

# A review of the deposits and beneficiation of lower-grade chromite

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## SYNOPSIS

This paper reviews the major deposits of lower-grade chromite in the world, and a wide variety of methods used for the recovery of chromium from them. Gangue materials in more coarsely sized ores can be separated by gravity means, whereas flotation techniques are required for finer-grained materials. However, unless there is considerable iron in the ores, physical means cannot increase the Cr/Fe ratios. Chemical techniques such as hydrometallurgical methods, chlorination, roasting and leaching, and smelting are required for this purpose.

A greater understanding of the physical properties of chromites and the chemical reactions that take place in the recovery operations is required before the recoveries from lower-grade chromites can be maximized. More efficient recovery operations can be realized if it can be shown definitively that the reduction of chromites occurs via either a gas-solid or solid-solid mechanism, for example. The effects of specific impurities on the chromite reduction reactions need to be better understood, as do reagent and pH control in the flotation of chromite.

## SAMEVATTING

Hierdie referaat gee 'n oorsig oor die belangrikste afsettings van laergraadse chromiet in die wêreld en 'n groot verskeidenheid metodes wat vir die herwinning van chromium uit sulke afsettings gebruik word. Aarsteemateriaal in die growwer ertse kan deur middel van swaartekrag geskei word, terwyl flottasietegnieke vir fynerkorrelrige materiaal gebruik moet word. Tensy daar heelwat yster in die ertse is, kan die Cr/Fe-verhouding egter nie deur fisiese metodes verhoog word nie. Chemiese tegnieke soos hidrometallurgiese metodes, chlorering, roosterling en logging, en uitsmelting moet vir die doel gebruik word.

'n Beter begrip van die fisiese eienskappe van chromiet en die chemiese reaksies wat in die herwinningsbewerkings plaasvind, is nodig om die herwinnings uit laergraadse chromiet te maksimeer. Doeltreffender herwinningsbewerkings sal byvoorbeeld moontlik wees as daar definitief getoon kan word dat die reduksie van chromiet via 'n gas-vastestof of 'n vastestof-vastestofmeganisme plaasvind. Die uitwerking van spesifieke onsuiverhede op die chromietreduksiereaksies asook reagens- en pH-beheer in die flottasie van chromiet moet ook beter begryp word.

## Introduction

Chromium is one of the most versatile and widely used elements. Its use in the metallurgical, chemical, and refractory industries is well known, and it is an essential element in the production of a wide variety of stainless steels, tool and alloy steels, nickel-chromium heating elements, and plating metals. Its widespread use in the metallurgical industry is attributed to its capability of enhancing properties such as resistance to corrosion or oxidation, creep and impact strengths, and hardenability. Chromium compounds are used extensively in the manufacture of paint pigments and chemicals, as oxidizing agents in organic syntheses, as electrolytes in chromium plating baths, and as agents for the tanning and dyeing of leather. In the form of chromite, it is used in the production of refractory bricks for the lining of high-temperature furnaces, and in the glassmaking and cement industries. There are few, if any, materials that can replace chromium economically and satisfactorily using present technology. Owing to these factors, chromium is considered a strategic material, a point that has been emphasized in a NMAB report<sup>1</sup>.

Before the early twentieth century, chromium from Maryland, Pennsylvania, Virginia, Turkey, and the Ural Mountains in Russia was used to supply the limited demands of the chemical industry. From that time, the demand increased substantially to satisfy the newly emerging metallurgical and refractory industries.

The world reserves of chromium are concentrated in the Eastern Hemisphere in over 20 countries (Fig. 1),

most of the producing countries containing limited reserves. Although chromium occurs in a variety of minerals, chromite ( $\text{FeCr}_2\text{O}_4$ ) is the sole commercial source.

Chromites can be classified on the basis of their Cr/Fe ratio. The highest-grade chromites<sup>2,3</sup> are those having a Cr/Fe ratio of more than 2.0 (usually approximately 2.8) and those containing a minimum of 46 to 48 per cent  $\text{Cr}_2\text{O}_3$ . These metallurgical-grade chromites occur in significant quantities in South Africa, Zimbabwe, and the U.S.S.R. Chemical and refractory-grade chromites typically have Cr/Fe ratios ranging from 1.4 to 2.0. Chemical-grade (high-iron) chromites contain large amounts of iron, which often results in Cr/Fe ratios of close to 1.0 (the ratios are usually from 1.5 to 2.1), although the absolute amount of contained chromium ranges from 40 to 46 per cent  $\text{Cr}_2\text{O}_3$ . However, it should be pointed out that South African high-carbon chromium is produced mainly from Transvaal chromite with a Cr/Fe ratio of approximately 1.5. Low-grade chromites are those that have low Cr/Fe ratios and contain relatively small amounts of chromium. Refractory-grade chromites contain relatively large quantities of  $\text{Al}_2\text{O}_3$  (greater than 20 per cent) and have  $\text{Cr}_2\text{O}_3 + \text{Al}_2\text{O}_3$  levels of more than 60 per cent. This paper concerns all classes of chromite except metallurgical grades.

The world-wide demand for primary chromium is expected to increase at an annual growth rate of 3.4 per cent from 1975 to 2000. The total demand for primary chromium in 2000 is forecast at 4 800 000 t (5 300 000 sh. t)<sup>4</sup>. Although world reserves of high-grade ores can meet this demand, these ores are often located at great distances from highly industrialized areas. Accordingly, demand for more readily available lower-grade chromite ores increases annually as the higher-grade ores become

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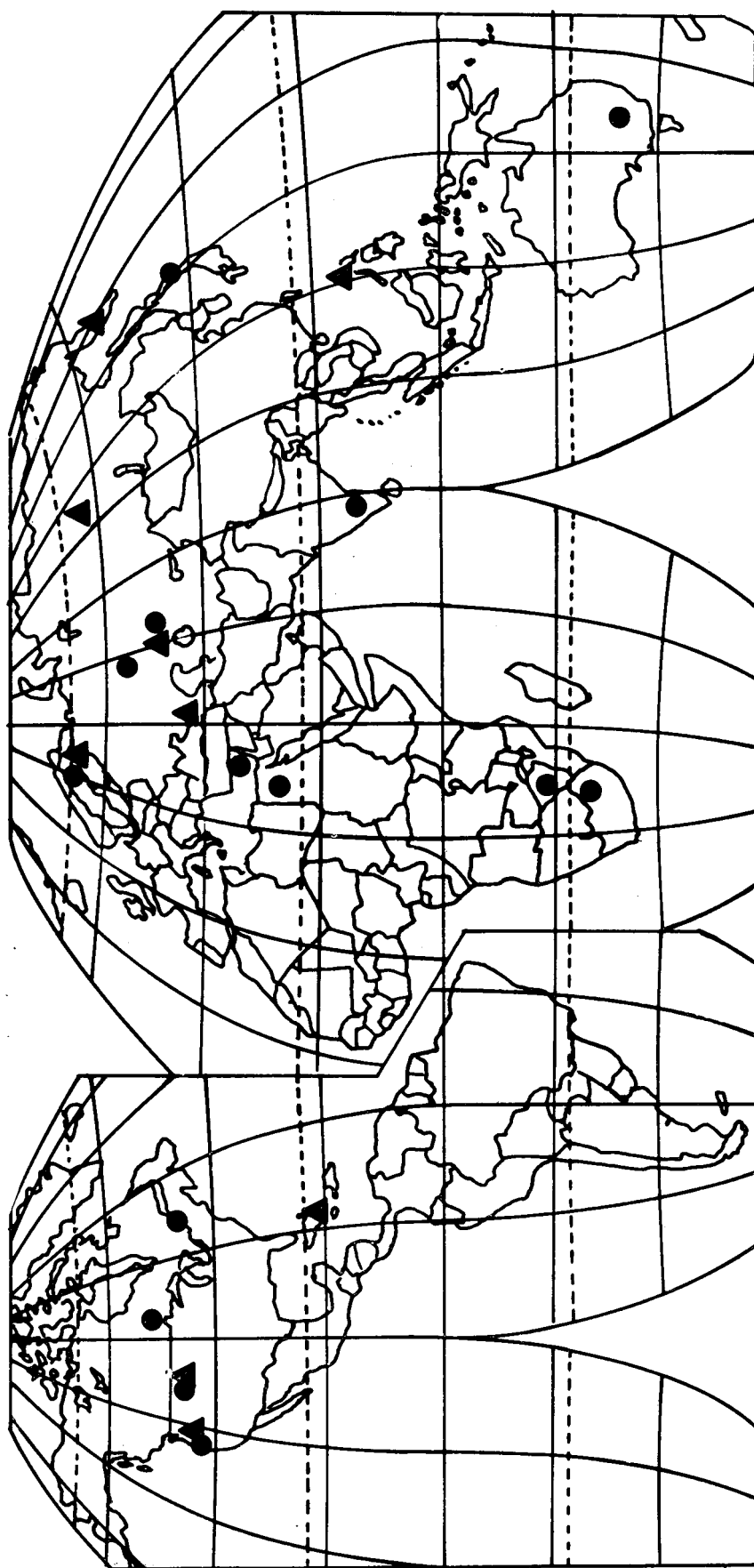


Fig. 1—Significant deposits of chromium in the world  
 ● Chemical-grade (high-iron) chromite  
 ▲ Refractory-grade chromite

TABLE I  
WORLDWIDE CHROMITE ORES (IN MILLIONS OF SHORT TONS)\*

Country	Chemical grade			Refractory grade			Total lower-grade ores
	Reserves	Other	Total	Reserves	Other	Total	
South Africa . . . . .	1 100	2 200	3 300	—	—	—	3 300
Zimbabwe . . . . .	56	56	112	—	—	—	112
U.S.S.R. . . . .	1,1	2,2	3,3	11	11	22	25,3
Finland . . . . .	11	5,6	16,6	—	—	—	16,6
Greenland . . . . .	—	11	11	—	—	—	11,0
Philippines . . . . .	—	—	—	4,5	2,2	6,7	6,7
Brazil . . . . .	3,9	2,2	6,1	0,2	0,1	0,3	6,4
United States . . . . .	—	5,6	5,6	—	0,1	0,1	5,7
India . . . . .	2,2	2,2	4,4	—	—	—	4,4
Malagasy Republic . . . . .	1,1	2,2	3,3	—	—	—	3,3
Canada . . . . .	—	2,8	2,8	—	—	—	2,8
Cuba . . . . .	—	—	—	0,3	1,1	1,4	1,4
Greece . . . . .	—	—	—	0,05	0,05	0,1	0,1

\* Data from reference 4, except for Canada (from reference 5).

depleted, and economic and efficient methods for the recovery of chromium from lower-grade ores are receiving more attention. With present technology, most of the low-grade ores cannot compete with the higher grades. An estimate of the world's lower-grade chromite ores is given in Table I, which was derived from surface geology and information on reserves, and indicates only orders of magnitude for comparative purposes.

The objects of this paper are to review methods for the recovery of chromium from lower-grade chromite ores, and to assess means whereby the recovery of chromium can be maximized from these deposits. A survey of the major lower-grade chromite deposits in the world and a review of the recovery methods used on them are included.

## United States of America

### Chromite Deposits

All the chromite deposits in the U.S.A. are relatively small and most are of lower grade. Being generally located in Alaska, Montana, Oregon, and California, a further complication is their distance from consuming

plants. As most of the podiform deposits in Alaska and California contain metallurgical-grade chromite, these are not discussed here.

The largest deposit in the United States lies in the coastal beach sands of south-west Oregon. Although relatively extensive, these deposits, which can be classified as high-iron deposits, are very low-grade and would require extensive beneficiation (Table II). The beach sands contain quartz, olivine, pyroxene, ilmenite, rutile, zircon, garnet, chromite, magnetite, hornblende, and epidote<sup>2</sup>.

The second most-extensive chromite deposit in the United States lies in the Stillwater Complex in south-central Montana. From the typical compositions of the concentrates produced from this deposit (Table II), it can be seen that they are either of chemical (high-iron) or refractory grade<sup>6,7</sup>.

A refractory-grade chromite deposit lies in east-central Oregon in Grant County, south-east of the town of John Day. The chromite occurs in belts of peridotite and dunite, which have largely been altered to serpentine. A representative chemical analysis is given in Table II.

TABLE II  
REPRESENTATIVE COMPOSITIONS OF CHROMITES IN THE U.S.A. IN MASS PERCENTAGES

Deposit	Cr <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	FeO	CaO	MgO	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	Cr/Fe	Footnote
Oregon coastal beach sands . . . . . (Shepard deposit)	9,40	*	14,1	8,10	3,50	14,4	34,8	0,59	†
Stillwater Complex, Montana:									
Mouat mine . . . . .	34,0	5,89	15,2	0,67	19,1	12,5	11,4	1,46	‡
Benbow mine . . . . .	46,1	*	24,1	NA	5,43	23,8	1,02	1,68	‡†
Gish mine . . . . .	46,0	3,87	18,4	0,04	11,2	19,4	0,28	1,85	‡†§
Grant County, Oregon . . . . . (Chambers mine)	37,8	0,8	14,6	0,3	15,2	27,0	1,9	2,17	† Δ
Seiad Creek area, California:									
Emma Belle <sup>8</sup> . . . . .	20,0	*	11,4	1,21	34,4	4,40	26,0	1,54	
Seiad Creek <sup>8</sup> . . . . .	18,3	*	11,3	3,40	30,4	5,34	27,2	1,42	°

NA = Not available.

\* Total iron as FeO.

† Dr George H. Reynolds, personal communication, 1977.

‡ Concentrate, ore contains more than 20 per cent Cr<sub>2</sub>O<sub>3</sub> by mass.

