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Chromium-Chromite: Bureau of Mines Assessment and Research

Proceedings of Bureau of Mines Briefing Held at Oregon State University, Corvallis, OR, June 4-5, 1985

Compiled by Charles B. Daellenbach

UNITED STATES DEPARTMENT OF THE INTERIOR

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PREFACE

Chromium is vital to the Nation's economy and is one of its most important critical and strategic materials. Chromium has a wide range of uses in chemical, metallurgical, and refractory industries. Although the United States is the world's leading consumer of chromium-bearing materials, it currently has no domestic production of chromite ore. The mineral chromite is the sole commercial source of chromium. Today the United States is totally dependent on foreign sources for its primary chromium materials.

With this background of national concern for chromium and chromite resources, the Bureau of Mines has had, for some time, a comprehensive program of chromium assessment and research. The objective of this 1985 Chromium-Chromite Briefing was to draw together the various elements of the current program and to present to industry, the public, and Government agencies the Bureau's multifaceted activities. Authors were drawn from three of the Bureau's directorates: Minerals Data Analysis, Minerals Information, and Minerals and Materials Research. The authors covered, through 18 presentations, a variety of topics including U.S. chromite and chromium trends and usage patterns; foreign and domestic resources; and research activities on mineral characterization and beneficiation, chemical and pyrometallurgical processing of chromite and chromium-bearing wastes, new low-chromium alloy and coating substitutes, corrosion- and oxidation-resistant stainless steels, and chromium-containing refractories. This report is a compilation of the papers presented at the briefing held at Corvallis, OR, June 4-5, 1985.

Special recognition goes to Julie A. Searcy and her staff at the Oregon State University, LaSells Steward Center, for their part in organizing and hosting the briefing activities. The assistance of Duggan Flanakin, Bureau of Mines, Division of Publication, in compiling the many manuscripts is gratefully acknowledged.

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Proceedings of Bureau of Mines Briefing Held at Oregon State University, Corvallis, OR, June 4-5, 1985

Compiled by Charles B. Daellenbach[1]

ABSTRACT

This briefing was sponsored by the Bureau of Mines to summarize ongoing and recently completed chromium-chromite research and resource assessment activities by the Bureau. Through the series of 18 presentations compiled herein, Bureau personnel covered a wide range of topics including U.S. chromite and chromium trends and usage patterns; foreign and domestic resources; and research activities on mineral characterization and beneficiation, chemical and pryometallurgical processing of chromite and chromium-bearing wastes, new low-chromium alloy and coating substitutes, corrosion- and oxidation-resistant stainless steels, and chromium-containing refractories.

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CHROMIUM CONTAINED IN U.S.-PRODUCED STAINLESS AND HEAT-RESISTING STEELS

By John F. Papp[1]

ABSTRACT

The primary objective of this Bureau of Mines study is to calculate an accurate, reliable Cr content of stainless and heat-resisting steel produced in the United States. Such a content is required for estimating the quantity of Cr recovered from recycled stainless steel and consumed by market sector.

The Unified Numbering System is a unified identification system of chemical specifications for metals and alloys developed as a collective effort among organizations publishing specifications. This system defines the Cr composition of U.S.-produced stainless and heat-resisting steels. The American Iron and Steel Institute's production data define the quantities of U.S.-produced stainless and heat-resisting steels. These Cr composition and production data were used to calculate the average Cr composition of stainless and heat-resisting steel produced in the United States from 1962 through 1983 as 16.7 pct. A historical series of the quantity of Cr contained in U.S.-produced stainless and heat-resisting steels was calculated, and those steels that accounted for the greatest amount of Cr were identified.

INTRODUCTION

The Bureau of Mines has reported Cr mineral production, consumption (*1*),[2] and availability (*2-3*) and has undertaken a supply-demand study. A result of the production-consumption report is apparent consumption (AC)[3] of Cr in the United States, a measure of national Cr consumption also called industrial demand. Chromium AC is compared with availability to determine adequacy of supply; it averaged 516,000 st/yr in the United States from 1973 through 1983. U.S. production now consists only of secondary production measured as Cr contained in purchased stainless steel scrap. Imports, exports, and inventories are measured as Cr contained in chromite ore and concentrate, Cr ferroalloys and metal, and Cr chemicals.

The major Cr-consuming industries are the refractory industry, the chemical industry, and the metallurgical industry. Chromite ore is consumed by the refractory industry for its chromite mineral content, while the chemical and metallurgical industries consume chromite ore for its Cr content. Chromium ferroalloys are consumed by the metallurgical industry for their Cr content. Over the 1973-83 time period the metallurgical industry accounted for 70 pct of industrial demand. Over the same time period the chemical industry accounted for 18 pct, and the refractory industry for 12 pct, of industrial demand. Based on the 1977-83 period, reported consumption of Cr materials by specific end use shows that stainless and heat-resisting (S&HR) steels account for 70 pct of the reported consumption. It is because S&HR steels account for 70 pct of metallurgical demand, which in turn accounts for 70 pct of industrial demand, that one can say: "As stainless steel goes, so goes chromium."

For the purpose of computing U.S. apparent consumption, secondary production (i.e., the Cr contained in purchased S&HR steel scrap) is the only component of domestic Cr production, to calculate secondary production, the Cr content of S&HR steel is required, hereafter called Cr/S&HR factor. The primary objective of this work is to calculate an accurate, reliable Cr/S&HR factor. This conversion factor is also useful for estimating the quality of Cr consumed by market sector, recoverable by recycling, and required to produce S&HR steel.

Abbreviations Used in This Paper

mt	metric ton
pct	percent
st	short ton
st/yr	short ton per year
yr	year

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[2] In each paper in these Proceedings, italic numbers in parentheses refer to items in the list of references at the end of that particular paper.

[3] Apparent consumption = primary production + secondary production + imports − exports + beginning inventories − ending inventories.

PROCEDURE

METHOD

The Cr content of S&HR steel production was calculated using Unified Numbering System (UNS) and American Iron and Steel Institute (AISI) data. This calculation was carried out for the time period 1962-83. The Unified Numbering System for Metals and Alloys (*4*) defined the universe of S&HR steel grades and the Cr composition limits of those grades. Annual AISI S&HR steel production by AISI Type data (*5*) defined production. To calculate the Cr content of S&HR steel, UNS Grades were associated with AISI Types; then constituent Grade Cr composition defined Type Cr compositions. The Type Cr composition-production products were calculated and summed to get annual values. The Cr/S&HR factor was then calculated as the 1962-83 time average of the composition average of maximum and minimum Cr content of S&HR steels divided by total S&HR steel production.

Prior to calculating a historical series of chromium contained in S&HR steel in more detail than an aggregated annual total, it was necessary to combine AISI Types into Type Groups, hereafter called Groups. AISI reported production among 63 Types in combinations that varied from year to year, so Types had to be combined to form Groups for which a production value was available over the entire analysis period. (Exceptions to this definition are discussed below.) Having associated AISI Types into Groups for the analysis period, Group Cr compositions were calculated based on AISI Type Cr compositions. The Groups that accounted for the predominant amount of chromium use were identified by quantity used. The market classes, as identified by the American Society for Metals (*6*), were related to the Groups.

AISI TYPES BASIS SET

The S&HR steel categories about which the most detailed production data are available are the AISI S&HR steel Types. An AISI Type basis set was chosen to categorize 1962-83 S&HR steel production. The Type categories used by AISI to report production changed from the 1962-76 to the 1977-83 time periods. In 1977 AISI introduced many new specific Types and eliminated several descriptive Type categories. Table 1 contains definitions for specific and descriptive Types. In 1977 AISI introduced the specific Types 205, S30430, 304N, 316F, 316N, 317L, 329, 330, 384, 409, 420F, 422, 429, 434, and 436; 406 and 443 were eliminated. The eight descriptive categories under "Other chromium nickel stainless steels with:" were contracted into four descriptive categories under the name "Other Chromium Nickel Stainless Steels With:," and the "All other" category was subdivided into "All Other 15% Chromium or Less" and "All Other Over 15% Chromium."

The objectives in choosing a basis set were to (1) take advantage of the similarities between the 1962-76 and the 1977-83 sets, (2) eliminate rarely used categories, and (3) retain detailed production data. These objectives were satisfied by choice of the 1977-83 set to be the AISI Type basis set. This basis set contains 63 AISI Types, of which 55 are specific Types and 8 are descriptive Types.

Having chosen the AISI basis set as that of 1977-83, it was necessary to make the 1962-76 AISI S&HR steel production data consistent with 1977-83 Type set. This rationalization is necessary because of the category name changes made by AISI as described above. Each of the resulting special cases is discussed below. No changes in the 200 series or 300 series were required. In the 400 series, Types 406 and 443 appeared during the 1962-76 period but not during the 1977-83 period. Throughout the 1962-76 period, AISI combined production to Type 406 with that of Type 405. Except for 1965 and 1966, AISI combined production of Type 443 with that of Type 442. To adjust production values, Type 406 was treated as Type 405, and Type 443 was treated as Type 442. Prior to 1977, each of the "Other chromium nickel stainless steels" categories was subdivided into two categories: one for other alloys under 10 pct, and one for other alloys over 10 pct. Except for 1966-69, AISI combined production of the other alloy under 10 pct and over 10 pct into a single value for each nickel category. That AISI combination procedure was used in this study. The 1962-76 Type "All other" was subdivided into "All Other 15% Chromium or Less" and "All Other Over 15% Chromium" in 1977. In this study all of the pre-1977 "All other" category production was treated as "All Other 15% Chromium or Less." The 1962-76 category "501, 502, and All Other high chromium heat resisting steels" was subdivided into Types "501," "502," and "All Other High Chromium Heat Resisting Steels." In this study all of the pre-1977 "501, 502, and All Other High Chromium heat resisting steels," category production was treated as Type 501. Because of the AISI 1977-83 basis set used here, a few production values from the 1960's had to be combined.

TABLE 1.—Association of UNS Grades with descriptive AISI Types [1]

Descriptive AISI Type	Unified Numbering System, Unified Number
Other Chromium Nickel Stainless Steel With:	
Nickel under 8%	S20300, S21400, S21460, S21600, S21603, S21900, S21904, S24000, S24100, S31100, S31500, S36200, S41008, S41025, S41800, S43035, S43036, S44020, S44023, S44300, S44400, S44625, S44626, S44700, S44800, S4500
Nickel 8-16%	S14800, S16800, S20910, S21800, S30310, S30330, S30345, S30360, S30490, S30452, S30940, S31609, S32109, S34709, S34720, S34723, S34809, S45500
Nickel over 16-24%	S33100, S38100
Chromium 15% or less	S41040, S41610, S42023
Chromium over 15%	S18200
All Other High Chromium Heat Resisting Steels	S50300, S50400
Production Not Shown By Type [2]	S13800, S15500, S15700, S17400, S17600, S17700, S35000, S35500, S42300

[1] A *specific* AISI Type is an alphanumerically named AISI Type category that specifies a single grade, such as Types 304, 304N, and 409. A *descriptive* AISI Type is an AISI Type category whose name describes the category contents, such as Other Chromium Nickel Stainless With Nickel under 8%.

[2] PNSBT. This descriptive AISI Type name was Production Not Reported by Type (PNRBT) from 1962 through 1976.

UNS GRADES TO AISI TYPES

The largest single group of S&HR steel categories for which detailed chemical composition data are available are the UNS Grades. The UNS set of S&HR steels is composed of 116 Grades, each specifically numbered and having an elemental composition specification. Of these 116 UNS Grades, 115 are from the "Heat and Corrosion Resistant (Stainless Steels)" series and one is from the "Nickel and Nickel Alloys" series. The UNS Grades were distributed over the AISI Type basis set to define the Cr composition limits of the AISI Types.

Only one UNS Grade corresponded to each of the 55 specific AISI Types. For these 55 Types, the Type Cr composition is the same as the corresponding Grade Cr composition. There were multiple UNS Grades for seven of the remaining eight descriptive AISI Types. For one descriptive AISI Type (Nickel Over 24%), there was no USN Grade. The association of UNS Grades that correspond to specific AISI Types is straightforward because the USN Grades are cross-referenced with AISI Types (*4*). Those UNS Grades were assigned first. The remaining UNS Grades then belonged to one of the descriptive AISI Type categories. These remaining UNS Grades were distributed among the descriptive AISI Types as follows:

1. All UNS Grades that had no AISI Type name were assigned to the "Other Chromium Nickel Stainless Steels" Types if they contained nickel, or to the "All Other" Types if they were nickel-free.
2. All UNS Grades that had an AISI Type name were assigned to the "Production Not Shown By Type" (PNSBT) Type.

Table 1 details the result of these associations. In each case where more than one UNS Grade contributed to an AISI Type, the constituent Grade Cr compositions were averaged to obtain the Type Cr composition.

Having defined the AISI Type basis set Cr content via UNS Grades and production via AISI S&HR steel production reports, the Cr/S&HR factor can be calculated. Let Cr_{mi} be the fractional Cr content of Type i, where m represents minimum, median, or maximum. Let P_{ij} be the AISI S&HR steel production reported as Type i in year j. Then F, the Cr/S&HR factor, was calculated as

$$F_m = [\sum_{j=1962}^{1983} \sum_{i=1}^{63} Cr_{mi}\, p_{ij}] \,/ \sum_{j=1962}^{1983} \sum_{i=1}^{63} p_{ij}.$$

AISI TYPES TO GROUPS

To produce a historical series of chromium contained in S&HR steel in more than annual aggregate detail, many AISI Types had to be collected into Groups that have an annual production value composed of the same AISI Type production values over the entire analysis period.

The necessity to combine Types into Groups results from AISI's variation of (1) Type categories and (2) Types among which production was collected. To collect as few Types as possible together, when the effect of combined production was small, the Types were not combined and the definition of Groups set forth above was not strictly followed. Groups 201, 304, 317, and 429 were affected. For example, S30430, a constitutent of Group 304, was introduced in 1977 and combined with Type 304 in 1980, 1982, and 1983. To have rigidly adhered to the Group definition would have meant assigning Type 304 to PNSBT Type category, when S30430 production was only 2 pct of that of Type 304. Both Group production and Cr composition were defined by those of the constituent Types.

Over the time period of this analysis, AISI published production data for most AISI Types, although not for each Type each year. Since production data were available, those data were used to define the relative importance of the contribution of each AISI Type to a Group. The relative importance, the weight factor, was calculated as the production-based fractional contribution of each AISI Type to its Group. The fraction, for a given year, is the production for an AISI Type divided by the Group production and is called the annual weight factor.

Thus, the Cr composition of a Group is defined as the production-based, weighted average of the constituent AISI Types times the Cr composition of constituent AISI Types summed over the constituent Types. For example, suppose that a Group is composed of three AISI Types; the Type i production in year j is Pij and Group g production in year j is

$$p_{gj} = \sum_{i=1}^{3} p_{ij} \qquad (1)$$

The annual weight factor for Type i in year j is $w_{ij} = P_{ij}/P_{gj}$. Let the uniqueness of Type i reported production in year j be

$$u_{ij} = \begin{matrix} 0 \text{ for composite production, or} \\ 1 \text{ for unique production.} \end{matrix}$$

Here composite means Type i reported production in year j was combined with that of another Type(s). Unique means Type i reported production in year j represented only Type i. Let

$$U_i = \sum_{j=1962}^{1983} u_{ij}.$$

Cr_{mi} is the fractional Cr content of Type i, where m is minimum, median, or maximum; the Cr composition of Group g is defined as

$$Cr_{mg} = \sum_{j=1962}^{1983} \sum_{i=1}^{3} [Cr_{mi}\, w_{ij}\, u_{ij}/U_i].$$

Interchanging the sums over i and j, and defining the average weight factor as

$$W_i = (\sum_{j=1962}^{1983} w_{ij}\, u_{ij}/U_i,$$

one obtains

$$Cr_{mg} = \sum_{i=1}^{3} W_i\, Cr_{mi}. \qquad (2)$$

This example illustrates the computation method used to obtain Group production, equation 1, and Group Cr composition, equation 2.

Actual computation differed in that–

1. The number of AISI Types that make up a Group varied from as few as one to as many as nine.

2. Average weight factors were calculated for two time periods, 1962-76 and 1977-83.

3. A few special cases arose where the constituent Type weight factor had to be assumed owing to lack of production data.

The association of AISI Types into Groups and the resulting Cr compositions (minimum and maximum Cr fractions) are shown in table 2. From 63 AISI Types, 33 Groups were formed.

TABLE 2.—Chromium compositions of the Groups and their constituent AISI Types [1]

AISI Type and Group Name	Chromium fraction	
	Minimum	Maximum
201 Group	0.1607	0.1807
201 Type	.1600	.1800
202 Type	.1700	.1900
205 Type	.1600	.1800
347 Group	.1680	.1880
347 Type	.1700	.1900
348 Type	.1700	.1900
384 Type	.1500	.1700
Ni.GT.16-24% Group	.1200	.1400
314 Type	.2300	.2600
Ni.GT.16-24% Type [2]	.1200	.1400
Ni.GT.24% Group	.1615	.1817
410 Group	.1168	.1368
410 Type	.1150	.1350
414 Type	.1150	.1350
416 Type	.1200	.1400
416 Se Type	.1200	.1400
429 Group	.1600	.1800
429 Type	.1400	.1600
430 Type	.1600	.1800
442 Group	0.2281	0.2685
442 Type	.1800	.2300
446 Type	.2300	.2700
Cr(Ni = O) Group	.1386	.1586
Cr.LE. 15% Type [3]	.1183	.1383
Cr.GT. 15% Type [4]	.1750	.1950
NRBT Group	.1534	.1761
316F Type	.1700	.1900
316N Type	.1600	.1800
329 Type	.2300	.2800
330 Type	.1700	.2000
409 Type	.1050	.1175
420F Type	.1200	.1400
422 Type	.1150	.1350
434 Type	.1600	.1800
436 Type	.1600	.1800
PNSBT Type [5]	.1442	.1586

[1] The following Groups are composed of one AISI Type of the same name: 301, 305, 308, 309, 309S, 316, 316L, 321, Ni under 8%, Ni 8-16%, 403, 405, 420, and 431. The following Groups are composed of AISI Types (shown in parentheses) of the same minimum and maximum chromium fraction contents: 302 Group (302 + 302B), 303 Group (303 + 303Se), 304 Group (304 + S30430), 304N Group (304 + 304L), 310 Group (310 + 310S), 317 Group (317 + 317L), 430F Group (430F + 430FSe), 440A Group (440A + 440B + 440C), 501 group (501 + 502, and Other Group (All Other High Chromium Heat Resisting Steels, which is S50300 + S50400).

