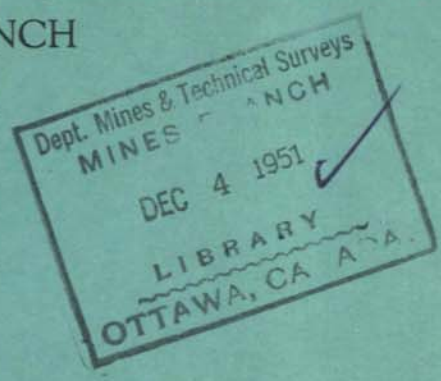CANADA

DEPARTMENT OF MINES AND TECHNICAL SURVEYS
MINES BRANCH

OTTAWA

THE UTILIZATION OF
LOW GRADE DOMESTIC CHROMITE

by

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THE UTILIZATION OF LOW GRADE DOMESTIC CHROMITE

A Survey of the General Problem with Details of
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by

K.W. Downes and D.W. Morgan[*]

I.   INTRODUCTION

During the past few years the problem of the utilization of chromite ores and concentrates of low chromium-iron ratio has been under investigation in many laboratories. At the Mines Branch two beneficiation schemes for raising the chromium-iron ratio of concentrates have been developed to the laboratory stage, two methods originating elsewhere have been checked, and the literature relating to the utilization of chromite of low chromium-iron ratio has been critically examined.

This investigation was undertaken because of the dependence of the North American continent upon overseas deposits of high-grade chromite, the only commercial sources of chromium for industry. Should supplies of chromite from abroad be cut off during any emergency it would be necessary to use domestic ores, which are almost entirely low grade and of low chromium-iron ratio. It was desired to find a method of employing these ores without incurring excessive costs, and particularly without reducing the production capacity of that part of the economy affected.

Although none of the processes investigated is considered cheap enough to encourage the exploitation of domestic resources under normal conditions, methods of beneficiating chromite which have been advanced to the laboratory stage are believed quite satisfactory to meet emergency requirements

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for a concentrate of high chromium-iron ratio. Methods of directly utilizing concentrates of lower ratio which do not unduly hinder production capacity are available for use in certain applications.

II. A BRIEF SURVEY OF CHROMIUM METALLURGY

Chromium has wide and essential uses in industry. As a metal it is used in the pure state as a plating, and alloyed with iron it enhances the strength, hardness, and corrosion resistance of structural steel, tool steel, bearings, crushing machinery parts, armour plate, and stainless steel. In refractories, as chromite, it is valued for furnace linings because of its high melting point (1900°C) and chemical inactivity, since it does not react with acid or basic fluxes. In chemicals it is used in tanning, in pigments in the paint and dye industries, and in electroplating.

The only commercial source of chromium is the mineral chromite. This mineral is a member of the spinel group, essentially $(FeMg)O(CrAl)_2O_3$. The amounts of chromium and iron may vary considerably. The use to which a sample of chromite is put, i.e. metallurgical, refractory or chemical, depends partly upon its chemical composition and partly upon its physical condition. In 1949 the consumption of chromite by grades in United States was as follows: (Preprint from U.S. Bureau of Mines Minerals Yearbook, 1949; section "Chromite").

Table 1

Consumption of Chromite By Grades in United States, 1949

Grade	Tons	Per Cent
Metallurgical	288,518	43
Refractory	268,925	40
Chemical	115,330	17
Total	672,773	100

At present chromite enters industry in the following ways:

1. Alloy with Iron and Steel

    (a) Metallurgical Grade:

    Standard specifications for metallurgical grade ore require a chromic oxide (Cr_2O_3) content of 48 per cent, a chromium-iron ratio of 3:1, and the ore must be in lumpy form. During the war a chromium-iron ratio of 2.5:1 was accepted, and fines were permitted to a limited extent (H500).[1] The bulk of this ore is made into ferrochrome, in which form chromium is added to steel.

    Ferrochrome is made by reducing chromite in the electric furnace. The chromium-iron ratio in the chromite controls the proportion of chromium in the resulting ferrochrome. In practice, a chromium content in ferrochrome of from 66 to 72 per cent has been found most suitable by steel makers. With higher proportions of chromium the ferrochrome is difficult to dissolve in the molten steel because of its high melting point. With lower proportions, more ferrochrome has to be added to introduce a given amount of chromium into the steel. This lowers the temperature of the melt and so increases the time required to make a heat of steel, and also increases the loss of chromium into the slag. These requirements for ferrochrome control the specifications for chromite ore.

    Ferrochrome is classed as high-carbon or low-carbon according to its carbon content. Low-carbon ferrochrome is made by re-smelting high-carbon ferrochrome with chromite ore.
    (H 523, 636 et. seq.; R.I. 3322[2]).

[1] Page 500 in the Hearings before the Subcommittee on Mines and Mining, Committee on Public Lands, U.S. House of Representatives, Part 2, (1948)

[2] U.S. Bureau of Mines Report of Investigation.

(b) <u>Off-grade metallurgical chromite ore</u>, that is, ore having a chromium-iron ratio less than 3:1, may enter industry in the following ways:

(i) It may be used to make Chrom-X, which is the trade name for low chromium ferrochrome made by Chromium Mining & Smelting Corporation Limited at Sault Ste. Marie, Ontario. Off-grade chromite is smelted in the same way as for standard ferrochrome, to make a low-chromium ferrochrome. To make Chrom-X the low-chromium ferrochrome is crushed and blended with ferrosilicon and sodium nitrate, and then briquetted. When the Chrom-X is added to molten steel the sodium nitrate oxidizes the silicon to sodium silicate, forming slag. About two per cent of the carbon is oxidized at the same time. The heat generated by these reactions melts the ferrochrome. There is thus no chilling of the molten steel, and the chief objection of the steel maker to low-chromium ferrochrome is eliminated. The recovery of chromium from Chrom-X in the steel is 90-95 per cent as compared with 85-90 per cent for standard ferrochrome.

Both high and low-carbon Chrom-X can be made. High-carbon Chrom-X is currently being manufactured and used in the steel industry. The cost is about two cents per pound of contained chromium more than standard high-carbon ferrochrome.

Chrom-X may be made from chromite having a chromium-iron ratio as low as 1.35:1, but is most economical between 1.8:1 and 3:1. Almost all the production of low-grade chromite from Montana during the last war was converted to Chrom-X and used in making iron and steel. Fine ores and concentrates are acceptable after sintering. Chrom-X can be made from Montana

ores as mentioned, and also from Oregon, California, Alaska, Bird River (Manitoba), and Black Lake (Quebec) ores.

Using ore with a chromium-iron ratio of 1.5:1, a 6000 KVA electric furnace produces 35-40 tons of crude metal per day, consuming 4200-4400 KWH per ton.

(H 524, 610, 629, 639: Metals and Alloys, Vol. 14, p. 52 (1941): Metals and Alloys, Vol. 15, p. 249 (1942)

(ii) It may be directly converted into stainless steel by the Wild process, which is currently being done by the American Rolling Mill Company, Rustless Division, Baltimore, Maryland. This process avoids the use of ferrochrome entirely. Chromite ore is added to the slag of an open hearth furnace, and ferrosilicon is added to the steel. The silicon reduces the chromite and chromium enters the steel. The process does not require any special chromium-iron ratio, anything down to 2:1 being satisfactory, and fines are acceptable. Recovery of chromium is about 96 per cent. The American Rolling Mill Company has used domestic ores in the process, and California ores have been similarly used in England.

(H 524, 617: Iron Age, Vol. 132, p. 18, Aug. 10 (1933): Metal Progress, Vol. 23, p. 13 (1935): Proc. A.I.M.M.E., Vol. 3, p. 133 (1945)

2. **As a Refractory**

The acceptance of chromite as a refractory is based primarily on actual performance rather than on chemical composition. The chromium-iron ratio is of no importance here. In general, FeO should be less than 16 per cent, Cr_2O_3 more than 30 per cent, and SiO_2 less than six per cent. The ore should be in hard lumps.

In recent years the chrome-magnesite brick has been developed, which is made from crushed chromite ore and magnesite clinker. The latter is chiefly

magnesium oxide. By adding suitable amounts of clinker, a chromite
with indifferent refractory properties can be made into a high
grade refractory. Since chromite concentrates as fine as 28-mesh
can be used, this makes possible the exploitation of chromite
deposits which would otherwise be useless.

(H 500, 602, 605, 640: Trans. Eng. Ceramic Soc., Vol. 38,
p. 211: Iron Age, Vol. 152, Nov. 18 (1943)

3. **As a Source of Chromium Chemicals**

The specifications for chemical grade chromite are not as rigid as
for metallurgical grade. In general, the minimum content of Cr_2O_3
should be 44 per cent, and it should not contain more than 15 per cent
Al_2O_3, 20 per cent FeO or three per cent SiO_2. Fines are acceptable
since the ore is ground before treatment.

In use, the ore is ground with sodium or potassium carbonate and
lime, and roasted in a reverberatory furnace. The chromium is oxidized
to chromate and then extracted from the calcine as sodium or potassium
chromate by leaching with hot water. Other chemicals such as zinc
chromate and the dichromates can be made from sodium chromate. Lower
grade ores than those specified above can be used in the process, but
furnace capacity is reduced thereby, and the consumption of reagents
per pound of recovered chromate is increased.

(H 582, 597, 641).

III. NORTH AMERICAN ORE SUPPLIES

Virtually all the chromite used in United States and Canada is
imported, the principal sources being Cuba, Union of South Africa, Southern
Rhodesia, Russia, Turkey, New Caledonia, and the Phillipines. Although there are
some chromite deposits in North America they are either too small, or the grade
of the ore is too low to make a domestic chromite industry possible in normal

times. Nonetheless, much attention has been given to the domestic chromite deposits. The present situation in regard to chromite is as follows:

The reserves of chromite in North America are small in relation to consumption. The total reserves of metallurgical grade lump ore, in California, Oregon, and Alaska, amount to 25,000 tons, or less than two months' supply. There are no known reserves of refractory grade ore on the continent, although the deposits in Cuba are adequate to take care of the requirements of the United States for several years (H 505). Even assuming that all the known chromite ores in United States could be utilized regardless of grade, the total would amount to about six years' supply (H 509). In Canada, the low-grade Bird River deposits are by far the largest and have been estimated at 10 million tons of ore with an average grade of 18 to 26 per cent Cr_2O_3 (Trans. C.I.M.M., vol. 46, p. 154 (1943). This corresponds roughly to an additional six years' supply for the continent. Thus it is clear that, in the long run, the North American continent must depend upon foreign chromite.

No serious attempt appears to have been made to use domestic chromite for refractory purposes (H641). During the last two wars some small Canadian and American deposits were mined for metallurgical grade. The Montana deposit, which is 75 per cent of the total United States chromite, has a chromium-iron ratio of from 1.4 to 1.7:1, which is too low grade to be attractive metallurgically, and it was mined only in case all shipments of higher grade foreign ores should fail. The Bird River deposits, discovered in 1942, have a chromium-iron ratio of 1.2 to 1.5:1 and are even less attractive.

In the event that all foreign shipments of chromite were cut off, the Montana, Bird River, and similar low-grade deposits would have to supply the needs of the continent until exhausted.

It would probably take from 18 months to two years to bring the Bird River deposits to a production of 1500 tons of ore per day or approximately one-half the North American requirements. Production from the Montana deposits might be brought up to 17 per cent of the total United States requirements in as little as one year (H 516). No estimate is available for the time necessary to attain greater production.

IV. UTILIZATION OF NORTH AMERICAN DEPOSITS

1. Introduction

The problem of employing low-grade ores in the metallurgical industry may be approached from two directions: the grade of the ore may be improved to come closer to present standards, which may be costly, or the metallurgical practice may be adapted to using low-grade ores which may reduce production capacity. The degree of beneficiation and the degree of adaptation for any specific purpose would have to be determined by a careful balance of the metallurgical and economic factors involved.

Chromite ores are mixtures of the mineral chromite and gangue, and the composition is therefore a combination of two factors, (1) the proportion of chromite to gangue, and (2) the composition of the chromite itself. Ores low in grade because of a high proportion of gangue can be brought up to grade by mechanical concentration, but if the chromite mineral itself is low in chromium or low in chromium-iron ratio, no mechanical process can produce a concentrate to meet specifications. Because the mineral chromite is of variable composition, its formula is written $(FeMg)O(CrAl)_2O_3$.

2. Mechanical Beneficiation

The low grade of the Montana and Bird River chromites is due to a combination of both the factors (1) and (2), referred to above. Thus, mechanical concentration will produce some beneficiation, but not sufficient to meet the recognized specifications for metallurgical or chemical grade chromite.

The following table indicates the results that have been obtained:

Table 2

Mechanical Concentration of Bird River and Montana Chromites

Deposit	Raw Ore	Concentrate		Recovery of Cr_2O_3
	Per Cent Cr_2O_3	Per Cent Cr_2O_3	Cr/Fe	
Bird River	18-26	41	1.5:1	78 per cent [1]
Montana	20	41	1.2-1.5:1	Up to 89 per cent [2]

[1] Tabling only.

[2] Tabling and flotation.

(Allsman and Newman, "Exploration of Stillwater Chromite Deposits, Stillwater and Sweetgrass Counties, Montana", A.I.M.M.E. Technical Publication 1751, (1944).

R.I. 3834, p.4; 4079.

Mines Branch, Ottawa, Investigation No. 1327, 1360, 1361.

Bateman, "Bird River Chromite Deposits, Manitoba", Trans. C.I.M.M., vol. 46, p. 154 (1943).