§ 0,18 per cent MnO and 0,50 per cent TiO<sub>2</sub> by mass.

Δ 0,3 per cent TiO<sub>2</sub> by mass.

° Average of 2 samples<sup>8</sup>.

One of the few chromite deposits in California that are not considered to be of metallurgical grade is that in Siskiyou County, near Seiad Creek in the extreme northern portion of the state. The ore is disseminated in serpentinized dunite. Associated minerals include olivine with chlorite, limonite, quartz, feldspar, kammererite, serpentine, calcite, epidote, orthopyroxene, actinolite, mangetite, and rutile. An examination of typical chemical analyses of the ore from two prospects (Table II) shows that this ore can be classified as chemical grade (high-iron).

Minor low-grade, widely scattered deposits also exist in Washington, Wyoming, North Carolina, Maryland, and Pennsylvania. Some of these were mined in the early twentieth century, but this is no longer economically feasible.

### *Beneficiation*

During World War II, the beach-sand deposits in Oregon were gravity-concentrated by tabling or by the use of Humphreys spirals. Some of these concentrates were further beneficiated by magnetic separation after drying, but the recoveries of approximately 65 per cent were considered low<sup>2</sup>. The concentrate contained from 40.4 to 41.9 per cent  $\text{Cr}_2\text{O}_3$  by mass, and a Cr/Fe ratio averaging 1.59 was obtained. Flotation techniques could not be recommended owing to the low recoveries (57 per cent). The best flotation concentrate contained 36 per cent  $\text{Cr}_2\text{O}_3$  by mass.

Considerable beneficiation work was conducted on the chromites from Montana over several decades. Early work by the Bureau of Mines focused on the roasting of the ore under strongly reducing conditions with carbon at 1300°C to reduce the iron, which was soluble in dilute  $\text{H}_2\text{SO}_4$  while most of the chromium was insoluble. In pilot-scale reduction experiments with coke, Cr/Fe ratios of 2.4 were obtained after leaching with acid<sup>9</sup>. At lower temperatures, the Cr/Fe ratio was greater than 3, and a deep bed was preferred. An increase in the carbon contents raised both the soluble iron and the soluble chromium. The Cr/Fe ratio of the leached residue increased to a maximum when increasing amounts of carbon were used, but then decreased as more carbon was added<sup>9</sup>.

Hunter and Paulson<sup>10</sup> conducted laboratory-scale reduction experiments with graphite on chromite from the Mouat Mine, starting the reduction at approximately 1150°C. A reduction of nearly 50 per cent was achieved slightly above 1300°C, while approximately 80 per cent was obtained at 1450°C. The evaluation of several carbonaceous reductants on the Mouat chromite showed that coal char yielded the most reduction between 1100 and 1300°C, whereas metallurgical coke was the preferred reductant<sup>7</sup> at 1400 and 1500°C. The same relationships applied with respect to the degree of metallization. The rate of reduction was greatest during the first 15 minutes, and higher temperatures increased the degree of reduction and metallization.

The Bureau of Mines conducted extensive smelting tests on Mouat chromite. In one series of tests, the chromite was smelted with either a sub-bituminous coal or a char made from that coal, the carbon-to-chromium

ratio of the charge being 1.02 for each test<sup>11</sup>. In another series of tests, in which the carbon-to-chromium ratio was varied, decreases in the ratio resulted in lower chromium and iron recoveries in the metal, lower yield, and lower Cr/Fe ratios in the metal. An acceptable ferrochromium could be prepared having an average Cr/Fe ratio of 1.32, and higher Cr/Fe ratios were obtained when the smelting operation was conducted on a silica (acid) hearth<sup>11</sup>.

Further smelting tests showed that Mouat chromite can be used for the production of acceptable ferro-alloys, although the Cr/Fe ratio could not be improved. It was found that approximately 130 per cent of the stoichiometric carbon requirement to reduce the chromium and iron appeared to be optimum<sup>12</sup>. This work also demonstrated that low-carbon ferrochromium-silicon can be prepared by a two-stage process that involves the addition of silica after an initial direct smelting step, its reduction to silicon with sufficient reductant, and melting to produce low-carbon ferrochromium-silicon.

In another study, iron was reduced selectively from chromite by carbothermic reduction in an electric-arc furnace. The use of basic slags resulted in better chromium recovery in the slag, and higher Cr/Fe ratios were obtained with acid slags<sup>13</sup>. Experiments were also conducted to remove much of the iron by the chlorination of mixtures of carbon and chromite. Higher temperatures produced greater Cr/Fe ratios, and additions of  $\text{CaF}_2$  improved the ratios. The upgraded slags were smelted in an electric-arc furnace to produce high-carbon ferrochromium containing up to 65 per cent Cr. Coke and hogged wood were used as reductants in these tests.

In a few smelting tests conducted on the chromite ores of central Oregon, low-carbon ferrochromium-silicon was produced in a two-step process as previously described. A recovery of up to 85 per cent Cr was realized. However, higher chromium recoveries were obtained by the smelting of the ores than by gravity concentration of the ores and smelting of the concentrate<sup>14</sup>. These chromites were judged to be suitable for the production of refractory brick with appropriate additions of  $\text{MgO}$ .

Methods for the utilization of chromite from Seiad Creek are described by Hunter and Sullivan<sup>8</sup>. Initially, an average of 86 per cent Cr was recovered in the sink product (35 per cent  $\text{Cr}_2\text{O}_3$  by mass) from sink-float tests. Tabling resulted in concentrates containing at least 49 per cent  $\text{Cr}_2\text{O}_3$  by mass, but the recoveries were low (33 to 45 per cent). The recoveries were improved (to 73 per cent) when tabling and electrostatic separation of the table middlings were used. The chromite can be selectively concentrated by flotation in the presence of slimes. Concentrates containing up to 45 per cent  $\text{Cr}_2\text{O}_3$  by mass were recovered, the Cr recoveries ranging from 83 to 91 per cent. Somewhat higher  $\text{Cr}_2\text{O}_3$  levels were obtained with lower recoveries when a combination of flotation of the minus 200-mesh fraction and electrostatic precipitation of the plus 200-mesh fraction was used. Magnetic separation resulted in lower chromium recoveries and  $\text{Cr}_2\text{O}_3$  contents. The results of smelting tests on the ore showed that a higher-carbon ferrochromium containing 47 to 51 per cent Cr could be prepared, with Cr recoveries as high as 86 per cent. Smelting of the

TABLE III  
ANALYSES OF REPRESENTATIVE SOUTH AFRICAN CHROMITES IN MASS PERCENTAGES

Deposit	FeO	Fe <sub>2</sub> O <sub>3</sub>	Cr <sub>2</sub> O <sub>3</sub>	Cr/Fe	CaO	Al <sub>2</sub> O <sub>3</sub>	MgO	MnO	SiO <sub>2</sub>	Reference
Union Corporation† . . . . .	26,4	*	47,2	1,57	NA	14,9	9,4	0,14	0,3	18
Moreesberg . . . . .	20,7	*	30,5	1,30	NA	16,9	10,8	NA	15,4	
Bushveld Complex, Steelpoort Seam:										
Winterveld mine, Transvaal .	16,8	7,9	42,9	1,58	0,5	14,1	12,4	NA	4,7	
Winterveld mine, Transvaal .	†	28,3	43,6	1,51	0,2	15,4	8,6	0	1,2	19
Winterveld mine, Transvaal .	24,6	*	44,3	1,59	0,4	16,1	11,2	NA	2,3	20
Kroondal ore, Transvaal . . . .	16,4	6,21	35,3	1,41	1,27	12,7	13,2	0,18	13,0	15
Grootboom ore . . . . .	25,0	*	42,4	1,49	0,09	15,7	9,5	NA	6,0	5

NA = Not available.

\* Total iron computed as FeO.

† Total iron computed as Fe<sub>2</sub>O<sub>3</sub>.

‡ TiO<sub>2</sub> = 0,5 per cent by mass.

sink-float concentrates with hogged-wood waste yielded a high-carbon ferrochromium containing 52 to 58 per cent Cr with a Cr recovery of 72 per cent. The energy requirements were lower when the concentrates were smelted than when the ore was smelted. Commercial-grade ferrochromium was produced by a combination of concentration and smelting<sup>8</sup>.

### Republic of South Africa

#### *Chromite Deposits*

The large Bushveld Complex in South Africa is a major world source of chromium, having estimated<sup>15</sup> reserves of up to 10 billion tons\*. The Complex is located in the north-eastern portion of the country in the Transvaal, north of Pretoria. The chromite deposits in the eastern portion of the Complex occur in a layered sequence of mafic to ultramafic rocks, which contain olivine, pyroxenes, and plagioclase<sup>16</sup>, the layers being up to 18 m thick. Most of the Bushveld chromite is classified as chemical-grade (high-iron), and representative analyses are presented in Table III. Thin seams of chromite also occur in the Merensky Reef<sup>17</sup>.

#### *Beneficiation*

In an investigation<sup>18</sup> aimed to improve both the grade and the Cr/Fe ratio of a chromite ore from Moreesberg (Table III), samples were crushed to minus 14 mesh and gravity-separated. One sample was separated into four size fractions, portions of which were mixed with coal (in the proportions 4 to 1) and reduced at 1200 and 1300°C. The metallic phase was removed by 10 per cent sulphuric acid. Increases in temperature and time, and/or decreases in particle size, resulted in increases in the Cr/Fe ratio but also decreases in chromium recovery. The chromium recoveries and Cr/Fe ratios were best at short time intervals. The fine particle size necessary for liberation made removal of the metallic phase by gravity separation unsuccessful. Corrosion tests to remove metallic iron with brine solutions, sea water, and ammonium chloride solutions were equally ineffective. Leaching of iron in a ferric salt solution was partially successful.

\* This and subsequent references to tons in this paper are to short tons.

Since chromite is weakly magnetic, it cannot be separated from the metallic phase by magnetic separation<sup>18</sup>.

Several investigations have been conducted to determine the reducibility of South African chromites as a function of temperature and composition<sup>3,5,10,19-22</sup>.

When Hunter and Paulson<sup>10</sup> reduced beneficiated Transvaal chromite with graphite in the temperature range 940 to 1600°C in a horizontal-tube furnace under argon, reduction began at 1150°C and reached over 80 per cent above 1300°C. The chromite reduction was affected by temperature, ferric iron and alumina contents, and ferrous iron content, in that order.

Rankin<sup>5,21</sup> investigated the reduction of beneficiated Kroondal ore thermogravimetrically (Table III) with graphite under an argon or carbon monoxide atmosphere. With graphite and temperatures of up to 1200°C, he found that iron formed first, followed by an impure Cr<sub>2</sub>O<sub>3</sub>. At higher temperatures, the formation of iron was followed by that of Fe<sub>3</sub>C and (Fe, Cr<sub>7</sub>C<sub>3</sub>). The initial metallic iron was eventually converted to Fe<sub>3</sub>C, and the chromite spinel gradually transformed to MgAl<sub>2</sub>O<sub>4</sub>. A similar reaction sequence occurred when carbon monoxide was used as the reductant. These results suggest Transvaal chromite is reduced through carbon monoxide, an interpretation supported by microstructural evidence that the initial reduction occurred at the edges of the chromite particles (topochemical<sup>5</sup>).

Dewar and See<sup>20</sup> conducted reducing experiments on chromite from the Winterveld mine (Table III) using chars, coke, coal, and graphite as reducing agents in a thermogravimetric furnace. In the 1h tests, 35 to 45 per cent reduction occurred at 1500°C, whereas negligible reduction occurred at 1350°C, the reduction mechanisms being independent of the type of reductant used. The rates of reduction increased with increased reactivities of the reducing agents towards carbon dioxide. In the later stages of reduction, the reduction was influenced both by the above factors and by the fixed-carbon content of the reducing agent.

Another sample of chromite from the Winterveld mine (Table III) was subjected to a series of reduction tests at 1200 to 1500°C<sup>19,22</sup>. Observations showed a topochemical reaction, but other mechanisms may operate over such a wide temperature range. Up to 1500°C, Urquhart believed that the reduction of this

Transvaal chromite ore occurred via a solid-state reaction with a solid reductant.

Cohen and Yalcin<sup>3</sup> conducted experiments on a South African chromite (Table III) using chromium as a reducing agent. The advantages claimed for this process are that only the iron oxide is reduced, the reduction is exothermic, and the product is carbon-free and not otherwise contaminated by the reductant. Chromite and chromium (17,5 per cent by mass) were briquetted and heated to temperatures between 700 and 1100°C for 1h. Total iron reduction was possible only at temperatures above 1050° C. It was found that the amount of chromium reductant influences the time required to complete the reduction reaction, approximately 17,5 per cent chromium being optimum; thorough mixing is necessary to maintain the chromium losses at a minimum, the iron can be leached subsequently with sulphuric acid, and the resulting concentrates can be used for the production of chromic oxide. Low-carbon ferrochromium can also be produced but, as a result of the advent of the argon-oxygen decarburization (AOD) process, this product is not required.

Zimbabwe

The reserves of high-iron chromites in the Transvaal and Zimbabwe constitute probably the greatest resource of chromium known in the world. In Zimbabwe, the chromites occur as seams in the Great Dyke, an extensive layered intrusion extending NNE-SSW for almost the length of the country and consisting of four ultrabasic complexes. Associated minerals include pyroxenes, olivines, and plagioclase<sup>23</sup>. Chromite occurs as the dominant phase in the chromite seams and as disseminated crystals in the olivine-bearing rocks. Intrusions of chromiferous peridotite also occur in the Selukwe area in central Zimbabwe. Most of the mines in this area yield metallurgical-grade chromites, the average analyses of the high-iron ore from Mount Claims and the Great Dyke being given in Table IV.