There are small changes in content fraction from the 1962-76 time period to the 1977-83 time period for a few Groups. These changes result from changes in the AISI production reporting practice between those time periods. The values reported here are the 1977-83 values.

[2] Other Chromium Nickel Stainless Steels With: Nickel over 16-24%.

[3] All Other, 15% Chromium or Less.

[4] All Other, over 15% Chromium.

[5] Production Not Shown By Type.

RESULTS

Over the 1962-83 period, the content of S&HR steel produced was calculated based on the minimum, average, and maximum Cr fractions per AISI Type. The resulting minimum Cr content was 0.1574; average, 0.6171; and maximum, 0.1768. Thus, the Cr/S&HR factor was found to be 0.1672 ± 0.0097. The Cr/S&HR factor of 0.1671 was found to have a mean square deviation of 0.0004 over the time period. This average Cr fraction represents about 5,768,000 st Cr contained in about 34,518,000 st of S&HR steel production.

Over the analysis time period (1962-83) only one of the 33 Groups accounted for a substantial fraction of Cr contained in S&HR steel production. The 304 Group, composed of AISI Type 304 and S30430, accounted for 36 pct of the Cr contained in production. Three Groups (i.e., 304 Group, NRBT Group, and 301 Group) accounted for 53 pct of the Cr contained in S&HR steel production. Only 13 Groups accounted for 90 pct of the Cr. Table 3 summarizes these results. At 36 pct, the 304 Group accounts for the largest share. This contribution is more than four time greater than

TABLE 3.—Summary of chromium contained in S&HR steel production by Group in descending order of chromium contained in production for the analysis period 1962 through 1983

Group name	S&HR steel production [1] st	Cr content of production st	Cr content, pct of total	
			Group	Accumulated
304	11,373,020	2,160,099	36.2	36.2
NRBT	3,051,374	502,756	8.4	44.6
301	2,833,684	481,726	8.1	52.7
429	2,686,547	456,713	7.7	60.4
Cr(Ni = O)	2,078,918	308,950	5.2	65.6
316	1,634,761	277,909	4.7	70.2
410	1,900,017	240,891	4.0	74.3
304N	1,164,646	221,283	3.7	78.0
Ni.LT.8%	971,967	186,169	3.1	81.1
303	831,776	149,720	2.5	83.6
316L	876,236	148,960	2.5	86.1
201	867,138	148,066	2.5	88.6
302	532,134	95,784	1.6	90.2
Remaining 20	3,715,925	585,627	9.8	100.0
Total	34,518,143	5,964,653		

[1] American Iron and Steel Institute AIS 104 reports for 1962-83.

that of the next nearest Group. The Cr share of the next three Groups is similar, each Group accounting for about 8 pct of the Cr contained in S&HR steel production.

Figures 1 and 2 detail the chromium contained in S&HR steel production for the seven Groups that accounted for 74 pct of the Cr. These figures show the quantity of Cr contained in Group production by year for each of the seven Groups. It is apparent from these figures that there are fairly large variations in the quantity of Cr contained in S&HR steel production from year to year. These variations are due primarily to changes in annual production. The NRBT and Cr(Ni = 0) Groups show significant changes, in opposite directions, between 1976 and 1977. The AISI Type composition of these two Groups is shown in table 2. The composition of the PNSBT Type changed significantly in 1977 when many specific Type categories were introduced – presumably separated from the 1962-76 PNRBT category.

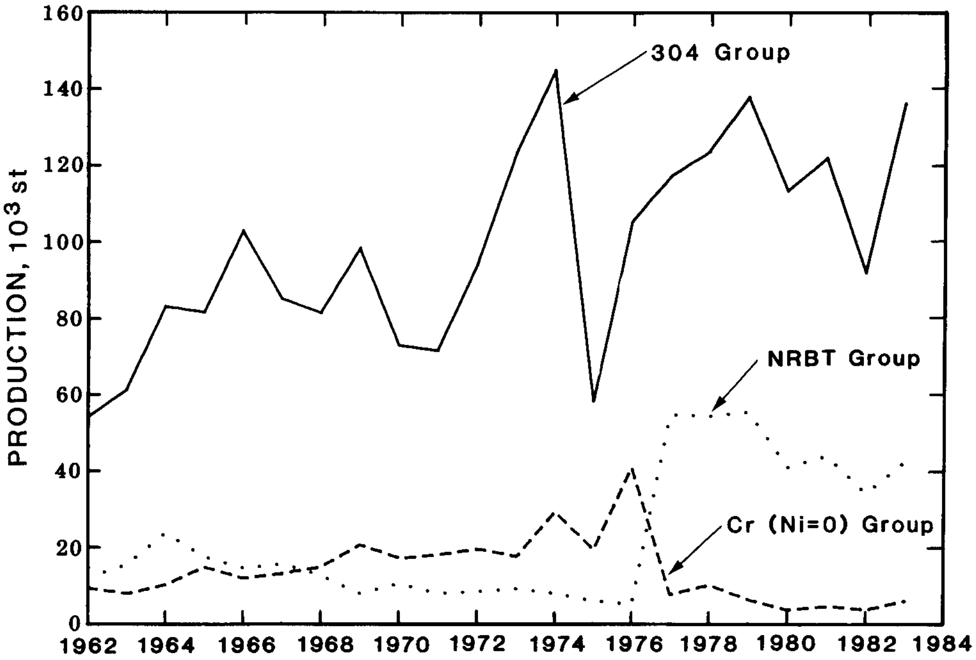

FIGURE 1.—Chromium contained in S&HR steel production. Groups 304, Cr(Ni = 0), and NRBT by year.

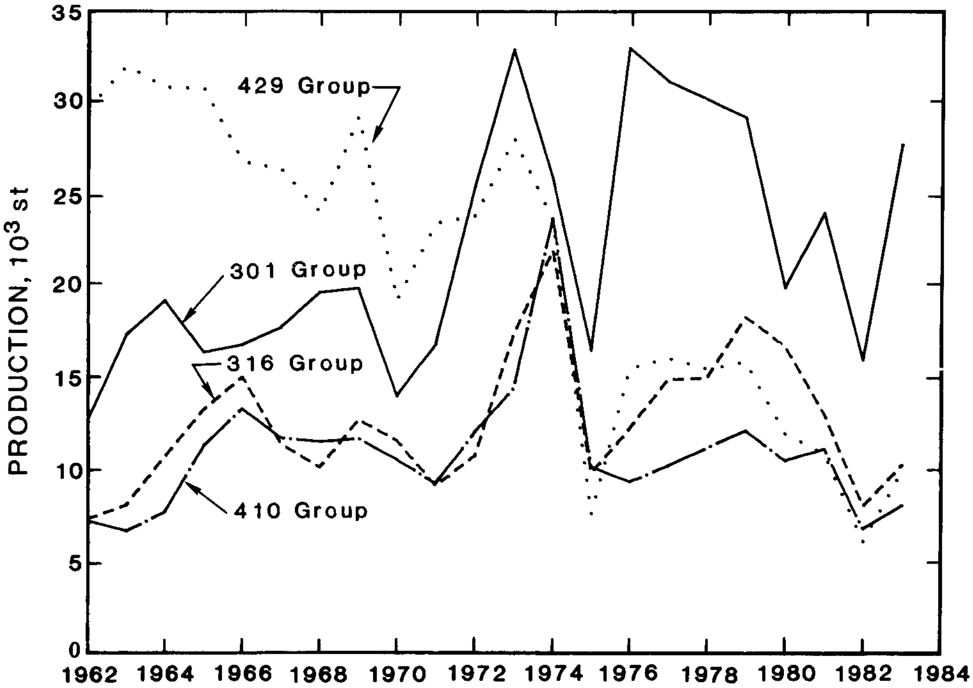

FIGURE 2.—Chromium contained in S&HR steel production. Groups 301, 316, 410, and 429 by year.

DISCUSSION

Together, AISI Types 304 and S30430 make up Group 304. AISI Type 304 has been described (*6*) as a low-carbon modification of AISI Type 302. The carbon is lower to restrict carbide precipitation during welding. The major end uses of Type 304 are chemical and food processing equipment, brewing equipment, cryogenic vessels, gutters, downspouts, and flashing. Type S30430 work-hardens less readily than does Type 305, and thus finds major use in servere cold-heading applications.

Group 304 accounts for by far the greatest amount of Cr contained in S&HR steel production. The large quantity of Group 304 production suggests a variety of end uses and, therefore, a variety of reasons for using this steel. The large quantity of Group 304 production suggests that this material is likely to be a major constituent of S&HR steel scrap. The large quantity of Group 304 production suggests that Group 304 is likely to account for a large share of recycled stainless steel scrap.

Between 1976 and 1977, the Cr contained in NRBT Group production rose sharply, while that of Cr(Ni = 0) Group declined sharply (fig. 1). The author concluded that these 1976-77 production changes resulted from the movement of Type 409 production from the Cr(Ni = 0) Group during 1962-76 to the NRBT Group during 1977-83. This movement occurred because Type 409 production was listed in the 1962-76 "All other" category, which was associated with the Cr(Ni = 0) Group; but in 1977 it was associated with the NRBT Group when Type 409 became a specific AISI Type used to report production. One cannot know with certainty the allocation of Grades and Types among descriptive AISI Type categories, because such information is not published. The following points are offered in support of the conclusion:

1. The general organization of the AIS 104 Form suggests that 400 series stainless steels not specifically listed belong in the "All other" category.
2. The sharp NRBT and Cr(Ni = 0) Group Cr content 1976-77 changes are not characteristic of the remainder of the Cr content time series for either Group, before or after the 1976-77 changes.
3. Type 409 is a stainless steel used primarily in automobiles. Its automotive use increased in the 1970's and is thought to have changed from little to extensive during the 1973-75 period. Increasing Cr content of production for the Cr(Ni = 0) Group and decreasing content for the NRBT Group over the 1970-76 period implies that the increasing Type 409 production was included in the Cr(Ni = 0) Group category during the 1962-76 period.
4. The changes in association of Type 409 production from the Cr(Ni = 0) to the NRBT Group in 1977 would account for the 1976-77 changes of both Groups.

Until about 1970, Type 409 was only used for parts in automobile exhaust system components. Its use then increased when automobile manufacturers elected to comply with the Federal Clean Air Act of 1970 by equipping automobiles with catalytic converters. Type 409 provided the desired lifetime for these converters at the higher operating temperatures resulting from converter use. By 1975, the majority of automoblies were equipped with catalytic converter exhaust systems (*9*).

Because the Type Cr compositions are average in forming a Group, one might expect little effect on the Cr composition of a Group to result from the assignment of one or two Types to a Group category of several constitutents. Such is not the case for the association of Type 409 with the NRBT Group or the Cr(Ni = 0) Group because Type 409 production is very large and has a low Cr fraction (0.1050 to 0.1175) compared with the S&HR steel average of 0.1671. The false nature of such a supposition is shown by calculation of the average Cr content of S&HR steel based on the Group data in table 3. Such a calculation yields an erroneous average Cr value 3 pct greater than the recommended value of 0.1671.

Based on the methodology described, the average Cr fraction of S&HR steel production was calculated to be 0.1671, with a mean square deviation of 0.0004 and a chemical composition specification uncertainty of ±0.0097. The consistency of this value over the time period suggests that this value could be reliably used to estimate the secondary Cr production component of apparent consumption. Secondary Cr production is Cr contained in purchased stainless steel scrap. In-house scrap is not a Cr production source for the purpose of computing apparent consumption.

The quantity of purchased scrap is the subject of a Bureau of Mines industry survey. The results of that survey are published monthly in the Iron and Steel Scrap Mineral Industry Surveys and annually in the Minerals Yearbook. Until 1983, a Cr/S&HR factor of about 12 pct was used to estimate secondary Cr production. In 1982, a cursory study, similar to the one on which the results in this paper are based, estimated the Cr/S&HR factor at about 0.16. Therefore, in 1983, secondary production was estimated using about 0.16 to calculate the Cr content of purchased stainless steel scrap. The National Materials Advisory Board (NMAB) (*7*) has suggested 16.4 pct, and a Bureau study (*8*) 16.7 pct, for the average Cr content of S&HR steel. NMAB does not explain its methodology, rendering impossible a critical comparison between the value reported here and that reported by the NMAB. The value reported in IC 8822 (*8*) was determined by multiplying the median Cr compositon by production for the years 1957 and 1977. The methodology of IC 8822 differs from that of this study in that–

1. IC 8822 (table A-3, p. 41) identifies the Cr composition of AISI Types 430, 430F, and 430F Se as 14.00 to 18.00 pct. The UNS composition used here is 15.00 to 18.00 pct.
2. IC 8822 does not specify Cr compositions for the AISI Types 329, 409, 422, 434, 436, and 442. These grades were apparently disregarded in the computation of average Cr content.
3. IC 8822 makes no Cr composition definition for the descriptive categories "Nickel Under 8%," "Nickel 8–16%," "Nickel Over 16–24%," "Nickel Over 24%," "All Other High Chromium Heat Resisting Steels," and "PNRBT."
4. The data base used in IC 8822 (2 yr) is small compared with that used in this study (22 yr).

Although IC 8822 does not specify chemical compositions for AISI Types 304N, 316F, 416, and 420F, it does have chemical compositions for AISI Types of the same number series. For example, IC 8822 includes Types 304 and 304L, but not 304N.

Among this author's objectives in calculating the average Cr content of S&HR steel were to (1) use as much of the detailed Type composition and production data as possible, (2) take advantage of the similarity of AISI annual production reports and the consistency of AISI Type Cr composition, and (3) account for production categorized by descriptive AISI Types. Short of treating each year's production on an individual basis, this approach represents the most thorough use of available data.

CONCLUSION

Three conclusions appear apporpriate from the preceding results and discussion. First, the factor 0.1671 ± 0.0097 should be used to calculate the Cr content of stainless and heat-resisting steel unless specific Cr composition information is available. Second, in combining AISI Types into Groups of consistent historical constitutent structure, the 400 series AISI Types that first appeared in 1977 (i.e., Types 409, 420F, 422, 429, 434, and 436) should be asociated with the Cr(Ni = 0) Group. Third, the criteria used to associate UNS Grades with AISI Types should be modified. As done in this study, all UNS Grades that correspond to a specific AISI Type should be so associated. The difference comes in distributing the remainder of the UNS Grades among the descriptive AISI Types. All remaining 100-300 series UNS "Heat and Corrosion Resistant" steels should be associated with the AISI "Other Chromium Nickel Stainless Steel" Types; and all remaining 400 series should be associated with the AISI "All Other 15% Chromium or Less" and "All Other Over 15% Chromium" Types. As done in this study, all remaining 500 series should be associated with AISI "All Other High Chromium Heat Resisting Steels." This leaves no Grades for the "PNSBT" Type. This Type category should be presumed to have a composition equal to the average of the other categories.

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CHROMITE RESOURCES—MARKET ECONOMY COUNTRIES

By Edward H. Boyle, Jr.[1] and Paul R. Thomas[2]

ABSTRACT

The Bureau of Mines has analyzed the long-term total cost and availability of chromite and high-C ferrochromium from 80 operations or deposits in 10 market economy countries (*1*). The appraisal presented economic evaluations for the extraction of 1.2 billion mt of in situ demonstrated resources of chromite ore contained within the 80 operations or deposits and addressed the long-term production potential of each of the 10 nations involved. It was estimated that approximately 649 million mt of marketable chromite products could be produced from the in situ demonstrated resource.

This paper summarizes the overall availability of chromite products and high-C ferrochromium from the demonstrated resources as of the early 1980's for the 10 countries and addresses specific resource aspects for each.

INTRODUCTION

This paper is a brief summary of the chromite resource position and of production potential for chromite and ferrochromium in 10 major chromite-producing market economy countries (MEC's): Republic of South Africa, Zimbabwe, Turkey, Philippines, India, Brazil, Finland, New Caledonia, Greece, and Madagascar. Two introductory comments are necessary to explain the context of the coverage involved in this paper.

First, although the 10 countries represented 99.2 pct of total 1982 MEC chromite production, they represented only about 50 pct of total world production of chromite in 1982. This is because two centrally planned economy country (CPEC) producers, the U.S.S.R. and Albania, were not analyzed. These two CPEC countries accounted for a combined 48 pct of world production in 1982 and have been, respectively, the first- and third-ranked world producers since 1981. They were not included in the analysis because of a lack of comprehensive and detailed information on their chromite and ferrochromium industries and because the differences between MEC and CPEC economic systems precluded any meaningful comparative cost analyses.

Second, table 1 presents a list of major, undeveloped MEC chromite deposits that were not analyzed in the study because of a lack of detailed data, and thus are not included in any of the total available tonnages discussed in this paper. For the reasons shown in the last column of table 1, it is not likely that these deposits will be developed in the near future owing to economics or, more importantly, because of marketability (usage) problems.

Abbreviations Used in This Paper

km^2	square kilometer
m	meter
mt	metric ton
mt/yr	metric ton per year
pct	percent
yr	year

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[1] Physical scientist.
[2] Economist.

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TABLE 1.—Chromite resources, market economy countries [1]

Country	Deposit	Type of resource	Estimated in situ tonnage, 10^3 mt	Grade pct Cr_2O_3	Cr-Fe ratio	Problems and status
Australia	Coobina	High-grade, podiform-type deposits.	2,100	28–49	1.5	Remote location, refractory-grade material.
Canada	Winnepeg District	Low-grade, seam-type deposits.	18,600	8.7	1.0–1.48	Very low Cr-Fe ratios.
Greeland	Fiskenaesset	....do	2,500	20–26	1.0–1.2	Remote location, very low Cr-Fe ratio.
Indonesia	None announced	Residual deposits and laterites.	NA	NA	NA	Exploration being conducted for low-grade eluvial chromite deposits. Also chromite in Ni-Co laterites.
Papua New Guinea.	Ramu River	....do	100,000	5–10	NA	Remote location, low-grade, some of economics will depend on Ni-Co laterite technology and economies.
South Africa, Republic of.	East and West Bushveld Complex.	UG2 seam	630,000	5.5	1.2–1.3	Extractable at certain operations on the Complex, but economic and marketing aspects questionable. Low Cr-Fe ratio of concentrate product. More promising for platinum values.