The mechanical concentration of the Bird River and Montana chromites is a straightforward and cheap process. As a source of metallurgical chromite, the concentrates can be used directly either by converting to Chrom-X or by direct addition to the open hearth furnace using the Wild process. Either course seems feasible, since fines can be used in both processes, although a chromium-iron ratio of 1.8 is preferred for Chrom-X, and a Cr_2O_3 content of 42 per cent is preferred for the Wild process (H 617, 630). Nothing seems to be known as to what can be done with these concentrates for making refractories, and some work may be needed here (H 641). Such concentrates can be used in the manufacture of chemicals, although plant capacity would be rather less than when using standard 44 per cent ore (H641, R.I. 3480, p. 55).

3. <u>Chemical Beneficiation</u>

Since the steel industry is accustomed to using ore running 48 per cent Cr_2O_3 and with a chromium-iron ratio of 3:1, it would obviously be most convenient, and hence least harmful to production, if the chromite concentrates could be raised to these specifications. This necessitates a chemical attack on the chromite either to remove sufficient of the iron and gangue, or to separate the chromium entirely, the product in the latter case being used to sweeten untreated material. Several methods of attacking the chromite have been developed, namely:

(1) <u>Reduction with carbon or methane and leaching with sulphuric acid</u>   (U.S. Bureau of Mines)

Chromite concentrates are roasted in a kiln at 1200°C or higher with carbon or at 1000-1100°C with a reducing gas such as methane. The calcine is leached in hot 10 per cent sulphuric acid for one hour which preferentially dissolves out iron. The chromium-iron ratio is easily raised to 3:1, and may be raised to 10:1 or higher. Recovery of chromium is about 90 per cent (R.I. 3834, p. 35). No complete estimate of costs is given, but it has been calculated approximately (R.I. 3847, p. 13) that one ton of concentrate can be reduced in the kiln for $0.48 using natural gas at 15 cents per 1000 cu. ft., or for $1.47 using coke at $6 per ton and fuel oil at $6\frac{1}{2}$ cents per gallon. These are 1946 costs. The process has been operated on a pilot plant scale.

(R.I. 3813, 3817, 3834, 3847: H 525. Also investigated by Hudson Bay Mining and Smelting Co., Flin Flon, Manitoba, and the Mines Branch. See Section V (2).

(2) <u>Oxidation to chromate and reduction of chromate with</u>
    <u>carbon</u>   (Mines Branch, Ottawa)

Ground chromite concentrate is pelletized with soda ash and lime, and roasted at 850°C. The sodium chromate produced is leached out with water and crystallized. The dried crystals are mixed with carbon and heated in a reducing atmosphere to 750°C, chromic oxide (Cr_2O_3) being formed and some of the soda ash regenerated. Recovery of chromium is about 90 per cent. The product is 90 per cent Cr_2O_3 and can be used to sweeten untreated concentrates. The cost to treat Bird River concentrates is estimated at from $15 to $21 per ton, depending on the price of soda ash. This process could be brought to pilot plant stage in a short time. The investigation is fully described in Section V (3).

(3) <u>Leaching in sulphuric acid under pressure</u>
    (Mines Branch, Ottawa)

Finely ground chromite concentrate is leached with a limited amount of sulphuric acid solution at elevated temperatures and pressures. Both chromium and iron are sulphated and dissolved, the chromium being later precipitated as an insoluble basic sulphate as the acid is used up. Ferrous sulphate remains in the solution, which is filtered off to leave a beneficiated residue. Considerable sulphur is found in the residue after leaching, but may be removed by sintering or thermal decomposition. Chromium recovery is over 95 per cent. The cost of beneficiating Bird River concentrate has been roughly estimated at $17.25 per ton of concentrate treated. Details of this investigation are given in Section V (4).

(4) <u>Leaching in sulphuric and chromic acid, and precipit-
ation of chromium trioxide (CrO_3) by evaporation.</u>

(Commonwealth Scientific and Industrial Research
Organization, Australia)

Chromite ore or concentrate is leached with sulphuric acid in
the presence of chromium trioxide at 140-160°C. Chromium dissolves as
the sulphate and is oxidized to the trioxide in a diaphragm cell. The oxidized
solution is purified of iron, aluminium, and magnesium by evaporation and
crystallization, and then chromium trioxide is crystallized by further
evaporation. The acid mother liquor is recycled. The product is 90 per cent
CrO_3 which can be used to sweeten untreated concentrate.

The recovery is about 75 per cent. Cost is estimated by Wark at
10d per pound of CrO_3 so that to produce one ton of beneficiated Bird River
concentrate having a chromium-iron ratio of 3:1 would cost about $70.
This process is in the pilot plant stage in Australia, and has been in-
vestigated by the Mines Branch (Canada). There is at present no indication
that the recovery can be raised, or the costs lowered.

(Letter I.W. Wark to C.S. Parsons, 14 June, 1949: Australian
Jour. App. Science, Vol. 1, No. 4, pp. 376 et. seq.: Progress
Report on Utilization of Bird River Chromite, Mines Branch,
Ottawa, 18 May, 1949.)

(5) <u>Decomposition of chromite by fusion with lime,
silica and coke</u> (Udy Process)

Lump ore or sintered chromite is charged into an electric furnace
with lime, silica, and coke. On smelting, some of the iron is reduced
to the metallic state, and lime, alumina, and silica form a slag in which
the chromic oxide is not soluble. When the melt is cooled the slag
disintegrates, and the altered chromic oxide is recovered by water classification.
The product described in the report referred to below was 50-60 per cent
Cr_2O_3 with a chromium-iron ratio of about 20:1. Recovery varied from 30

to 77 per cent, but no doubt could be brought under better control.
No information on cost is available, but the costs would not be
excessive if reasonable recovery were obtained. The process is owned
by Chromium Mining & Smelting Corporation, Limited, Sault Ste. Marie,
Ontario, which presumably possesses complete data.

(Mines Branch, Ottawa, Investigation
No. 1492, Sept. 1943)

(6) <u>Electrolytic chromium</u>   (United States Bureau of Mines)

Ground chromite concentrate is leached with sulphuric acid and
chromium trioxide at 120°C. The leaching medium is return electrolyte
from the electrolytic cells and contains sodium and ammonium sulphates.
After separation of aluminium, iron, and magnesium by crystallization,
chrome alum is separated by further crystallization. This is re-
dissolved and electrolyzed, ampere efficiency being about 45 per cent.
The process is continuous and cyclic and has been used to produce 50 lb.
of metallic chromium per day from Montana chromite. The product is
about 99 per cent chromium metal and has been estimated to cost 25 cents
a pound on a large scale. Details of this estimate are not available.

(H 532: Trans. Electrochem. Soc., vol. 89,
p. 443, 1946.)

(7) <u>Sponge chromium</u>   (United States Bureau of Mines)

Finely ground chromite mixed with quartz or coke is heated to
1000°C and treated with chlorine. The volatile chlorides of iron,
aluminium, magnesium, and chromium are removed at about 900°C and
fractionally condensed, chromium chloride being obtained substantially
free of other chlorides. The chromium chloride is reduced with hydrogen,
hydrogen chloride being formed as a by-product. The product is 99 per
cent metallic chromium. Recovery is about 90 per cent. No costs are
available and the process, although very completely reported, is still

in the laboratory stage. There are serious technical difficulties

in handling chlorides on a large scale at these temperatures.

(R.I. 3480, p. 12: U.S. Bureau of Mines
Bulletin 436 (1942).

This list of proposed processes is not exhaustive. Methods which

appear to have been abandoned, such as the United States Bureau of Mines

matte smelting process, are not included. No mention has been made of the

many treatments which have been tried and found wanting.

V. PROCESSES INVESTIGATED BY THE MINES BRANCH

1. Introduction

At the Mines Branch, methods (1), (2) and (3), briefly described

in the previous section were investigated recently. The process of carbon

reduction followed by sulphuric acid leaching, as developed by the United

States Bureau of Mines and as modified by Hudson Bay Mining and Smelting Company

(Method No. 1), appeared to be the most promising of the methods already worked

out, being reasonable in cost and simple in operation. For this reason it was

checked and examined by the Mines Branch. Methods (2) and (3) were developed

at the Mines Branch and seemed worth following up. As they have not been reported

they are described in some detail.

All the tests at the Mines Branch were made on a mechanically

beneficiated concentrate from the Bird River area. The analysis of this

concentrate is:

Per Cent	Cr	Fe	Ca	Mg	Al	SiO_2
	28.44	19.10	0.48	4.22	9.54	3.16

This concentrate is typical of that obtained from Bird River ores and

is similar to that obtained from low-grade ores in United States.

The cost of this concentrate is estimated at $12 per ton, based on an

estimate of mining costs by Hudson Bay Mining and Smelting Company, and on

concentration tests by the Mines Branch.

2. **Reduction with Carbon or Methane and Leaching with Sulphuric Acid**

(a) **Introduction**

Processes have been developed by the United States Bureau of Mines and by Hudson Bay Mining and Smelting Company for beneficiating chromite by leaching with sulphuric acid after preferentially reducing some of the iron oxide in the mineral to metallic iron. These processes appeared sufficiently attractive, in particular that of Hudson Bay Mining and Smelting Company, to justify examination in some detail at the Mines Branch with a view to making an independent assessment of their value.

These processes depend upon the fact that oxides of iron are more easily reduced to the metal by carbon or methane than are the oxides of chromium, and that metallic iron and chromium are dissolved by sulphuric acid much more readily than are their ignited oxides.

As carried out by the United States Bureau of Mines, the concentrate is roasted with carbon or methane gas, and leached with hot 10 per cent sulphuric acid to remove the reduced iron. Although a carbon-chromite mixture may be roasted at temperatures where the iron oxides are reduced but the chromic oxides are not, the rate of reaction at these temperatures is prohibitively slow with the grind of concentrate used at the United States Bureau of Mines (90 per cent minus 100-mesh). Therefore the process is carried out at higher temperatures and controlled by the time of roast, quantity of reducer, time of leach, and strength of leaching acid.

Hudson Bay Mining and Smelting Company found, however, that by fine grinding of the concentrate (80 per cent minus 325-mesh) the roasting could take place at temperatures where the iron oxides were

reduced yet the chromium oxides were not. With the fine grind the process could be controlled by roasting temperature alone. An unpublished paper by L. Griffith on this process, as investigated by Hudson Bay Mining and Smelting Company, is on file at the Mines Branch. A detailed abstract of the paper is given later in this report.

(b) Results of Mines Branch Investigation

The method of beneficiation is to hold a mixture of finely ground (80 per cent minus 325-mesh) chromite concentrate and coal at such a temperature, in practice around 1150°C, that reducing conditions are set up over the coal which will reduce iron in the chromite but not chromium. The reduced iron is then leached out with sulphuric acid, leaving a residue with an increased chromium-iron ratio.

In the laboratory tests at the Mines Branch, as at Hudson Bay Mining and Smelting Company, 100 grams of concentrate was mixed with 20 grams of coal and placed in a covered crucible. The charge was put into a hot Globar furnace, and timing was begun when the furnace had achieved the desired temperature. The charge was cooled in the crucible.

Two series of roasts were run, one series using Algoma coke breeze, the other Michel coal, as the reducer. In each series, roasts were made at different temperatures throughout the critical range. The calcines were leached, and both residue and liquor were analysed for chromium and iron content. The acid consumption during leaching was determined, and a beneficiated residue was analysed for sulphur.

Results of experiments carried out by Hudson Bay Mining and Smelting Company were found reproducible within reasonable limits. The

acid consumption during leaching can be accounted for by the iron and chromium leached out, with a small allowance for lime and magnesia. Residual sulphur was low, analysing 0.063 per cent in the sample examined. The results of the experiments carried out at the Mines Branch indicate that Bird River chromite can be satisfactorily beneficiated by this process to a chromium-iron ratio of at least 5:1, with a chromium recovery of 95 per cent, using Michel coal, or 8.6:1, with a chromium recovery of 86 per cent, using coke. No exhaustive search was made for optimum roasting conditions. The laboratory work gave no indication that difficulties would arise which would hinder commercial application. The calcines, while somewhat fritted together, crumbled easily, and the leach solution filtered readily.

The results of these experiments, in conjunction with results given by Hudson Bay Mining and Smelting Company, and the United States Bureau of Mines, for similar selective reduction processes, show the effect of varying the reducing agent. The United States Bureau of Mines has carried out extensive tests using methane-hydrogen gas mixtures as the reducer (R.I. 3847) and coke (R.I. 3834). It has been shown that methane-hydrogen or natural gas mixtures will reduce iron in chromite at temperatures as low as $1000^\circ C$, whereas atmospheres set up over coke require temperatures of $1200^\circ C$ for equivalent reduction. However, the reduction using methane-hydrogen is much less selective than that using coke, an appreciable amount of chromium being reduced together with the iron. Experiments using coal to set up the reducing atmosphere reveal a behaviour between these two extremes. It is indicated that the amount of volatile matter, largely made up of methane and hydrogen, in the coal governs the properties of the reducing atmosphere.

In terms of the final leached residue, for a constant chromium recovery, as the reducing agent varies from methane-hydrogen gas through

coal to coke, steadily increasing chromium-iron ratios are obtained. Alternatively, for a given chromium-iron ratio, as the reducing agent is varied from methane-hydrogen through coal to coke, steadily increasing chromium recoveries are obtained. Some idea of the relative effects of different reducing agents may be obtained from the following table:

Table 3

The Effect of Reducing Agent on Temperature
of Roast and Chromium-Iron Ratio Obtained

Reducing Agent	Temperature, °C	Cr/Fe	Chromium Recovery, Per Cent	Reference
Methane-hydrogen	1000	2.6	94	R.I. 3847
Crow's Nest Coal	1150	4.04	93.6	H.B.M. & S. Co.
Michel Coal	1200	5.18	94.9	Mines Branch
Coke	1300	·7.4	93.4	R.I. 3834
Coke	1400	8.7	93.3	R.I. 3834

The United States Bureau of Mines, in R.I. 3847, has compared methane-hydrogen gas or natural gas mixtures with coke as reducing agents in its process. This comparison favours coke as the reducing agent from the point of view of maximum beneficiation and recovery, and the gaseous reducer from the point of view of cost of reducing agent and fuel, temperature, and rate of reaction, and cost of furnace construction. Gaseous reducing agents were not used in Hudson Bay Mining and Smelting Company's process.