Hunter and Paulson<sup>10</sup> conducted laboratory-scale reduction experiments with graphite in a horizontal-tube furnace under argon to determine the degree of reduction possible as a function of temperature and chromite composition. They found that temperatures of at least 1400°C were required to obtain a significant degree of reduction, most of the reduction occurring between 1400 and 1500°C. This chromite was more difficult to reduce than the other chromites tested (Stillwater, Transvaal, U.S.S.R.). The Zimbabwean chromite concentrate tested contained more ferric iron than the others.

U.S.S.R.

Chromite Deposits

Major chromite deposits in the Soviet Union occur in the Ural and Caucasus Mountains, in central and eastern Siberia, and in Kamchatka, Chukotka, and Sakhalin. All of the ores are contained in ultramafic massifs in folded rocks, the most important deposits being located in the Ural Mountains<sup>25</sup>. These ores are associated with peridotite rocks in which harzburgites predominate. The primary minerals include olivine, orthopyroxene, and accessory chromium spinel (chromite). The chromites, which are low in iron but contain considerable amounts of Al<sub>2</sub>O<sub>3</sub>, are classified as refractory-grade. Typical average analyses are given in Table V. The chromites of the Urals are associated with serpentinized dunites, and ferruginous chromium-picotites occur in troctolites (Table V). Metallurgical-grade chromite ores occur in the south-east but, being high-grade ores, are not considered in this paper. Several other areas in the Soviet Union contain chromites with less alumina and/or higher iron levels, and some can be considered to be chemical-grade chromites. Among these are deposits of the Shorzha massif in Armenia, near Lake Sevan (in peridotites and dunites) and ores in the Saranovsk massif on the western slopes of the Ural Mountains (in dunites).

Beneficiation

Sobieraj and Laskowski<sup>26</sup> investigated the flotation responses of a Russian chromite (Table V, last column) in 10<sup>-4</sup> M solutions of sodium laurate and dodecylammonium hydrochloride. The tests were conducted on a minus 0,2 plus 0,075 mm size fraction in a modified Hallimond tube with conditioning and flotation times of 5 min at an air flow of 5 l/h. Nearly 100 per cent recovery was realized with sodium laurate in a pH range of 2,5 to 8,5, and approximately 65 per cent recovery was obtained at pH values of 10 to 12. With the dodecylammonium hydrochloride, complete recovery was attained in a pH range of 5 to 12. Comparisons with other chromites indicated that the differences in flotation response were due to variations in the composition of the gangue minerals. Ionic and molecular adsorption is believed to be responsible for the flotation capabilities of sodium laurate, whereas an electrostatic interaction between mineral and collector is suggested from the work with dodecylammonium hydrochloride.

The presence of aluminum in refractory chromites affects the flotation of chromite depending on the pH. For pH ranges between 2,5 and 4,5, no decrease in recovery was observed. However, for pH values between

TABLE IV  
ANALYSES OF REPRESENTATIVE CHROMITES IN ZIMBABWE IN MASS PERCENTAGES

Deposit	FeO*	Cr <sub>2</sub> O <sub>3</sub>	Cr/Fe	MnO	Reference
Great Dyke . . .	19,1-23,0	51,7-53,9	2,06-2,38	NA	23
Mount Claims . . .	25,5	41,6	1,52	0,89	24

NA = Not available.                      \* Total iron as FeO

TABLE V  
AVERAGE ANALYSES OF U.S.S.R. CHROMIUM-BEARING ORES IN PERCENTAGES<sup>25,26</sup>

	Chromites from harzburgites	Chromium picotites from troctolites	Chromites from dunites	Chromites from Shorza massif	Chromites from Saranovsk massif	Chromites of unspecified origin
Cr <sub>2</sub> O <sub>3</sub> . . . . .	38,9	35,0	37,5	47,5	40,6	41,8
Fe <sub>2</sub> O <sub>3</sub> . . . . .	2,5	5,2	4,9	5,2	7,5	4,4
FeO . . . . .	15,3	20,4	11,3	13,9	19,3	12,8
Al <sub>2</sub> O <sub>3</sub> . . . . .	27,1	25,4	27,5	13,2	16,3	23,8
MgO . . . . .	14,4	10,6	15,8	11,8	12,7	15,1
CaO . . . . .	0,0	0,0	0,0	0,6	0,1	0,8
SiO <sub>2</sub> . . . . .	1,2	2,2	1,5	2,2	2,4	1,2
Cr/Fe . . . . .	2,0	1,2	2,1	2,3	1,4	2,2
Density, g/cm . . . . .	ND	ND	4,15	ND	ND	ND

ND = Not determined.

8 and 10, the Al<sup>3+</sup> ions interacted strongly with the mineral surface. Depressed flotation occurred between pH 4,5 and 8, and activation between pH 10 and 12. This phenomenon is related to the region of stability of aluminum hydroxides and to the resulting precipitation of aluminium species on the mineral surface. It was concluded that the flotation of chromite ores should be conducted under alkaline conditions with a possible second upgrading in acid solutions.

### India

Indian lower-grade chromite ores contain up to 40 per cent Cr<sub>2</sub>O<sub>3</sub> and considerable iron, with Cr/Fe ratios ranging from approximately 1,0 to 1,8. They are usually associated with chlorite, serpentine, and magnesite or dolomite, and are typically hard and fine-grained<sup>27</sup>. The ores can be considered to be of chemical grade and are located in Karnataka (Mysore State).

The Indian chromites can be concentrated by conventional ore-dressing techniques owing to the difference in relative density between the ore and the gangue materials. However, chemical means are necessary to increase the Cr/Fe ratio substantially. The optimum method of concentration<sup>27</sup> is determined by the particle size of the ores.

Several techniques to decrease the iron content of the concentrates have been evaluated. One method involved the decomposition of the ore either with an alkali or with an acid. Sodium chromate or dichromate was produced in the alkali process, and these compounds were subsequently reduced to chromium oxide<sup>28</sup>. The acid process involved pressure leaching with concentrated sulphuric acid, which yielded a basic chromium sulphate that could be decomposed into the oxide.

Another technique involved the reduction of the iron oxide in chromite ore with gaseous reducing agents such as hydrogen, carbon monoxide, and coke-oven gas<sup>9,29</sup>. Coke-oven gas was used on Indian ores to obtain a Cr/Fe ratio of 3 and a chromium recovery of 80 per cent. The ore was roasted for 1h at 1100°C and then leached with 10 per cent sulphuric acid for 1 h<sup>30</sup>.

Solid-state carbon reduction to preferentially reduce the iron in the Indian chromites, followed by sulphuric acid leaching, was attempted on a laboratory scale<sup>27,31</sup>. The Cr/Fe ratio of the ores ranged from 1,01 to 1,33. In one investigation, ore briquetted with a 1 per cent

dextrin binder and coke was heated to 1300°C, and the reduced product was leached with 10 per cent boiling sulphuric acid for 1h to yield a product with a Cr/Fe ratio of 3. The use of a 5 per cent NaCl binder improved the solid-state reduction process when graphite, charcoal, and coke were employed. Selective reduction was conducted at 1150°C for 2,5 h and subsequently at 1350°C for 0,25 h. The same leaching solution was used to obtain a product with a Cr/Fe ratio ranging from 2,7 to 3.

In a two-stage reduction process using a 25 kV·A electric furnace, 80 per cent of the stoichiometric carbon requirement was smelted with Indian chromite ore having a Cr/Fe ratio of 1,0. A chromium-rich slag with a Cr/Fe ratio of 2,7 was obtained when a slag basicity of 0,9 was used, although this variable had a minor influence on the chromium recovery<sup>27</sup>. In the second stage, the slag was smelted to produce a high-carbon ferrochromium. The economics of the process are dependent on the cost of electric power.

Athwale and Altekar<sup>32</sup> investigated the chlorination of chromite with hydrochloric acid using a fluidized-bed technique. Improvements in the Cr/Fe ratio were noted but the economics on a large scale are unknown.

### Canada

#### Chromite Deposits

Major chromite deposits in Canada are located in British Columbia, south-eastern Manitoba, Ontario, Quebec, and Newfoundland. The lower-grade ores contain a relatively large amount of iron, and therefore possess a low Cr/Fe ratio and are classified as chemical-grade. One of the largest single chromite deposits in North America is located in south-eastern Manitoba (Bird River). The ores include epidote and serpentine, in addition to an impure chromite (Fe, Mg)O (Cr, Al, Fe)<sub>2</sub>O<sub>3</sub>. An average grade of approximately 11,5 Cr<sub>2</sub>O<sub>3</sub> (7,8 per cent chromium) has been estimated<sup>33</sup>. Concentrates containing approximately 44 per cent Cr<sub>2</sub>O<sub>3</sub> should be possible, based on mineralogical examinations, and should contain approximately 21 per cent iron, yielding a Cr/Fe ratio of 1,5.

#### Beneficiation

A variety of physical methods, such as sink-float, jigging, tabling, magnetic separation, and flotation, have been employed on Bird River ores. The resulting Cr<sub>2</sub>O<sub>3</sub>

contents ranged from 36 to 42 per cent, with iron contents ranging from 19 to 24 per cent. This yields Cr/Fe ratios ranging from 1,1 to 1,5, which is insufficient for most metallurgical applications.

Several pyrometallurgical and hydrometallurgical methods have been devised to remove iron and gangue materials from Bird River chromite ores in order to increase the Cr/Fe ratio. An oxidation and reduction technique was developed to prepare a high-grade chromium oxide that would be added to the concentrate to achieve metallurgical-grade specifications<sup>34</sup>. Soda ash was added to the chromite to produce sodium chromate, followed by aqueous dissolution of the chromate. Filtration removed the iron-bearing residue, and a high-grade chromium oxide was produced by evaporation, crystallization, and reduction of the chromate (Na<sub>2</sub>CrO<sub>4</sub>) with coke. The chromium recovery was approximately 90 per cent of the chromium in the concentrate. When the high-grade chromium oxide was mixed with the lower-grade chromite concentrate in a 2:1 ratio, the resulting product assayed 57 per cent Cr<sub>2</sub>O<sub>3</sub> and 13 per cent Fe, yielding a Cr/Fe ratio of 3:1.

Smelting of the chromite concentrate with lime, silica, and coke in an electric-arc furnace produced iron and a chromium-containing slag<sup>34</sup>. The chromic oxide was recovered by water classification from the disintegrated slag. Although the Cr/Fe ratio was approximately 20, the overall chromium recoveries ranged from 30 to 77 per cent.

Leaching of the finely ground chromite concentrate with a 30 per cent sulphuric acid solution at 200 to 250°C and elevated pressure, followed by cooling, filtration, washing, and calcining at 1000°C, resulted<sup>34</sup> in a product containing 43,6 per cent Cr<sub>2</sub>O<sub>3</sub> with a Cr/Fe ratio of 3,17. The chromium recovered was about 96 per cent of the chromium in the concentrate.

Other methods<sup>34</sup> included leaching of the chromite with sulphuric acid and chromic acid at 140 to 160°C to produce CrO<sub>3</sub> after oxidation and evaporation in a diaphragm cell. This procedure yielded a product with 90 per cent CrO<sub>3</sub>, and the chromium recovery was approximately 75 per cent of the chromium in the ore. Bird River chromite concentrate can be roasted in a kiln at 1200°C or higher with carbon, or at 1000 to 1100°C with reducing gases (e.g. hydrogen, methane, natural gas), followed by atmospheric leaching of the calcine in 10 per cent hot sulphuric acid. The iron was dissolved selectively, and any Cr/Fe ratio can be obtained as a function of the amount of iron dissolved. A series of tests yielded a concentrate with 43,2 per cent Cr<sub>2</sub>O<sub>3</sub> and a Cr/Fe ratio of 2,82. The recovery was approximately 90 per cent of the chromium in the original concentrate.

More-recent investigations have emphasized the direct production of chromium metal, carbides, and sodium chromates. The Ontario Research Foundation reduced Bird River chromite with carbon in the solid state<sup>35</sup> between 1025 and 1425°C to produce chromium carbide. The carbide (Cr<sub>7</sub>C<sub>3</sub>) is recovered as a magnetic fraction and contained 40 per cent chromium, 35 per cent iron, and 5,2 per cent carbon. High-grade chromium carbides can also be prepared from sodium chromate and carbon at temperatures from 1000 to 1270°C in a nitrogen

atmosphere<sup>36</sup>. The carbide can be used to produce chromium metal or can be employed as an alloying addition. Ferrochromium can be prepared direct<sup>37</sup> from Bird River chromite concentrate by reduction of chromite-carbon pellets in a methane-hydrogen mixture at 800 to 1050°C. Solid-state reduction of chromium carbides with chromium oxide at temperatures ranging from 1300 to 1750°C or the reduction of sodium dichromate with carbon can produce sponge chromium metal<sup>36</sup>. High-purity sodium chromate can be prepared from an acidified solution that causes precipitation of alumina and silica<sup>35,36</sup>.