NA Not available.

[1] Not evaluated in this study for product availability or costs. Major questions of geology, economics, technology of extraction, or marketability raise doubts about production for the near term. In addition to these nondeveloped resources, other countries such as Cyprus, Iran, Japan, Pakistan, and Sudan produce very small amounts of chromite (140,000 mt combined production for 1980, including 82,000 mt of Iranian production).

AVAILABILITY OF CHROMITE PRODUCTS AND HIGH-CARBON FERROCHROMIUM

As shown in table 2, there are many ways to classify a particular chromite deposit and the products to be extracted from it, depending upon the criteria used for the classification. In table 2, the first four classification criteria (usage, Cr-Fe ratio, Al_2O_3 content, and product size) are product-related as well as interrelated, while the last two criteria (geologic structure and mineralogic occurrence) are deposit-related and interrelated.

TABLE 2.—Various classifications of chromite ores and concentrates in relation to classification criteria

Usage	Metallurgical, chemical, refractory.
Cr-Fe ratio	High-Fe, high-Cr.
Al_2O_3 content	Refractory, nonrefractory.
Product size	Lump ore, fines (friable) ore, concentrates.
Geologic structure	Podiform, stratiform, eluvial-alluvial-lateritic.
Mineralogy	Massive, disseminated, schlieren.

As shown in figure 1, the 1.2 billion mt of in situ ore that has been cost-evaluated and forms the base of the results mentioned in this paper represents only 17 pct of the total demonstrated resources in the 10 countries. The difference is almost entirely represented by non-cost-evaluated demonstrated tonnages in the Great Dyke of Zimbabwe and the Bushveld Complex of South Africa. As such, the resource analyzed is very conservative.

Figure 2 summarizes the demonstrated resources of recoverable chromite ore and concentrates (products), as analyzed in this study, according to the Cr-Fe ratio in products that could be used for metallurgical purposes and the tonnage that was indicated to have specific refractory markets as of 1980. Approximately 260 million mt of high-Cr (>2.0 Cr-Fe ratio) products are available for metallurgical use, and 372 million mt of high-Fe (< 2.0 Cr-Fe ratio) products are available for metallurgical or chemical use. In addition, about 17 million mt of refractory-grade and foundry sand chromite products were estimated to be available from a select few of the mines and deposits analyzed. This combined 649 million mt of available chromite products would represent 134 yr of production at 1982 levels from all producing nations excluding the U.S.S.R. and Albania.

Figure 3 shows the distribution of the combined 632 million mt of high-Cr and high-Fe products according to their presence in either stratiform, podiform, podiform-stratiform (basically unclassified), and eluvial-alluvial-lateritic type deposits. The stratiform deposits (represented by the Bushveld Complex in South Africa, the Greak Dyke in Zimbabwe, the Campo Formosa District in Brazil, and the Kemi operations in Finland) contain 87.2 pct of the chromite products estimated to be available. The podiform deposits (represented by the Selukwe and Belingwe Districts in Zimbabwe, the Hassan District in India, the high-grade Philippine deposits, the large majority of the Turkish deposits, and the chromite deposits in Madagascar, New Caledonia, and Greece) account for only 5.2 pct of the total amount of products. The podiform-stratiform deposits (represented by the Cuttack, Dhenkenal, and Keonjhar Districts in Orissa State, India) account for 6.5 pct, and eluvial-alluvial-lateritic deposits in the Philippines and Zimbabwe represent only 1.1 pct of the total amount of available chromite products. The

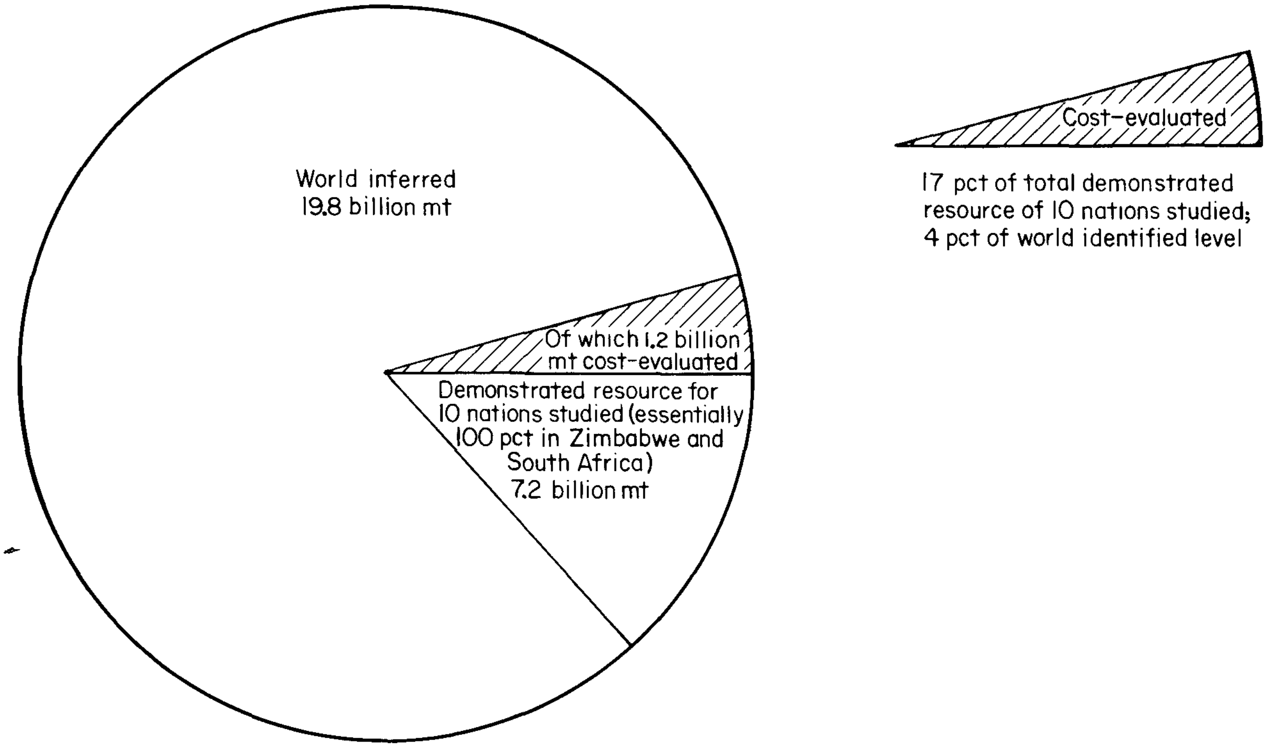


FIGURE 1.—Relationship of cost-evaluated tonnage to an estimate of the total demonstrated and identified resource levels within the 10 nations under study.

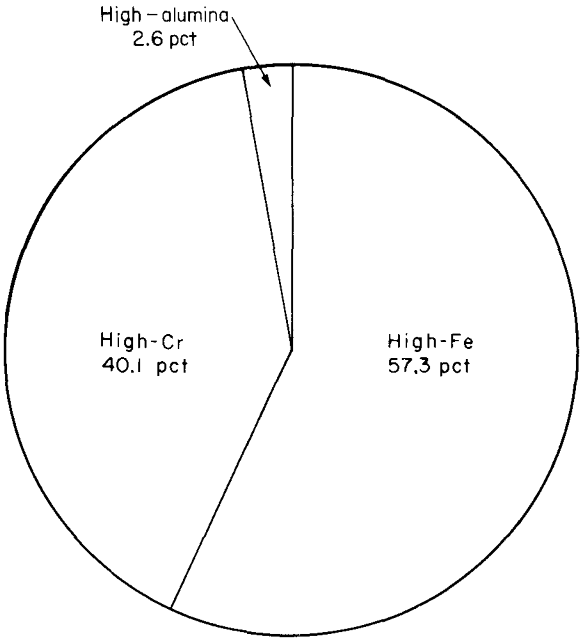


FIGURE 2.—Total estimated available high-Cr, high-Fe, and refractory chromite products.

bar graph of figure 3 presents these relative proportions in a more dramatic fashion.

The preponderance of products from stratiform deposits shown in figure 3 would be significantly larger except for the limitations (see figure 1) put on the resource-cost analysis of the demonstrated chromite resource potential of the Bushveld Complex in South Africa and the Great Dyke seam deposits in Zimbabwe. Even with this limitation, the importance of Zimbabwe and South Africa to the total available chromite products in both the high-Cr and high-Fe categories is in great evidence, as shown in the bar charts of figure 4.

In the course of the analysis, it was realized that the utilization and economics of producing high-C ferrochromium from these available chromite products would have to be addressed. Figure 5 presents a simplified relationship between the Cr-Fe ratio in a particular chromite product and the grade of high-C ferrochromium that could be produced by the smelting of that chromite product. In this diagram, a grade C, high-C ferrochromium of 50 to 55 pct contained Cr can be produced from a chromite ore or concentrate with a Cr-Fe ratio of 1.4 to 1.8, while a 56- to 64-pct-contained-Cr, grade B, high-C ferrochromium can be produced from 1.8 to 2.45 Cr-Fe ratio chromite products, and a >64-pct-contained-Cr, grade A, high-C ferrochromium can be produced from ores and concentrates with Cr-Fe ratios exceeding 2.45.

Applying this simplified relationship to the 80 mines or deposits analyzed gives the ferrochromium data shown in figure 6. If the entire 632 million mt of available high-Cr and high-Fe chromite products were smelted to produce high-C ferrochromium products, it would result in production of 280 million mt of high-C ferrochromium. Of this total, the majority (173.6 million mt) would be grade C ferrochromium, 44.3 million mt would be grade B ferrochromium, and 61.9 million mt would be grade A ferrochromium. South Africa represents 95 pct of the available grade C ferrochromium, Zimbabwe represents 87.3 pct of the available grade A ferrochromium, and South Africa and India represent 55 pct and 40 pct, respectively, of the available grade B ferrochromium.

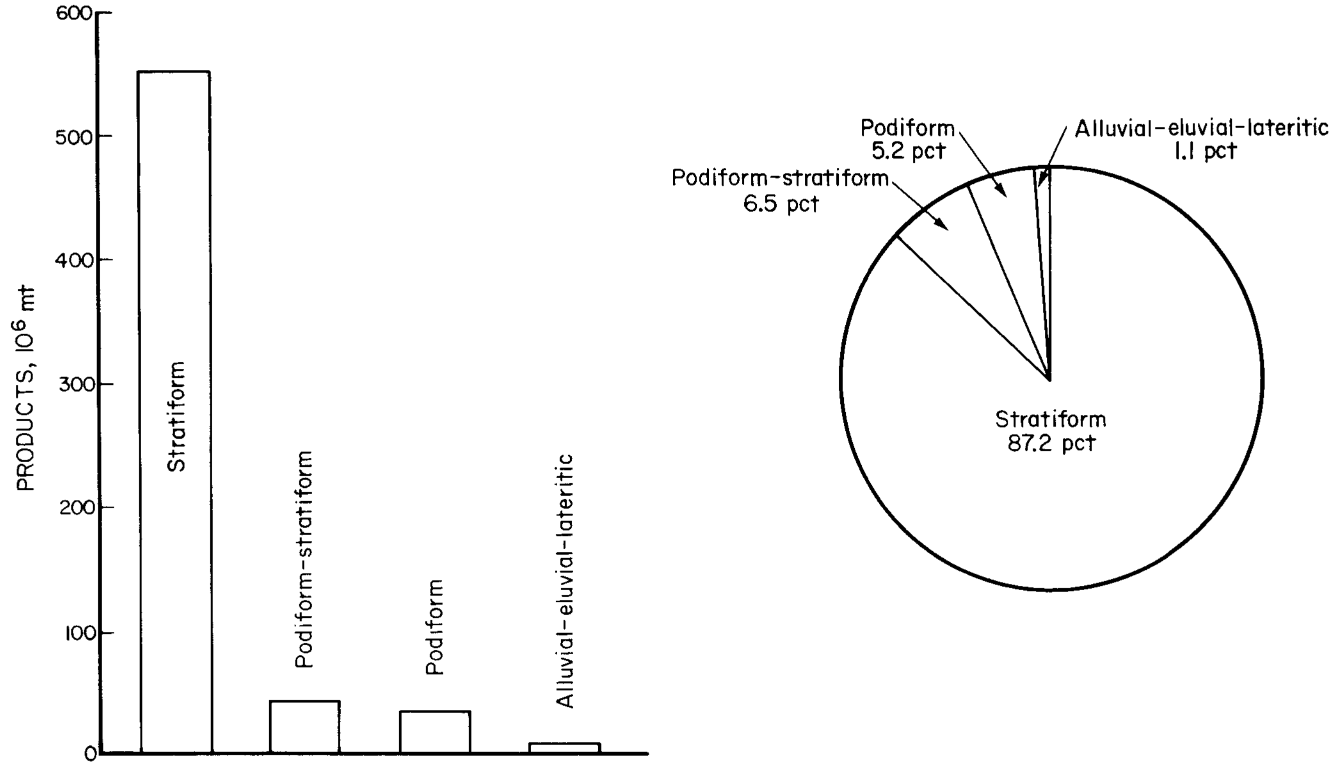
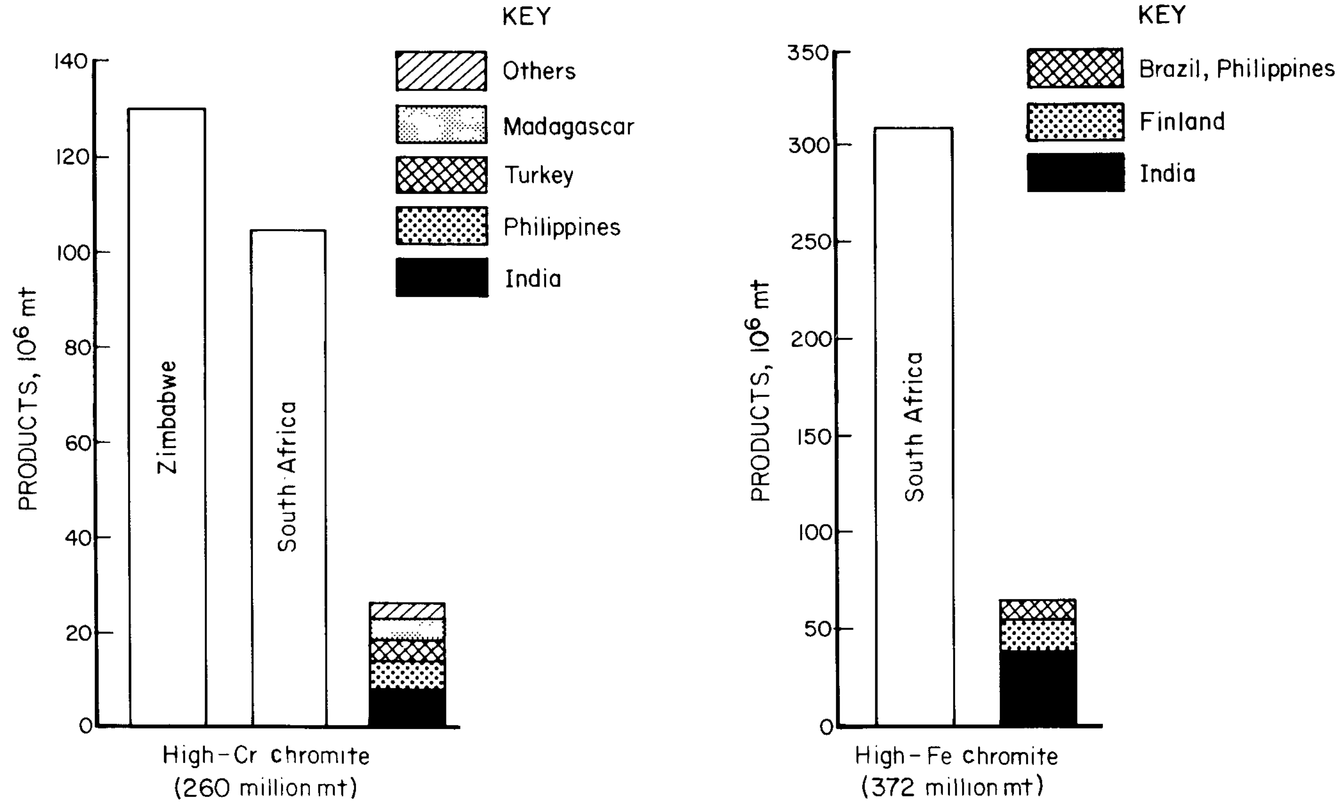


FIGURE 3.—Total estimated available high-Cr and high-Fe products; distribution by product type.



High-Cr chromite (260 million mt)

High-Fe chromite (372 million mt)

FIGURE 4.—Total estimated available high-Cr and high-Fe products; distribution by country.