(c) Estimate of Cost of Beneficiation

An estimate of the costs of treatment of chromite concentrate made by Hudson Bay Mining and Smelting Company, revised to 1949 rates, is

reproduced below with a more recent revision of the cost of sulphuric acid:

(Basis, 250 tons of concentrate, at about 100 per cent minus 48-mesh, per day; the ferrous sulphate formed in the leaching to be crystallized out and used in a contact plant as the principal source of sulphuric acid.)

		Per Ton of Concentrate Treated
Grinding, dry, to 80 per cent minus 325-mesh	-	$ 0.50
Reducing roast:		
Operating, maintenance, misc., $2.00 Coal, 0.32 ton @ $11.00, $3.52	-	5.52
Leaching	-	0.73
Crystallization of ferrous sulphate	-	0.20
0.28 ton H_2SO_4 at $15	-	4.20
Miscellaneous at 10 per cent	-	1.11
		$12.26

Recovery, about 95 per cent

Since natural gas is not readily available in central and eastern Canada, and in view of the higher chromium-iron ratios obtainable through the use of coke, it was considered worthwhile to make an estimate of the cost of using coke to beneficiate some concentrate to a chromium-iron ratio of 8:1 and using the resultant material to sweeten untreated concentrate to a ratio of 3:1. The costs are based on Hudson Bay Mining Company's estimates for 1949, with sulphuric acid again at $15.00 per ton.

		Per Ton of Concentrate Treated
Grinding, dry, to 80 per cent minus 325-mesh	-	$ 0.50
Reducing roast:		
Operating, maintenance, misc., $2.00 Coke, 0.32 ton @ $11.00, $3.52 Grinding coke @ $2.00/ton, $0.64	-	6.16
Leaching	-	0.73
Crystallization of ferrous sulphate	-	0.20
Sulphuric acid, 0.416 ton @ $15.00	-	6.25
Miscellaneous at 10 per cent	-	1.38
Cost per ton concentrate beneficiated to Cr/Fe = 8	-	$15.22

If used to sweeten 0.6 ton of raw concentrate to Cr/Fe = 3, cost per ton concentrate beneficiated is $9.50.
Recovery, about 95 per cent

This cost may be compared with the estimate of $12.26 based on 1949 costs for beneficiating to a chromium-iron ratio of 3:1 using coal. Though the difference between these two figures is not numerically very significant because of the approximations involved in the estimates, it indicates a tendency towards lower costs by sweetening, a tendency which might be exploited by using coke, or coal low in volatile matter. Since methane and hydrogen react very readily with chromite, a fairly minor change in the amount of volatile matter in the coal used could have an appreciable effect on the chromium-iron ratio of the product and on the chromium recovery of the process. It is worthy of note that in Canada there are large amounts of western coals low in volatile matter which are, in addition, extremely friable, and hence, easily pulverized. However, the choice of reducing agent, natural gas, coke, or coal, is dependent upon

economic factors not now determinate and in particular upon plant
location.

For commercial-scale roasting, three possibilities have been
suggested: roasting in saggers in brick kilns, Wedge or Herreshoff
roasters, and rotary kilns. The temperatures required, particularly if
coke is used, are considered high for a multiple-hearth roaster. A
rotary kiln was employed successfully by the United States Bureau of
Mines for roasting chromite with coke. This kiln was run up to 72
hours at temperatures in excess of 1340°C. In view of the experience of
the United States Bureau of Mines a rotary kiln appears suitable for
the process.

(d) Summary

It is believed, on the basis of laboratory results and comparison
with work done on a similar process on a pilot-plant scale by the United
States Bureau of Mines, that Hudson Bay Mining and Smelting Company's process
is technically feasible and can be carried through at a very reasonable cost.

(e) Abstract of Unpublished Results Obtained by Hudson Bay
    Mining and Smelting Company ("Beneficiation of Chrome
    Ores by Low-Temperature Selective Reduction,"
    unpublished paper by Laurence Griffith.)

General Principles

A theoretical equilibrium diagram is drawn from thermodynamic
considerations which indicates the feasibility of selectively reducing iron
from chromite by roasting in contact with air within a limited temperature
range. This diagram is illustrated in Figure 1. From the diagram it may be
seen that iron in chromite can be selectively reduced by carbon over the
temperature range 850°C to 1190°C in contact with air, and over the range
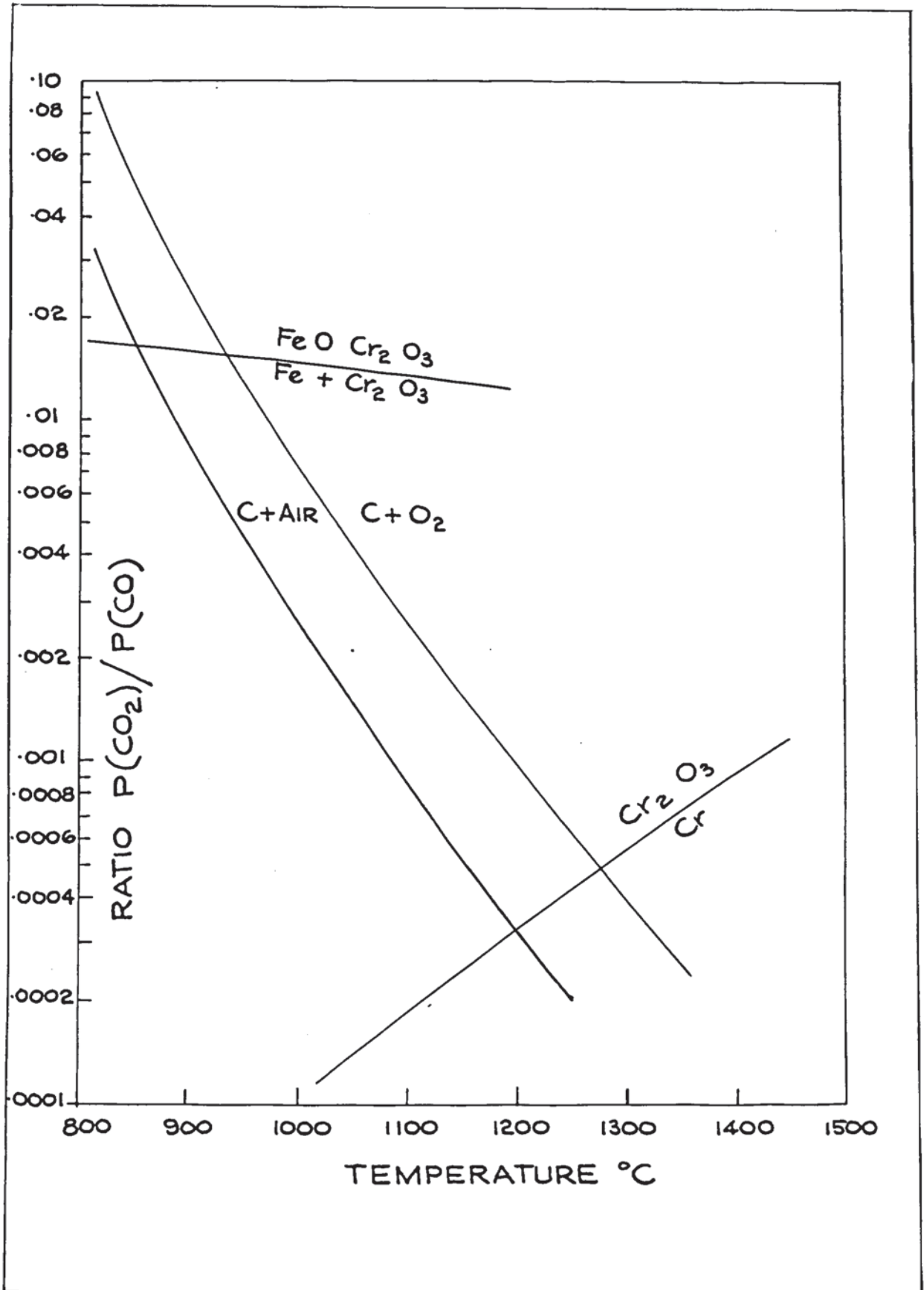950°C to 1260°C in the absence of air.

Figure 1 - Phase diagram showing limits of stability of oxides of iron and chromium in contact with carbon, with respect to temperature.

Experimental Methods

A typical analysis of the chromite concentrate used in this investigation is:

Per Cent	Cr	Fe	SiO_2	Al_2O_3	CaO	MgO	Mn	P
	27.4	21.0	2.9	18.7	3.4	6.9	0.2	0.03

Before use the concentrates were ground to 80 per cent minus 325-mesh, except where noted otherwise. The reducer was Crow's Nest coal, 90 per cent minus 200-mesh.

In most of the tests 100 grams of concentrates was mixed with 20 grams of coal and then placed in a 200-gram assay crucible which was covered with an assay scorifier. The pots were placed in a hot Burrell Globar furnace and as soon (5 to 10 minutes) as the pyrometer indicated the desired temperature, timing was begun. The furnace pyrometer and the heat distribution in the furnace were frequently checked with a master pyrometer and spot temperatures are believed to be within 10°C of true. In three-hour tests the temperatures may have varied as much as 25°C too high or too low for short periods. Generally the pots were allowed to cool with the lids still in place, but no re-oxidation occurred if the lids were removed, or if the contents were poured into pans to cool. The charge was somewhat fritted together but broke easily to a powder between the fingers.

Originally the calcines were tested by running leaches in an excess of 10 per cent sulphuric acid, weighing the residue and having it assayed for chromium and iron. Later it proved more convenient to analyse the calcines for total chromium, total iron, acid soluble chromium, and acid soluble iron (an excess of 10 per cent sulphuric acid was used in the acid-soluble assays). The two methods gave about the same results. Later, as described below, continuous leaching tests, simulating leaching on a practical scale, were carried out. These did not extract as much iron or chromium as

was indicated by the acid-soluble iron and chromium assays, but the amounts were sufficiently close to serve as an operating guide.

Experimental Determination of the Best Roasting Temperature

Table 4 gives a summary of the experiments run to find the best temperature for selective reduction.

Table 4

Effect of Temperature on the Selective Reduction (20 gm. coal per 100 gm. conc.)

Temperature, °C	Time of Roast, Hours	Leach Cake		Per Cent of Metal Rendered Soluble	
		Cr/Fe Ratio	Cr Recovery Per Cent	Cr	Fe
Leached but not roasted		1.35	100.0	0	7.2
675	13	1.38	100.0	0	9.5
800	4	1.43	100.0	0	12.7
925	4.5	1.46	100.0	0	16.3
1095	3	1.93	100.4	0	35.3
1150	3	4.04	93.6	6.4	71.4
1175	4	5.44	88.6	11.4	78.1
1200	2	4.58	84.6	15.4	77.6
1230	3	3.28	80.6	19.4	69.4
1260	3	2.69	69.8	30.2	67.1

Some of these results are shown graphically in Figure 2.

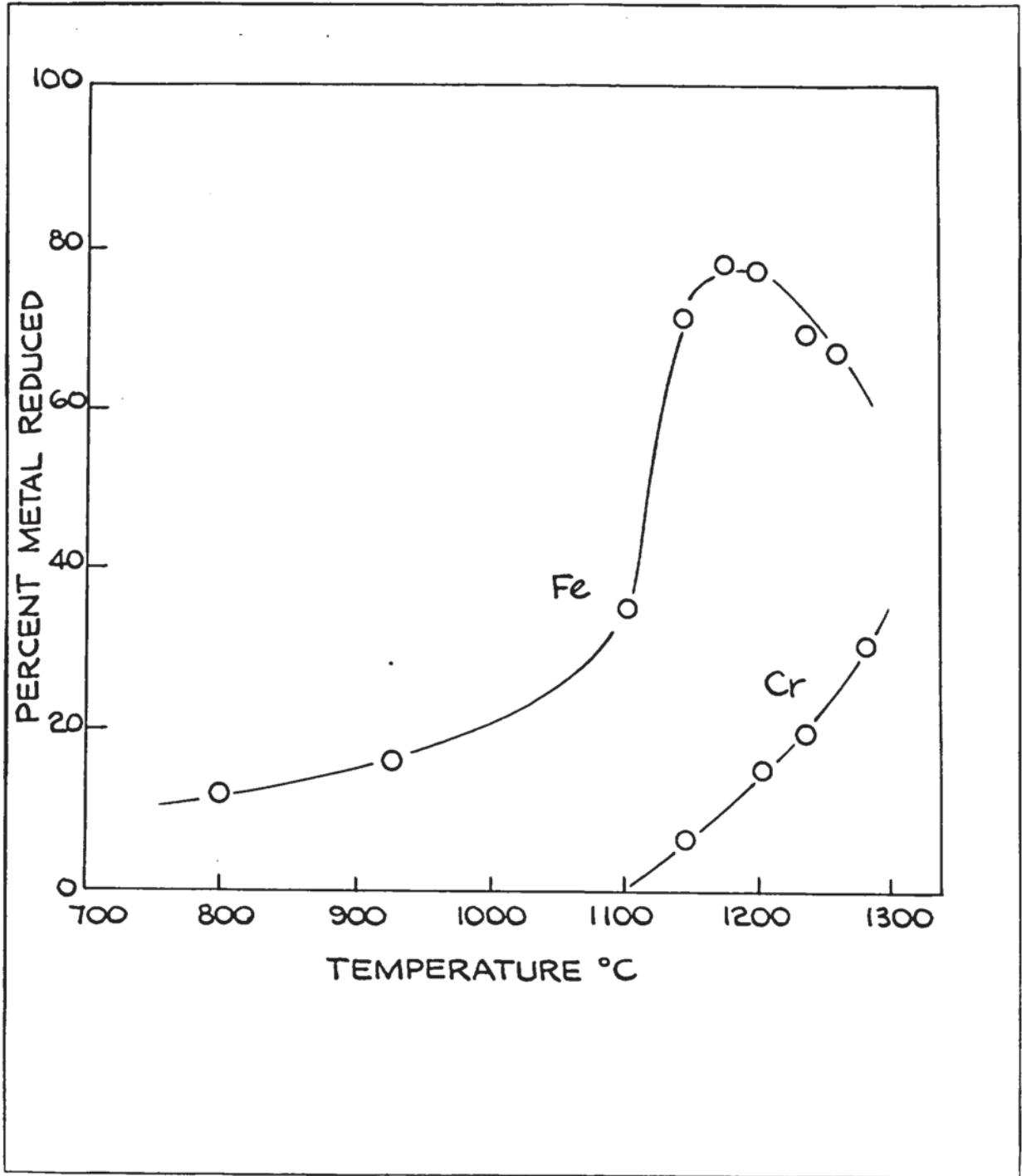No explanation is offered for the drop in percentage iron rendered soluble.

