78 pct range for some of the poor-grade materials, such as the southern Oregon beach sands and the Dust Mountain and Halibut Bay submarginal materials from Alaska. Chromium extractions for the high-grade materials were in the 92 to 99 pct range.

Chromium extractions in the large reactor were generally slightly higher than those obtained in the small reactor. This is shown in the results for the Mouat, Eight Dollar Mountain laterite, Red Bluff Bay, and Red Mountain tests.

The best chromium extractions obtained for each of the chromite concentrates tested is shown in table 6. The concentrates are arranged according to the chromium extraction obtained, with the best extraction listed at the top and the worst extraction at the bottom. As can be seen from this table, the general trend was for the extraction to decrease as the iron content increased. Also, a higher ratio of sodium hydroxide-to-chromite was required for good extraction as the iron content increased. As the silicon plus aluminum content increased, the viscosity of the mixture also

generally increased although this did not necessarily result in lower chromium extraction. The most notable exceptions to this trend of lower chromium extraction and high viscosity as the iron content increased were the two chromites from the Bar-Ric property in northern California. These were relatively high-grade chromites compared with the other chromites tested. However, the worst extractions were unexpectedly obtained with this material. The reason for this low extraction was not determined because only a limited amount of material was available for testing.

#### VISCOSITY OF REACTION MIXTURE

The viscosity of the fused reaction mixture ranged from almost waterlike to a pastelike consistency that would not flow out of the reactor. A quantitative measure of viscosity was not obtained in these studies, and this report will be confined to a qualitative discussion. The lower grade chromites containing a high percentage of iron or a large amount of silicon plus aluminum generally tended to result in reaction products with greater viscosity. Operating conditions resulting in very high viscosities also tended to result in somewhat lower chromium extractions. Reaction products with moderate viscosity could still result in chromium extractions in the 90-pct area, however. The viscosity of the fused reaction mixtures obtained with each concentrate are also summarized in table 6.

The iron in chromites having a low Cr:Fe ratio generally results because  $\text{Fe}^{3+}$  substitutes for  $\text{Cr}^{3+}$  in the chromite lattice. However, the high iron content in the Dust Mountain and Halibut Bay submarginal concentrates resulted from magnetite ( $\text{Fe}_3\text{O}_4$ ) coatings on the chromite grains. To determine whether such coatings affected the viscosity of the reaction mixture, magnetite was added to the Red Mountain concentrate (the reaction products of which are normally very fluid) in an amount sufficient to lower the Cr:Fe ratio from 2.8:1 to 0.8:1. This mixture was reacted at a temperature of  $650^\circ\text{C}$ , a reaction time of 4 h, and a

TABLE 5. - Results of chromite fusion tests on 10 other materials

(Small reactor)

NaOH- chromite, wt ratio	Temp, °C	Time, h	Extraction, pct			NaOH- chromite, wt ratio	Temp, °C	Time, h	Extraction, pct		
			Cr	Al	Si				Cr	Al	Si
RED MOUNTAIN						KANUTI RIVER--TABLE CONCENTRATE					
4:1.....	650	4	98.8	87.1	65.3	4:1.....	650	4	92.5	76.2	72.5
	650	2	95.2	88.9	71.4		650	2	86.6	73.1	71.4
	550	4	98.0	75.7	71.4		550	4	92.9	72.4	94.5
2:1.....	550	2	94.8	80.6	77.6	2:1.....	550	2	83.6	69.0	85.7
	650	4	92.6	65.0	27.7		650	4	89.3	64.0	39.7
	650	2	92.6	79.4	50.8		550	4	81.6	41.1	38.0
2:1 <sup>1</sup> .....	550	4	95.5	81.3	72.3	2:1 <sup>1</sup> .....	450	4	27.1	23.2	63.6
	550	2	94.9	81.8	53.8		650	4	77.8	58.4	58.7
	650	4	89.0	81.5	67.7		550	4	61.9	42.1	84.3
550	4	90.5	80.9	64.6	KANUTI RIVER--TABLE MIDDINGS						
BAR-RIC 1466						4:1.....	650	4	85.4	63.9	65.5
4:1.....	650	4	73.2	66.8	67.5		650	2	80.4	63.2	69.4
	550	4	66.6	68.5	88.9		550	4	79.5	56.4	46.7
2:1.....	650	4	65.5	56.9	50.8	550	2	74.6	56.9	80.1	
	550	4	53.3	45.7	67.5	4:1 <sup>2</sup> .....	650	4	71.7	48.9	70.4
BAR-RIC 1467						550	4	79.9	40.0	92.7	
4:1.....	650	4	68.2	59.5	69.9	4:1 <sup>1</sup> .....	650	4	69.0	50.1	74.3
	550	4	69.5	62.6	86.2	550	4	61.4	22.8	85.9	
DUST MOUNTAIN						2:1.....	650	.5	37.8	25.6	55.5
6:1.....	650	4	80.8	64.5	41.9	550	1	66.3	16.2	82.5	
	550	4	50.1	33.4	64.5	2:1 <sup>1</sup> .....	650	4	62.7	41.6	52.9
4:1.....	650	4	80.2	66.2	33.5	550	4	37.0	29.9	70.4	
	650	4	72.1	53.8	29.9	SHEPARD MINE BEACH SANDS					
	650	2	65.3	49.8	32.9	4:1.....	750	4	78.1	79.1	28.6
	550	4	46.5	33.4	49.4		650	4	52.7	52.9	48.6
HALIBUT BAY--HIGH CHROMIUM						550	4	41.8	33.3	57.1	
4:1.....	650	4	98.9	61.9	66.2	WILD FINN					
	650	2	98.3	88.2	84.8	3:1.....	650	2	97.1	92.4	77.9
	550	4	98.7	80.1	90.7		550	2	97.2	90.0	92.9
2:1.....	550	2	97.8	87.7	95.4	2:1.....	650	4	97.1	74.3	45.7
	650	2	94.6	67.7	45.3		650	2	96.8	80.3	56.4
	550	4	95.5	65.7	48.8		550	4	98.0	70.3	62.9
	550	2	93.2	62.0	50.2		550	2	96.4	77.4	63.6
	650	2	93.2	62.0	50.2		HALIBUT BAY--SUBMARGINAL				
4:1.....	650	4	77.8	36.8	67.0	HALIBUT BAY--SUBMARGINAL					
	550	4	66.4	52.0	47.9	HALIBUT BAY--SUBMARGINAL					