Canadian chromite-ore fines having a Cr/Fe ratio of 1,7 with 45,3 per cent Cr<sub>2</sub>O<sub>3</sub> and 23,2 per cent FeO were melted in an extended arc flash reactor (EAFR), which employs an indirect arc to melt metal and slag by radiation from a soft diffuse plasma that is derived from gas introduced through axial holes in graphite electrodes<sup>38</sup>. The advantages of this system over conventional submerged-arc processes are that low electrical resistivity of the slag is not a factor for efficient processing, there is no sharp temperature gradient in the bath, fluid slags are more easily obtained, the composition and size of the charge are less critical, a higher-quality product is obtained, and slag-metal reactions are enhanced. Chromite ore fines were mixed with appropriate reductants and flux additives and heated to approximately 800°C in a preheater, the iron oxide in the charge being reduced in a reactor column at temperatures of 1600 to 2000°C. Alternatively, the ore can be fed through the preheater without a carbon addition. Anthracite in the hearth produced the required reducing gases. Ferrochromium metal containing an average of 56 per cent chromium, 28 per cent iron, and 7,7 per cent carbon was obtained. This molten metal could be charged direct to an AOD unit or vacuum furnace for decarburization, and appropriate scrap and alloy additions made to produce stainless steel. However, on a laboratory scale, the energy consumption was three times higher per unit mass than that realized in conventional operations.

Cuba

Cuban chromite ores contain considerable Al<sub>2</sub>O<sub>3</sub> (25 per cent) and are therefore classified as refractory-grade materials. A typical analysis is given in Table VI. The ores occur in peridotites and are associated with dunites, troctolites, and harzburgites in the Majari-Baracoa region.

Sobieraj and Laskowski<sup>26</sup> conducted flotation tests on a Cuban chromite using procedures and equipment similar to those previously described for the beneficiation of Russian chromites. The results were similar to those

TABLE VI  
ANALYSIS OF A CUBAN CHROMITE IN MASS PERCENTAGES<sup>26</sup>

Cr <sub>2</sub> O <sub>3</sub>	39,8
Fe <sub>2</sub> O <sub>3</sub>	6,4
FeO	9,5
CaO	0,3
MgO	17,4
Al <sub>2</sub> O <sub>3</sub>	25,2
SiO <sub>2</sub>	1,1
Cr/Fe	2,3



TABLE VII  
TYPICAL ANALYSIS OF RUN-OF-MINE CHROMITE ORE FROM TROODOS,  
CYPRUS, IN MASS PERCENTAGES

Cr <sub>2</sub> O <sub>3</sub>	31,7
Fe <sub>2</sub> O <sub>3</sub>	14,5
FeO	13,1
Cr/Fe	1,07
CaO	4,5
MgO	11,2
Al <sub>2</sub> O <sub>3</sub>	9,8
SiO <sub>2</sub>	14,3
TiO <sub>2</sub>	0,3
MnO	0,2

obtained with the Russian material. Maximum chromium recovery occurred in a slightly narrower pH range (3 to 8) with sodium laurate, and at a slightly higher pH (nearly 6) with dodecylammonium hydrochloride than that achieved with the Russian chromite. The behaviour of both these refractory chromites was generally similar, although the Russian chromite exhibited better flotation properties at pH values ranging from 10,5 to 12.

### Cyprus

Podiform chromite deposits are located in dunites in the Troodos area of the island of Cyprus. These ores contain massive and disseminated chromites<sup>39</sup>. A typical analysis of run-of-mine ore is given in Table VII. The Troodos chromites can be classified as high-iron chromite ores.

Preliminary tests on this ore were designed to recover a maximum amount of massive ore in the feed while simultaneously minimizing the size reduction<sup>39</sup>. The recovery of the massive chromite was accomplished by two heavy-medium drums, and one heavy-medium cyclone separator was used to recover chromite grains down to 1 mm. Liberation, followed by grinding, jigging, and screening, was used, and the fine fraction was taken for final treatment. The fine fraction was recovered on diagonal shaking tables. This procedure provided an overall Cr<sub>2</sub>O<sub>3</sub> recovery of 93 per cent and a recovery of massive coarse chromite of more than 80 per cent. The coarse, 'intermediate', and fine concentrates contained 48 to 49 per cent Cr<sub>2</sub>O<sub>3</sub> by mass, giving a Cr/Fe ratio of 2,75. Although this is a satisfactory concentrate, it was not accomplished without some disadvantages. These included the use of low-capacity and bulk shaking tables, some costly handpicking, and a relatively slow feed rate owing to the size of the ore.

### Egypt

#### Chromite Deposits

Barramya chromite ore is located in the Eastern Desert, approximately 130 km west of Marsa Alam. It is a high-iron podiform deposit, and typical chemical analyses of the ore are presented in Table VIII (samples 1 and 2). Chromite [(Mg, Fe)O (Cr, Al, Fe)<sub>2</sub>O<sub>3</sub>] constitutes 60 to 70 per cent of the ore, with serpentine comprising much of the remainder (20 to 30 per cent)<sup>40,41</sup>. Minor amounts of magnetite and chromium-bearing silicates, such as kammererite and uvaronite, are also present. The analyses of another Egyptian chromite ore with similar mineralogy are also given in Table VIII (sample 3). This ore also contains small amounts of

chromium silicates such as kammererite and uvaronite<sup>42</sup>.

#### Beneficiation

Barramya chromite was concentrated on a shaking table to separate the lighter silicate minerals from the chromite minerals. The results for sample 1 (Table VIII) showed that higher feed rates and water flowrates decreased the recovery and quality of the chromite. Optimum motor speeds of 370 r/min and a deck slope of 4 degrees from the horizontal yielded the greatest recovery of chromites<sup>41</sup>. Cleaning was conducted on the table concentrate and middling, which resulted in concentrates containing 51,2 and 43,8 per cent Cr<sub>2</sub>O<sub>3</sub>, respectively. These concentrates are suitable for the production of ferrochromium and chemical applications, respectively. Similar tabling operations for sample 2 (Table VIII) yielded a concentrate containing 36,0 per cent Cr<sub>2</sub>O<sub>3</sub>, which is suitable for refractory applications. Experiments using a cross-belt high-intensity separator were conducted in an attempt to remove most of the iron and gangue materials in the concentrates. The optimum main-belt speed was found to be approximately 6 m/min at a current of 1 A. These variables gave a Cr<sub>2</sub>O<sub>3</sub> content of 54,6 per cent, with a recovery of 69 per cent and a Cr/Fe ratio of 3,4. Smaller particle sizes increased the Cr<sub>2</sub>O<sub>3</sub> content of the concentrate. In chlorination experiments to increase the Cr/Fe ratio, various amounts of carbon were added to reduce the iron and chromium oxides and chlorine gas was allowed to react with the ores<sup>40</sup>. Preliminary tests indicated that fine-grained ore chlorinated most satisfactorily, and that a gas flowrate of 3 l/g per hour was optimum. Four times the stoichiometric carbon requirement was found to provide the maximum degree of chlorination. Higher temperatures (up to 800°C) and times of reaction (up to 5 h) increased the degree of chlorination.

Laboratory-scale beneficiation work on the second Egyptian chromite was directed towards depression of the serpentine and trapping of magnetite in a flotation cell. Deslimed feed was added to the magnetoflotation apparatus (a flotation cell positioned between the poles of a C-shaped magnet). Selective flotation of chromite using dilute hydrofluoric acid to obtain a pH of 5,5, Na<sub>2</sub>SiF<sub>6</sub> as a serpentine depressant, oleic acid in kerosene as a collector, and pine oil as a frother resulted in a concentrate with a Cr/Fe ratio of 3,2 and a Cr<sub>2</sub>O<sub>3</sub>

TABLE VIII  
ANALYSES OF EGYPTIAN CHROMITE ORES, IN MASS PERCENTAGES

	Barramya Ore		
	Sample 1	Sample 2	Sample 3
Cr <sub>2</sub> O <sub>3</sub>	38,2	35,5	40,2
Fe <sub>2</sub> O <sub>3</sub>	5,6	5,3	*
FeO	9,1	21,3	18,7
Cr/Fe	1,9	1,3	1,9
CaO	4,1	5,8	4,3
MgO	21,0	10,5	8,0
Al <sub>2</sub> O <sub>3</sub>	18,5	9,0	18,2
SiO <sub>2</sub>	7,2	10,4	9,5
Reference	38	39	40

\* Total iron given as FeO

recovery of approximately 57 per cent. A Cr/Fe ratio of only 2,5 was obtained without use of the magnetic field<sup>42</sup>. However, high magnetic field intensities are detrimental for grade and recovery.

Finland

The chromites of the Kemi district in Finland comprise eight orebodies in association with a basic-ultrabasic plutonic intrusion. Chromium in the ores typically ranges from 16,8 to 20,8 per cent, and iron ranges from 11,1 to 12,8 per cent. In general, the Cr/Fe ratio varies from 1,52 to 1,65, making these chemical or refractory-grade chromites. Mineralogically, the chromites are associated with serpentines, tremolite, or talc and carbonates.

Lukkarinen<sup>43</sup> summarized the results of an extensive series of tests to establish optimum conditions for the concentrating of Finnish ores. Mixed results were obtained during flotation experiments owing to the alteration of gangue minerals, which produces similar surface characteristics for different minerals. Rapid changes in ore grade and magnetic layers on fractured chromite surfaces made flotation control difficult, but gravity separation was effective in concentrating the chromite and magnetite, most of which is altered. Low-intensity magnetic separation caused the magnetite layer on chromite particles to be drawn into the concentrate, thus decreasing the chromite recovery. Fine-grained magnetite attached to silicate minerals reported to the concentrate in high-intensity magnetic separation, but the chromite recovery was improved by completion of the magnetic separation with gravity methods. The resulting middling could be ground to remove silicates from the chromite. It was found that each orebody requires its own concentrating procedures for maximum recovery.

Philippines

Refractory chromites are mined from the Masinloc mine in Zambales Province in northern Luzon<sup>44</sup>, which is one of the two largest producing mines in the Philippines. (The other produces metallurgical-grade chromite.) The chromites are located in a belt of peridotitic rock adjacent to a north-northeast-trending belt of olivine-rich gabbroic rock, which has been serpentized to some extent. The analysis, in mass (percentages), of the ore is as follows<sup>44</sup>:

Cr <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	FeO	Cr/Fe	Al <sub>2</sub> O <sub>3</sub>	MgO+CaO	SiO <sub>2</sub>
36,5	4,75	10,8	2,1	31,0	17,2	0,85

Australia

A chemical-grade high-iron chromite from Australia containing enstatite (MgSiO<sub>3</sub>), pyrope (Mg<sub>3</sub>Al<sub>2</sub>Si<sub>3</sub>O<sub>12</sub>), and hohmannite [Fe<sub>2</sub>(OH)<sub>2</sub>(SO<sub>4</sub>)<sub>2</sub>·7H<sub>2</sub>O] was the subject

TABLE IX  
ANALYSIS OF AUSTRALIAN CHROMITE IN MASS PERCENTAGES<sup>45</sup>

Cr <sub>2</sub> O <sub>3</sub>	49,4
Total Fe (as FeO)	24,7
CaO	0,3
MgO	6,5
Al <sub>2</sub> O <sub>3</sub>	9,5
SiO <sub>2</sub>	9,2
Cr/Fe	1,8

of hydrochlorination tests by Maude and Sale<sup>45</sup>. A chemical analysis of this ore is given in Table IX.

Experiments on the reduction of carbon at relatively low temperatures (approximately 700 to 1060°C) yielded only a 17 per cent reduction after 16 hours when 32,2 per cent carbon by mass was added<sup>45</sup>. At 1060°C, considerable chlorination of the chromite occurred when 49 per cent calcium chloride dihydrate (by mass) was added. At that temperature, nearly all the iron and 22 per cent of the chromium were removed from the ore. Higher iron and chromium yields than those obtained in experiments where no carbon had been added were found to be possible<sup>32</sup>. Increases in the Cr/Fe ratio can be obtained by chlorination without carbon, but carbon is required if both the chromium and the iron are to be chlorinated. The decomposition of calcium chloride dihydrate to generate HCl gas resulted in lower chromium yields than those achieved with pure anhydrous HCl, owing to the formation of β-calcium chromium oxide from the CaO decomposed from the calcium chloride dihydrate.

Other Countries

Other smaller, lower-grade chromite deposits occur in Greenland, Colombia, Brazil, the Malagasy Republic, and Japan.

Recovery of Chromium

Both surface and underground mining techniques are used to obtain raw chromite ore. Most of the podiform or lens-like deposits are surface mined, whereas the stratiform (layered) deposits such as those in South Africa and Zimbabwe are usually mined by underground methods. Specific mining techniques vary widely depending on the locality<sup>46</sup>.

Usually, chromite is cleaned by hand-sorting, washing, and screening, or by gravity concentration. Concentrates are prepared from fines or crushed lower-grade ore using jigs, tables, spirals, or magnetic separators. Gravity-separation methods predominate over flotation techniques.

The successful beneficiation of lower-grade chromite ores depends on the ore mineralogy, the size requirements of the concentrates, and the chemical composition of the ore. Gangue materials can be separated by physical methods such as gravity concentration (mainly tabling and jigging). Low-intensity magnetic separation can be used to reject the magnetite, but physical methods cannot be used to increase the Cr/Fe ratio or to separate the chromites that are present in fine intergrowths with other materials. Upgrading to yield higher Cr/Fe ratios requires pyrometallurgical and/or hydrometallurgical treatment.

Pyrometallurgical techniques are used to produce chromium alloys or additives for the metallurgical industry. Chromite ore, fluxes, and reducing agents are usually smelted in electric-arc furnaces, adjustments being made to the composition of the charge and the process variables to produce the desired ferrochromium products.

Either electrochemical or pyrometallurgical processes are used to produce chromium metal. In the electrochemical process, a solution of ferrochromium is used to produce a purified chromium-alum solution, which is

electrolysed to chromium metal. The pyrometallurgical process involves the aluminothermic reduction of pure  $\text{Cr}_2\text{O}_3$ .

A pyrometallurgical-hydrometallurgical process, which includes the roasting of chromite with sodium carbonate and lime, followed by water leaching to remove sodium dichromate and sodium sulphate, is often used. The leach liquor is purified, the sodium sulphate is removed, and the purified sodium dichromate solution is crystallized, the product being used either directly or to produce a variety of chromium chemicals.