Figure 2 - Effect of temperature on fraction of total iron and chromium reduced.

Table 5

Effect of Duration of the Roast

Time of Roast, Hours	Temperature, °C	Cr/fe Ratio	Cr Recovery Per Cent
1	1150	2.01	94.8
2	1150	3.71	94.0
3	1150	4.04	93.6
4	1150	3.16	89.6

The data from Table 5 are plotted in Figure 3.

Effect of Quantity of Coal Used

The effect of variation in the quantity of coal used is shown in Tables 6 and 7, and in Figure 4. These results show the importance of temperature control. At 1200°C, no amount of coal will produce the desired chromium-iron ratio, while at 1150°C, a chromium-iron ratio greater than three is obtained, the ratio being almost independent of the amount of coal used.

Table 6

Effect of Quantity of Coal Used - 1150°C, 3-Hour Roasts.

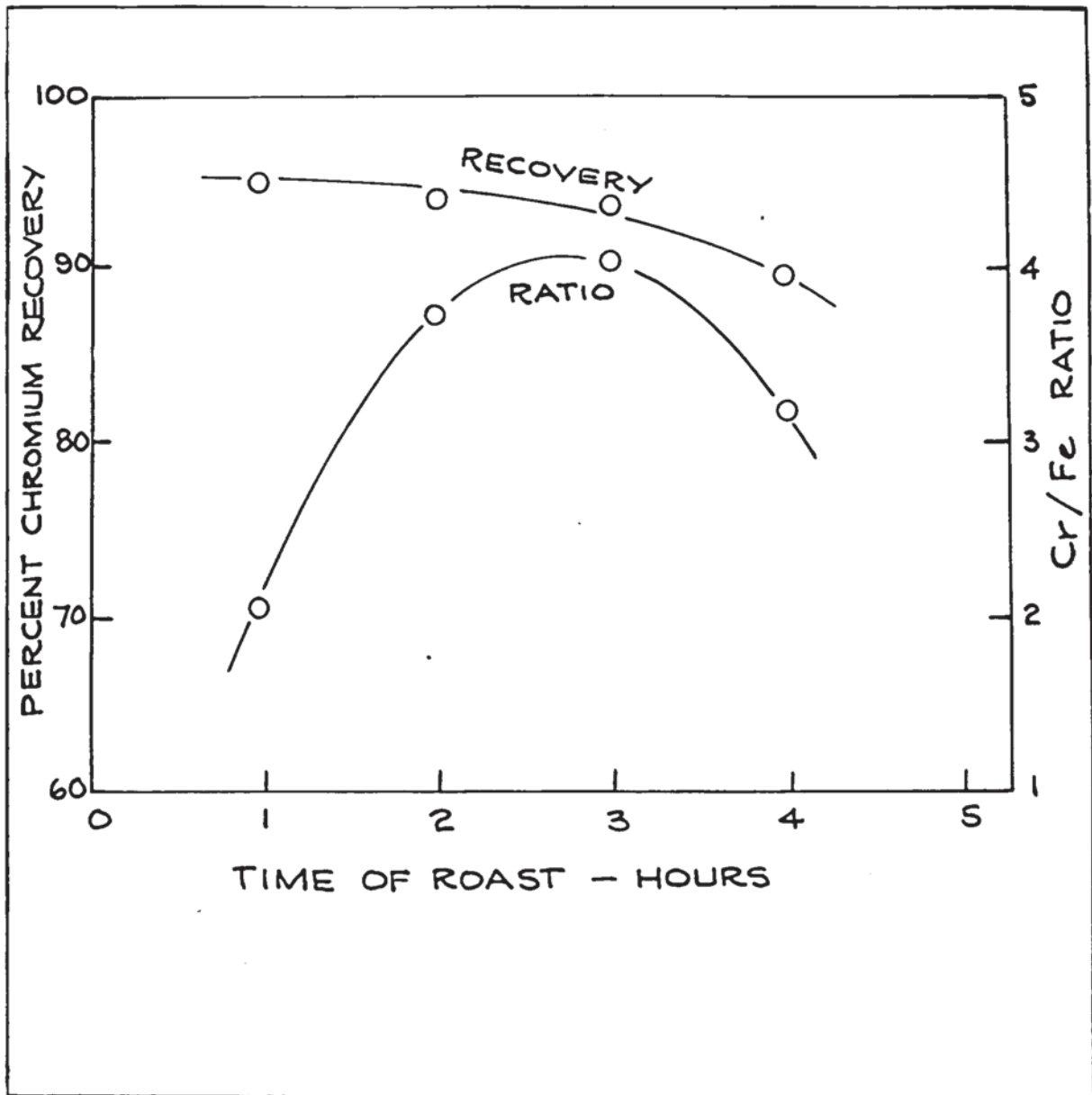| Gm. Coal per 100 gm. Concentrate	Temp., °C	Calcine				Leach Cake		Per Cent Fe Rendered Soluble
		Fe Per Cent	Cr Per Cent	ASFe Per Cent	ASCr Per Cent	Cr/Fe Ratio	Cr Recovery Per Cent	
10	1150	21.7	29.0	8.6	0.4	2.18	98.6	39.6
20	1150	21.0	28.4	14.0	1.2	3.88	95.6	66.6
30	1150	21.2	28.3	14.1	1.4	3.79	95.1	66.5
40	1150	20.3	27.5	13.3	1.4	3.70	94.9	65.5
50	1150	19.9	27.2	13.0	1.7	3.72	93.8	65.3

Note: ASFe = Acid Soluble Iron, etc.

Figure 3 - Effect of roasting time on chromium recovery and Cr/Fe ratio in finished product. Roasting Temperature 1150°C.
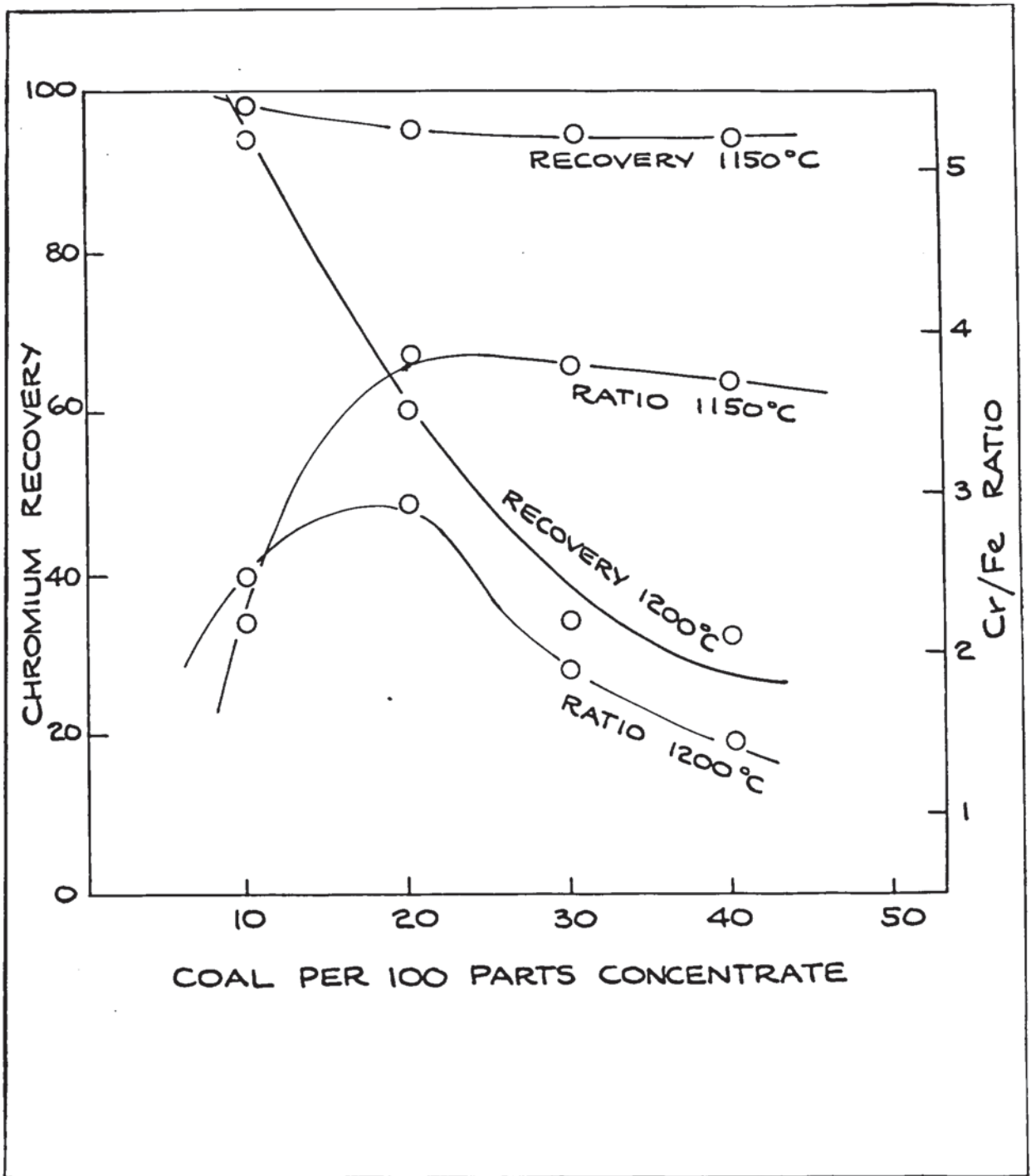
Figure 4 – Effect of quantity of reducing agent in chromium recovery and Cr/Fe ratio in finished product.

Table 7

Effect of Quantity of Coal Used - 1200°C, 5-Hour Roasts

Gm. Coal per 100 gm. Concentrates	Temperature, °C	Leach Cake		Per Cent Fe Rendered Soluble
		Cr/Fe Ratio	Cr Recovery Per Cent	
10	1200	2.42	94.2	51.3
20	1200	2.95	60.3	74.4
30	1200	1.90	34.2	77.5
40	1200	1.46	32.3	72.4

Effect of the Time of Leaching

The materials rendered soluble in the roast leach out quickly, after which the residue changes but slightly. This conclusion is drawn from the data obtained by leaching a calcine prepared at 1175°C, which are illustrated in Figure 5. As will be noted, the recoveries are some-what low as 1175°C is a little too high a temperature for selective roasting.

Effect of Grind on the Roast

That fine grinding is essential is shown by the data of Table 8 which are illustrated in Figure 6.