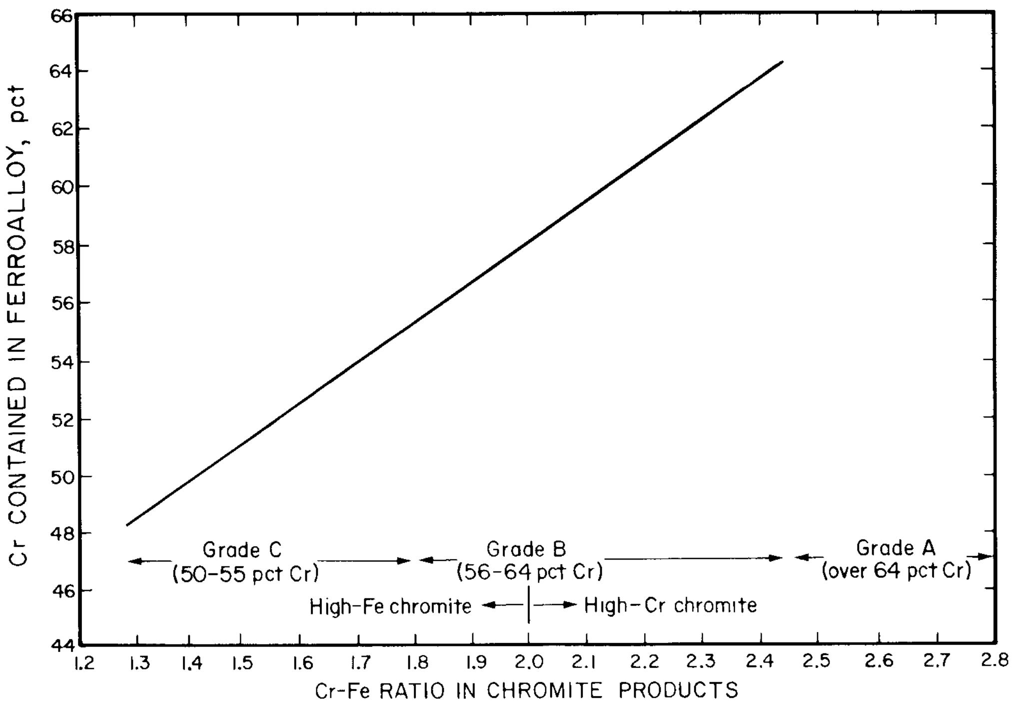


FIGURE 5.—Relationship between Cr-Fe ratio of chromite ores and Cr contained within a high-C ferrochromium product.

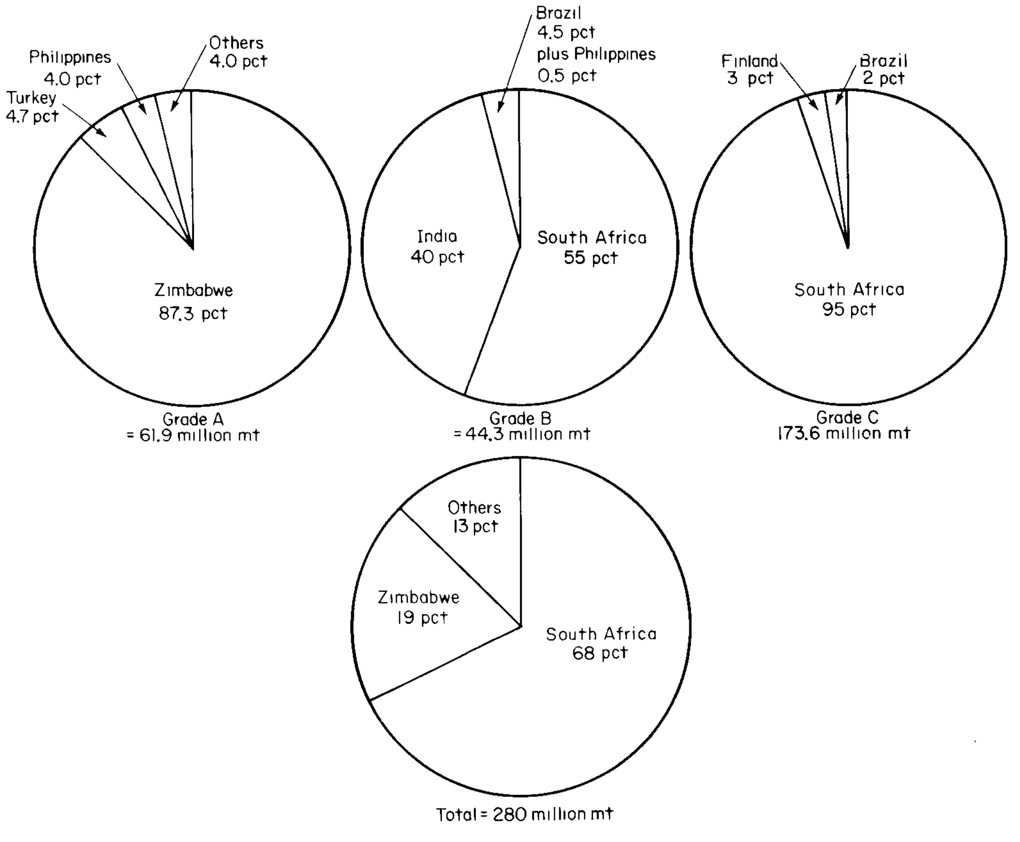


FIGURE 6.—Percentage contribution, by country, to total high-C ferrochromium availability estimates by product grades A, B, and C

SUMMARY, BY COUNTRY

The following pages summarize pertinent aspects of chromite and ferrochromium availability in the 10 countries that were analyzed.

REPUBLIC OF SOUTH AFRICA

1. The Bushveld Complex contains all of the available chromite resource that was analyzed.

2. An estimated 104.4 million mt of high-Cr chromite products and 307.6 million mt of high-Fe chromite products are available. This constitutes an immense resource of relatively low-cost chromite products.

3. The analysis was limited to producing operations as of 1979-80 and to vertical depths of 300 to 600 m. This resulted in only about 20 pct of the total demonstrated chromite resource being analyzed for costs. (See figure 7.)

ZIMBABWE

1. There are four historical sources of chromite production:

A. Seam deposits of the Great Dyke.

B. Podiform deposits of the Selukwe District.

C. Podiform deposits of the Belingwe District.

D. Eluvial (residual) deposits in the northern portion of the Great Dyke.

2. An estimated 116.7 million mt of products are available from Great Dyke seam deposits, 12.7 million mt from podiform deposits, and 0.8 million mt from eluvial deposits. All products are high Cr at 2.0 to 3.8 Cr-Fe ratios.

3. Approximately 130 million mt of chromite products are available; however, the majority of the Great Dyke chromite resource (seam-stratiform) is relatively high cost.

4. Analysis of Great Dyke seam deposits was limited to certain sections known to have had producing operations in 1979-80 or in the past. As a result, only about 47 pct of the most commonly accepted total Great Dyke resource estimate was analyzed.

5. Podiform deposits have good economics but limited resources; seam deposits have virtually unlimited resources but relatively poor economics.

TURKEY

1. The country has approximately 23,000 km^2 of ultramafic rock outcrops which could serve as hosts for chromite deposits.

2. The Government exploration agency has identified over 330 individual chromite deposits or deposit groups in 40 of Turkey's 67 Provinces and in at least 90 separate regions or districts (*2-3*).

3. The tonnage evaluated represents the demonstrated resources in only 25 individual deposits at 6 major mining operations, and it should be considered as a very conservative appraisal of Turkey's chromite potential.

4. Total in situ ore tonnage was estimated at 11.7 million mt ore at a weighted-average Cr_2O_3 grade of 38.0 pct. This tonnage would result in production of about 7.6 million mt of high-Cr chromite products with Cr-Fe ratios mostly greater than 2.8. The assumption that the entire output would be smelted to high-C ferrochromium would result in production of 2.9 million mt of grade A high-C ferrochromium.

5. Over 75 pct of the evaluated in situ ore tonnage is contained in podiform deposits. As in every country where most of the chromite resource consists of podiform deposits, the lack of podiform deposits of a significant size to allow fairly large production levels and reasonable economics for underground mining is a constant concern. It is believed that the response in Turkey has been the same as in the Philippines, in that recent work has been concentrated on the location and study of chromite deposits that could be mined by large-tonnage surface mining methods.

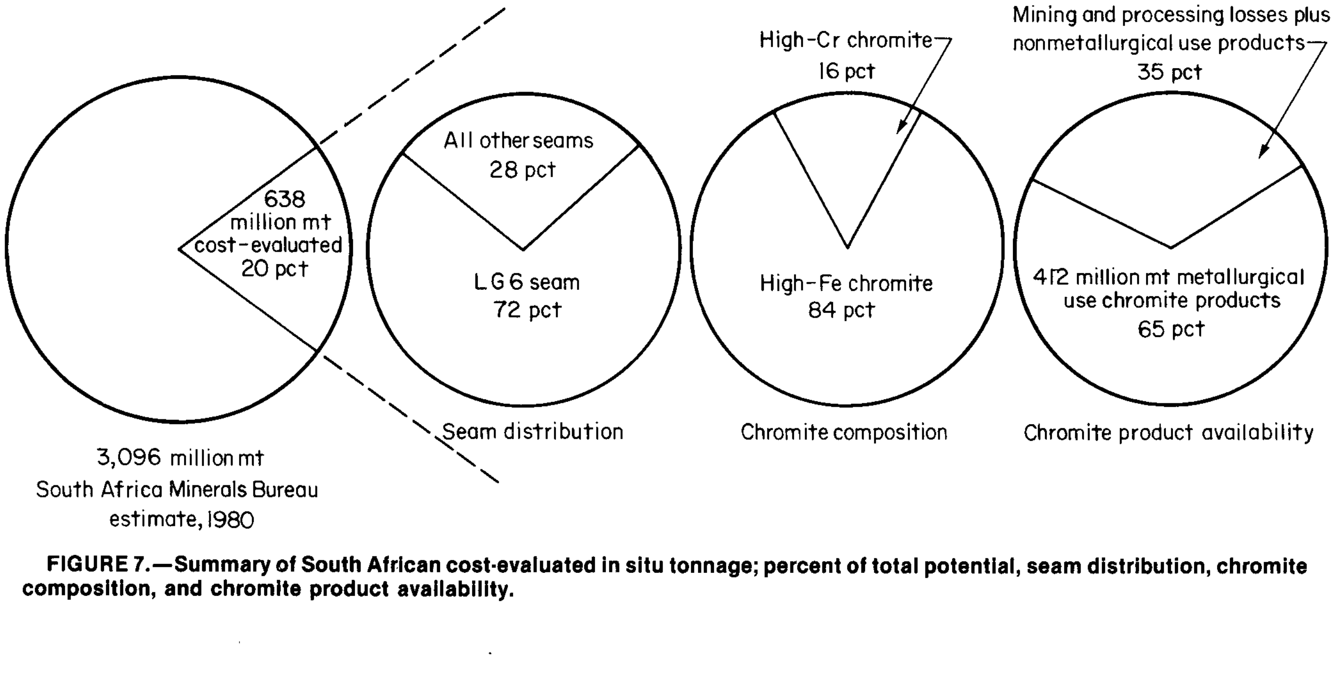


FIGURE 7.—Summary of South African cost-evaluated in situ tonnage; percent of total potential, seam distribution, chromite composition, and chromite product availability.

PHILIPPINES

1. Approximately 11,500 km^2 of area contain outcrops of ultramafic complexes and serpentine rocks, which are typical host rocks for chromite deposits.

2. In 1976, a total of 125 chromite deposits or occurrences were listed by the Philippine Bureau of Mines (*4*). Approximately 50 pct were located at Zambales Province, and 34 pct were located in Mindoro, Palawan, Samar, and Dinagat Provinces.

3. As of 1976, all of the known chromite reserves in the Philippines were contained in podiform deposits. Because of the endemic problem of limited reserves and resources in podiform deposits, a major program was instituted in the mid- to late-1970's which emphasized the investigation of low-grade eluvial, alluvial, and lateritic chromite deposits.

4. It was estimated that approximately 6.2 million mt of high-Cr chromite products would be available from four major podiform deposits or operations and 5.9 million mt of high-Fe chromite products would be available from five major eluvial, alluvial, or lateritic chromite deposits. In addition, approximately 4.5 million mt of refractory-grade chromite products would be available from two major podiform operations.

5. Because of their small sizes (the vast majority contained less than 100,000 mt contained ore), the analysis did not address the economics of 1.8 million mt of high-Cr metallurgical-grade ore contained in 21 podiform deposits and 1.1 million mt of refractory-grade ore contained in 12 podiform deposits.

6. Because of very low (1.3 to 7.0 pct) Cr_2O_3 grades in the in situ ore, the low-grade eluvial, alluvial, lateritic deposits are presently estimated to be uneconomic, especially in relation to the low-cost Finnish and South African products they would compete with.

INDIA

1. In 1975, India's demonstrated resource of in situ chromite ore was reported as 17 million mt. Subsequent reevaluation of resources by lowering the cutoff grade from 40 to 30 pct Cr_2O_3 resulted in a dramatic increase to 112 million mt of in situ ore, 60 million mt of which was considered as proven (*5*). All of the additional tonnage is located in the Cuttack, Keonjhar, and Dhenkenal districts of Orissa State. As a result, in 1980 about 96 pct of the demonstrated chromite resource in India was located in Orissa State, with only 2 pct in Karnataka State (the Hassan district) and the remainder scattered among small deposits in other States.

2. At the time of the analysis, indications were that much of the additional tonnage was probably low-grade (25 to 35 pct Cr_2O_3) and high-Fe (1.3 to 1.7 Cr-Fe ratio) material represented mainly by the "lower and upper brown" ores of the Sukinda Valley (Cuttack and Dhenkenal districts). Metallurgical tests have indicated that nearly all of this material will require tabling and that some would possibly require magnetic separation to produce chromite products with Cr-Fe ratios sufficiently high to be used in the new "charge" ferrochromium smelters being built in India (*6*).

3. A strict tonnage classification of Orissa chromite ores into podiform or stratiform deposits is impossible at present; hence, they are classified for this paper as podiform-stratiform. Significant tonnages in both types of ore bodies are present in the Sukinda Valley and the Keonjhar district, although most appears to be in podiform ore bodies.

4. It appears that, for internal country usage, any chromite product with a Cr-Fe ratio <1.6 will be used for chemical production, and any chromite products with a Cr-Fe ratio >1.6 will be used for metallurgical purposes.

5. A total of 81.2 million of in situ ore was estimated to represent the demonstrated chromite resources in India, with 69.3 million mt in the Cuttack district (including the Dhenkenal district) and 9.4 million mt in the Keonjhar district–both in Orissa State–and 2.5 million mt at three deposits in the Hassan district of Karnataka State. Overall, this in situ resource could represent eventual production of 43 million mt of chromite products, of which 4.9 million mt is high-Cr products (>2.0 Cr-Fe ratio) and 38.1 million mt is high-Fe products for metallurgical and chemical usage.

6. The foregoing items represent a summary of the finding in 1980-81. The following items represent recent updated data that may signify a variance from these data.

A. The output capacity of the four planned high-C ferrochromium smelters will be a combined total of 200,000 mt/yr. As of 1984, two smelters had been constructed and two were scheduled for completion during 1985.

B. Total Orissa State in situ tonnage is 112.6 million mt ore with the following indicated characteristics (*7*):

65 pct is below a vertical depth of 70 m; much of this will require underground mining with possible recoveries of only 65 pct.

Only 23 pct is proven; 66.6 million mt is classified as proven and probable.

Only about 10 pct is lump ore.

Grade breakdown by usage is 55.0 pct metallurgical grade (>48 pct Cr_2O_3, >2.8 Cr-Fe ratio), 32.2 pct "charge Cr" grade (42 to 46 pct Cr_2O_3, >1.6 Cr-Fe ratio), and 12.8 pct inferior grade (<40 pct Cr_2O_3, <1.6 Cr-Fe ratio).

BRAZIL

1. In 1977, chromite resources in Brazil at the inferred level were reported as 24 million mt of in situ material (*8*). Of this total, 57 pct was located in the Campo Formosa District, 2 pct in the Jacurici Valley, 4 pct in the Alvarado do Minas area, and 37 pct in 100 other small deposits scattered throughout Brazil.

2. The analysis of chromite resources resulted in an estimated 18.6 million mt of in situ ore at the demonstrated level and 39.0 million mt of identified resources. These totals included the Campo Formosa District, Jacurici Valley, and Alvarado do Minas deposits but did not include the 100 other small deposits.

3. The chromite deposits of the Campo Formosa district, which comprised 17.0 million mt of the demonstrated and 37.0 million mt of the identified resources, are classified as stratiform deposits, while the Jacurici Valley and Alvarado do Minas deposits are podiform in nature. The additional tonnage for the identified level is comprised almost entirely of material that would have to be mined by underground methods in the Campo Formosa District.

4. The Campo Formosa District mines account for about 85 pct of Brazil's current (early 1980's) chromite production. The present surface mining operations are characterized by very low mill feed grades of 17.0 to 21.0 pct Cr_2O_3, reflecting high dilution. The Cr-Fe ratios in various products range from 1.5 to 2.5. The demonstrated resource in the Campo

Formosa District would account for about 4.6 million mt of chromite products suitable for chemical and metallurgical uses, which is just sufficient to supply the country's only ferrochromium smelter at Pojuca.

FINLAND

1. The Kemi operations at the north end of the Gulf of Bothnia contained the only demonstrated chromite resource analyzed.

2. The surface-minable resource was estimated to be 29.2 million mt of in situ ore at an average grade of 27.0 pct Cr_2O_3 and a Cr-Fe ratio of 1.5 to 1.6. This in situ tonnage should result in production of 17.0 million mt of high-Fe chromite for metallurgical and chemical use and 2.5 million mt of chromite concentrates for foundry sand usage.

3. Surface-minable material was estimated to a maximum depth of 110 m at seven separate ore bodies. There could be greater than 30.0 million mt of additional material that could be mined by underground methods, but the Kemi operation will probably not have to address this aspect for at least 25 to 30 yr.

4. The chromite deposits at Kemi are classified as stratiform deposits although they do "pinch and swell" to become "lenslike" in places. As much as 85 pct of the ore is classified as a "soft, talcose" ore and 15 pct as a "hard, serpentinite" ore (*9*).

5. The surface-minable chromite resource at Kemi is a very low cost source of high-Fe chromite products. As of 1980, about 25 pct of the ore and concentrate products were required for the nearby ferrochromium smelter at Tornio. Usage of Kemi output as feed for the Tornio smelter could double, depending upon company plans. The remainder of Kemi's output is exported overseas; the Vargon ferrochromium smelter in Sweden is believed to take a fair amount of the exports.

NEW CALEDONIA

1. About 8,000 km^2 of the country's surface area is covered by ultramafic rocks. The entire country contains at least 50 individual podiform chromite deposits in 12 separate ultramafic "massifs" (*10*).

2. As of 1980, 82.8 pct of all of New Caledonia's past chromite production had come from the Tiebaghi Massif (*10*). The demonstrated resource of chromite ore in the Tiebaghi and Fantouche "pipelike" deposits, which provided nearly all of this past production, was the only demonstrated resource analyzed.