<sup>1</sup>Na<sub>2</sub>CO<sub>3</sub> added, 100 pct of concentrate weight.<sup>2</sup>Na<sub>2</sub>CO<sub>3</sub> added, 67 pct of concentrate weight.

sodium hydroxide-to-chromite ratio of 4:1. The reaction product became very viscous almost immediately, and the chromium extraction dropped from 98.8 pct to 82.0 pct. While this did not exactly duplicate the manner in which the magnetite was associated with the chromites, it did illustrate the effect of magnetite.

In another test, hematite (Fe<sub>2</sub>O<sub>3</sub>) was added to the Red Mountain concentrate to give a Cr:Fe ratio of 0.8:1, and the mixture was reacted under the same conditions as above. The iron in this case only increased the viscosity of the reaction product slightly and not nearly to the level caused by the magnetite. The

chromium extraction was 97.4 pct in this case, which was essentially the same value obtained without the hematite addition.

One of the major silicon-containing gangue constituents is serpentine, a magnesium silicate mineral. To test the effect of silicon on the viscosity of the reaction mixture, serpentine in the amount sufficient to raise the silica

content from 1.4 pct to 4.0 pct and to 6.5 pct was added to the Red Mountain concentrate, and the resulting mixtures were reacted. The fusion reaction product became more viscous but not nearly to the extent as that resulting from the magnetite addition. The chromium extractions were 98.9 and 96.1 pct at the two silicon levels.

TABLE 6. - Best chromium extractions obtained for each concentrate

(Small reactor)

Concentrate	Cr:Fe, wt ratio	Analysis, pct				NaOH- chro- mite, wt ratio	Cr extrac- tion, pct	Viscosity of melts <sup>1</sup>
		Cr <sub>2</sub> O <sub>3</sub>	Fe	SiO <sub>2</sub>	SiO <sub>2</sub> + Al <sub>2</sub> O <sub>3</sub>			
Halibut Bay--high Cr.	3.2	53.5	11.6	4.3	12.9	{ 4:1 2:1	98.9 95.5	Very fluid. Fairly fluid.
Red Mountain.....	2.8	56.4	13.7	1.4	10.2	{ 4:1 2:1	98.8 95.5	Very fluid. Fluid.
Wild Finn.....	3.0	57.7	13.2	3.0	10.2	{ 2:1 3:1	98.0 97.2	Fairly fluid. Fluid.
Red Bluff Bay.....	2.0	41.7	14.3	8.0	17.2	4:1	95.0	Fairly thick.
Eight Dollar Mountain laterite.	1.8	41.5	16.1	1.7	24.0	4:1	93.5	Very fluid.
Mouat.....	1.5	36.1	16.7	8.5	23.5	{ 4:1 6:1	94.3 92.6	Very thick. Thick.
Kanuti River:								
Table concentrate..	1.7	49.5	20.4	2.6	10.0	4:1	92.9	Fairly fluid.
Table middlings....	2.2	46.3	14.6	5.9	16.3	4:1	85.4	Fairly thick.
Dust Mountain.....	.6	25.1	30.4	2.2	24.0	{ 6:1 4:1	80.8 80.8	Fairly fluid. Very thick.
Shepard Mine beach sands.	1.2	40.9	24.2	.8	10.6	4:1	78.1	Fluid.
Halibut Bay-- submarginal.	.9	31.4	23.8	5.0	20.8	4:1	77.8	Very thick.
Bar-Ric 1466.....	2.0	44.6	14.9	2.7	16.5	4:1	73.2	Fairly fluid.
Bar-Ric 1467.....	1.9	45.6	16.7	3.5	15.0	4:1	69.5	Do.