Table 8

Effect of Fineness of Grind, Roasts run 3 hours at 1150°C

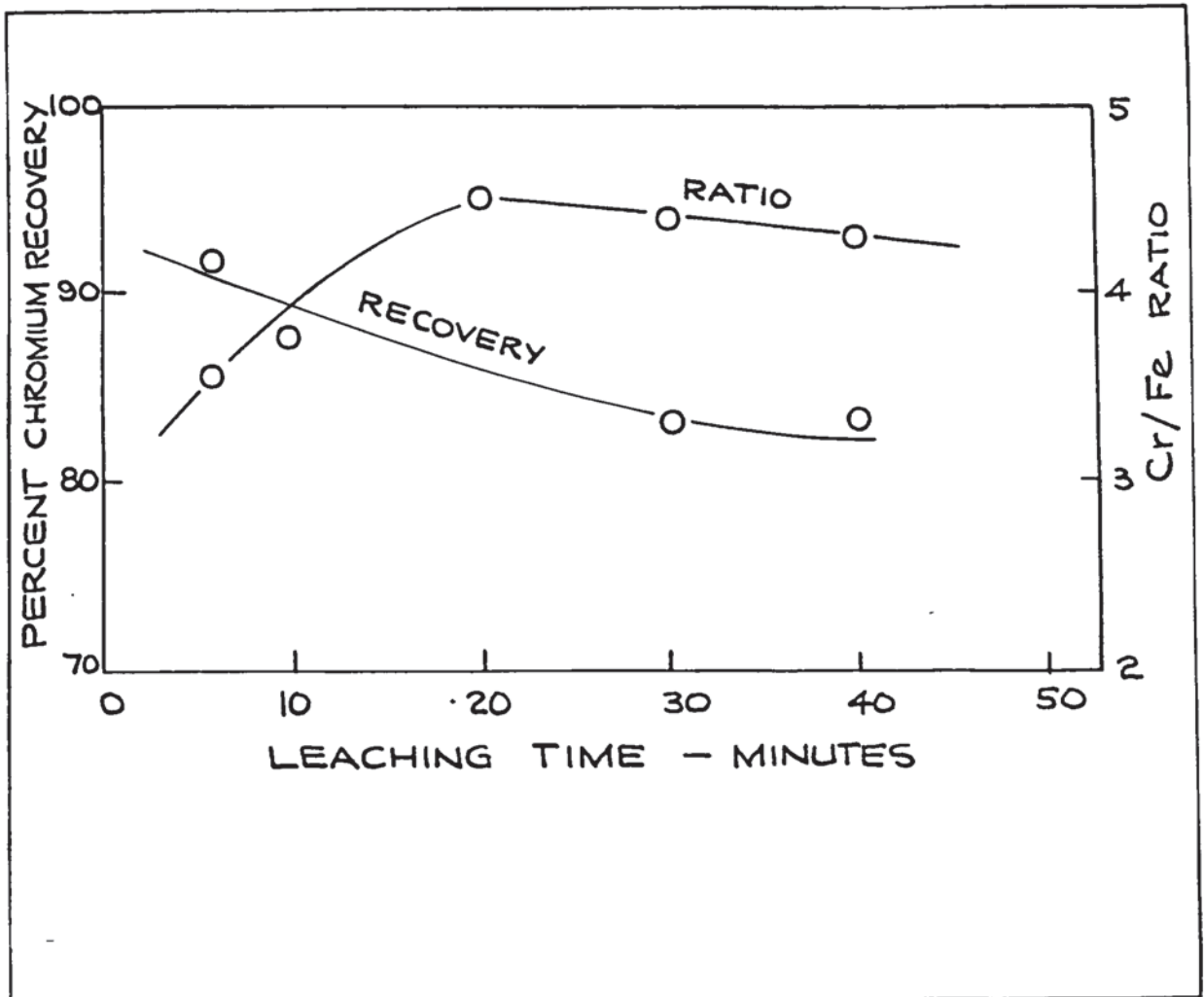|		Charge 1	Charge 2	Charge 3	Charge 4
Screen Analysis of Charge	(+48 mesh	4.3	0	0	0
	(-48 +65 mesh	18.5	0.2	0.1	0
	(-65 +100 "	30.9	3.8	0.1	0.1
	(-100 +150 "	23.5	13.3	0.5	0.1
	(-150 +200 "	12.8	18.2	3.1	0.1
	(-200 +325 "	7.9	16.3	15.1	0.9
	(-325 "	2.1	48.2	81.1	99.0
Cr/Fe ratio of leach cake		1.44	2.16	3.61	4.04
Cr Recovery Per Cent		98.8	99.2	97.8	93.6
Per Cent Cr made soluble		1.2	0.8	2.2	6.4
Per Cent Fe made soluble		11.0	42.2	66.7	71.4

Figure 5 – Effect of leaching time on chromium recovery and Cr/Fe ratio in finished product. Roasting temperature 1175°C.

Retreating Material Roasted at Too High a Temperature

The following data show that, if chromite should be inadvertently roasted at too high a temperature, which would result in large losses of chromium in the acid leach, the condition may be corrected by re-roasting the material at the proper temperature.

A charge of 100 grams of concentrates plus 20 grams of coal was held at 1230°C for three hours. The product had the analysis:

Fe	-	23.6 Per Cent
Cr	-	29.4 " "
ASFe	-	16.4 " "
ASCr	-	5.7 " "

This on leaching yielded a product of chromium-iron ratio 3.29 but the chromium recovery was only 80.5 per cent. Thirty grams of the product was then mixed with 6 grams of coal and reheated at 1150°C for one hour. The product assayed:

Fe	-	21.4 Per Cent
Cr	-	26.1 " "
ASFe	-	16.0 " "
ASCr	-	5.1 " "

These figures yielded a leach cake of ratio 3.89 but the chromium recovery was still only 80.5 per cent. A second 30-gram sample was therefore mixed with 6 grams of coal and held at 1150°C for 3 hours. The product assayed:

Fe	-	22.0 Per Cent
Cr	-	26.3 " "
ASFe	-	16.0 " "
ASCr	-	1.8 " "

This yielded a leach cake of ratio 4.08 at a chromium recovery of 94.2 per cent.

This result would be of much importance in practice, for if, say, a Wedge or Herreshoff roaster were used, only the lower two or three hearths would need to be held to the critical temperature. The upper hearths could be run hot to speed up the reduction.

<u>Leaching Tests on Selectively Reduced Calcine</u>

In practice the calcine would be leached with hot dilute sulphuric acid. After removing the leach residue the solution would be cooled to crystallize $FeSO_4.7H_2O$ from it, the acidity would be brought up to strength by adding a concentrated sulphuric acid, and the mixture used to leach more calcine. It can be easily shown that if the calcine is leached while it is still hot from the furnace no external heating of the acid leach will be required. The production of acid should be from the ferrous sulphate crystals produced, small amounts of pyrite being used to make up losses. In the Bird River district it would be slightly cheaper to use pyrite as a source of all the acid, but the disposal of the ferrous sulphate is a serious problem which is best overcome by using this material as the source of acid. Since the acid need not be concentrated, a chamber-process or contact plant would be satisfactory.

A continuous series of leaches following the above procedure and under conditions simulating plant practice was carried out. No difficulties were encountered, but it should be noted that the leaching efficiency was not quite as good as would be expected from the acid-soluble iron and chromium assays on the calcines used. On the other hand, the chromium recoveries were better than indicated by the calcine assays.

There is a tendency towards frothing during the leach. This is apparently related to the quantity of residual coal in the calcine. If the calcine is under-roasted the froth is difficult to control. The gases

given off in the leach have a very obnoxious odor.

The beneficiated concentrates resulting from this series of leaches were combined and analysed. The composition was as follows:

Cr	-	29.6 Per Cent or	Cr_2O_3 =	43.2 Per Cent
Fe	-	10.5 "	"	
SiO_2	-	4.0 "	"	
Al_2O_3	-	21.4 "	"	
CaO	-	1.4 "	"	
MgO	-	8.7 "	"	
Cr/Fe	-	2.82 "	"	

Analyses on similar material indicate that it contains only a trace of sulphur and no phosphorus.

The acid consumption in the continuous leach test was 0.28 gm. H_2SO_4 per gram of calcine. The calculated consumption for solution of the iron is only 0.233 gram per gram of calcine.

Operating Costs of Beneficiation

A detailed cost estimate, totalling $7.54 to treat one ton of concentrates, is given, based on 1942 rates.

A general flowsheet of a proposed plant is shown in Figure 7.

3. ### Oxidation to Chromate and Reduction of Chromate with Carbon (No. 2)

(a) ### Laboratory Experiments and Discussion

This method of beneficiation involves the oxidation of the chromium in chromite concentrates to sodium chromate by roasting in air with sodium carbonate, and then the reduction of the sodium chromate with carbon, producing chromic oxide, and regenerating sodium carbonate. The resultant chromic oxide is used to raise the grade of raw chromite concentrate to an acceptable chromium content and chromium-iron ratio.

A tentative flowsheet for production of chromic oxide is shown in Figure 8.

COAL

TABLE
CONC.

GRIND

REDUCING ROAST

LEACH TANKS

FILTER

WASH WATER

WATER

COOLER

FILTER
Fe SO₄·7H₂O

EVAPORATOR

DRYER

BENEFICIATED
CONC.