Conventional crushing equipment is used to size-reduce chromite for refractory applications. Screening to various particle ranges follows, and specific quantities of these ranges are blended with magnesite and pressed into suitable refractory shapes.

#### Gravity Concentration

Crushing and grinding of chromite ores often result in the production of excessive amounts of fines owing to the brittle, fractured nature of the ore. These fines can be recovered only with difficulty by gravity processes. Massive and disseminated ores require the use of tables, jigs, and spirals for effective concentration.

The U.S. Bureau of Mines has for many years conducted extensive tabling tests on lower-grade chromite ores. The early work involved crushing and grinding of the ores to minus 28 mesh, hydraulic sizing of the ore, and tabling<sup>47,48</sup>. The results for ores from California, Montana, and Oregon are summarized in Table X. Magnetic separation of the gravity concentrates from the table feed was not satisfactory and failed to increase the Cr/Fe ratio. Chromium was lost primarily in a slime fraction that could not be beneficiated by either gravity or flotation methods. For the Montana ores, the degree of chromium recovery in the concentrate from the table feed was often inversely proportional to the grade.

Further research on Seiad Creek chromites showed that a considerable amount of chromium was present in the middling fractions after tabling<sup>8</sup>. Although the chromite was essentially liberated from the gangue materials,

significant amounts of either concentrates or tailings could not be prepared by repeated tabling. The chromium recoveries from tabling methods alone were relatively low (Table X).

The chromium recoveries for Stillwater chromite were higher from tabling methods (Table X), but significant amounts of chromium remained in the middling fraction<sup>49</sup>. Tabling with middling retreatment represented one of the two most satisfactory concentrating schemes.

Tabling was found to be effective on other ores containing serpentine gangue materials owing to the differences in size between the chromite and the serpentine particles<sup>41</sup>. Complete slime separation was also accomplished. Tabling is often regarded as an effective way of removing gangue materials.

The U.S. Bureau of Mines conducted jigging experiments on several samples of domestic chromites. The jigging of a plus 20-mesh fraction of a California ore containing 18,1 per cent  $\text{Cr}_2\text{O}_3$  by mass resulted<sup>47</sup> in a recovery of 77 per cent of the chromite in the product with 43,5 per cent  $\text{Cr}_2\text{O}_3$ , 8,9 per cent  $\text{SiO}_2$ , and a Cr/Fe ratio of 2,38. However, the liberation at that size was not sufficiently satisfactory to produce a low-silica product. Jigging could be an appropriate coarse beneficiation technique for other ores, such as those from the Stillwater Complex, in combination with sink-float methods.

Panning was used to separate metallics from partially reduced chromite ores that had been ground to minus 270 mesh<sup>18</sup>. Poor results were obtained, possibly due either to the lack of separation of the metallics or to the extremely fine grain size.

Heavy-liquid separations on chromite ore from Seiad Lake sized to plus 100 mesh showed that considerable coarse gangue can be rejected at a solution density of 3,32 or higher without excessive chromium losses when thalious formate solutions are used as the separation media<sup>8</sup>. Typical sink products contained 35,0 per cent  $\text{Cr}_2\text{O}_3$  by mass and 86 per cent of the chromium fed to the unit.

TABLE X  
RESULTS FROM THE TABELING OF CHROMITE ORES

Ore	Ore size mesh	$\text{Cr}_2\text{O}_3$ in ore % (by mass)	$\text{Cr}_2\text{O}_3$ reporting to concentrate %	Concentrate Cr/Fe	$\text{Cr}_2\text{O}_3$ in concentrate % (by mass)	Reference
Seiad Creek, California . . .	-20	NA	22	2,35	51,1	47*
	-20	NA	64	2,30	51,0	47†
	-28	9,1	58	1,96	52,9	46
	-48 to -200	20,0	34	2,24	49,7	5
	-48 to -200	18,3	45	2,33	49,0	5
	-65	NA	76	2,25	50,6	47*
Stillwater Complex, Montana .	-28	9,95	84	1,49	40,7	48
	-28	22,8	89	1,22	40,0	46
	-35	13,5	81	1,21	37,8	46
	-35	8,04	69	1,32	38,5	48
	-48	7,75	69	1,40	40,1	48
	-20 to -100	28,8	82	2,58	48,0	46
John Day, Oregon . . . . .	-28 to -100	24,5	74	1,69	33,8	46
	-48 to -100	20,9	68	1,50	37,6	46

NA = Not available.

\* Wet table.

† Air table.

### *Magnetic Separation*

Magnetic separation was not as satisfactory as other methods such as gravity separation and flotation for the recovery of chromium from California chromites<sup>8</sup>. The chromium recoveries did not exceed 62 per cent, and the magnetic concentrates graded from 41 to 42 per cent  $\text{Cr}_2\text{O}_3$  by mass. The limited chromite recovery may be due to the presence of a magnetite layer on the chromite particles that draws the chromite into the concentrator of a low-intensity separator. However, controlled magnetic separation can be used on table or flotation concentrates to reject the magnetite and improve the Cr/Fe ratio. Magnetic separation has also been used to eliminate most of the iron and gangue materials in table concentrates<sup>41</sup>. Slower main-belt speeds, magnetic field strengths of 1 A, and finer particle sizes improved the Cr/Fe ratios. Recoveries of up to 80 per cent chromium, Cr/Fe ratios of 3,7, and concentrates containing up to 68 per cent  $\text{Cr}_2\text{O}_3$  by mass were realized.

### *Electrostatic Separation*

Electrostatic separation at 15 000 to 20 000 V produced a high-grade chromite concentrate<sup>8</sup> containing 54 per cent  $\text{Cr}_2\text{O}_3$  by mass with a Cr/Fe ratio of 2,42. However, the chromium recovery was only 58 per cent owing to the fine material that was not treated and that was masked by adhering dust, so precluding selective separation. Combinations of tabling and electrostatic separation, or electrostatic separation and flotation, failed to improve the chromium recoveries.

Comparative electrostatic-separation experiments on sized and unsized material from Montana indicate that sizing can improve the chromium recovery<sup>49</sup>. High-tension electrostatic separation of a tabling concentrate resulted in recoveries of 86 per cent and a  $\text{Cr}_2\text{O}_3$  content of 42 per cent by mass. Ores that contain considerable serpentine do not respond well to electrostatic separation because serpentine can respond as a conductor. Some improvement resulted when electrostatic separation was conducted on tabling concentrates.

### *Flotation*

Although gravity methods are well known and widely used for the concentration of chromites, such techniques fail to recover the size fractions below approximately 100  $\mu\text{m}$ . Recovery from the fine size fractions is particularly important in finely disseminated ores. Flotation offers an alternative concentration process for the separation of the fine materials and the avoidance of chromium losses. In general, earlier results of flotation of lower-grade chromite ores were inferior to those obtained by tabling. Flotation required fine grinding, which necessitated greater slime loss and careful reagent control. Slimes were depressed by a variety of materials, and the use of a fluoride ion with an anionic (fatty acid) collector for the selective flotation of chromite ores is effective for sands, residues from gravity plants, and other deslimed ores<sup>50</sup>. However, fine-grained disseminated ores do not respond well to this technique. It was found that additional dispersing depressants were required for the gangue materials. Some ions such as iron and lead activated the chromite for flotation. Chromite could not be floated below pH 6, the prevention of flotation of the gangue materials being the major problem.

Tabling of flotation concentrates improved the results, but a recovery of only 55 per cent in a product containing 37 per cent  $\text{Cr}_2\text{O}_3$  by mass with a Cr/Fe ratio of 0,89 was obtained from one Montana ore<sup>47</sup>. With an ore from the Stillwater Complex, the recoveries were improved to 89 per cent, which was lower than those obtained by tabling treatments alone. The concentrates obtained using the most efficient size ranges contained up to 40 per cent  $\text{Cr}_2\text{O}_3$  by mass and had a Cr/Fe ratio of 1,23.

Further studies by the U.S. Bureau of Mines showed that lower-grade chromites could be selectively concentrated by flotation in the presence of slimes. Preconditioning with fuel oil permitted flotation of the chromite from the flocculated siliceous-gangue slimes. Recoveries of up to 91 per cent were realized with products containing up to 45 per cent  $\text{Cr}_2\text{O}_3$  by mass<sup>8</sup>. The Cr/Fe ratios ranged from 2,17 to 2,46. Oleic acid was used for flotation. Sodium fluoride and sulphuric acid yielded better results than dilute hydrofluoric acid when these reagents were added to free the 'flocs' from the siliceous gangue.

Flotation results have shown that the composition of the chromite phase in the ore affects the grade of the concentrate more than does the grade or the composition of the ore. This was particularly evident in work conducted on chromite ores in the north-western United States<sup>51</sup> in which cheaper collectors than oleic acid were investigated. Taggart and Arbiter<sup>52</sup> showed that fuel oil alone does not collect in many cases, and that fatty acid alone results in non-selective collection. The use of both reagents allows a neutral oil film to support a weakly anchored fatty acid. The recoveries ranged from 78 to 91 per cent, with concentrates grading from 36 to 43 per cent  $\text{Cr}_2\text{O}_3$  by mass. For the concentrates derived from north-western ores, the Cr/Fe ratios averaged 2,41. This technique was also used on Montana ores, which yielded concentrates ranging from 24 to 38 per cent  $\text{Cr}_2\text{O}_3$  by mass, with recoveries from 65 to 89 per cent.

One problem in the development of flotation techniques for chromite ores is the variability of the ores themselves. A process developed for one ore does not usually yield optimum results for another ore of different origin. It is thought that differences in the composition of the gangue materials, as well as in the composition of the chromium spinels, are responsible for these variations in flotation behaviour. Fundamental research is required to alleviate this problem. Investigations involving the flotation of a pure chromite and a pure serpentine using sodium oleate as the collector showed<sup>53</sup> that the chromite can be collected at collector concentrations of between 0,3 and 1000 mg/l. Effective flotation occurs when the collector concentration is between 10 and 100 mg/l at pH values between 3 and 11. Sodium oleate floats serpentine poorly, but appears to be an effective separator for chromite and serpentine. Metal ions such as  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ , and  $\text{Fe}^{3+}$  depress chromite and do not influence serpentine, but the depression of chromite by  $\text{Mg}^{2+}$  depends on the anions in the solution. The precipitation or chelation of such potentially harmful ions is required for selective flotation of chromite. Other collectors such as alizarin red S or hexametaphosphate in acid pulps, or sodium silicate or carbonylmethyl cellulose in alkaline media, offer no selectivity<sup>42</sup>. The best

depressant for serpentines in an acid circuit is  $\text{Na}_2\text{SiF}_6$  at pH 5.5 with oleic acid as collector. The grade of chromite can be improved by the use of a magnetic field, but high field intensities are detrimental to grade and recovery.

Among the various ions that can be present in the pulp,  $\text{Al}^{3+}$  ions exert the most influence on the flotation behaviour of refractory-grade chromites. These ions cause depression in the pH range 4.5 to 8 and activation between pH 10 and 12. The properties of the minerals apparently do not affect depression, whereas activation is influenced by the surface characteristics of the mineral<sup>26</sup>.

Amines have been used as collectors in the flotation of chromites containing olivine and serpentine<sup>54,55</sup>. It was found that serpentine could be floated in the pH range 3 to 12, olivine in neutral solutions, and chromite in acid and alkaline solutions. Amines with 8 to 14 carbon atoms were the optimum collectors. Improved flotation of chromite in the second acid step resulted from extensive conditioning of the pulp in an alkaline environment. Morawietz<sup>56</sup> found amines with 12 to 18 carbon atoms to be effective collectors for a pure chromite. Regulators including HCl, NaOH,  $\text{H}_2\text{SO}_4$ , and  $\text{H}_3\text{PO}_4$  could be used in different pH ranges. There is evidence of an electrostatic interaction between collector ions and mineral surfaces. For some chromite ores, sodium fluorosilicate was found to be an effective regulator<sup>57</sup>. Abido<sup>58</sup> showed that hydrofluoric acid also has good selectivity in the amine flotation of chromite, in contrast to sodium fluorosilicate. Again, the degree to which a given fluoride ion influences the floatability of chromite depends on the source and composition of the mineral phase.

Sommerlatte<sup>59</sup> mentions a flotation plant having a capacity of 10 000 tons of chromite concentrate per month that yielded a recovery of only 55 per cent and a concentrate with 54 per cent  $\text{Cr}_2\text{O}_3$  by mass. Tall oil, sulphated kerosene, fuel oil, and sulphuric acid were used<sup>59</sup> to reach a pulp pH of 6. Organic regulators and selective flocculants facilitated the flotation without desliming.

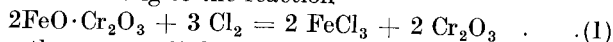
The flotation of chromite ores should be conducted in alkaline conditions with a possible second upgrading in acid solutions, owing to a high consumption of acid.

#### *Hydrometallurgy*

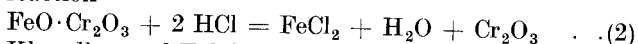
For the production of ferrochromium, the Cr/Fe ratio of the starting material should be as high as possible. Conventional methods of beneficiation such as gravity concentration and flotation can increase the metal content of chromite ores by removing gangue materials, but the Cr/Fe ratio is difficult to change since it depends on the spinel composition. To increase the Cr/Fe ratio, iron must be removed by structural dissociation of the spinel. This can be accomplished in two ways: by selective reduction of the iron oxides with carbon, gases, or chlorine at temperatures below 1350°C, followed by leaching of the metallic iron with dilute sulphuric acid; or by selective chlorination of the iron oxides using a reducing agent with chlorine or hydrochloric acid. Gaseous reduction with or without a prior oxidative roasting step has also been evaluated, and solvent extraction techniques have been employed for the recovery of chromic oxide.