3. It was estimated that at least 2.3 million mt of in situ ore were available in the Tiebaghi and Fantouche pipes for underground mining. This resource could result in production of 1.7 million mt of high-Cr chromite products with Cr-Fe ratios of 3.0 to 3.6. All production is expected to be exported.

GREECE

1. Of 12 ultramafic rock complexes in Greece containing chromite deposits, only 4 are of large proportions. Metallurgical-grade ores are associated with the ultramafic complexes in the northern portion of Greece, while refractory-grade chromite ores are typically associated with the ultramafic complexes in the central portion (*11*).

2. Nearly all of the metallurgical chromite production in the past has come from the deposits in the Xerolivado (Skoumsta) and Voidolakkos areas, which are both located in the Mount Vourinos ultramafic complex.

3. The demonstrated resources analyzed represent the tonnage present in the Xerolivado (Skoumsta) mining area only. The total in situ tonnage of 2.2 million mt at 18.0 pct Cr_2O_3 is a podiform resource that should result in the production of 590,000 mt of high-Cr products at a Cr-Fe ratio of around 3.0.

4. The estimated output from Xerolivado (Skoumsta) alone would only provide about two-thirds of the feed requirements for the new high-C ferrochromium smelter located at Almyros. Indications are that the Anexitika, Koursoumia, and Kersitsa deposits of the Mount Vourinos complex would probably provide the additional tonnage needed for the Almyros smelter to produce 30,000 mt/yr of high-C ferrochromium.

MADAGASCAR

1. Chromite deposits occur in three major districts (Andriamenha, Befandriana, and Ranomena), all located in the northern half of the country. All deposits are podiform in nature (mostly lenses) and are mined by surface methods. The deposits in the Andriamenha and Befandriana districts are high-Cr deposits with Cr-Fe ratios of 2.4 to 3.3. The Ranomena district deposits are high-Fe chromite deposits with Cr-Fe ratios of 1.3 to 1.5.

2. Chromite ores from the Ranomena district were only produced from 1960 to 1964, the Andriamenha district began production in 1964, and deposits in the Befandriana district were brought into production in 1975. As of 1980, the Andriamenha district was accounting for about 70 pct of production and the Befandriana district for 30 pct. Expectations were that by 1984 the Andriamenha district would be the sole producer. This district has accounted for about 95 pct of all past chromite production in Madagascar.

3. Demonstrated resources consisted of 10.0 million mt of ore at 31.4 pct Cr_2O_3 for the Andriamenha district, 250,000 mt of ore at 37.0 pct Cr_2O_3 at the Ranomena district, and 100,000 mt of 45.0 pct Cr_2O_3 ore in the Befandriana district. This tonnage could result in production of 3.8 million mt of high-Cr chromite products and 100,000 mt of high-Fe chromite products.

4. As many as 300 individual deposits have been identified in the Andriamenha district (*12*). The 10.0 million mt

of ore estimated to be present in the Andriamenha district consists of 4.5 million mt at the Ankazatoalana deposit, 1.0 million mt at the Bemanevika deposit, and an estimated 4.5 million mt contained in 25 of the other large lens deposits.

5. There has never been a ferrochromium smelter in Madagascar, although studies on construction of a smelter were conducted in the mid-1970's and in the early 1980's.

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CHROMITE RESOURCES IN ALASKA

By Jeffrey Y. Foley,[1] James C. Barker,[2] and Lawrence L. Brown[3]

ABSTRACT

The Bureau of Mines investigated chromite deposits and occurrences in Alaska between 1979 and 1984 as part of the Bureau's critical and strategic minerals program. Chromite-bearing ultramafic rocks are known to occur in 8 regions in Alaska; 132 subeconomic podiform-type deposits and 1 placer deposit are estimated to contain 3.4 million to 4.3 million st chromic oxide (Cr_2O_3) in high-Cr and high-Fe chromite. Most of the deposits contain between 5 and 10 pct chromite, and minesite beneficiation would be required to produce shipping-grade concentrates. In the Chugach trend, an inferred reserve base comprises 2.8 million st Cr_2O_3 in 42 deposits that are all within 10 miles of tidewater or existing transportation routes. Most of these reserves are contained in the Turner stringer zone (1.25 million st) and Windy River placer deposit (556,000 st) at Red Mountain on Kenai Peninsula and in the Halibut Bay complex on Kodiak Island (201,000 st). Seventy less accessible deposits in the remote western Brooks Range contain between 576,000 and 1.4 million st high-Cr chromite. The Rampart, Yukon-Koyukuk, and Southeast regions contain deposits with minor production potential. No resource estimates are available for deposits in the Yukon-Tanana, Alaska Range, and Southwest regions.

INTRODUCTION

In Alaska, 132 exposed subeconomic podiform-type deposits and 1 placer deposit are estimated to contain from 3.4 to 4.3 million st of chromic oxide (Cr_2O_3), mostly in high-Cr chromite. Based on 1983 consumption statistics, these supplies are adequate to satisfy total domestic chromium demands for between 9 and 12 yr (*16*).

These estimates are based on published descriptions of deposits in eight regions, information released to the Bureau of Mines by industry, and on-site examination of deposits by the Bureau. These estimates include only known deposits containing greater than 1,000 st Cr_2O_3 and are considered conservative. Additional unmeasured resources are present in deposits of unknown size. Potential also exists for additional exposed and buried deposits in each of the eight regions, which have not been completely explored.

Although small high-grade deposits exist, most chromite in Alaska is found in low-grade zones that contain between 5 and 10 pct chromite. These low-grade zones consist of numerous bands of disseminated, coalescent, and massive chromite that alternate with nearly barren dunite and peridotite layers. Recovery of chromite from the low-grade zones would require mine-site concentration in most cases. Metallurgical tests by the Bureau's Albany Research Center indicate that much of the chromite in Alaska is of high quality and that high-Cr concentrates suitable for metallurgical use may be produced.

Access to chromite deposits in Alaska and land status range from practicable to prohibitive. From 65 to 80 pct of the estimated reserves are within 10 miles of tidewater or existing roads and are on lands open to mineral development. Other deposits are inaccessible except by airplane, and some are in areas such as National Parks that are closed to mineral development. These factors must be considered in assessing the mineral development potential of a given area.

Abbreviations Used in This Paper

ft	foot
mi^2	square mile
pct	weight percent
st	short ton
yr	year

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CHROMITE-BEARING REGIONS

Chromite-bearing ultramafic rocks are concentrated in eight larger regions (fig. 1) that are variably defined on the basis of geology, geography, and physiography. Of these regions, several are appropriately called trends because they parallel mountain ranges, major faults, and related geologic features. Other, less well-defined regions contain scattered chromite-bearing ultramafic bodies that are of uncertain relation to one another. The only potentially significant lode chromite deposits in Alaska are found in the ultramafic portions of alpine peridotite and alpine peridotite-gabbro complexes. Many of these complexes are associated with pillow basalt, diabase, and chert and are therefore interpreted as ophiolite fragments that are erosional remnants of ocenaic crust that were tectonically emplaced along the magrins of accreting continental crust. The chromite-bearing peridotite bodies range from less than 1 mi^2 to almost 100 mi^2 in area, but most are smaller than 10 mi^2.

Chromite also occurs in minor amounts in zoned ultramafic and other igneous complexes that were intruded into the earth's crust. Many of these are found in southeast Alaska, and one is known in southwest Alaska. More rarely, chromite occurs in igneous rocks of mafic to intermediate composition such as monzonite and alkali gabbro.

In the alpine peridotite and zoned ultramafic complexes, chromite occurs as disseminated grains and as magmatic segregations. The magmatic segregations form layers, lenses, irregularly shaped masses, and nodular aggregates in dunite and peridotite that are generally referred to as podiform-type deposits. Often, parallel layers from less than 1 inch to several feet wide are concentrated in zones that measure tens, hundreds, or even thousands of feet in area and thickness. The largest known deposit of this type is the Turner stringer zone at Red Mountain on Kenai Peninsula.

Chromite is also concentrated in placer deposits on beaches and in alluvial deposits that are proximal to chromite-bearing rocks, but little exploration has been done for placer chromite in Alaska. Most reported placer chromite occurrences, however, consist of accessory to minor chromite in highly concentrated black sands (*2–4*) that were produced during placer gold mining operations or sediment sampling where very little ultramafic rock is known, and most of the reported placer occurrences are therefore not likely to be significant resources. Potential does, however, exist for recoverable placer chromite in valleys draining some of the areas described in this report.

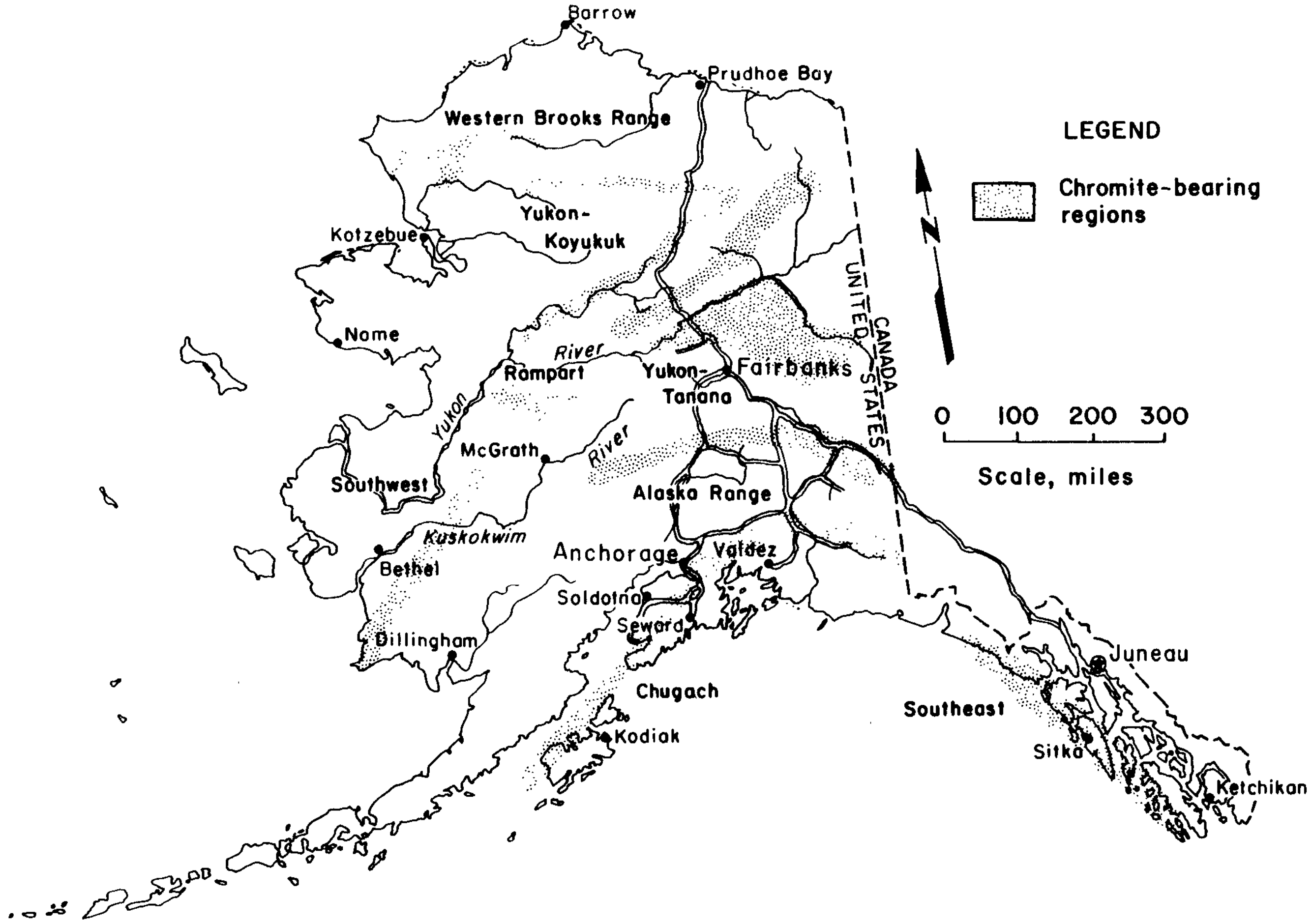

FIGURE 1.—Chromite-bearing regions in Alaska.

CHUGACH TREND

Foremost among the chromite-bearing regions in Alaska is the Chugach trend from which Alaska's only chromite production has come. This trend is a narrow belt that parallels the arcuate Border Ranges Fault and the Chugach Mountains for over 600 miles in southern Alaska. Within this trend, fault-bounded masses of chromite bearing alpine peridotite and associated gabbroic rocks are discontinuously present from near the Canadian Border to Kodiak Island (fig. 2). Podiform chromite deposits are present in ultarmafic rocks near Tonsina, Palmer, and Eklutna, at Red Mountain and Claim Point on Kenai Peninsula, and in the Halibut Bay Complex on Kodiak Island (*6-7*). About 2.8 million st of Cr_2O_3 in high-Cr chromite is estimated in 41 hard-rock and 1 placer deposits (table 1) that are all within 10 miles of tidewater or existing roads (*6-7*).

At Bernard Mountain, near Tonsina, 343,000 st of Cr_2O_3 is estimated in three deposits containing about 5 pct chromite each (*7*). Twelve smaller and higher grade deposits are also present. Twenty-six thousand short tons of Cr_2O_3 is estimated in one deposit at Sheep Hill, about 4 miles east of Bernard Mountain. Because of their small size or high-Fe content in contained chromian spinels, no tonnages were estimated for 11 other occurrences and deposits at Sheep Hill and adjacent Dust Mountain.

Within the Wolverine Complex, near Palmer, are seven occurrences for which no tonnage estimates were made.

TABLE 1.—Summary of chromite deposits along the Border Ranges Fault

Complexes	Deposits	Cr_2O_3, 10^3 st
Tonsina area:		
Bernard Mountain	3	343
Sheep Hill	1	26
Palmer area:		
Eklutna	1	1
Kenai Peninsula:		
Red Mountain	23	1,575
Windy River	1	556
Claim Point	10	90
Kodiak Island:		
Halibut Bay area	3	201
Total	42	2,792

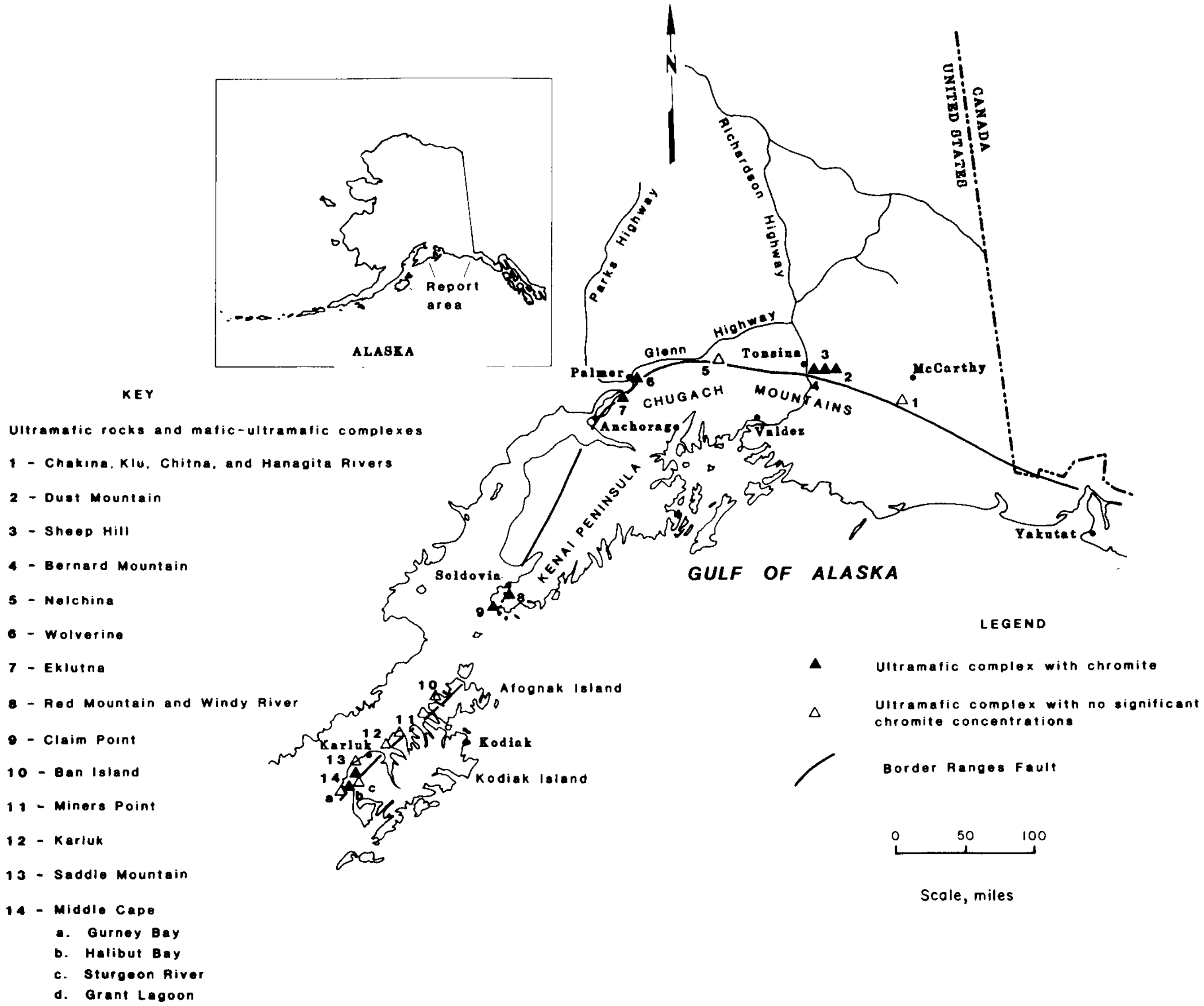

FIGURE 2.—Chugach trend.

Most of these occurrences consist of banded and massive chromian spinel in talus and morainal debris. Metallurgical tests on a bulk sample from the largest occurrence in the Wolverine Complex indicate marginal-quality chromite with a Cr-Fe ratio of about 1.6 is present.