PART TO
WASTE

CAKE TO DISPOSAL

GROUND PYRITE
AIR

WATER

| PYRITE BURNER | DUST CHAMBER | HOT COTTRELL | LEAD TOWER | GAS COOLER | WET COKE PACKED BOLES | DRY | DRYING TOWER |

H₂SO₄

98%
H₂SO₄

ABSORB.
TOWER

H₂SO₄
STORAGE

SO₃
COOLER

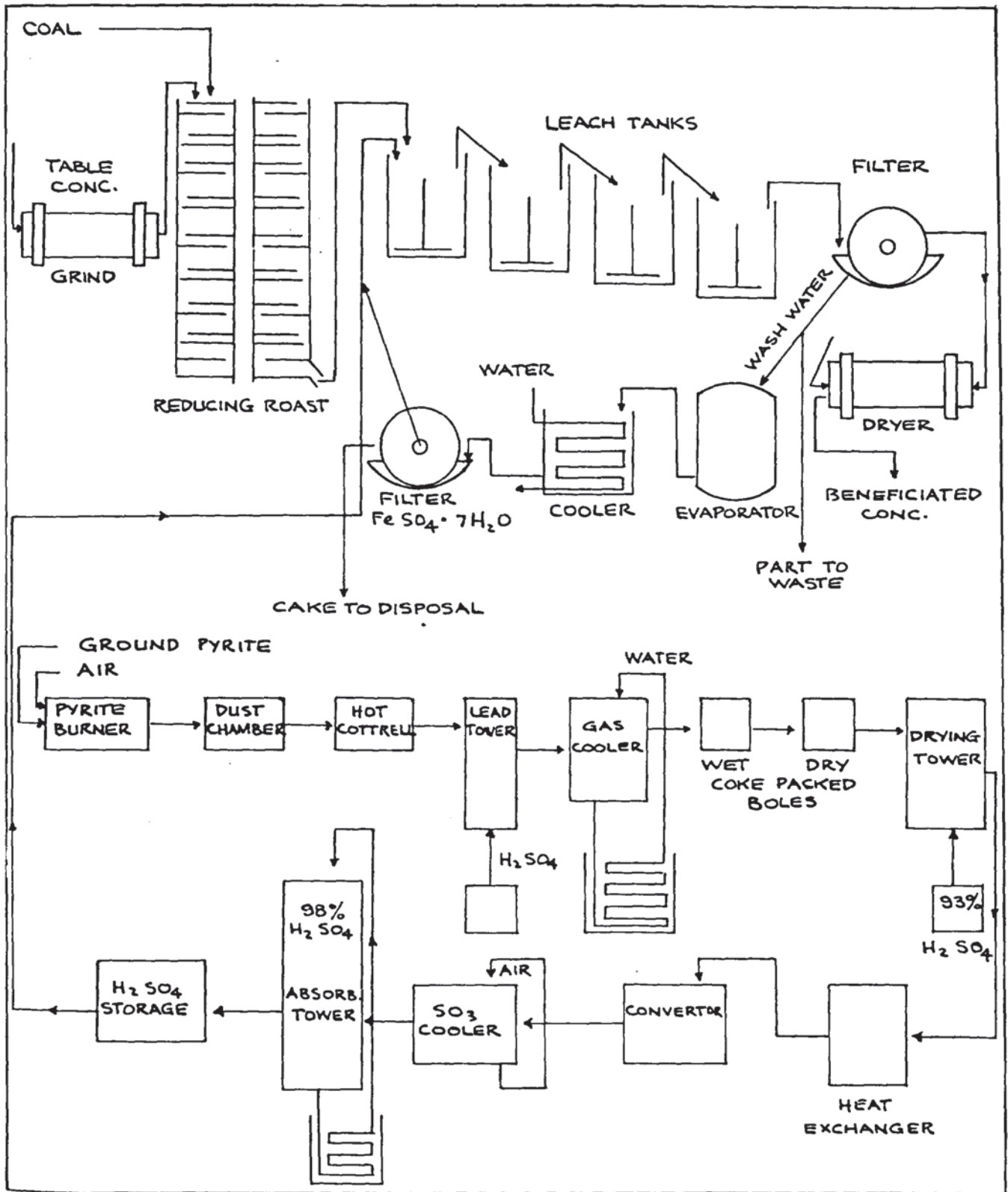AIR

CONVERTOR

HEAT
EXCHANGER
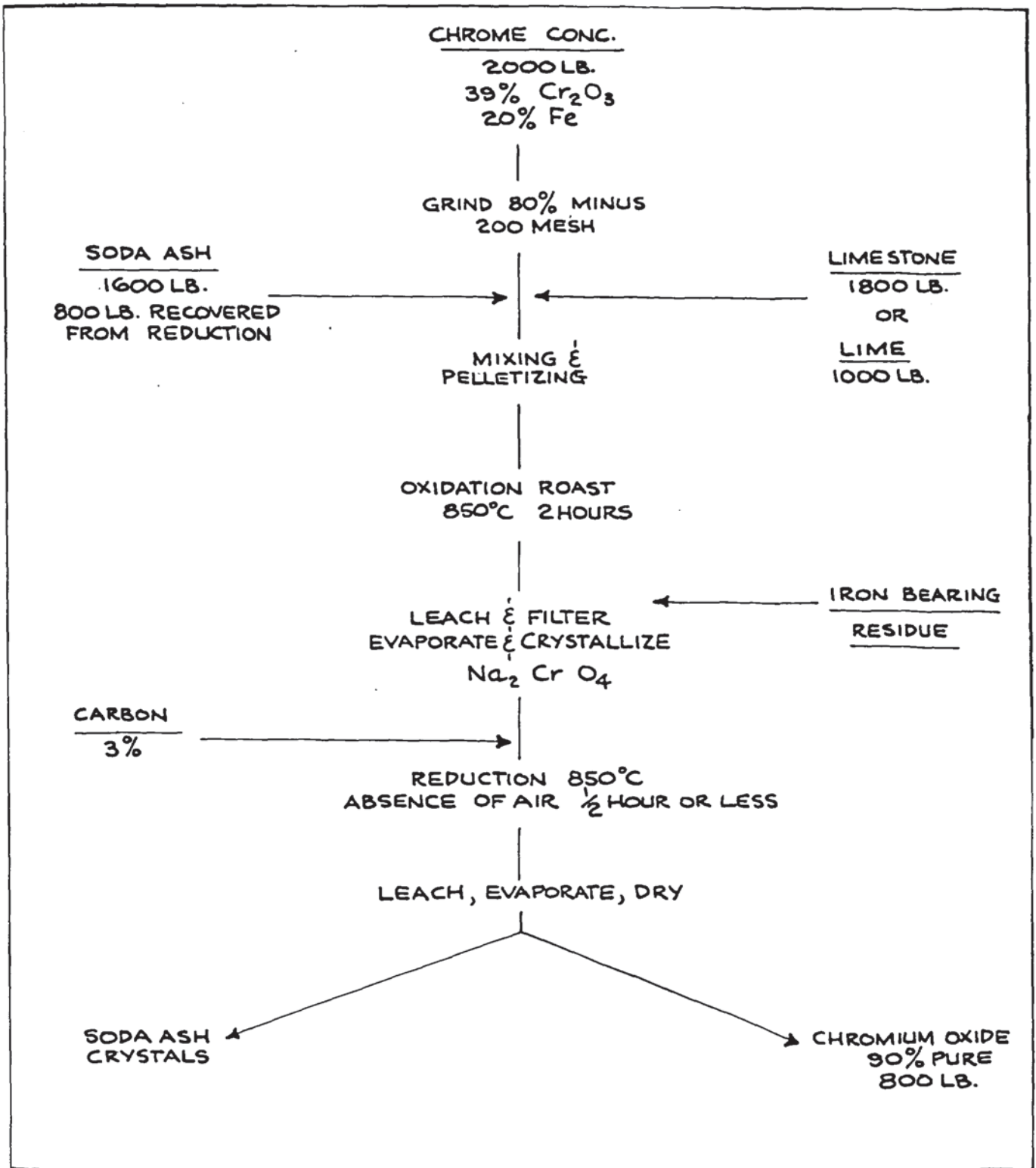
93%

H₂SO₄

Figure 7 - Flow Sheet

Figure 8 - Tentative flowsheet, for production of chromium oxide from Bird River chromite.

Investigative work on a laboratory scale has proven the feasibility of the separate steps shown in the flowsheet.

On a laboratory scale it was found that the charge could be made into pellets and that the chromite in the pellets could be 98 per cent oxidized to chromate in 2 hours at 850°C without disturbing the charge by rabbling of any sort.

Leaching produced a chromate solution from which, in evaporation, 98.7 per cent pure Na_2CrO_4 crystals were produced.

Preliminary work on the reduction of this sodium chromate by carbon indicated that the Cr_2O_3 product is approximately 90 per cent pure.

One essential step in this process is the recovery of soda. From the reduction process, 78 per cent of the equivalent Na_2CO_3 in the chromate was regenerated and recovered in the filtrate. This, as indicated in the flowsheet, could be returned to the pelletization step, thus greatly reducing the net soda ash requirements of the process.

The percentage of soda ash utilized in the oxidation stage to form chromate was not determined with this mixture (i.e. with lime present). However, tests using soda ash and chromite indicated that about 83 per cent of the soda went into sodium chromate. Although not confirmed by analysis, it is assumed that the lost 17 per cent was consumed in formation of silicates or aluminates. Using these two figures for the oxidation and reduction steps would give an overall recovery or regeneration of approximately 55 per cent of the soda used.

Although the process is feasible on a laboratory scale, its large-scale application hinges on the efficiency and capacity of the oxidation step in large scale production. Using a pelletized mixture of chromite concentrate, lime and soda ash in the proportions 1:0.5:0.8, the

progress of the reaction was as follows: at 45 minutes, 80 per cent oxidized to chromate; at two hours, 98 per cent; and at four hours, 99 per cent. The temperature was 850°C. This experiment was conducted in open dishes without rabbling in a muffle furnace in a current of air. Tests using oxygen enriched air showed no increase in the rate of reaction at higher oxygen concentration.

The chromic oxide product would be used to raise the grade and chromium-iron ratio of raw concentrate so that it would be acceptable for ferrochrome smelting. If the chromium-iron ratio of the concentrate were raised to 3:1 the grade would be 57 per cent. The considerable increase in grade is an advantage of this method.

(b) Rough Estimate of Cost of Beneficiation

This estimate is an approximation only. No provision has been made for power, labour, or capital. Although only 50 per cent recovery of soda ash is assumed in the oxidation step, the heat requirements in the reduction step have been calculated assuming complete recovery of the soda by evaporation of the soda ash solution.

(i)   Oxidation, Leaching, and Evaporation to Dry Na_2CrO_4

Based on 50 per cent recovery of soda ash. The United States Bureau of Mines estimated (R.I. 3480) heat requirements equal to 0.7 ton coal (12,000 BTU per ton) per ton of concentrate for oxidation. Assuming Na_2CrO_4 obtained in solution at 350 gm/l, specific gravity 1.25, evaporation will require 0.2 ton coal (12,000 BTU per ton) per ton of concentrate.

To beneficiate a ton of concentrate to a chromium-iron ratio of 3:1, the chromium is extracted from 0.566 ton of the concentrate and used to sweeten the remaining 0.434 ton.

Grind (dry) 0.566 ton concentrate to 80 per cent minus 200-mesh ($0.50 per ton)	- $ 0.28
453 lb. soda ash at $22 per ton	- 4.98
1020 lb. limestone at $4 per ton	- 2.04
0.51 ton coal at $11 per ton	- 5.61
Yield, 906 lb. Na_2CrO_4 (95 per cent recovery)	- $12.91

(ii) <u>Reduction with Carbon, Leaching out Soda Ash, and Evaporation of Soda Ash Solution</u>

Based on heat required to raise charge (Na_2CrO_4 + 3 per cent carbon) to 850°C, assuming specific heat of 0.3. No credit is given for heat developed by the reaction, which is slightly exothermic. Assume Na_2CO_3 obtained in solution at 200 gm/l, specific gravity 1.2, and evaporated.

0.159 ton coal at $11 per ton	- $ 1.75
Leach and dry	- 0.24
906 lb. Na_2CrO_4	- 12.91
Yield, 408 lb. Cr_2O_3, 90 per cent pure (95 per cent recovery)	- $ 14.90

The 408 lb. 90 per cent Cr_2O_3 is sufficient to sweeten 0.434 ton concentrate to a chromium-iron ratio of 3:1, containing 57 per cent Cr_2O_3. Thus $14.90 represents the cost of beneficiating one ton of concentrate to the required ratio. The cost of soda ash used in the above estimate, $22 per ton, represents the current price in the United States. The Canadian price ranges considerably higher, from $48 to $60 per ton. With soda ash at $50 per ton the beneficiation costs become $21.20 per ton of concentrate treated. It is felt that the American price is the better guide in

estimating costs for a large-scale emergency operation.

4. <u>Leaching in Sulphuric Acid Under Pressure</u> (No. 3)

(a) <u>Introduction</u>

It was found at the Mines Branch that chromite concentrate can be leached in sulphuric acid solution to yield a high-chromium low-iron residue.

The leaching is done at elevated temperatures and pressures. During the leach, iron, chromium, magnesium, and calcium, which occur in the chromite as oxides, react with the sulphuric acid and are taken into solution. If there is an excess of acid beyond that necessary to sulphate all the charge, chromic sulphate remains in solution, but if the acid is insufficient to form the normal sulphates, the chromium is reprecipitated as what is presumed to be a basic sulphate as the reaction progresses and the acid is used up. Ferrous, magnesium, and calcium sulphates remain in solution to be separated from the beneficiated residue by filtration. Sodium chloride may be added to the leach as a catalyst.

(b) <u>Experimental</u>

The experimental method used was to place finely ground (80 per cent minus 200-mesh) concentrate and sulphuric acid solution in a pyrex glass tube, seal, and heat to the desired temperature, generally about 200° to 250°C, with or without agitation. The charge was cooled, filtered, and washed. Both the beneficiated residues and the filtrates were examined.

Analyses of the chromite concentrate before and after a test follow:

	Per Cent	Cr	Fe	Ca	Mg	Al	SiO_2	S
Concentrate	-	28.44	19.10	0.48	4.22	9.54	3.16	
Beneficiated residue	-	21.7	6.85	0.07	0.78	7.48	2.63	10.09

The chromium recovery in the beneficiated residue was 95.5 per cent and the resultant chromium-iron ratio 3.17.

In this test the charge, heated six hours at 220°C, consisted of:

    10 gm. concentrate, 80 per cent minus 200-mesh
    5 ml. H_2SO_4
    12 ml. H_2O
    2 gm. NaCl

The sulphur content of the beneficiated residue was lowered to 0.23 per cent by heating at 1000°C in a crucible.

Assuming removal of all volatiles, the final analysis of the beneficiated chromite was calculated to be:

Cr	Fe	Ca	Mg	Al	SiO_2
29.8	9.42	0.10	1.07	10.1	3.62

These data show that, in the final product, the chromium-iron ratio was 3.17, the grade was 43.6 per cent Cr_2O_3, and the chromium recovery was 95 per cent.

The amount of beneficiation obtained by leaching in various amounts of acid is illustrated in Figure 9. The results shown were all obtained by complete reaction as defined by less than 5 per cent of the chromium remaining in solution. The chromium-iron ratio in the beneficiated residue does not continue to rise with increased amounts of acid but reaches a maximum at a ratio of about 3.5. The reason for this is explained later, in the discussion of the reaction mechanism.

A leach test was run with sufficient acid to sulphate all the chromium, magnesium, calcium, and iron in the concentrate. The specimen was held at temperature for a length of time considered ample for complete reaction. The iron found in the liquor was 15.7 per cent of the original concentrate (82 per cent of the total iron), roughly equivalent to the amount of iron in the ferrous state. This appears to be close to the maximum possible removal of iron by this type of leach.
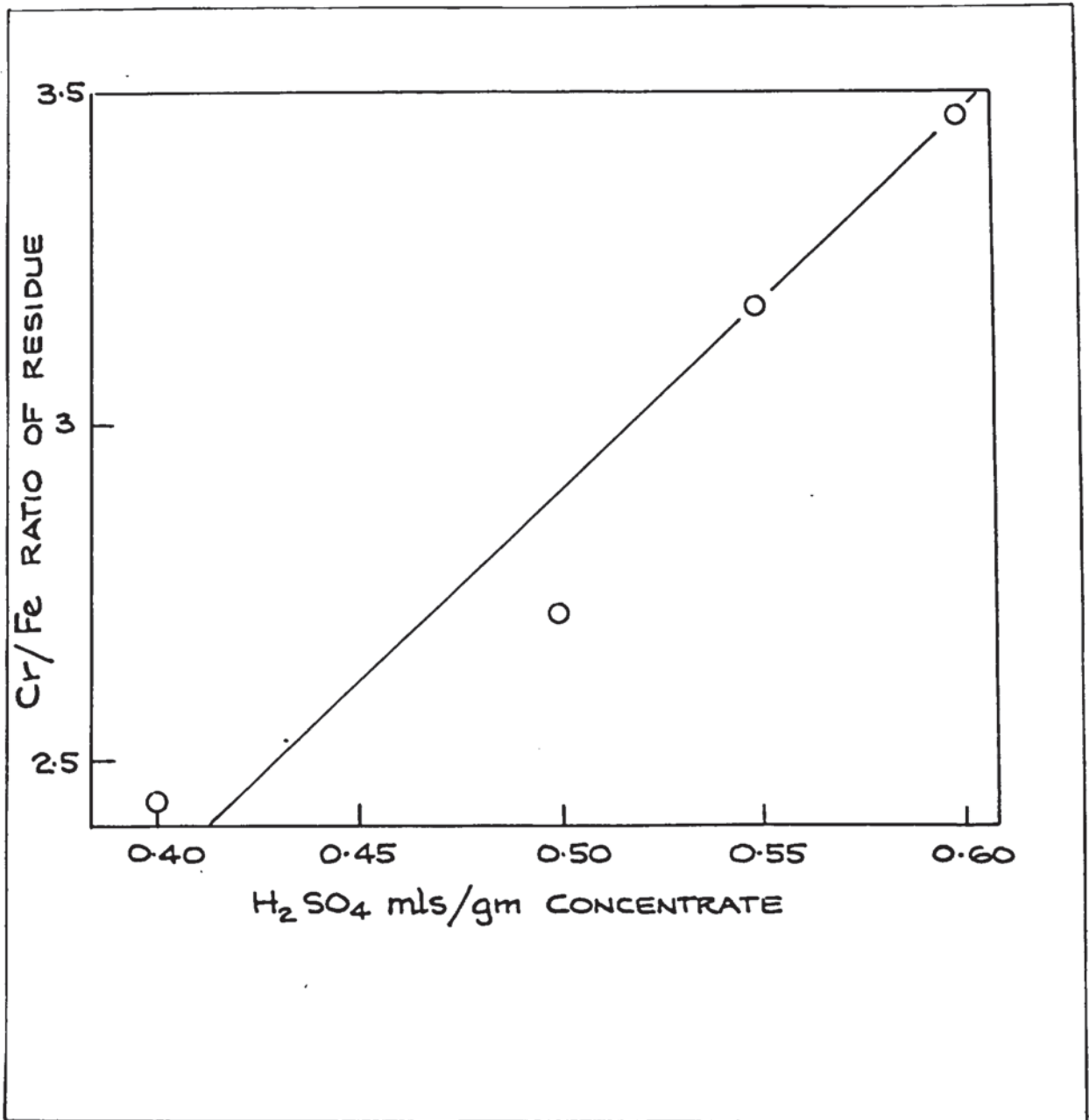
Figure 9 - Effect of quantity of leaching acid on Cr/Fe ratio of leached product.