#### *Chemical Upgrading*

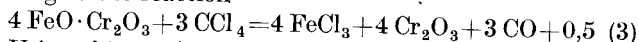
Early U.S. and British patents described the chlorination of chromium-bearing materials. In one<sup>60</sup>, iron as ferric chloride is separated by the use of a gas containing CO,  $\text{S}_2\text{Cl}_2$ , and  $\text{Cl}_2$  at temperatures ranging from 600 to 900°C according to the reaction



In other patents<sup>61</sup>, hydrochloric acid with excess hydrogen is used to upgrade chromites according to the reaction

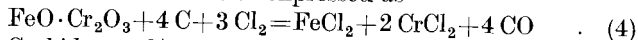


Khundkar and Talukdar<sup>62</sup> used  $\text{CCl}_4$  to chlorinate chromite ores at temperatures between 700 and 800°C according to the reaction



Using this method, they chlorinated 80 per cent of the iron and 30 per cent of the chromium in 2 h, and increased the Cr/Fe ratio more than threefold. Subsequent separation of the chlorides is required.

Reducing agents such as carbon increase the degree of chlorination of chromites, depending on the amount of stoichiometric carbon used, and the presence of carbon may cause incipient reduction of the oxides. Generally, lower oxides are chlorinated more readily. Iron oxides in the ore chlorinate more readily than chromium oxides, and from four to five times the stoichiometric carbon requirements are necessary to completely chlorinate the chromites<sup>40</sup>. The use of this amount of carbon requires a temperature of approximately 800°C for maximum chlorination. Periods from 1 to 5 h exert a minimal influence on the degree of chlorination. The overall chlorination reaction can be expressed as



Carbides and/or  $\text{COCl}_2$  can also be formed during the chlorination process. The phosgene can form at lower temperatures and decompose into CO and  $\text{Cl}_2$  at 800°C or above, which may result in less chlorination than has been observed at 900 to 1000°C. The formation of carbides would also result in more difficult chlorination conditions.

Pokorny<sup>63</sup> has shown that complete chlorination of the iron and chromium constituents in chromites can be accomplished with HCl or  $\text{Cl}_2$  at 800°C if the chromite is briquetted with a mixture of coke, pitch, and tar. Maier<sup>64</sup> used a stepwise chlorination process with briquettes of ore and carbon reductant. At 700°C,  $\text{CrCl}_3$  formed, which made the briquettes very dense, and at 800°C, some  $\text{CrCl}_3$  began to volatilize and  $\text{CrCl}_2$  appeared. Chlorination proceeded rapidly at temperatures between 900 and 1000°C. Chlorination of chromite concentrates by a fluosolids-reductive chlorination technique using coke, CO, and fluorspar increased the Cr/Fe ratios by up to ten times<sup>32</sup>. In general, the iron and chromium oxides are chlorinated in proportion to their molar ratio. Chlorination of iron oxide is favoured over chromium oxide especially when  $\text{Al}_2\text{O}_3$  is present, but also in the presence of  $\text{MgO}$ <sup>65</sup>. Maude and Sale<sup>45</sup> showed that hydrochlorination of chromite ore with carbon can be achieved at temperatures approximating 1000°C. The HCl gas was generated by the thermal decomposition of calcium chloride hydrate. This reaction produced CaO, which reacted with the  $\text{Cr}_2\text{O}_3$  in the chromite to produce

$\beta$ -calcium chromium oxide. The chromium yields were therefore lower than those obtained with pure anhydrous HCl.

#### *Pyrometallurgical-Hydrometallurgical Treatment*

Chromite ores have been roasted with  $\text{Na}_2\text{CO}_3$  to form water-soluble sodium chromates<sup>66,67</sup>. The impurities can be precipitated by adjustment of the pH, and  $\text{Na}_2\text{CrO}_4$  can be recovered<sup>66</sup> at pH 6, or  $\text{Na}_2\text{Cr}_2\text{O}_7$  at pH 3. The chromates can be reacted with carbon to form  $\text{Cr}_2\text{O}_3$  for further reduction, and  $\text{Na}_2\text{CO}_3$  can be recovered for recycling.

Chromite ores can be processed with either an alkali or an acid treatment. The alkali process consists of the production of sodium chromate or dichromate and the subsequent reduction to  $\text{Cr}_2\text{O}_3$  for blending with untreated ores<sup>28</sup>. In the acid process, pressure leaching of chromite ores with  $\text{H}_2\text{SO}_4$  yields a basic chromium sulphate that can be decomposed to  $\text{Cr}_2\text{O}_3$ . Chromium also can be obtained by  $\text{H}_2\text{SO}_4$  leaching in the presence of chromic oxide and subsequent electrolytic oxidation of the chromium sulphate to chromic acid, which can be separated by fractional crystallization. The leaching of lower-grade chromite ores produces chromic acid, which can be electrolysed to produce electrolytic chromium.

Early work by the U.S. Bureau of Mines focused on the selective reduction of iron in chromite ores with carbon, which subsequently was removed by acid leaching, leaving a chromium-containing residue<sup>9</sup>. Laboratory-scale investigations showed that finely divided chromite (minus 28 mesh), carbon, and a minimum temperature of 1200°C are required. The use of excess carbon over the stoichiometric amounts required to reduce all the iron is not recommended, although excess carbon increases the oxidation resistance of the products<sup>68,69</sup>. Pilot-scale work in an oil-fired kiln designed to minimize troublesome temperature gradients and premature reductant oxidation produced a calcine at 1395°C, which could be leached at 85 to 90°C with 8 per cent  $\text{H}_2\text{SO}_4$  to yield a residue with a Cr/Fe ratio higher than 3.

Harris<sup>70</sup> continued this approach and showed that an off-grade chromite could be reduced by the use of excess reductant, with the selective leaching action dependent on the formation of carbide. At lower temperatures such as 1150°C,  $\text{Cr}_3\text{C}_2$  is formed, together with iron or iron carbide. Acid leaching dissolves the iron and iron carbide, and the  $\text{Cr}_3\text{C}_2$  and unreduced chromite remain in the residue. At higher temperatures (1350°C),  $\text{Cr}_7\text{C}_3$  is formed. This carbide is acid-soluble and causes chromium losses in the residue. Various leaching agents were tested; the results showed ferric sulphate to be an effective substitute, with the advantages of closed-cycle leaching and a minimal disposal problem. However, the build-up of aluminium and magnesium salts in the electrolyte might pose problems. Fluxes added prior to roasting, such as borates or carbonates, increased the Cr/Fe ratios by increasing the rate and extent of reduction, but the chromium losses were excessive. Fine grinding and pelletization were beneficial by decreasing the dust losses, easing the density, and improving the handling characteristics. A treatment involving sulphating roasting and leaching with ammonium sulphate was not considered economic owing to excessive losses of ammonia

and the required crystallization steps for separation.

McRae conducted experiments in which coal was used as the reductant at 1200 and 1300°C to reduce a chromite<sup>18</sup> and the metallic phase was leached with 10 per cent  $\text{H}_2\text{SO}_4$ . The chromium recovery decreased as the Cr/Fe ratio increased in the residue. Smaller particle sizes yielded higher Cr/Fe ratios. Other leaching techniques such as rusting and the use of a ferric salt solution were attempted. Rusting with water at pH 4, brine, and seawater was unsuccessful, possibly owing to the effects of the chromium content of the metallic phase. The ferric salt solution separated some of the iron, but further research is required.

Various gases have been used to selectively reduce chromites followed by acid leaching<sup>70</sup>. Carbon monoxide gas reduced the chromites at temperatures ranging from 1130 to 1250°C, yielding a maximum Cr/Fe ratio of 3.38. A considerable amount of chromium as well as iron was reduced. However, the percentage of gas used in the reaction is low. When methane gas was used as a reductant at 1190°C, a maximum Cr/Fe ratio of approximately 2.5 was obtained. Longer roasting resulted in greater chromium and iron losses. The use of gaseous mixtures of  $\text{SO}_2$  and air in partial equilibrium with  $\text{SO}_3$  yielded only a superficial sulphation of the chromite. The best results were obtained at 470°C. Still less sulphation occurred at temperatures above 860°C.

Another process that has been investigated is roasting followed by gaseous reduction. Experiments using oxygen and wood charcoal to form CO were unsatisfactory<sup>71</sup>. However, the optimum conditions were found to include pre-oxidation with oxygen at 1200°C, followed by reduction roasting with town gas at 1175°C. Both the Cr/Fe ratio and the chromium recovery were excellent (6.4:1 and 90.9 per cent respectively). The pre-oxidation step precludes a maximum particle-size limitation. The pre-oxidation roast oxidizes the FeO to a hematite-type phase, which breaks the iron-chromium oxide bonds. Reduction then forms carbides throughout the grains rather than on the surface only. Evidently, the hematite-type phase enhances the permeability to the reducing gas and the iron oxide is reduced to iron carbide. The enriched chromium-containing phase is less susceptible to reduction, and the chromium recovery is enhanced.

In most of these investigations, the ultimate goal was to prepare suitable material for the production of ferrochromium. In some applications in the chemical industry, however, chromic oxide is the desired product. One process involves the fusion of finely ground chromite ore with sodium carbonate at 900°C for 16 hours<sup>72</sup>. The resulting sodium chromate was leached in boiling water or in a molten mixture of NaCl and  $\text{Na}_2\text{O} \cdot 2 \text{B}_2\text{O}_3$ , and an effective separation of chromium was achieved from iron and vanadium by use of the latter method. The salt phase, which contained most of the chromium, was melted under reducing conditions and reacted with boric oxide and sodium carbonate. Chromic oxide formed as a fine solid dispersion throughout the oxide phase. This treatment further decreased the iron. The borate glass containing the chromic oxide product was crushed, boiled in water, and filtered, the boric oxide being recycled. When borate glass from the first step was crushed, boiled,

and filtered, the residue was  $\text{Cr}_2\text{O}_3$  that could be combined.

#### *Electrometallurgy*

In the 1940s, the Bureau of Mines developed a new commercial method for the production of electrolytic chromium from lower-grade chromites. This technique has been the basis for nearly all the electrolytic chromium metal produced in the United States<sup>4</sup>. Small lots of room-temperature ductile chromium used for metallurgical and medical research were produced by another technique developed by the Bureau of Mines. Ductile wire for permanently irradiated implants in the treatment of cancer was produced by this method. Chromium metal produced electrolytically in fused salt baths has been used for basic research applications<sup>4</sup>.

#### *Pyrometallurgy*

In 1979, 61 per cent of the chromite consumed in the U.S.A. was used in the metallurgical industry for the production of ferro-alloys that are used primarily in the manufacture of stainless steels<sup>73</sup>. Chromium alloys or additives are produced by pyrometallurgical techniques, which makes pyrometallurgical processing one of the most important methods for the recovery of chromium values. Traditionally, chromite ore, fluxes, and reducing agents are smelted in three-phase submerged-arc furnaces. Chromite fines should be agglomerated prior to being charged into the furnace. More recently, various methods for prereduction of the chromites prior to melting have attracted considerable attention.

Pelletizing and briquetting are the two major techniques for the agglomeration of finely divided chromite ores, which represent the majority of the ores. Lankes and Boehm<sup>74</sup> have described a method for the production of pellets used as charge material for the travelling grate-rotary kiln LEPOL process. Bentonite (1 per cent) is used as a binder for the pelletization, which is conducted on a disc pelletizer. During the operation of the LEPOL process, the pellets are strengthened in the rotary kiln at temperatures ranging from 1300 to 1500°C. Excellent compressive strengths were obtained, and the pellets were judged to be completely satisfactory for smelting purposes.

The Japanese developed a similar process<sup>75</sup> using an annular vertical kiln for the firing of pellets containing 2.5 to 3 per cent bentonite by mass at 1150°C. The advantages claimed are that less area is required than for a rotary kiln, the thermal efficiency is better, and no separate preheating equipment is required. Pelletizing offers the following advantages over the use of lumpy ores: variations in the composition of the charge can be handled well, and the permeability and reactivity are better than those of lumpy ores.

South African investigators showed that additions of hydraulic binders of up to 10 per cent by mass for the pelletizing of Transvaal chromite fines resulted in pellets with very low strengths<sup>76</sup>. A bentonite binder (up to 2.5 per cent by mass) was preferred. The addition of a reducing agent in the form of char did not significantly alter the pelletizing characteristics of the ore. The firing temperature should be below the softening point of the chromite pellets.

Because pelletization requires very fine grinding and

subsequent induration at high temperatures, briquetting that involves a reductant and a binder, such as calcium lignosulphate, molasses and lime, or mixtures of these materials, has been investigated. Two South African companies now prefer briquetting to pelletization<sup>77</sup>.

Several techniques have been proposed for the reduction of chromites using gaseous reductants including carbon monoxide and mixtures of methane and hydrogen.

Basic investigations have used chromium sesquioxide with mixtures of methane and hydrogen, and have shown that methane is generally an inert component with respect to the reduction reaction, carbides are formed when excess carbon is available, hydrogen exerts a catalytic effect on the solid-state reduction reaction with CO decreasing this effect, and reduction reactions occur at 100 to 150°C lower in hydrogen than when CO or an inert atmosphere is used<sup>78</sup>. Additional work on chromites using mixtures of methane and hydrogen showed that chromite reduction can begin at 800°C when methane produced by the hydrogenation of carbon is used<sup>37</sup>. Only the iron and chromium oxides are reduced, the other oxide impurities remaining inert. The presence of these impurities decreases the reduction rate. Excess carbon results in exothermic hydrogenation reactions, which provide some of the heat required for single-step reduction. Further investigations<sup>5,21</sup> using CO demonstrated that iron and  $\text{Cr}_2\text{C}_3$  are formed up to 1200°C. At higher temperatures, iron forms first, followed by  $(\text{Cr},\text{Fe})_7\text{C}_3$ , and the original iron is then transformed to  $\text{Fe}_3\text{C}$ .