Near Eklutna, between Palmer and Anchorage, are six chromite occurrences and deposits that were drilled and trenched in the 1940's by the Bureau. These deposits are small and probably insignificant, but it is likely that additional and perhaps more significant deposits there are obscured by vegetation so dense that it has already completely overgrown the Bureau's earlier excavations.

Chromite was produced from two areas on Kenai Peninsula: Red Mountain and Claim Point (fig. 2). During the First and Second World Wars and the Korean conflict, a total of about 30,000 st chromite ore with reported grades between 38 and 43 pct Cr_2O_3 was produced from the Star No. 4 and Chrome Queen Mines at Red Mountain and the Reef Mine at Claim Point (*7*). Of the chromite ore produced on Kenai Peninsula, about 8,000 st was shipped to Japan in 1976. (*18*).

A 10-mile road reaches Red Mountain from tidewater on Jakolof Bay near the community of Seldovia. Thirty-three chromite deposits at Red Mountain have been described by U.S. Geological Survey, Bureau of Mines, and Anaconda Minerals geologists. Prior to recent Anaconda and Bureau investegations, 97,000 st contained Cr_2O_3 was inferred in 20 deposits that contain 30 pct or more chromite (*11-12*). Based on mapping, drilling, and trenching by Anaconda, and metallurgical testing by the Bureau of Mines, about 1.5 million additional short tons of Cr_2O_3 is estimated in three low-grade deposits (*1, 6-7*). These include the Turner, Star, and Horseshoe stringer zones. The Turner stringer zone contains 1.25 million st Cr_2O_3 at an average grade of 5.6 pct Cr_2O_3, the Star stringer zone 208,000 st at 6.9 pct Cr_2O_3, and the Horseshoe stringer zone 29,000 st at 4.5 pct Cr_2O_3. Three other low-grade deposits, the Tram Road, Richards, and Tom stringer zones, remain unevaluated, and no tonnage estimates are presented.

Of all the chromite deposits in Alaska, those at Red Mountain are prehaps the best exposed and certainly the most explored. Based on surface sampling, drilling, seismic surveys, and metallurgical tests by Anaconda and the Bureau, 556,000 st of contained Cr_2O_3 is estimated in gravels with a grade of 1.3 pct Cr_2O_3 in the Windy River placer deposit at Red Mountain.

Ninety thousand short tons of Cr_2O_3 is estimated in 8 of 16 hard-rock chromite deposits that have been described at Claim Point, on the southern tip of Kenai Peninsula (fig. 3). Over 2,000 st of chromite ore was produced from the Reef deposit in the First World War. This deposit contains at least 15,000 st Cr_2O_3 at grades greater than 40 pct chromite. The deposit is largely under water and probably contains more chromite than present estimates indicate. Banded chromite typical of the Reef deposit is shown in figure 4.

The largest deposit at Claim Point is deposit 10, which was trenched and drilled by the Bureau in the 1940's. By lowering cutoff grades, indicated reserves for this deposit were increased from about 54,000 st to over 71,000 st during recent Bureau investigations. Other smaller deposits at Claim Point include low-grade stringer zones and higher grade, massive chromite bands such as the one at deposit 2 (fig. 5).

Chromite-bearing alpine-peridotite bodies are present at several locations on the southwest end of Kodiak Island. These include ultramafic bodies near Halibut Bay, Miners Point, Grant Lagoon, Gurney Bay, Saddle Mountain, and the Sturgeon River. Similar rocks are reported on Ban and Afognak Islands. Most occurrences observed by the Bureau are small and low grade, but one large deposit, with 5 pct chromite, in the Halibut Bay complex is estimated to contain 196,000 st Cr_2O_3. Two other deposits there contain 5,000 st Cr_2O_3 combined; no estimates were made for eight other occurrences in the complex.

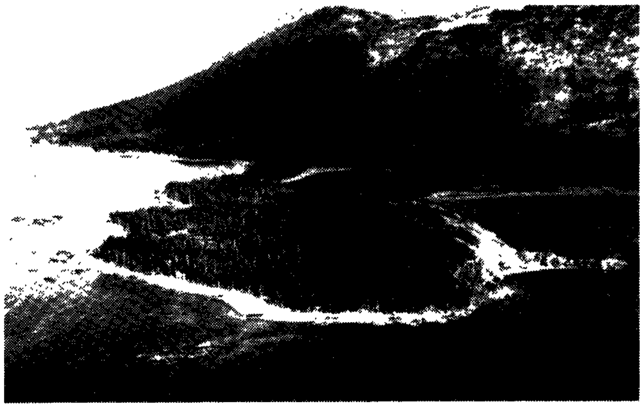

FIGURE 3.—Claim Point, Kenai Peninsula.

FIGURE 4.—Banded chromite in the Reef deposit, Claim Point.

FIGURE 5.—Massive chromite band at deposit 2, Claim Point.

SOUTHEAST TREND

Minor chromite is reported in ultramafic rocks at numerous locations in southeast Alaska (fig. 1). Most of these occurrences are in dunite portions of Alaskan-type ultramafic complexes that show concentric zoning of rock types and are interpreted to be exposed subvolcanic magma chambers (*14*). The only complex in southeast Alaska for which resource estimates are available is Red Bluff Bay on Baranof Island, where 32,000 st of low-grade material with about 12 pct Cr_2O_3 is present in eight deposits that comprise small lenses, thin layers, and disseminated chromite in dunite (*13, 15*).

WESTERN BROOKS RANGE TREND

The western Brooks Range trend (figs. 1 and 6) in northwestern Alaska comprises chromite-bearing ultramafic rocks at Iyikrok Mountain, in the Avan Hills, and at Misheguk, Siniktanneyak, and Asik Mountains. This ophiolite trend extends from the Chukchi Sea to Howard Pass, a distance of about 200 miles, and contains between 576,000 and 1.4 million st Cr_2O_3 in 70 high-Cr and high-Fe chromite deposits (*10*). These estimates are based on traverses made by four people in a 200 -mi^2 area, during two

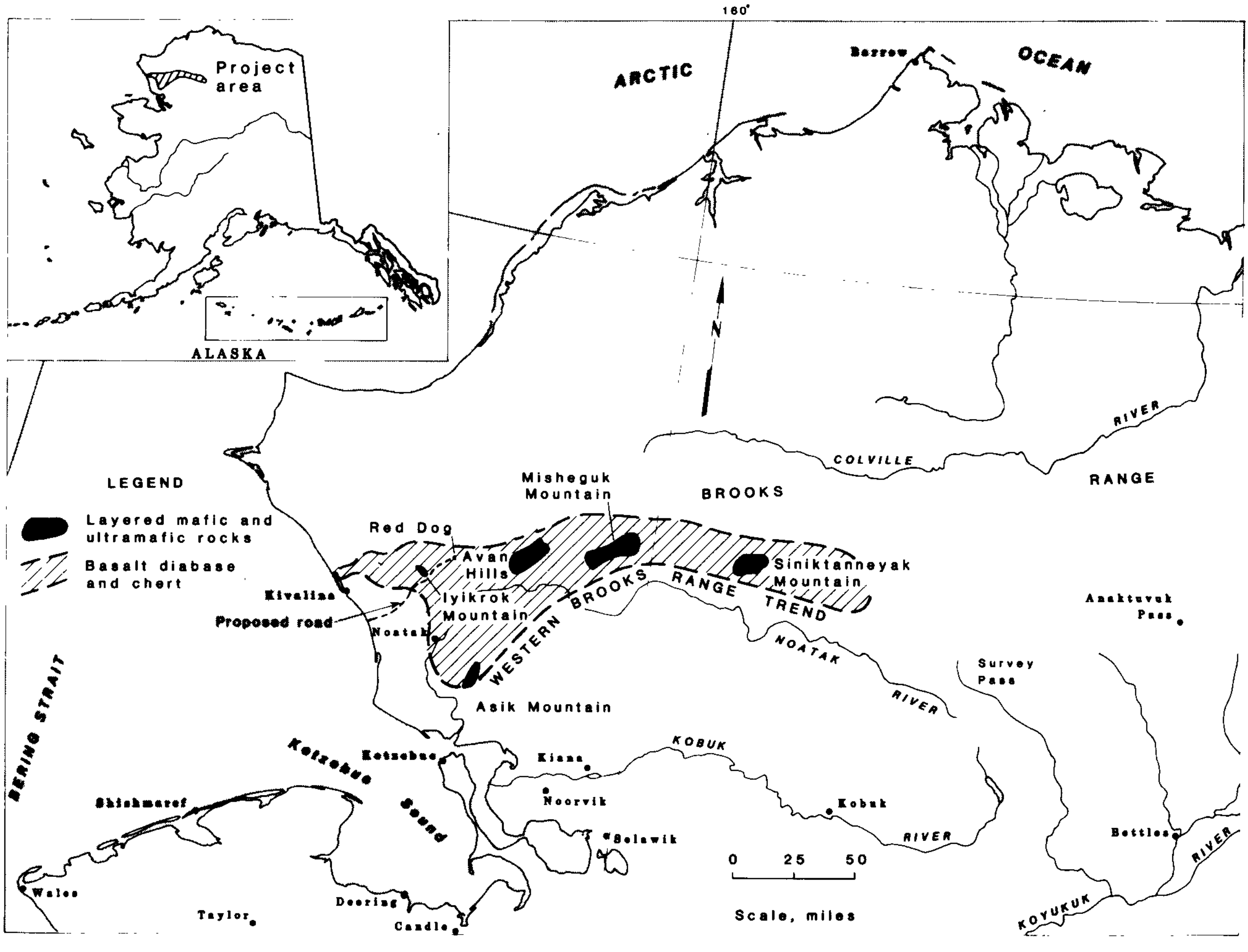

FIGURE 6.—Western Brooks Range trend.

2-week periods, and additional deposits undoubtedly exist. Next to deposits in the Chugach trend, deposits at Iyikrok Mountain and in the Avan Hills are prehaps the most likely to be developed, as they would be made accessible by a proposed road from a port site on the Bering Sea coast near Kivalina to the Red Dog lead-zinc-silver deposit, where production may begin as early as 1989. Some of the western Brooks Range deposits are within the Noatak National Preserve, administered by the National Park Service.

YUKON-KOYUKUK TREND

The Yukon-Koyukuk basin in northern and central Alaska (fig. 1) is bounded on the north and southeast by ophiolitic rocks that locally contain high-Cr chromite. Podiform-type deposits are present at Caribou Mountain, along the Kanuti and Kilolitna Rivers, and near Holonada Creek (*5, 9*). Except for the small deposits at Caribou Mountain on the Dalton Highway, helicopters provide the only practical access to chromite deposits in this region. Except for one deposit in the Holonada mass that contains between 13,000 and 26,000 st Cr_2O_3, exposed deposits in the Yukon-Koyukuk trend are estimated to contain less than 1,000 st each (*10*).

RAMPART TREND

Parallel to the southeast limb of the Yukon-Koyukuk trend are poorly exposed ophiolitic rocks of the Rampart trend (fig. 1), which are offset right-laterally along the Kaltag Fault. There are no roads, and access to this region is generally difficult. Podiform-type deposits are present in the Kaiyuh Hills at the southwest end, and minor chromite has been observed in the Christian River mass to the northeast. Of 21 occurrences and deposits in the Kaiyuh Hills, 4 contain between 17,000 and 37,000 st Cr_2O_3 (*8*).

YUKON-TANANA UPLANDS REGION

Minor chromite is reported at numerous locations in the Yukon-Tanana uplands region (fig. 1), but no significant concentrations are known. The region is largely covered by unconsolidated surficial deposits and vegetation, and where exposed, ultramafic rocks are typically small, extensively faulted and altered, and contain only accessory chromite. Metallurgical tests by the Bureau of Mines on low-grade material from Nail Ridge, one of the larger and better exposed masses, indicate the chromium spinel there is unsuitable for industrial use.

ALASKA RANGE TREND

Fault-bounded and intrusive masses of alpine peridotite and serpentinite of Paleozoic and Mesozoic age crop out at numerous locations in a narrow, 400-mile-long trend that parallels the Alaska Range from near the Canadian border to near Farewell (fig. 1). The origins and relative ages of these ultramafic rocks are unknown, but most are elongated parallel to the Denali Fault and were possibly emplaced into the crust during deformation along the fault. Although the Alaska Range is crossed by two highways and a railroad, access to chromite deposits in this trend is limited to helicopter travel.

Chromite is reported in alpine peridotite and serpentinite masses at several locations in the Alaska Range trend, but few of the masses have been thoroughly investigated for their chromite potential. No reserve estimates are available. Of the reported chromite occurrences in the Alaska Range, those near Lacuna and Yentna Glaciers and in the Chulitna area have the greatest reserve potential. Chromite is reported at several locations in the Lacuna and Yentna Glaciers area, where the largest occurrence is an 8-ft by 60-ft lens of massive, high-Cr chromite (*17*). Similar, nearly massive chromite bands up to 1-ft thick are also present near Copeland Creek in the Chulitna area.

SOUTHWEST REGION

The southwest region includes chromite-bearing alpine peridotite and alpine peridotite-gabbro masses of varied origin and ages at Mount Hurst, Tatlignagpeke Mountain, Mitlak Mountain, Red Mountain, and Susie Mountain, and chromite-bearing monzonite near Moore Creek and Fourth of July Creek (fig.). This region extends southwest from Mount Hurst, near Tolstoi, to Goodnews Bay, a distance of about 450 miles. Deposits in this region are some of the most remote in the State. Ultramafic rocks at Mount Hurst may be related to ultramafic and related rocks in the Kaiyuh Hills, 75 miles to the north, which are in the Rampart ophiolite belt. Tatlignagpeke Mountain and Mitlak Mountain, between the Arolik and Goodnews Rivers, consist of serpentinized, strongly tectonized, and layered peridotite and gabbroic rocks that structurally overlie Mesozoic and Paleozoic sedimentary and volcanic rocks. At Goodnews Bay, an Alaskan-type ultramafic complex with accessory chromite is the source of platinum-group metals in the Salmon River placer deposit. Small chromite-bearing monzonite plutons are intruded into sedimentary rocks of the Cretaceous Kuskokwim Group near Moore Creek and Fourth of July Creek. No reserves are estimated for any of the southwest chromite occurrences.

SUMMARY

Estimates of Cr contained in Alaskan deposits are summarized in table 2. Most of these estimates are based on surface observations made during examination of the chromite-bearing masses; additional reserves probably exist in undiscovered buried deposits, covered extensions of known deposits, and placer deposits in streams adjacent to the chromite-bearing masses. The deposits occur within eight geographic or geologic regions. The podiform-type deposits range in size from a few tons to over 1 million st of contained Cr_2O_3. The total estimated reserve potential is 3.4 million to 4.3 million st contained Cr_2O_3 and is sufficient to satisfy total domestic Cr demands for 9 to 12 yr. These tonnages are mostly contained in low-grade deposits with less than 10 pct chromite. Mine site beneficiation of the chromite would be required to produce shipping-grade concentrates. Metallurgical tests and geochemical analyses on samples from most of these deposits indicate that high-Cr concentrates can be recovered.

Only the Chugach trend contains deposits that are large enough (2.8 million st Cr_2O_3 in 42 low-grade deposits) and close enough to tidewater or existing transportation routes to significantly offset chromium shortages in the event of an interruption of foreign supplies.

Seventy low-grade deposits in the remote Western Brooks Range trend contain an estimated 576,000 to 1.4 million st Cr_2O_3. Most of the Western Brooks Range deposits will become more accessible when the proposed road to the Red Dog lead-zinc-silver deposit is constructed.

TABLE 2.—Summary of chromite deposits in Alaska

Region	Number of deposits[1]		Contained Cr_2O_3, 10^3 st
	Type 1	Type 2	
Western Brooks Range trend	70	>100	576-1,394
Yukon-Koyukuk trend	9	>50	17- 31
Rampart trend	4	20	17- 37
Yukon-Tanana uplands region	0	>5	0
Alaska Range trend	0	>15	0
Southwest region	0	>30	0
Chugach trend	42	>94	2,800
Southeast region	8	>22	4
Total	133	>336	3,414-4,266

[1] Type 1 includes only deposits for which estimated reserves or estimated reserve potential is inferred. Type 2 comprises identified deposits and occurrences, including those for which no reserve estimates are available.

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CHROMIUM RESOURCES IN THE CONTERMINOUS UNITED STATES

By Nicholas Wetzel[1]

ABSTRACT

The Bureau of Mines is evaluating Cr resources in the conterminous United States (suitable for both metallurgical and chemical use) for Cr availability by State, county, deposit, and operation. The investigation to date has identified more potential resources than previously believed to be present.

Low-Fe Cr resources (Cr-Fe ratios >2.0) are estimated at 1.6 million mt Cr_2O_3 contained in 14.6 million mt of chromite-bearing material in California (95 pct), Oregon (4.5 pct), and Washington (0.5 pct) podiform deposits. High-Fe resources (Cr-Fe ratios of 1.5 to 2.0) are estimated at 12.4 million mt Cr_2O_3 contained in 138.5 million mt of chromite-bearing material in Montana (75.5 pct), California (20 pct), Oregon (3.7 pct), Wyoming (0.7 pct), and the Appalachian region (<0.1 pct).

Additional resources with excessively high Fe contents (Cr-Fe ratios <1.5) that may be a potential Cr source in the future total 7.6 million mt Cr_2O_3 contained in 448.5 million mt of chromite-bearing material in Oregon beach sands and laterites (57 pct), California laterites and asbestos properties (40 pct), Washington iron deposits (3 pct), and Montana podiform deposits (<0.1 pct).

INTRODUCTION

The objective of this report is to estimate the quantity and quality of identified domestic Cr resources[2] present in the conterminous 48 States. For purposes of this study, domestic resources have been classified into two categories based on Fe content: low-Fe and high-Fe. These categories roughly parallel the distinction between metallurgical and chemical grades; however, owing to the increasing interchangeability among grades, a dollar value per metric ton of product is more applicable. "Low-Fe" chromites comprise ores and concentrates similar in product grade to those produced in Turkey that have a Cr-Fe ratio near 3.0 and are estimated to be valued at $110/mt. "High-Fe" chromites comprise ores and concentrates similar in product grade to those produced in South Africa that have Cr-Fe ratios ranging from 1.5 to slightly over 2.0 and are estimated to be valued at $52/mt.