Following the use of chlorides to catalyse other reactions
involving the destruction of the chromite lattice, as in producing sodium
chromate by reacting chromite with sodium carbonate (Handbuch der
Anorganischen Chemie - R. Abegg und Fr. Auerbach - Liepzig 1921), sodium
chloride was included in the leach. The temperature of reaction was
lowered slightly, and equivalent reaction took place in charges containing
20 per cent sodium chloride at temperatures about 15° to 20° below the
temperatures for charges without sodium chloride. Apart from this no
differences in leach behaviour or end products were noted. It is doubtful,
however, if the use of sodium chloride would have any practical value,
as the corrosive properties of chloride solutions tend to be more serious
than those of sulphate solutions, and in any case, the decrease in
temperature of leach is small.

(c) Reaction Mechanism.

The phenomena which were observed to be associated with the leach
throw some light on the mechanism of the reaction. It was noted that:

    (a)   Chromium is initially put into solution and later reprecipitated.

    (b)   Chromium is not reprecipitated if there is an excess of acid
           beyond that required to sulphate the chromium, iron, magnesium,
           and calcium.

    (c)   A considerable amount of sulphur is found in the beneficiated
           residue.

    (d)   The iron leached out is in the ferrous state.

    (e)   The amount of iron which may be removed while still retaining the
           chromium is limited.

The following theory is proposed for the mechanism of the leach.
Chromite is composed principally of the oxides of chromium and ferrous and
ferric iron, along with smaller amounts of aluminum, magnesium, and calcium
oxides. In the initial stages of the leaching all these oxides react with

sulphuric acid, forming the sulphates of the metals and water. Eventually the acidity of the solution is reduced to the point where chromic and ferric sulphates begin to hydrolyse, forming insoluble basic sulphates. This hydrolysis frees acid which continues to attack the ferrous, magnesium, and calcium oxides, and possibly also aluminum oxide. The final result, if the correct amount of acid has been added, is a solution containing principally ferrous sulphate, along with other soluble sulphates, and an insoluble residue containing the basic sulphates of chromium and ferric iron. Thus, neglecting the roles played by elements other than chromium and iron, the net result of the leaching is the extraction of ferrous iron from the chromite.

This theory satisfactorily accounts for all phenomena observed: the initial dissolution and subsequent reprecipitation of chromium, the non-precipitation of chromium in excess acid, the sulphur in the residue, and the limited amount of iron that can be removed without removing chromium. Since only a limited amount of iron can be removed without removing chromium, there is a limit to the chromium-iron ratio which can be obtained in the beneficiated residue.

(d) Conditions of Leach

The general scheme of beneficiation having been set up, it was thought advisable to investigate the conditions of attack on the chromite to estimate the minimum temperature and pressure at which the process could be carried out. The rate of attack oñ the chromite was followed by determining the amount of ferrous sulphate taken into solution. The charges were leached in sealed glass tubes, 1" x 3", agitated in a rocking-type autoclave. The times recorded were times at temperature. The heating and cooling periods

were essentially the same for all tests. The pertinent data from this
series of experiments are presented in Figures 10, 11, and 12.

It must be noted that the data shown for these tests do not
represent the results of complete reaction but rather the rate of reaction
as indicated by the amount of iron dissolved in a given time.

In all tests the amount of acid in the charge was the same,
sufficient to produce a residue having a chromium-iron ratio of 3:1 if the
reaction were carried to completion.

Effect of Temperature

Figure 10 shows the effect of temperature on the rate of attack for
two series of leaches differing in strength of acid solution. These results
were obtained by leaching similar charges at three temperatures, keeping the
leaching time the same in all cases. The curves indicate that an increase
in temperature increases the rate of attack.

Effect of Time

Figure 11 shows the rates of reaction observed for two different
leaches. These two curves may not be directly compared, since not only the
temperature but also the acid strength is different in each.

Effect of Acid Concentration

Figure 12 shows the importance of the strength of the acid solution
on the leach for three different leaching temperatures. In this group of tests,
charges with the same amount of chromite and sulphuric acid, but with varying
amounts of water, were caused to react, keeping the time and temperature of
leach the same for all tests in each series.

Up to an acid strength of about 1:2 by volume, an increased
concentration of acid leads to a higher rate of attack as indicated by ferrous
sulphate leached out. At higher concentrations, although a change in appearance
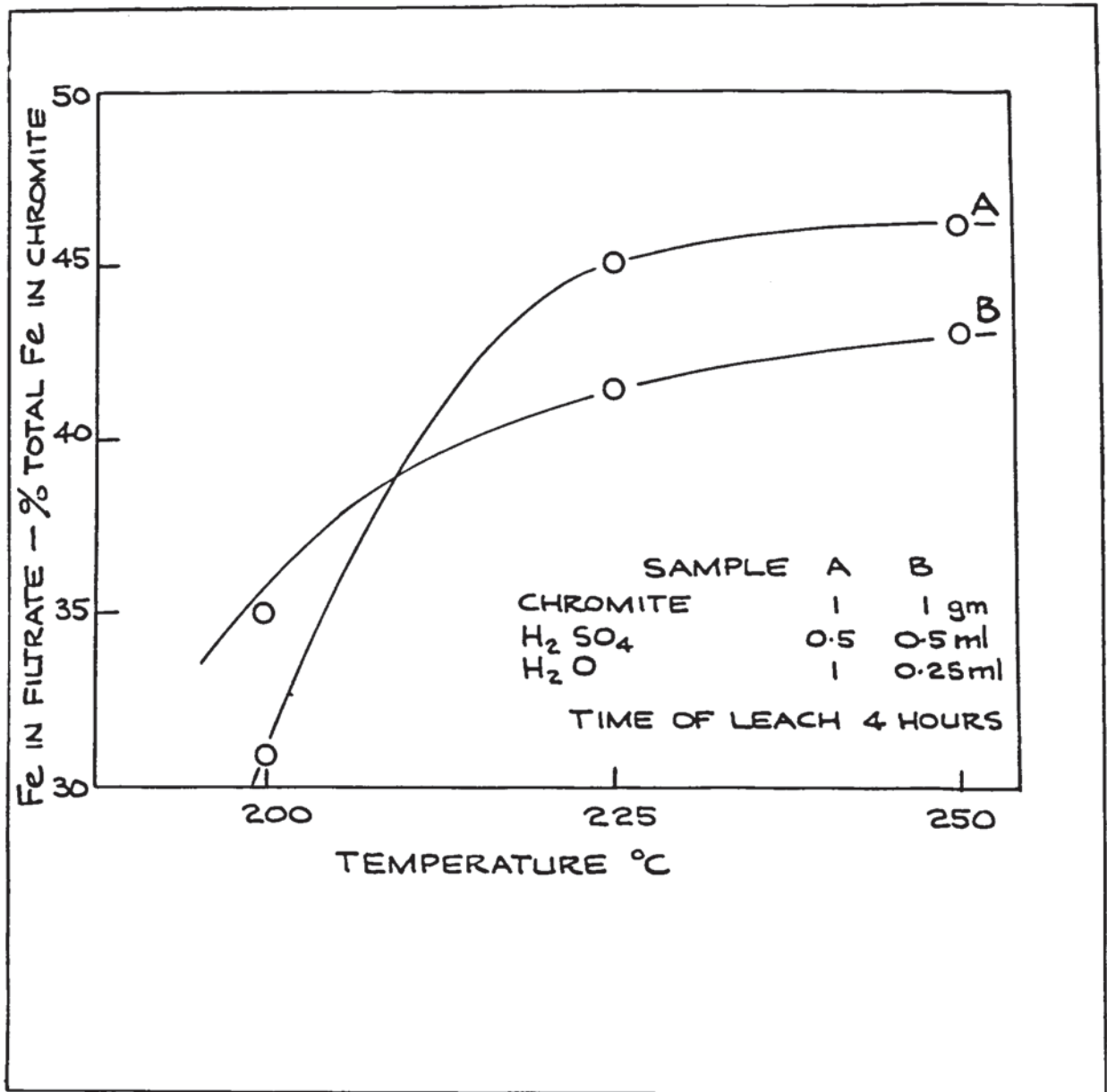of the charge indicates that sulphation takes place rapidly, there is a sharp

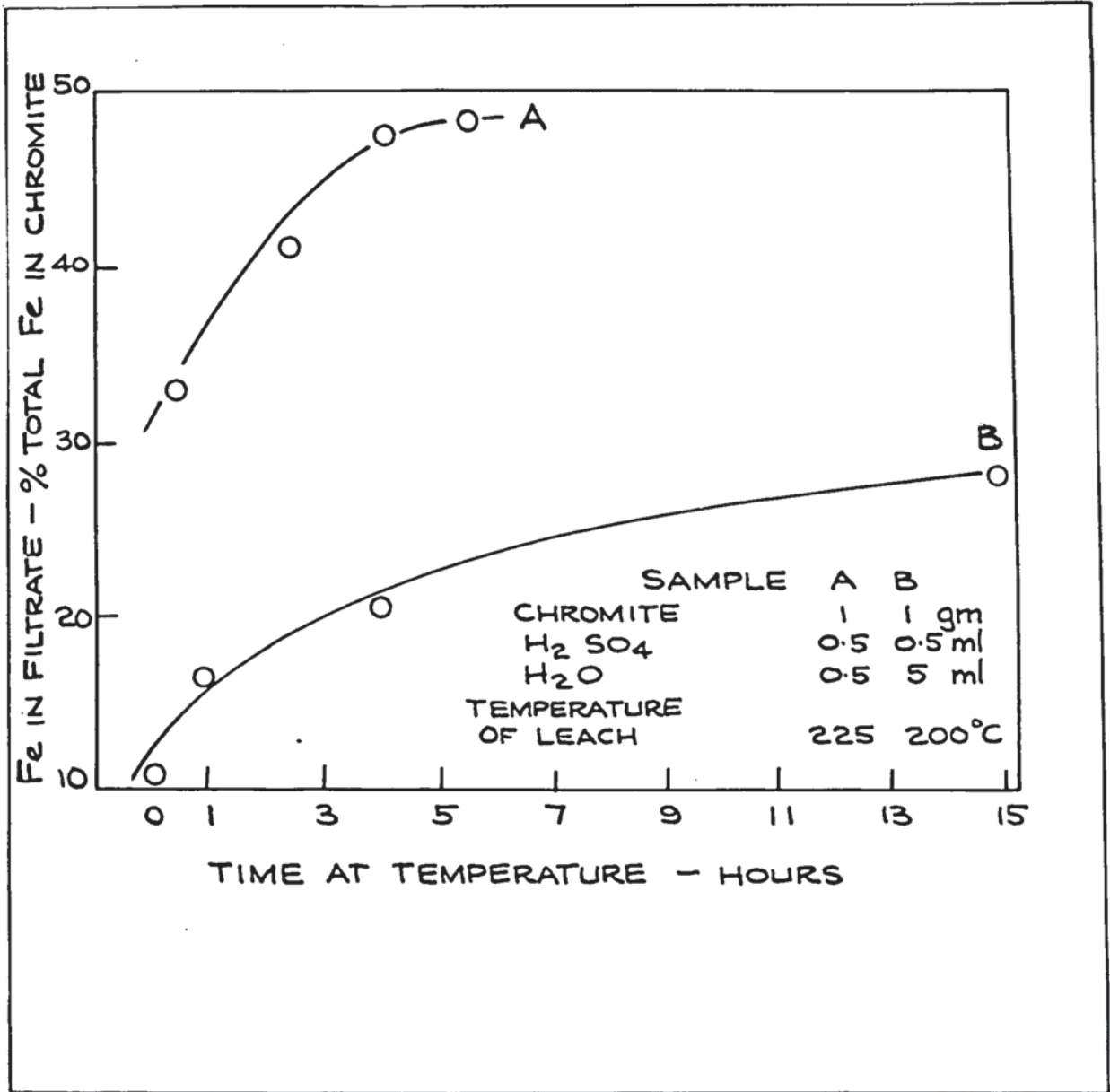Figure 10 - Effect of leaching temperature on fraction of total iron leached out.