<sup>1</sup>Qualitative measure of viscosity:

Term	Consistency indicated
Very fluid..	Water.
Fluid.....	Light household oil.
Fairly fluid	30w oil.
Fairly thick	Latex paint.
Thick.....	Molasses.
Very thick..	Paste.

## IMPURITY EXTRACTION

The major impurities that were solubilized by the fusion reaction were silicon and aluminum. A minor amount of ferrous iron was also soluble but oxidized on exposure to air and precipitated from solution. Magnesium was a major impurity in the chromite concentrates but did not become soluble to any extent. Solution concentrations were typically 1 ppm or less. As shown in tables 2 through 5 and figures 2 through 6, the aluminum extraction generally tended to follow the same trend as the chromium extraction. This would be expected because the aluminum substitutes for chromium in the chromite lattice. As the chromium was reacted, the aluminum would also be exposed and react with the sodium hydroxide.

The silicon extraction appeared to be more random, although it generally decreased with time after increasing for the first hour of the reaction. Also, as shown in tables 2 through 5 and figures 2 through 6, reaction at a temperature of 550° C often resulted in greater extractions than at 650° C. These lower extractions may be due to the formation of higher molecular weight insoluble sodium silicates as the reaction time and temperature increase. Increasing the sodium hydroxide-to-chromite ratio generally resulted in an increased silicon extraction.

### ADDITIVES TO REACTION MIXTURE

As previously mentioned in the discussion of the Mouat results, sodium carbonate was added to some of the reaction mixtures to decrease the viscosity of the fused reactants. This additive was effective in reducing viscosity but also decreased the chromium extraction. A more effective means to reduce viscosity was to add additional sodium hydroxide. Sodium hydroxide additions not only improved the chromium extractions, but this additive did not introduce an additional chemical species that would have to be separated from the sodium chromate in final recovery steps.

Sodium sulfate ( $\text{Na}_2\text{SO}_4$ ) was also evaluated as a viscosity reducing agent. Use of this additive was not pursued because it resulted in a greater decrease in chromium extraction than did the sodium carbonate additive.

The insoluble residue remaining after water leaching the fusion product from several Mouat and laterite tests was examined by scanning electron microscope (SEM)-microprobe methods. Residue from tests conducted for 1, 2, 3, and 4 h were examined. It was observed that discrete particles of a silicon-containing phase were present at the 1-hr reaction time, and as the reaction time became longer, the chromite grains were coated with a progressively thicker layer of this phase. It appears that this phase was molten at the reaction temperature and glassy on cooling.

A semiquantitative analysis of this phase indicated the approximate composition shown below, in percent:

Na...	8	Si...	6	Cr..	0.7
Mg...	9	Ca...	.8	Fe..	33
Al...	5	Ti...	.5	O...	Balance

Another phase was present that is high in iron and magnesium but low in aluminum and silicon. This material also formed coatings on the chromite grains.

In an attempt to suppress the formation of the coating on the chromite grains, and thereby increase the chromium extraction and/or reaction rate, several additives were tested in the fusion reaction. Among these additives were magnesium oxide ( $\text{MgO}$ ), calcium oxide ( $\text{CaO}$ ), aluminum oxide ( $\text{Al}_2\text{O}_3$ ), magnesium sulfate ( $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ ), calcium carbonate ( $\text{CaCO}_3$ ), and calcium sulfate ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ). None of these materials was effective, although some did decrease the viscosity of the reaction mixture slightly. The additives containing calcium also tended to decrease the chromium extractions.

## SUMMARY AND CONCLUSIONS

Laboratory-scale testing showed that low-grade domestic chromites that are not suitable for chemical processing by present commercial methods can be treated successfully by a procedure devised by the Bureau of Mines. The procedure involves reacting the chromites with fused sodium hydroxide under oxidizing conditions to form sodium chromate. The

sodium chromate is then recovered by leaching and crystallization. Chromium extractions as high as 98.9 pct were obtained from high-chromium concentrates. Marginal high-iron concentrates resulted in chromium extractions in the 90- to 94-pct range, and submarginal chromites resulted in chromium extractions in the 68- to 81-pct range.

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