To date, total domestic production has been <2 million mt of lump ore and concentrates averaging 41.1 pct Cr_2O_3 with an average Cr-Fe ratio of 2.0. Of this total, 30 pct was low-Fe material derived solely from podiform deposits in California and Oregon (table 1). The remaining production was of the high-Fe variety, the bulk of which came from the Stillwater Complex in Montana (70 pct) or podiform deposits in Pennsylvania and Maryland (19 pct). The balance of high-Fe chromites came from podiform or beach sand deposits in Oregon (7 pct) and California (4 pct) (table 2).

Domestic resources are contained in four types of deposits: (1) podiform, (2) stratiform, (3) lateritic soil, and (4) placer.

Podiform deposits are associated with alpine-type peridotite bodies in California, Oregon, and Washington that have been tectonically emplaced from marginal basins over areas of active island-arc volcanism. Typically, these peridotites are approximately 95 pct harzburgite, with the remaining 5 pct composed of scattered patches of dunite and irregular seams of orthopyroxenite. Dunite and chromite normally occur together in harzburgite, with chromite usually found in the dunite or its most common alteration product, serpentine. The dunite typically occurs as irregular patches, tabular lenses, or pods ranging from a few cubic meters to thousands of cubic meters.

Stratiform deposits of the Stillwater Complex are contained in a large layered igneous intrusive. Chromite

Abbreviations Used in This Paper

ft	foot
in	inch
km	kilometer
m	meter
mt	metric ton
pct	weight percent
yr	year

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[1] Physical scientist, Western Field Operations Center, Bureau of Mines, East 360 Third Ave., Spokane, WA 99202.

[2] Identified resources – Resources whose location, grade, quality, and quantity are known or estimated from specific geologic evidence; include economic, marginally economic, and subeconomic components.

TABLE 1.—Production by type and quality[1]

Type	Ore shipped, mt	Cr_2O_3, pct	Cr-Fe ratio	Contained Cr_2O_3, mt	Source, State and pct
			LOW-Fe		
Podiform:					
Disseminated	242,300	45.5	2.6	110,300	94 CA, 6 OR.
Massive	333,100	46.5	2.9	154,900	85 CA, 15 OR.
Total	575,400	46.1	2.8	265,200	89 CA, 11 OR.
			HIGH-Fe		
Podiform:					
Disseminated	70,300	42.4	2.0	29,800	51 CA, 28 OR, 21 MT.
Massive	280,600	39.8	1.6	111,600	84 MD-PA,[2] 10 OR, 6 CA.
Stratiform	954,600	38.6	1.6	368,500	100 MT.
Placers	68,600	39.5	1.5	27,100	70 OR, 30 MD-PA.
Total	1,374,100	39.1	1.6	537,000	70 MT, 7 OR, 19 MD-PA, 4 CA.

[1] Production reported in this table is considered conservative. Where detailed production data were not available or the records appeared duplicative, minimum figures are used.

[2] All production from Maryland and Pennsylvania podiform deposits occurred prior to 1900 (*16*).

Sources: References 2-4, 6, 16, 20, 23-24, 33, 35-37.

minerals and enclosing harzburgite originally formed in horizontal layers as a cumulate or "magmatic sediment" during fractionation of a basaltic magma (*14*).

Lateritic soil deposits occur in the northern California-southern Oregon coastal region and are derived from weathering of alpine peridotites which host podiform chromite deposits. Chromite concentrations rarely exceed 3 pct Cr_2O_3.

Placer deposits occur along the southern coast of Oregon where black sands were concentrated by wave action and currents and deposited along former coastlines adjacent to the cliffs and in offshore depressions (*8*).

TABLE 2.—Production and resources by State

State	Contained Cr_2O_3, mt	
	Production	Resources
Montana	375,900	9,464,600
California	257,500	6,910,100
Oregon	66,800	4,817,100
Washington	0	252,400
Wyoming	0	92,500
Maryland	[1] 102,000	7,300
Pennsylvania		6,300
North Carolina	0	3,500
Georgia	0	600

[1] All prior to 1900.

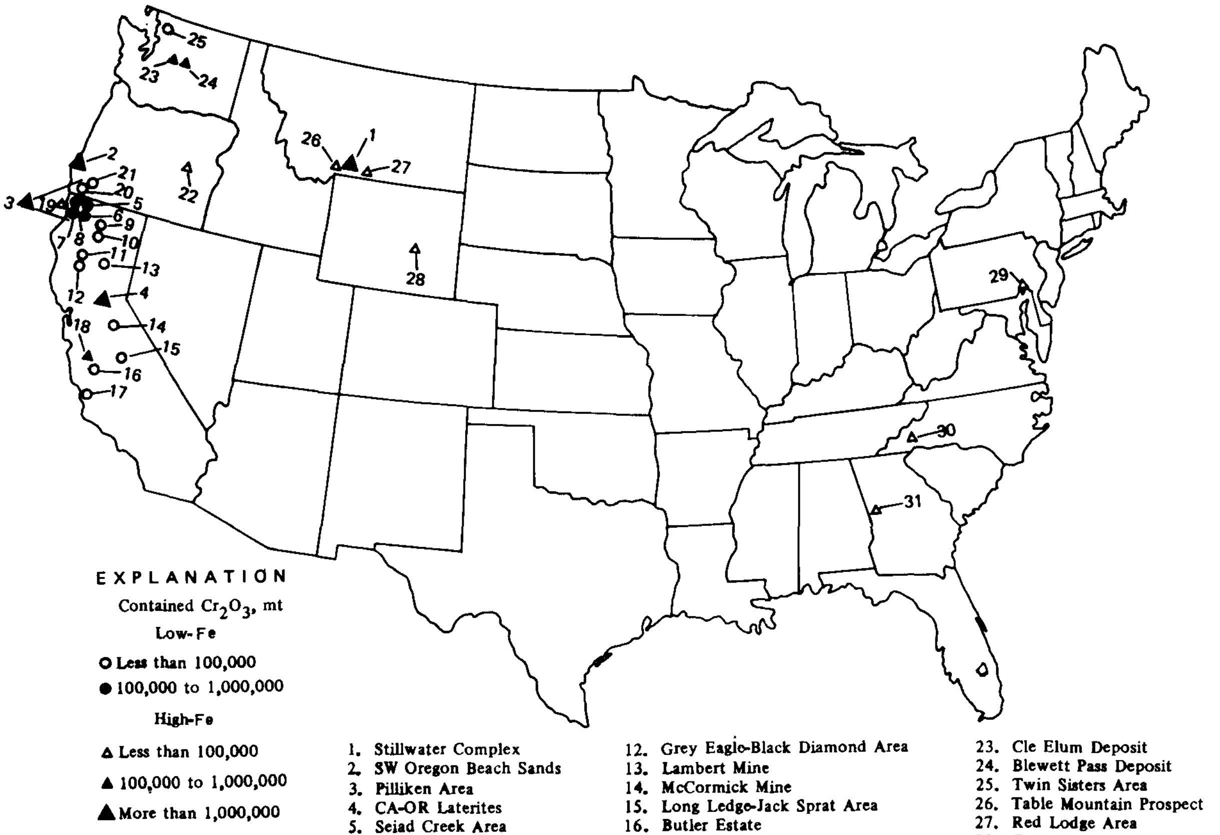
OVERVIEW

Low-Fe chromite resources in the conterminous United States are estimated at 1.6 million mt contained Cr_2O_3 in 14.6 million mt of chromite-bearing material (table 3). Over 99 pct of these resources are contained in podiform deposits of California and Oregon (fig. 1). Within these deposits over 97 pct of the resource is contained within the larger

TABLE 3.—Resources by type and quality

Type	Ore, mt	Cr_2O_3, pct	Cr-Fe ratio	Contained Cr_2O_3, mt	Source, State and pct
			LOW-Fe		
Podiform:					
Disseminated	14,422,600	10.2	2.5	1,474,000	95.0 CA, 4.0 OR, 1.0 WA.
Massive	189,000	42.9	2.9	81,000	76.0 CA, 24.0 OR.
Total	14,611,600	10.6	2.5	1,555,000	95.0 CA, 4.5 OR, .5 WA.
			HIGH-Fe		
Stratiform	46,215,900	20.6	1.6	9,514,200	98.9 MT, 1.1 WY.
Placer:					
Beach sands	8,768,700	4.9	1.4	433,500	88.7 OR, 11.3 CA.
Placer	1,247,700	1.4	1.5	17,700	41.2 MD, 35.6 PA. 19.8 NC, 3.4 GA.
Podiform:					
Disseminated	82,040,700	3.0	2.0	2,420,200	98.5 CA, 1.5 MT.
Massive	188,500	22.6	2.0	42,500	100.0 OR.
Total	138,461,500	9.0	1.8	12,428,000	75.5 MT, 20.0 CA, 3.7 OR, .7 WY, .1 others
			POTENTIAL SOURCES		
Beach sands	200,000,000	1.0	NAp	2,000,000	100.0 OR.
Laterites	196,819,000	2.6	NAp	5,073,000	54.0 CA, 46.0 OR.
Asbestos	41,058,000	.7	NAp	271,000	100.0 CA.
Iron ore	10,591,300	2.1	.6	221,700	100.0 WA.
Podiform	18,000	30.0	1.1	5,400	100.0 MT.
Total	448,486,300	1.7	1.0	7,571,100	57.2 OR, 39.8 CA, 2.9 WA, .1 MT.

NAp Not applicable.



1. Stillwater Complex
2. SW Oregon Beach Sands
3. Pilliken Area
4. CA-OR Laterites
5. Seiad Creek Area
6. Hamburg-McGuffy Creek Area
7. Bar Rick Mine
8. Broken Ladder Area
9. Coggins Mine
10. Little Castle Creek Mine
11. North Elder Creek Area
12. Grey Eagle-Black Diamond Area
13. Lambert Mine
14. McCormick Mine
15. Long Ledge-Jack Sprat Area
16. Butler Estate
17. San Luis Obispo County Area
18. San Benito-Tulare-Fresno Asbestos
19. Crescent City Beach Sands
20. Sourdough Area
21. Chrome Ridge Area
22. John Day Area
23. Cle Elum Deposit
24. Blewett Pass Deposit
25. Twin Sisters Area
26. Table Mountain Prospect
27. Red Lodge Area
28. Casper Mountain Deposit
29. State Line District
30. Morgan Hill-Lancaster-Holcombe Deposits
31. Louise Deposits

FIGURE 1.—Location of significant chromite deposits in the conterminous United States.

disseminated deposits grading from 5 to 20 pct Cr_2O_3 rather than the small scattered pods of shipping-grade ore.

High-Fe chromite resources are estimated at 12.4 million mt contained Cr_2O_3 in 138.5 million mt of chromite-bearing material. Of this total, 75 pct is contained in stratiform deposits of the Stillwater Complex, 21 pct in disseminated podiform deposits of California, and 3 pct in beach sand deposits of southwest Oregon. Less than 1 pct is contained in stratiform deposits of Wyoming, disseminated deposits of Montana, or alluvial deposits of Pennsylvania, Maryland, Georgia, and North Carolina.

Additional chromite resources are available from lower grade beach sand deposits in southern Oregon and as potential byproducts from laterites, asbestos deposits, and iron ore deposits. These resources contain nearly 7.6 million mt Cr_2O_3 in 448.5 million mt of material. Over 67 pct of this resource is contained in laterite deposits of California and Oregon, 26 pct in southwest Oregon beach sands, 3.5 pct in asbestos properties in California, 3.1 pct in Washington iron ore deposits, and < 0.1 pct in exceedingly high-Fe podiform deposits in Montana.

MONTANA

Montana's estimated resources are 42.9 million mt ore containing 9.5 million mt Cr_2O_3. More than 99 pct of this total is in stratiform deposits of the Stillwater Complex. The remaining resource occurs in several small massive and disseminated podiform deposits in the Red Lodge District, some 50 km southeast of the Stillwater Complex, and the Table Mountain asbestos prospect in the Spanish Peaks Primitive Area, approximately 100 km west of the Stillwater Complex. All chromite resources in Montana are high in Fe, with Cr-Fe ratios averaging 1.6.

STILLWATER COMPLEX

The Stillwater Complex, a large layered intrusive body, lies along the northern margin of the Beartooth Mountains and is exposed along a strike length of 45 km; exposed width ranges between 3 and 6 km. The 2.9-billion-year-old Archean Age complex intrudes even older metasediments to the south and is uncomformably overlain by Middle Cambrian sediments to the north. The complex, for classification purposes, has been divided into three zones, the Basal, Ultramafic, and Banded Zones (*30*). Chromite is concentrated in 13 separate, alphabetically designated (oldest to youngest) chromitite layers within olivine-rich rocks of the Ultramafic Zone in the lower part of the complex (*13*). Individual layers are not omnipresent; only two, the G and H layers, are believed to contain potential chromite resources. All significant occurrences are associated with poikilitic rock of harzburgite composition.

Chromite was first noted in the vicinity of the present Benbow Mine in 1918. From 1918 to 1929, Chromium Products Corp. made several unsuccessful attempts to develop the property. In 1939, the Bureau of Mines began a 6-yr study which included trenching, drilling, and channel sampling of the G chromitite layer. During this study, a Canadian firm acquired the Benbow property and drove a 425-m exploration adit. When the Canadian firm relinquished its interests, the Anaconda Co., under Government contract to supply concentrates, initiated development. From 1941 to 1943, Anaconda developed 14,261 m of underground workings and completed 804 m of diamond drilling to define, in part, the resources of the G chromitite layer (*31*). During the 3-yr production period, Anaconda mined 203,844 mt ore at an average grade of 18.4 pct Cr_2O_3. About 169,000 mt of this total was processed at the Benbow mill to yield 65,832 mt of 41.5-pct-Cr_2O_3 concentrate.

The Mountain View chromite deposit was discovered and claimed in stages between 1880 and 1918. Development continued sporadically from 1918 to 1930; however, no significant production occurred until the Government contract was let to the Anaconda Co. in 1941. Anaconda completed about 12,000 m of underground development from 1941 to 1943. The mill processed 70,485 mt of 19.3-pct-Cr_2O_3 ore to produce 26,796 mt of 38.8-pct-Cr_2O_3 concentrate. An additional 95,711 mt was mined and stockpiled.

The American Chrome Co., also under Government contract, reopened the Mountain View Mine in 1953. From 1953 to 1961, 18,832 m of development work was completed. During the 8-yr period of operation, 862,000 mt of 38.6-pct-Cr_2O_3 concentrate was produced. In 1958, a pilot ferrochromium plant was constructed that yielded promising test results (*31*).

The Gish property, located in 1918, was not developed until 1942 when Anaconda, under Government contract, completed 1,239 m of underground workings. None of the mined ore was milled.

The Nye Basin area was explored by trenching and diamond drilling by the Bureau during the 1930's and 1940's. No subsequent exploration has taken place.

The stockpile produced by American Chrome was completed at a cost to the Government of $33/mt. In 1974, the stockpile was sold to Metallurg Inc. of New York, at a reported sale price of $9/mt. In 1975, approximately half of the stockpile was hauled by truck to Columbus, MT, then shipped by rail to Great Lakes ports; some of the concentrate was subsequently shipped to Germany, Sweden, and the United States. Truck haulage was terminated in 1975 because of road damage. In the summer of 1982 truck haulage was resumed, and the remaining concentrates were moved to Columbus, MT.

Estimated resources included herein are determined for specific deposits within the complex. Resource calculations are based upon published company information, Bureau and U.S. Geological Survey project reports and publications, and inferences from reasonable extensions of ore zones based on available geologic data. Maximum depth of chromitites at the Mountain View, Benbow, and Nye Basin is as has been arbitrarily fixed at the Stillwater River Valley, i.e., 1,525 m above sea level. This elevation represents the lowest surface exposure of chromitite layers. Resources total 42,441,000 mt averaging 22.2 pct Cr_2O_3 (table 4).

TABLE 4.—Chromite resources of the Stillwater Complex

Deposit	Ore, mt	Cr_2O_3 grade, pct
Mountain View Mine	15,104,000	22.6
Benbow Mine	17,953,000	22.2
Nye Basin Area	8,530,000	22.2
Gish Mine	854,000	15.0
Total	42,441,000	22.2

Source: References 11 and 13 and Bureau estimates (1984).

RED LODGE DISTRICT

Chromite in the Red Lodge district occurs as lenses and pods scattered through sill-like masses of serpentinized peridotite that have intruded metasediments and metavolcanic rocks. These metasediments and metavolcanics now exist as roof pendants in gneissoidal Precambrian granite, which underlies most of the Beartooth Range (*15*).

Chromite was first discovered in the Red Lodge area in 1916. The only recorded production, however, took place from 1941 to 1943 when 51,200 mt ore averaging 12.5 pct Cr_2O_3 was mined and milled. This produced 10,600 mt concentrate averaging 40 pct Cr_2O_3 with a 1.4 Cr-Fe ratio (*15*). An additional 19,000 mt lump ore averaging 32 pct Cr_2O_3 was also produced during this time.

Resource estimates for the Red Lodge district total 18,000 mt averaging 30.0 pct Cr_2O_3 (*15*).

TABLE MOUNTAIN PROSPECT

The Table Mountain prospect was investigated by the Bureau in 1965 during the wilderness study of the Spanish Peaks Primitive Area. The deposit area is composed of granitic gneiss, hornblende schist, amphibolite, and chloritic schist. The chromite occurs within the amphibolite and chloritic schist (*1*). The amphibolite lens is approximately 100 m long and 10 m wide and is surrounded by an additional 11 m of chromite-bearing chloritic schist.

Resources are estimated at 352,000 mt averaging 10.6 pct Cr_2O_3 with Cr-Fe ratios between 1.5 and 1.7 (*1*).

CALIFORNIA

Chromite resources in California total 6.9 million mt Cr_2O_3 contained in 249.1 million mt of chromite-bearing material. Of this total, 1.5 million mt contained Cr_2O_3 is low in Fe, with Cr-Fe ratios ranging between 2.5 and >3, and 2.5 million mt contained Cr_2O_3 is high in Fe, with Cr-Fe ratios ranging between 1.6 and 2.2. The remaining resources consist of 2.75 millon mt Cr_2O_3 in 103.9 million mt of lateritic soils, and 271,000 mt Cr_2O_3 contained in 41.1 million mt of asbestos resources.