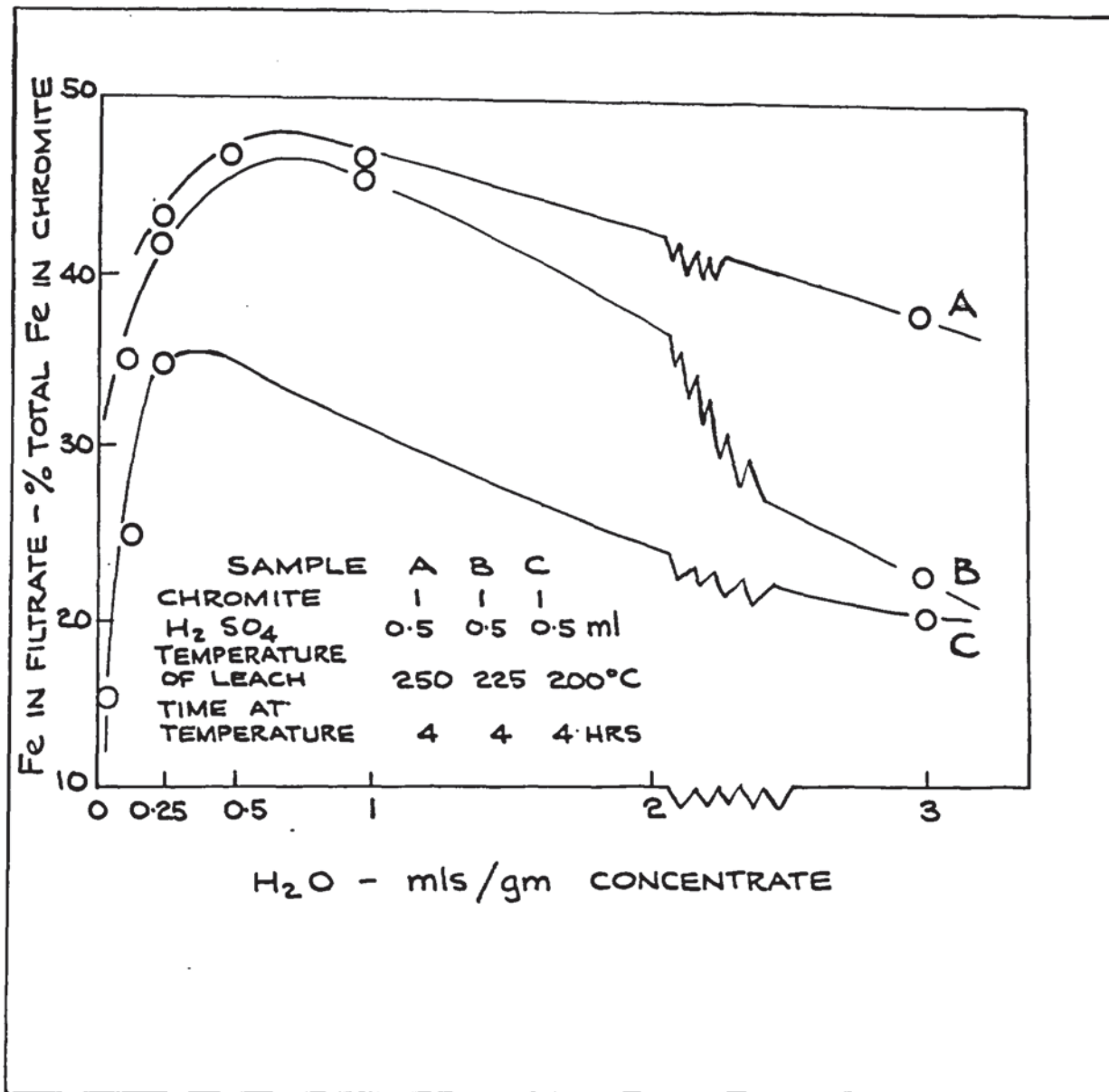Figure 11 - Effect of leaching time on fraction of total iron leached out.

Figure 12 - Effect of acid concentration on fraction of total iron leached out.

decrease in the amount of ferrous sulphate leached out.

Pressures Developed

Figure 13 shows the pressure set up over sulphuric acid solutions, strength 1:1 and 1:2 by volume, in the temperature range of interest. The pressures shown represent the pressures occurring at the beginning of leaches using such solution strengths. The pressure would not be expected to increase appreciably, if at all, during the leach.

Effect of Grinding

A test was made to determine the general effect of finer grinding on the acid attack. Two samples were leached in the same amount of acid six hours at $220^{\circ}C$, one sample screening 83 per cent minus 325-mesh, the other 80 per cent minus 200-mesh. With the sample of finer grind 46 per cent more iron was taken into solution than with that of coarser grind.

Evaluation

The data presented in Figures 10, 11, and 12 indicate that in order to carry out the reaction in a reasonable time the minimum temperature of reaction should be $225^{\circ}C$, preferably $250^{\circ}C$, and that the strength of acid solution should be about 1:2 by volume. The concentrate should be finely ground.

The temperature that can be used in practice will be limited by the reaction vessel, since both the pressure and corrosiveness of the acid solution increase with temperature.

The strength of acid used would have to be determined from a balance of several factors:

(a) The pressure developed, which is lower with more concentrated acid.

(b) The rate of reaction, which is higher with more concentrated acid.
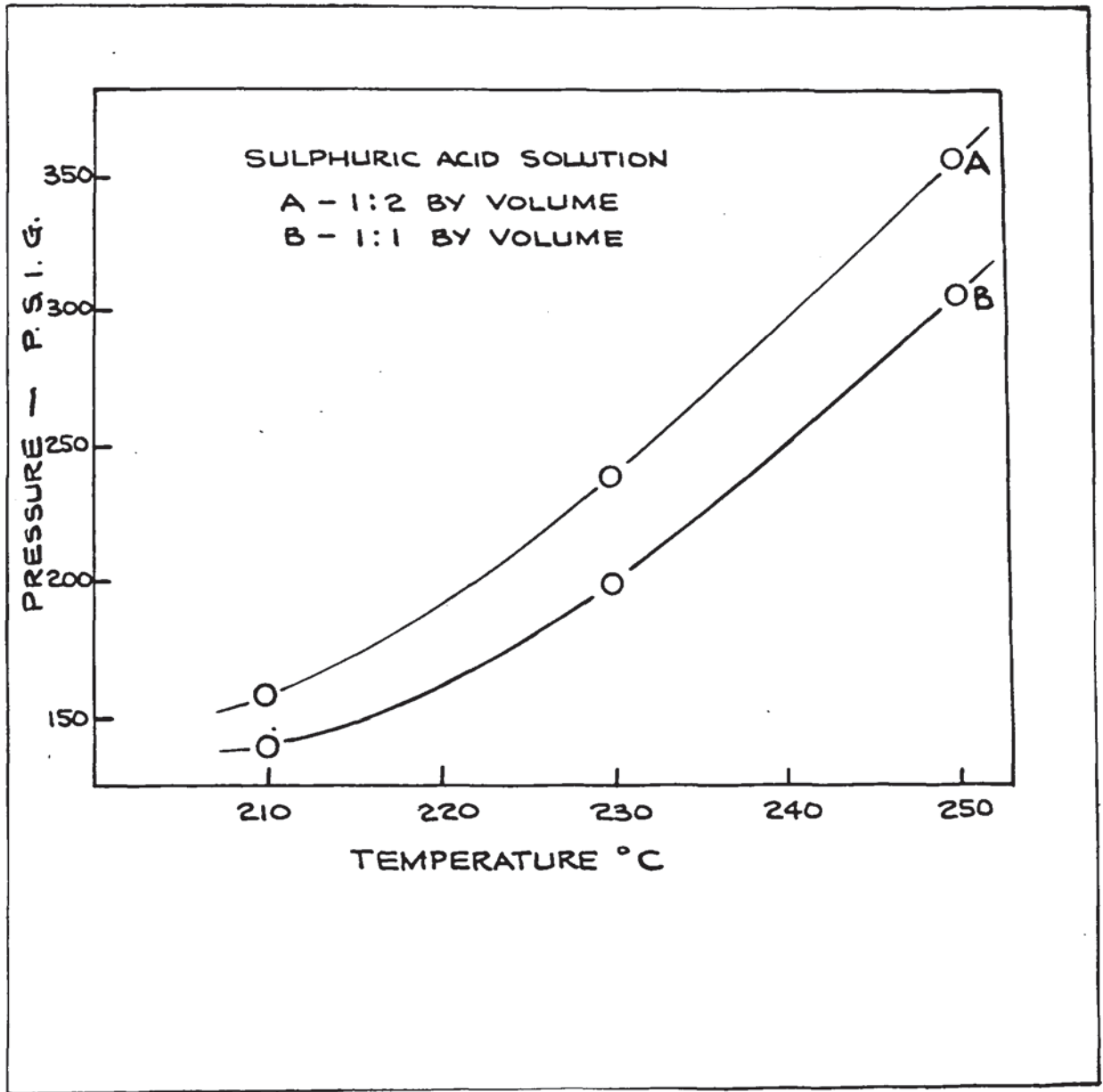
Figure 13 - Effect of acid concentration on equilibrium vapour pressure at various temperatures.

(c) Corrosion properties of solutions of varying acidity.

(d) Ease of agitating the sludge, which is more fluid with
     solutions of lower acid concentration, since the concentration
     is varied by varying the amount of water.

(e) Cost Estimate

A preliminary cost estimate has been made for producing a concentrate
having a chromium-iron ratio of 3, assuming that the sulphur will be eliminated
from the leached chromite by sintering at a cost of $2.00 per ton.

<div align="center">

Per ton concentrate treated

0.92 ton H_2SO_4 @ $15 per ton	-	$13.80
Grinding (wet)	-	0.25
Leaching	-	1.00
Filtering	-	0.20
Sintering	-	2.00
Recovery over 95 per cent		$17.25

</div>

The product would be suitable for ferrochrome smelting without further

treatment.

Since the greater part of the magnesium is leached from any concentrate

treated, thus using up an appreciable amount of acid, slightly lower costs

would be expected if the concentrate were more highly beneficiated and used

to sweeten untreated material.

(f) Summary of Sulphuric Acid Leaching

The process under consideration in this investigation entails leaching

at elevated pressures, an operation not at present in general use in the field

of metallurgy, although similar operations are common in the chemical industry.

No attempt has been made to design a process to be ready for immediate

application, but rather the chemical basis for the process has been sketched

out and some of the factors involved in the practical application have been

examined to gain a rough estimate of their magnitudes and importance.

No attempt has been made to determine the type of equipment that can be used for leaching. Equipment design will certainly present a problem, in view of the corrosive nature of the solutions used, and there has been little experience with such equipment in the metallurgical industry. However, in view of the rapid advances being made nowadays in pressure-reactors and corrosion-resistant surface coatings, it is felt that should the process be held economically attractive, no serious difficulty would be encountered in its application.

VI. GENERAL SUMMARY

The report summarizes the pertinent data regarding the extent of the Canadian and North American reserves of chromite ores, their quality, and possible uses, and methods that have been suggested for their beneficiation. Although the subject has been greatly condensed, sufficient references have been included to enable investigation of the background and authority for the important statements.

Although most of the information exists in the literature, the investigations of the Mines Branch and of Hudson Bay Mining and Smelting Company, Limited have not been published. Since these methods appear to have possibilities as large-scale chromite beneficiation processes, they are given quite extended treatment so that the data on which the final conclusions have been reached can be examined independently.

It is known that the Bird River and Montana deposits, the two largest deposits of chromite on the continent, can be mined and concentrated mechanically by tabling or by combined tabling and flotation to produce a concentrate containing about 40 per cent Cr_2O_3, chromium-iron ratio 1.3:1 to 5:1, with a recovery varying from 78 to 89 per cent. No unforeseen difficulties need be expected in these operations. The time required to attain the necessary production of

concentrates from these two deposits has been estimated at somewhat under two years.

These concentrates can be converted into high or low-carbon Chrom-X, in which form they can satisfy the metallurgical needs of the continent. No difficulty in making and using high-carbon Chrom-X exists, since it is being used in steel-making in competition with standard high-carbon ferrochrome. Low-carbon Chrom-X can be made if necessary, but is apparently not competitive with standard low-carbon ferrochrome. In many cases, the use of Chrom-X in place of standard ferrochrome in steel-making would have no detrimental effects on production.

Alternatively, the concentrates can be added directly to steel, using the Wild process which avoids the use of ferrochrome. This process is used by American Rolling Mill Company and is competitive with standard steel-making practice for many applications. These two methods of utilizing chromite of low chromium-iron ratio are thus proven, and since they compete with standard practice they cannot be unduly expensive or unwieldy.

In an emergency when maximum steel production is required it might be desirable to beneficiate the concentrates chemically to allow them to fit in with standard practice. To determine whether the chromite should be utilized as Chrom-X, or in the Wild process, or should be beneficiated to some degree, calls for a careful balance of the metallurgical and economic factors of the case under consideration.

In the Mines Branch laboratories two new methods for beneficiating domestic chromite concentrates have been worked out, viz., oxidation to chromate and reduction of the chromate with carbon, and pressurized leaching with sulphuric acid. These processes compared very favourably with others which were known both with regard to their technical feasibility and their economy in application.

It was at this point that the Mines Branch learned of the modification to the United States Bureau of Mines process of roasting chromite concentrates with carbon and leaching with sulphuric acid which had been developed by Hudson Bay Mining and Smelting Company. This company made its results available to the Mines Branch where the data were carefully checked, fully confirmed, and somewhat extended.

In view of the earlier pilot-scale work done by the United States Bureau of Mines on carbon reduction of chromite, and because Hudson Bay Mining and Smelting Company's modification consists only in the fineness of grind, this process should be regarded as having been through the pilot plant testing stage. It appears to be the simplest and most economical process so far proposed.

Assuming the most favourable conditions, namely, that a portion of the concentrates is highly beneficiated and used to sweeten raw concentrates, the process has been shown to cost roughly $9.50 per ton of beneficiated concentrates, chromium-iron ratio of 3:1. To this should be added the estimated cost of raw concentrate, $12.00 per ton, giving a total cost of $21.50 per ton of metallurgical grade chromite concentrates at Bird River. Even if these concentrates required sintering at $2.00 per ton to agglomerate them, the final cost of $23.50 per ton at Bird River compares favourably with the current price of imported chromite, about $39.00 at New York. The difference may not, however, be sufficient to justify a domestic chromite mining and beneficiating industry.

It may be concluded that chromite concentrates, obtained by the mechanical concentration of domestic chromite ores, can be beneficiated, raising the chromium-iron ratio to 3:1 if desired. And in view of the extensive pilot plant work done by the United States Bureau of Mines on their version of the process, no great technical difficulties need be expected in a commercial scale operation. For a few years at least, depending upon the extent of the ore deposits, and subject to a one-to two-year delay while the mines develop full production, the North American continent can supply its chromium requirements from its own resources.