Considerable work has been conducted on the solid-state reduction of chromites with carbon. Basic investigations<sup>79,80</sup> involving the delineation of the kinetics and mechanisms of chromite reduction with solid carbon (graphite) showed that the initial reaction at 1000 to 1050°C resulted in reduction of  $\text{Fe}^{3+}$  to  $\text{Fe}^{2+}$ . From 1050 to 1200°C, iron is totally reduced to the metal and a carbide. This is true for chromium if no impurities are present. Otherwise, chromium is totally reduced to a carbide at 1250°C. Hunter and Paulson<sup>10</sup> investigated the ease of reduction of four chromites with graphite as a function of composition in the temperature range 600 to 1400°C. Higher temperatures yielded a greater degree of reduction, the degree of reduction being inversely proportional to the ferric iron content and directly proportional to the alumina and ferrous iron levels. Barcza<sup>81</sup> further demonstrated that reduction (as represented by mass losses) was proportional to the amount and mineralogical composition of the contained gangue. The mechanism was believed to be a three-dimensional diffusion of the reactants through the reaction product. Rankin<sup>5,21</sup> showed that the solid-state reduction of chromites with graphite yielded phases similar to those obtained when chromites were reduced with CO. Nafziger *et al.*<sup>7</sup> investigated the solid-state reduction of two chromites with various reductants, and found that the use of more-reactive reductants such as coal char resulted in a greater degree of reduction. The ease of reduction for the two chromites was proportional to the amount of contained iron.

The data obtained for the solid-state reduction of chromites formed the basis for the development by the Japanese of reduction processes



involving shafts or grates and rotary kilns on a pilot scale in the late 1960s. Dried pellets prepared from low-grade chromite fines, a reductant (such as anthracite or coke), a binder, and a flux were reduced in a rotary kiln, one-half of the kiln being regarded as a preheating area. Approximately 30 per cent of the carbon in the pellets was lost by combustion. During roasting at 1300 to 1435°C, an outer shell of oxides was formed on the pellets from the flux materials in the zone between the preheating and reduction areas in the kiln. The exothermic oxidation increased the pellet temperature to a point sufficiently high for the subsequent reduction reaction to occur (greater than 1275°C). The temperature must be carefully controlled to avoid softening of the pellets and yet be high enough to effect sufficient metallization. A reduction of 60 per cent of the iron and chromium oxides was achieved in the kiln<sup>82</sup>. A plant was constructed in South Africa to process 120 kt of ferrochromium per year, at least 25 per cent of the production being exported to Japan<sup>83</sup>. Further reduction investigations<sup>84</sup> in South Africa were conducted using char in pellets containing a high-iron chromite at temperatures ranging from 1100 to 1400°C. At the higher temperatures, reduction proceeded faster, approximately 35 per cent of the iron being metallized before any significant amount of chromium was metallized. A maximum of 75 per cent reduction was achieved by the addition of 100 per cent of the stoichiometric carbon requirement to completely reduce all the iron and chromium oxides. Recent pilot-scale investigations have shown that off-grade chromites can be metallized up to 90 per cent in 2 to 3 hours, beginning at approximately 1150°C and ending at approximately 1350°C. The chromites were pelletized with 125 to 150 per cent of the stoichiometric carbon requirement (as coal char) to reduce all the iron and chromium oxides. These pellets were charged into a batch rotary kiln, together with a continuous addition of coke breeze during the test. The prereduced pellets were removed from the kiln under an inert atmosphere, and a layer of coal char was placed on top of the hot pellets to prevent reoxidation<sup>85</sup>.

The U.S. Bureau of Mines has conducted extensive smelting studies on unreduced lower-grade chromites over the past several decades. Wessel and Rasmussen<sup>11</sup> prepared ferrochromium with an average Cr/Fe ratio of 1.32 by smelting high-iron chromite with a sub-bituminous coal and coal char in an open-top electric-arc furnace. The average chromium and iron recoveries were 97 and 94 per cent, respectively. Walsted<sup>12</sup> noted that the Cr/Fe ratio was not improved, but that suitable ferro-alloys could be smelted from these chromites. The selective reduction of iron from other off-grade chromites resulted in Cr/Fe ratios greater than 4 in the metal, with Cr recoveries of 89 per cent in a chromium-bearing slag<sup>13</sup>. Additional research on one chromite ore showed that high-carbon ferrochromium containing approximately 50 per cent Cr by mass with Cr recoveries of up to 86 per cent could be prepared<sup>8</sup>. However, the consumption of electrical energy was high. The consumption of energy was less when the ore was beneficiated. Recent investigations<sup>85</sup> have shown that submerged-arc conditions are preferable to open-bath operations with respect to

chromium recovery, mass of metal, and reduction efficiency. Coal char (100 to 120 per cent of the stoichiometric carbon requirement for complete reduction) was generally the reductant of choice. Initial slag basicities (defined as  $(\text{CaO} + \text{MgO})/\text{SiO}_2$  on a mass basis) between 0.6 and 0.9 and a C/Cr mass ratio between 0.6 and 1.0 were recommended. Satisfactory ferrochromium for use in the AOD manufacture of stainless steel can be produced from lower-grade chromites under submerged-arc conditions provided that the operating variables are controlled within relatively narrow limits.

Other investigators have smelted chromite concentrates (with Cr/Fe ratios of 1.6 to 1.7) with a limited amount of coke and slagging constituents under submerged-arc conditions. In a two-stage operation, an iron alloy and a slag containing 27 per cent  $\text{Cr}_2\text{O}_3$  by mass were obtained initially. In the second stage, the chromium-rich slag was smelted with appropriate slagging components and a reductant to produce high-carbon ferrochromium containing 63 per cent Cr and a slag with only 1.8 per cent  $\text{Cr}_2\text{O}_3$  by mass. The slag-metal separation was difficult owing to the refractory nature of the first-stage slag<sup>70</sup>. A similar scheme has been reported by Mousoulou<sup>86</sup>, in which chromium contained in pig iron (equal to or less than 2 per cent Cr by mass) smelted from laterites is removed during steelmaking, and the ironmaking slag, which contains most of the chromium, is processed further. Seetharaman and Abraham<sup>27</sup> report that 80 per cent of the stoichiometric carbon requirement for complete reduction and a slag basicity of 0.9 were preferred for the first-stage smelting of a low-grade chromite ore with a Cr/Fe ratio of 1. The activity of  $\text{Cr}_2\text{O}_3$  in the slag should be as low as possible, whereas the activity of FeO should be high for optimum separation. A high-carbon ferrochromium was produced during the second-stage smelting operation. High carbon contents<sup>87</sup> are favoured by agglomeration of the ore with finely divided carbon, an  $\text{MgO}/\text{Al}_2\text{O}_3$  ratio in the slag greater than 1, the presence of CaO, and a C/Cr ratio greater than 1. A higher carbon content than normal can be expected in the high-carbon ferrochromium produced from lower-grade ores. Although alternative smelting schemes involving a silicon reductant have been proposed, it has been demonstrated that the power requirements are higher because silicochromium must be produced first and the lime-chromite slag melted<sup>88</sup>.

In summary, extensive testing has shown that low-grade chromites can be smelted to produce acceptable high-carbon ferrochromium. The use of wood wastes provides distinct advantages in a typical two-stage smelting operation for the upgrading of lower-grade chromites.

Considerable recent interest is evident in the processing of chromites for the production of high-carbon ferrochromium suitable for the production of stainless steel. Prereduction of the chromite prior to melting offers some advantages over direct smelting. Otani and Ichikawa<sup>82</sup> emphasized that, when hot prereduced pellets are continuously charged into an electric-arc furnace, the energy savings can be as high as 500 kW·h per ton of alloy produced, compared with operations in which charging techniques are used. In addition, the coke



requirements are halved, the total energy consumption is less, and the chromium recoveries are higher. Further advantages include higher productivity and a smoother, more controllable melting operation in the furnace<sup>85</sup>. Prereduction also possesses some inherent disadvantages such as the necessity for fine grinding and for very close temperature control to prevent excessive sintering, sensitivity to the carbon balance, and possible increased sulphur content in the metal<sup>76, 85</sup>.

#### *Special Alloys*

In addition to high-carbon ferrochromium, which accounts for the major metallurgical end-use of chromium, other metals and alloys can be produced. These include ferrochromium-silicide, chromium, and low-carbon ferrochromium. A single-stage process for the production of ferrochromium-silicide in two carbon-lined submerged-arc furnaces is described by Clark<sup>89</sup>, who used lumpy chromium ore, quartz, and coke as the charge. The alloy contained 39 per cent chromium and 43 per cent silicon by mass, and a chromium recovery of 90 to 93 per cent was realized. However, such alloys can be produced only from higher-grade chromite ores.

Cohen and Yalcin<sup>3</sup> describe a process, in which chromite is reduced by chromium, that they claim to be more selective in reducing iron oxides; it is exothermic, thus providing added heat, and very low carbon levels can be achieved in the alloys. A minimum temperature of 1050°C was required to achieve total reduction of the iron. Improvements in the Cr/Fe ratio were realized, but the use of chromium as a reducing agent is not attractive commercially.

A number of other processes have been used to produce low-carbon ferrochromium. However, with the advent of the AOD process for the production of stainless steel in 1967, the demand for special alloys including low-carbon ferrochromium diminished from 45 per cent of the total consumption in 1970 to 12 per cent in 1978. In addition, stainless steel can be made in an L.D. converter or in an electric furnace, and the carbon can be removed in a vacuum degassing vessel while oxygen is blown into the vessel. For these reasons, techniques for the production of low-carbon ferrochromium are not treated in this paper inasmuch as they have become of academic interest only.

#### *Special Melting Techniques*

The energy crisis prompted several investigators to seek alternative methods for the production of ferrochromium. One of these is plasma technology, which has the following advantages: it requires lower specific energy owing to the higher operating temperatures, which decrease the flux burden and increase the recovery of heat from off-gases; no agglomeration or preparation of the charge is required; and water-cooled electrodes can be used, instead of the more expensive graphite electrodes. Fey and Harvey<sup>90</sup> proposed a process in which lower-grade chromite ore is charged into a prereduction vessel where some of the iron oxide is selectively reduced and the iron removed. The upgraded chromite is then carbothermically reduced by a pyrolysed gaseous hydrocarbon such as natural gas at over 1700°C. At Bethlehem Steel, a reactor has been developed that employs a film rather than discrete particles entrained in the plasma

gas<sup>76</sup>. This process increases the residence time and provides intimate contact between the oxide and the carbon reductant. Hamblyn<sup>91</sup> compares the energy requirements for the production of ferrochromium using plasma technology with those in submerged electric-arc furnaces. The production of ferrochromium in a plasma furnace required less energy (between 13 and 18 per cent) owing to the lower reaction energies, heating of raw materials (e.g. fluxes), and higher heat recovery in off-gases during plasma melting. Preheating of the chromite could recover between 10 and 14 per cent of the theoretical input energy. Moore *et al.*<sup>92</sup> describe their equipment and results using a laboratory-scale sustained shock-wave plasma reactor to successfully reduce a low-grade domestic chromite in flight. Metallizations of 46 and 7.3 per cent for iron and chromium, respectively, were achieved by the use of lignite char as the reductant.

Pickles *et al.*<sup>38</sup> developed an extended-arc flash reactor to prepare very high-purity ferrochromium, using coke, coal, coke breeze, or graphite as reductants. The small scale of their work resulted in a very high consumption of energy. The temperatures in the plasma zone exceeded 2000°C. The advantages of this process are that no agglomeration is necessary, any grade of ore can be used, the reductant can be of any size and resistivity, the electrical efficiency is greater than for conventional smelting in a submerged electric-arc furnace, the process is simple and not capital-intensive, and the produced ferrochromium is pure.

## **Discussion and Conclusions**

### *Comparison of Recovery Techniques*

Although this paper has considered a wide variety of lower-grade chromite ores and concentrates, certain generalizations can be made with regard to maximizing the chromium recovery from these materials. Successful recovery depends on the chemical composition, mineralogy, and particle size of the material. Physical methods can be successful in removing some or all of the gangue materials. For example, gravity-concentration methods can be used effectively if the density difference between the ore and the gangue is sufficiently large (for example 0.8 g/cm<sup>3</sup>). However, chemical means (hydrometallurgical and/or pyrometallurgical) must be used to improve the Cr/Fe ratio in chromites. The techniques used often present a compromise between maximum Cr<sub>2</sub>O<sub>3</sub> content of the product, chromite recovery, Cr/Fe ratio, and economics.

Most lower-grade chromite ores respond to some type of gravity separation for the removal of gangue materials provided that the chromite is not finely intergrown with such materials. Finer grinding of a high-iron ore does not necessarily yield concentrates containing more Cr<sub>2</sub>O<sub>3</sub> or higher Cr/Fe ratios. Chromite fines are not generally amenable to gravity methods of separation owing to excessive chromium losses. High-iron ores containing less Cr<sub>2</sub>O<sub>3</sub> can provide concentrates by gravity methods such as tabling that have equal or greater Cr/Fe ratios and Cr<sub>2</sub>O<sub>3</sub> contents than concentrates from ores with higher Cr<sub>2</sub>O<sub>3</sub> levels. Chromite ores having significant size differentials between the chromite and the gangue materials can be tabled effectively. For more coarsely

sized ores, gravity methods generally provide superior results over flotation techniques in the beneficiation of most off-grade chromite ores.

Magnetite in the ores can be separated by magnetic means provided that the magnetite particles have not adhered to the surface of the chromite grains. Relatively low belt speeds and low magnetic fields are recommended. Electrostatic-separation techniques can be used in combination with other beneficiation techniques if the gangue contains little or no serpentine.

For fine-grained materials (less than 100  $\mu\text{m}$ ), flotation is an accepted technique for the beneficiation of chromites. Careful control of reagents and pH is required for maximum recovery. The composition of the chromite phase in the ore affects the selection of reagents and the grade of the concentrate more than it affects the bulk composition of the ore. For example, the presence of  $\text{Al}^{3+}$  profoundly affects the flotation behaviour of refractory-grade chromites and requires careful pH control. A variety of flotation reagents have been developed for chromites to depress slimes, to act as dispersants, and to selectively float the chromites. The wide variability of the ores precludes the recommendation of optimum reagents. Economics may also play an important part.

In some cases, it should be noted that a specific beneficiation technique (such as tabling) will increase the Cr/Fe ratio, but simultaneously decrease the Cr recovery and/or the  $\text{Cr}_2\text{O}_3$  content of the concentrate. Evidently, when some of the iron is removed, some chromium is interlocked with it and a certain amount is lost. More selective separation techniques are required.

A summary of the effect of some beneficiation techniques on selected ores is presented in Table XI, together with partial analyses of the ores. The recommended method of concentration cannot be correlated well with the ore composition. Detailed mineralogical studies are not available.

#### *Chemical Upgrading*

As has been demonstrated, ore-dressing methods can be used for the removal of gangue materials for upgrading purposes. However, physical beneficiation of chromite ores cannot increase the Cr/Fe ratio from that present in the ore unless the gangue materials contain considerable iron. As no ore-dressing process can change the Cr/Fe ratio of the chromite spinel in the ore, some form of pyrometallurgical and/or hydrometallurgical process involving chemical attack is required. Chemical beneficiation methods have not been enthusiastically received owing to economic considerations.

Accordingly, extensive smelting tests have shown that it is possible to produce a satisfactory high-carbon ferrochromium containing higher-than-normal carbon levels from lower-grade chromites. Hogged fuel such as wood waste and sawdust can be used effectively.

Originally, it was thought that high-carbon ferrochromium should contain 66 to 72 per cent chromium by mass, which required a Cr/Fe ratio in the ore of approximately 3. With the advent of new and improved processes for the production of stainless steel, lower grades of ferrochromium can be used. Such lower grades (50 to 55 per cent chromium by mass) can be smelted directly from lower-grade chromites. Therefore, there is less

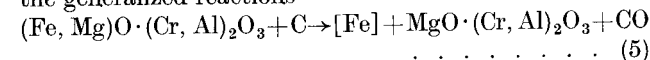
apparent need for chemical upgrading of the ore now than there was previously. However, chemical upgrading may be required to offset transportation costs to the market from remote chromite deposits.

In the past, high-carbon ferrochromium was unsuitable for the production of high-chromium steels such as austenitic stainless steels, which represent a large percentage of the market for ferrochromium. The carbides tended to precipitate at grain boundaries at certain temperatures, leading to selective corrosion at those sites and subsequent embrittlement of the alloy. However, with the development of the AOD process, in which molten steel is blown with a mixture of argon and oxygen to remove carbon and silicon, the argon decreases the partial pressure of carbon monoxide and alters the Cr-C equilibrium, resulting in stainless steels having carbon contents as low as 0.01 per cent by mass. Another development involves the removal of carbon by vacuum degassing while oxygen is simultaneously blown in the ladle. Therefore, there is essentially no demand for expensive low-carbon ferrochromium for metallurgical applications.

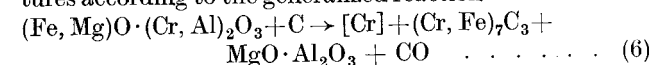
Techniques involving metallic chromium as a reductant do not appear to be a practical means for the production of ferrochromium.

#### *Pyrometallurgy*

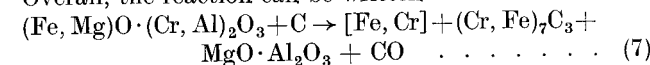
The reduction of lower-grade chromites with carbon is a complex multistep process, primarily owing to cation substitution and defects in the spinel structure. Experimental results<sup>7</sup> have indicated that the iron in the chromites reduces first at lower temperatures according to the generalized reactions



As the iron in the chromites is reduced, reduction of the chromium in the chromites begins at the higher temperatures according to the generalized reaction



Overall, the reaction can be written



If carbon monoxide is not an effective reducing agent for chromites<sup>37, 81</sup>, its removal from the system should not affect the rate of reduction. On the other hand, if  $\text{Fe}_3\text{C}$  is formed as a reaction product, as suggested by thermodynamics alone, this species can function as an effective reductant by permitting the transport of carbon through the carbide to the chromite. Such an intermediate carbide is short-lived and rarely appears as a reaction product<sup>7</sup>. The presence of carbides has a significant effect on the reduction of oxides containing chromium.

The question of whether chromite is reduced by a solid-solid reaction or by a gas-solid reaction has received considerable attention. Barcza showed that a solid-solid reaction was responsible and that carbon was the diffusing species. It is important to understand the reduction reactions more thoroughly so that high-carbon ferrochromium can be produced more efficiently<sup>93</sup>.

Reduction reactions for the production of high-carbon ferrochromium can be plotted on a Pourbaix diagram,

TABLE XI  
RESULTS OF BENEFICIATION TECHNIQUES AND RECOMMENDED TREATMENTS FOR SELECTED WORLDWIDE CHROMITE ORES

Ore	Cr <sub>2</sub> O <sub>3</sub> % by mass	Total Fe % by mass	Total oxides % by mass	Cr/Fe	Maximum reported values for concentrates			Recommended method of concentration	Recommended treat- ment for ferrochromium production	References
					Cr recovery %	Cr <sub>2</sub> O <sub>3</sub> % by mass	Cr/Fe			
Seiad Creek, Calif, USA . . . .	18,3	8,79	66,3	1,42	83-91	45	2,4	Selective flotation	Smelting ore directly (≤ 86 % Cr recovery)	8
Stillwater, Mont., USA . . . .	12,4	24,1	30,3	0,35	NA	NA	2,4-3,0	Reduction and acid leaching or tabling with middling retreatment	Acid smelting or chlori- nation of concentrates using CaF <sub>2</sub>	6, 7, 9-13
John Day, Oregon, USA . . . .	37,8	11,9	44,4	2,17	NA	48	2,6	Tabling	Smelting ore directly (> 85 % Cr recovery)	6, 14
SW Oregon Beach Sands, USA .	9,4	11,0	60,8	0,59	65	41	1,6	Tabling or spirals; magnetic separation	No good technique at present	2
Moreesberg, South Africa . . . .	30,5	16,1	43,1	1,30	99	NA	6,0	Reduction and acid leaching	ND	18
Soviet Union . . . . .	41,8	13,0	40,9	2,2	≈ 100	NA	NA	Flotation under alkaline conditions	ND	26
Mysore, India . . . . .	≤ 40	NA	NA	1,0-1,8	80	NA	3,0	Reduction and acid leaching	ND	9, 27, 29, 30
Bird River, Canada . . . . .	≈ 11,5	NA	NA	NA	NA	36-42	1,1-1,5	Physical methods	Smelting concentrate (upgrade-concentrate by pressure leaching)	33
Majari-Baracoa, Cuba . . . . .	39,8	11,9	44,0	2,3	≈ 100	NA	NA	Flotation	ND	26
Troodos, Cyprus . . . . .	31,7	20,3	39,8	1,07	93	48-49	2,75	Heavy-medium and gravity separation	ND	39
Barramyaia, Egypt . . . . .	36,9	15,7	43,3	1,6	69	55	3,4	Gravity and magnetic separation	ND	40, 41
Egypt . . . . .	40,2	14,5	40,0	1,9	57	NA	3,2	Flotation and magnetic separation	ND	42

NA = Not applicable.  
ND = No data.

which relates temperature and oxygen pressures. At higher temperatures, lower-carbon chromium carbides are more stable than those containing higher concentrations of carbon<sup>87</sup>. Carbide reactions occur at lower temperatures under reduced total pressures. At low temperatures and high oxygen pressures, the stable condensed phases are  $\text{Cr}_2\text{O}_3$  and carbon. As the temperature increases or the oxygen pressure decreases,  $\text{Cr}_3\text{C}_2$  and  $\text{Cr}_2\text{O}_3$  become the stable condensed phases<sup>94</sup>. Pourbaix diagrams are useful in determining the minimum temperature necessary to obtain a metal or specific carbide by carbothermic reduction at a specified oxygen pressure. For example, chromium can be obtained at a minimum temperature of 1255°C at  $10^{-4}$  atm. CO pressure or 1040°C at  $10^{-6}$  atm. CO pressure.

Of equal importance to the efficient reduction of chromites by carbon for the production of high-carbon ferrochromium is an understanding of the kinetics of the relevant reduction reactions. Early experiments under 1 atmosphere pressure conducted by Gel'd and Esin<sup>95</sup> on  $\text{Cr}_2\text{O}_3$  and chromite ores with graphite showed that the rate of reduction of the ore was significantly slower than that of the  $\text{Cr}_2\text{O}_3$ . Impurities retarding the diffusion of the reactive species in the ore were thought to be responsible. As expected, the reaction rates also depend inversely on the square root of the particle diameter of the ore and reductant. At total pressures of less than 1 atm., topochemical mechanisms were believed to describe the reactions in which reduction begins over the entire particle surface simultaneously. Others have found that  $\text{Cr}_2\text{O}_3$  in the presence of iron was reduced by a process that was diffusion-controlled at carbon contents of less than 1 per cent by mass, and was controlled by chemical reaction rates at carbon contents above 2 per cent by mass. The overall reduction rate of iron and chromium oxides by carbon increases with temperature. However, at constant temperatures, the reaction rate decelerates owing to a lower overall contact surface for diffusion of the reducing agent.

Urquhart<sup>19</sup> found that the presence of quartz did not affect the rate of reduction of iron from chromite ore, but increased the rate of reduction of chromium. Solid-state diffusion of the reacting species through a product layer most nearly described the experimental results. This is considered to be a topochemical reaction. Evidently, the diffusion of iron and chromium ions in the chromite spinel is the rate-limiting step.

Nafziger *et al.*<sup>7</sup> found that the reduction may be nucleation-controlled, although topochemical control may predominate under mildly reducing conditions. Diffusion control was suggested as the rate-determining step under mildly reducing conditions.

It is evident from this review that much more research is required for a full understanding of the behaviour of chromites in conventional beneficiation and smelting techniques. This includes a greater understanding of the physical properties, as well as of the reactions applicable to flotation, roasting, solid-state reduction, and smelting. Thermochemical and kinetic investigations are required, and emerging techniques such as prereduction and plasma-arc melting should be applied. The effective recovery of chromium also is dependent on a

more thorough knowledge of the spinel structure and the degree to which cations substitute into this structure. Detailed X-ray crystallographic studies are therefore required. A greater understanding of the fundamental physical, chemical, and metallurgical reactions in the extraction of chromium will permit a better recovery from lower-grade chromites, including very low-grade materials such as those found on the south-western coast of Oregon in the U.S.A.

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## Computer applications

The Institution of Mining and Metallurgy will hold the Eighteenth International Symposium on Computer Applications in the Mineral Industries (APCOM) from 26th to 30th March, 1984, at the Royal School of Mines, Imperial College, London.

The Symposium, in line with previous conferences, will cover a wide range of computer applications in the mining industry, emphasizing techniques of interest to the practising engineer. The special theme of the meeting — the first to be held in the United Kingdom — will be the comparison of actual operating experience with original models, forecasts, and feasibility estimates.

Since the APCOM series of conferences was begun in 1961 many examples must have accumulated of techniques having been put into practice and plans having been implemented. It is therefore timely to review the successes and failures of computer applications since computers became available as a management tool. Case studies of this general theme under any of the subject headings given below are particularly welcome.

### Papers

The Organizing Committee intends to invite a number of authors to present papers, but will welcome additional submissions on the following principal topics:

### Exploration

- Modelling mineral deposition processes
- Regional comparisons for target selection
- Computer-aided selection of target areas
- Experience with computer analysis of geophysical and geochemical data
- Geostatistics and ore-reserve estimation
- Techniques of estimation

Comparison of grade and tonnage estimates with production

Computer graphic applications

### Financial evaluation and planning

Techniques for making early estimates of capital and operating costs

Comparison of feasibility estimates with final costs and performance

### Mine design and operations

System modelling and evaluation

Rock mechanics in design applications

Materials-handling studies

Interactive graphics

### Mineral processing and metals extraction

Modelling applications for plant management, design and control

Comparison of designed and actual performance

### Market analysis and prediction

Simulation of commodity markets

Supply, demand and price studies

Comparison of predictions with actual outturns

### International climate for the mineral industries

Abstracts (250 to 300 words) should be submitted to the Secretary, The Institution of Mining and Metallurgy, 44 Portland Place, London WIN 4BR, England, before 1st January, 1983. Completed manuscripts of approved papers will be required in September 1983, and a pre-printed volume will be sent to registrants in advance of the conference. A range of micros and/or terminals will be available as an extension of visual aids. Intending authors should indicate whether they wish to make use of this facility.