PODIFORM DEPOSITS

Major podiform chromite resources in California are found in Siskiyou, Del Norte, El Dorado, San Luis Obispo, and Tehama Counties.

Siskiyou County

Seiad Creek District

Principal deposits in the Seiad Creek district of Siskiyou County are the Emma Bell and Seiad Creek properties. These deposits have produced only 3,500 mt of lump ore and concentrates with an average Cr-Fe ratio of 3.0. However, exploration, which began in 1941 and is ongoing today, has delineated some of the largest domestic deposits discovered to date. From April to October 1941, the Bureau completed 1,980 m of diamond drilling, 128 m of underground workings, and 956 m of trenching in an attempt to delineate the Seiad Creek deposit (*34*). In 1978, U.S. Chrome of Grants Pass, OR, initiated a diamond drilling program on its Seiad Creek property in an effort to expand the Bureau's work. By the end of 1978, seven drill holes totaling 508 m had been completed at the Seiad Creek Mine; three holes were drilled at the Emma Bell. During 1979, 14 more holes were drilled to delineate the upper portion of the Emma Bell. Drilling between 1980 and 1982 totaled 493 m on three new target areas southeast of the Emma Bell; however, no significant chromite intercepts were encountered.

In 1983, U.S. Chrome entered into a joint venture with Asamera Minerals. The partnership included the Seiad Creek, Emma Bell, Ladd, Fairview, and McGuffy Creek properties. Subsequent drilling at the Emma Bell consisted of two holes drilled by U.S. Chrome and two by Asamera.

Resource estimates for the Emma Bell are based on a total strike length of 1,200 m, a width that ranges between 20 and 50 m, and grades that average 3.4 pct Cr_2O_3. Higher grade chromite is concentrated within a 4- to 10-m width that averages 13.8 pct Cr_2O_3 and contains an estimated 466,000 mt Cr_2O_3 in 3,384,000 mt ore. Should the lower grade material prove a viable resource in the future, an additional 149,000 mt Cr_2O_3 contained in 14,558,000 mt ore is estimated to be available.

The Seiad Creek deposit is located approximately 1.5 km southeast of the southern end of the Emma Bell. The main ore body has a strike length of about 500 m with an average width of 45 m. The deposit hosts an estimated 110,000 mt Cr_2O_3 contained in 1,711,000 mt ore.

Additional resources in the Seiad Creek district are small and probably do not exceed more than a few thousand metric tons of contained Cr_2O_3.

Hamburg-McGuffy Creek Area

The major deposits of the Hamburg-McGuffy Creek area are the Ladd and Fairview Mines and the McGuffy Creek deposits. Exploration in the Hamburg-McGuffy Creek area was initiated during the intense search for Cr during World War I. Considerable exploration and development took place during this period but ceased with the fall of Cr prices at war's end; little more than assessment work was carried out between 1918 and 1942. The U.S. Geological Survey, in accordance with the Strategic Minerals Act of 1939, conducted an exploration program between May and June 1942 (*34*). The program consisted of 681 m of diamond drilling in the McGuffy Creek area. Ten holes were drilled on the Veta Chica Claim and four on the Cerro Colorado Claim. In addition, 150 trench channel samples were taken.

At the Ladd property, U.S. Chrome Corp. drilled four holes totaling 460 m during the spring of 1979 (*7*). During this same period, surface sampling and mapping were conducted on the Fairview property.

In fall 1983, Asamera Minerals began a diamond drilling program on the Veta Chica and Lady Grey Claims; by winter, over 1,000 m of drilling had been completed (*19*). During this period, Bureau personnel developed plane table maps of the Lady Grey, Veta Grande, Veta Chica, Grand Falls, and Grand Canyon Claims at McGuffy Creek; the Ladd Mine was also mapped.

The largest chromite deposits in the McGuffy Creek area occur at the Veta Chica, Lady Grey, and Cerro Colorado Claims. Minor deposits have been identified in the Grand Falls, Grand Canyon, and Veta Grande Claims. Total estimated resources for the McGuffy Creek deposits are 37,000 mt Cr_2O_3 contained in 417,000 mt ore.

At the Ladd Mine, minimal diamond drilling and surface mapping has roughly delineated two subparallel zones of disseminated and schlieren chromite with a combined width of 21 m and a surface outcrop length of 550 m; drilling has intersected the zones at a depth of 100 m. The zones strike roughly N 10° to 20° E and dip 55° to 80° NW. Higher grade zones are estimated to contain 120,000 mt Cr_2O_3 in 1,605,000 mt ore. An additional 53,000 mt Cr_2O_3 is contained in 3,497,000 mt dunite, which encloses the higher grade ore.

Data on the Fairview Mine are restricted to a surface map (1 in = 50 ft) and 10 channel samples taken from surface outcrops (*28*). The deposit consists primarily of a zone of heavily disseminated to banded and massive chromite from <1 m up to 3 m wide. The zone strikes roughly N 40° W and dips 65° to 85° SW. Surface exposures suggest a strike length of at least 150 m with no indication of the depth of downdip extension. Estimated resources are 23,000 mt Cr_2O_3 contained in 65,000 mt ore averaging 35.6 pct Cr_2O_3 with a 3.0 Cr-Fe ratio.

Del Norte County

Del Norte County is ranked second only to San Luis Obispo County for total production of chromite in California. Through the end of the Government buying program in 1958, more than 80 mines had produced a total of 86,600 mt of lump ore and concentrates (*32, 36*). Although more than half the past production has come from high-grade massive podiform deposits, resources are estimated for only 12 high-grade deposits with a total of 60,000 mt averaging about 50 pct Cr_2O_3 with Cr-Fe ratios ranging between 2.8 and 3.7. The majority of these resources are contained in the High Plateau Mine, which has produced the highest quality domestic ore to date (55 pct Cr_2O_3 with a 3.7 Cr-Fe ratio), and the French Hill Mine, which has produced more than 40 pct of the total production in Del Norte County. Both deposits, as well as other massive occurrences in the region, contain pods, lenses, and tabular bodies of nearly pure chromite enclosed by highly serpentinized dunite along shear zones.

The majority of the resources estimated for Del Norte County are contained in two deposits, the Bar Rick and the Broken Ladder.

The Bar Rick deposit was discovered in 1952 by C. H. McClendon, who operated the property in conjunction with several others from 1953 to 1958 (*18*). Exploration of the deposit consists of 500 m of diamond drilling by Inspiration Development Co. in 1971, and subsequent surface sampling and mapping by the Bureau in 1979, 1980, and 1983. Additional mapping and sampling were conducted by Del Norte Chrome Ltd., which purchased the property in 1981. Chromite resources are estimated by Del Norte Chrome at 2,196,000 mt averaging 5.9 pct Cr_2O_3 in the lower and upper benches, and 22,415,000 mt averaging 2.8 pct Cr_2O_3 in the remainder of the deposit (*5*). Chromite in the upper and lower benches consists of lenses and streaks, and clots of more massive chromite, scattered randomly through highly sheared and serpentinized dunite. Dunite between the upper and lower benches is less altered and contains <1 pct to >10 pct disseminated chromite.

The Broken Ladder deposit is located north of Gasquet Mountain. There is no recorded production or exploration history for the deposit; however, the Bureau mapped and sampled it in 1982 and 1983. Over a distance of more than 2 km, chromite occurs as streaks and lenses in shear zones and as massive clots to sparsely disseminated grains in less altered dunite. Although additional work is required before more accurate resource estimates can be made, it is estimated that at least 300,000 mt Cr_2O_3 contained in 6 million mt of chromite-bearing material can be developed.

El Dorado County

The Pilliken Mine area contains the most significant chromite deposits in El Dorado County, with a total production through 1958 of 28,815 mt of lump ore and concentrates (*4, 32*). Deposits in the Pilliken area occur in peridotites of the Western Metamorphic Belt of the Sierra Nevada foothills. Nine distinct subareas within the Pilliken area contain potential chromite resources. Chromite occurs in a wide variety of forms, from sparsely disseminated grains to irregular masses of nearly pure chromite. Resource estimates were calculated from deposit descriptions and assay data provided by Wells (*38*) and Bureau sample data collected in 1978 and 1979. The total resource potential for all nine areas consists of 344,000 mt Cr_2O_3 contained in 3,284,000 mt ore and an additional 1,336,500 mt Cr_2O_3 contained in 41,767,000 mt low-grade material. Resources are described in table 5.

TABLE 5.—Estimated resources for the Pilliken area

Location	Ore, mt	Cr_2O_3 grade, pct	Contained Cr_2O_3, mt
High-grade:			
Subarea 1	1,770,000	11.0	194,700
Subarea 2	377,000	9.0	33,900
Subarea 3	636,000	10.2	64,900
Subarea 4	88,000	10.2	9,000
Subarea 5	44,000	10.2	4,500
Subarea 6	73,000	9.6	7,000
Subarea 7	278,000	10.2	28,400
Subarea 8	18,000	7.2	1,300
Low-grade:			
Subareas 1-8	41,767,000	3.2	1,336,500
Total	45,051,000	3.7	1,680,200

Source: Reference 27 and Bureau estimates (1984).

Although the Pilliken Mine area hosts the largest single group of podiform chromite deposits in California, the majority of the lower grade ore contains unusually high quantities of Fe. Concentrates produced from ore containing <5 pct Cr_2O_3 had Cr-Fe ratios ranging between 0.8 and 1.4, whereas concentrates produced from ore containing 5 to 15 pct Cr_2O_3 had Cr-Fe ratios averaging 1.7. These ratios are similar to those obtained from Stillwater ores.

Resources have also been estimated for several smaller dunite masses that occur in El Dorado County. Six additional properites, the Darrington, Steele, Joerger, Walker, Murphy, and Chaix, are estimated to contain 132,000 mt of chromite-bearing dunites averaging 12.0 pct Cr_2O_3 (*4, 38*).

San Luis Obispo County

Chromite deposits in San Luis Obispo County comprise some of the largest past producers of disseminated chromite in California. Beginning as early as 1870, over 75 deposits have been developed that produced over 130,000 mt of low-Fe chromite concentrates and lump ore (*32-33*). A large majority of this production came from the Castro, New London, La Primera, Trinidad, Pick and Shovel, Sealy, Sweetwater, and Norcross deposits. Chromite contained in these deposits generally ranged in grade between 5 and 20 pct Cr_2O_3.

Several of the larger deposits were examined by the U.S. Geological Survey in the 1940's. In 1943, it was estimated that remaining resources were about 32,000 mt; however, during the 1950's, $>60,000$ mt was mined. Currently, total resources for San Luis Obispo County deposits have been estimated at 133,000 mt ore averaging 14.2 pct Cr_2O_3 (*27*). Although the Bureau has yet to determine the potential of chromite resources in lower grade deposits containing 5 to 10 pct Cr_2O_3, the probability is high of discovering large tonnages of low-grade resources similiar to those described in Siskiyou, Del Norte, and El Dorado Counties. These deposits should be investigated in order to properly ascertain their potential.

Tehama County

The North Elder Creek chromite deposits are located approximately 70 km west of Red Bluff in Tehama County. Nearly 32,000 mt of lump ore and concentrates have been produced from the Grau, Mill Gulch, and the Old Noble Electric Steel Co. deposits (*6, 32*). All occur in a large shear zone more than 5 km in length and varying in width from a few to several hundred meters. Chromite occurs as pods, lenses, and streaks enclosed by serpentinized dunite and massive serpentine, or in varying degrees of dissemination within less altered dunite.

Deposits of North Elder Creek were visited and sampled by the Bureau in 1979; a few disseminated resources are estimated to remain. Total resources are estimated at 104,000 mt averaging 11.9 pct Cr_2O_3 (*22*). Concentrates produced during past operations averaged 45 pct Cr_2O_3 with a 2.8 Cr-Fe ratio.

Since these resources are restricted to less than a few hundred meters of the total strike length, additional resources may be present north and south along strike.

Other Areas

Additional low-Fe resources are available in several smaller podiform deposits throughout California. These deposits are described in table 6. Deposits listed in table 6 contain published resources only. Permission to disclose Bureau individual property estimates was not received prior to publication.

LATERITE DEPOSITS

Laterite resources in California are estimated at 2,750,000 mt Cr_2O_3 contained in 103,897,000 mt of lateritic soil. The bulk of these resources were delineated during the Bureau's field program, which commenced in 1976 and continued through 1979. The majority of sampling was accomplished with backhoes and hand augers.

PLACER DEPOSITS

The only known placer deposit of interest in California is the beach sand deposit that extends for about 7 km south of the breakwater at Whaler Island (*36*) just south of Crescent City. Within this area is a strip of concentrated black sands 3 km by 75 m to 110 m averaging 1.2 m thick. This zone is estimated to contain 700,000 mt averaging 7.0 pct Cr_2O_3.

OTHER OCCURRENCES

An additional 270,000 mt Cr_2O_3 is contained in over 41 million mt of asbestos resources in San Benito, Fresno, and Tulare Counties.

TABLE 6.—Additional low-iron resources from California podiform deposits

Deposits by county	Past production Cr_2O_3, pct	Cr-Fe ratio	Published resource		
			Ore, mt	Cr_2O_3, pct	Reference
Butte:					
Lambert	44	2.8	W	W	W
Parks Ranch	38	2.6	W	W	W
Del Norte: Sunrise	47	2.6	W	W	W
Fresno:					
Butler Estate	46	3.0	W	W	17
Jack Sprat	44	2.6	1,200	30.0	23
Long Ledge	45	2.6	6,800	8.0	23
Glenn:					
Black Diamond	47	3.0	40,000	8.0	25
Grey Eagle	47	3.0	151,000	12.9	25
Nevada: Holsemann	33	2.5	W	W	W
Placer: Parker Ranch	40	1.6	5,000	8.0	24
Shasta: Little Castle Creek	45	2.8	5,000	23.0	37
Sierra:					
Milton	30	2.5	W	W	W
Oxford	NA	NA	W	W	W
Siskiyou:					
Coggins	38	3.2	W	W	W
Peg Leg	54	3.3	100	54.4	35
Stanislaus: Black Bart	34	2.5	2,000	33.8	9
Toulumne:					
Mum and Alice	35	3.2	7,500	15.0	2
Richards	37	NA	7,000	20.0	2
North End	NA	NA	W	W	W
McCormick	43-49	2.8-3.5	220	47.0	26
Trinity: Black Bear	NA	NA	W	W	W
Total	NAp	NAp	516,000	16.8	NAp

NA Not available. NAp Not applicable. W Withheld; included in total.

OREGON

Chromite resources in Oregon total 4.8 million mt Cr_2O_3 contained in 306.7 million mt of chromite-bearing material. Of this total, 85,000 mt contained Cr_2O_3 is low in Fe with Cr-Fe ratios ranging between 2.2 and 2.8; 2,409,100 mt contained Cr_2O_3 is high in Fe with Cr-Fe ratios ranging between 1.4 and 2.0. Remaining resources consist of 2,323,000 mt Cr_2O_3 in 92,922,000 mt of lateritic soils.

PODIFORM DEPOSITS

Major podiform chromite resources are found in the Josephine Peridotite located in portions of Josephine, Curry, Douglas, Jackson, and Coos Counties, and in the John Day area in Grant County.

Josephine Peridotite

Production from podiform deposits in the Josephine Peridotite totals 49,000 mt of lump ore averaging 48 pct Cr_2O_3 with a 2.8 Cr-Fe ratio, and approximately 2,000 mt of concentrates averaging 46 pct Cr_2O_3 with a 2.5 Cr-Fe ratio. Production has come from 58 properties in Josephine County, 19 in Curry County, 8 in Douglas County, 5 in Jackson County, and 2 in Coos County (*20*). Most of the deposits were high-grade lenses and pods that yielded less than a few hundred metric tons. The Oregon Chrome Mine, however, accounted for nearly 65 pct of the area's total production.

Only four deposits, the Oregon Chrome Mine, Chrome King, Shady Cove, and Dirty Face, have data available for determining high-grade resource potential. These contain an estimated 25,000 mt of nearly pure, massive chromite in the form of pods, lenses, and tabular bodies enclosed by highly serpentinized dunite. This resource averages 45 pct Cr_2O_3 with a Cr-Fe ratio of 2.7.

Areas of significant resource potential include the Chrome Ridge area in Josephine County and the Sourdough area in Curry County.

The Chrome Ridge area was investigated by the Bureau in 1983 and 1984; the deposits were mapped and 150 samples were collected. Three principal deposits with significant resources were identified: the Violet, Buster, and Shady Cove.

The Violet Mine consists of upper and lower workings situated along two shear zones in highly serpentinized and chloritized dunite. The upper workings are in a north-northwest-trending zone 6 m wide by almost 100 m long. The lower zone workings, some 100 m to the southwest, average 15 m wide over a 35-m strike length.

The Buster Mine lies in serpentinized dunite and is faulted against metamorphosed harzburgite along the western edge of the deposit. Chromite occurs as disseminations within the dunite and as layers in shear zones. Sampling from lower and upper benches defined a zone 25 m wide and 45 m long.

The Shady Cove Mine contains schlieren-type banded chromite in serpentinized shear zones associated with northeast-trending faults. Small massive chromite pods are associated with the serpentinite. Analyses of the massive chromite average 41.8 pct Cr_2O_3 and 55.0 pct Cr_2O_3 plus Al_2O_3, with a 2.9 Cr-Fe ratio.

Resource estimates total 200,000 mt at the Violet averaging 4.7 pct Cr_2O_3, 321,000 mt at the Buster averaging 8.3 pct Cr_2O_3, and 10,000 mt at the Shady Cove averaging 19.4 pct Cr_2O_3.

Resources have been estimated for the Sourdough area by Wells (*39*) at 100,000 mt averaging 15 pct Cr_2O_3, and for the Young's Dailey Dozen by Ramp (*20*) at 20,000 mt averaging 15 pct Cr_2O_3.

Detailed mapping and sampling should increase these estimates considerably.

John Day Area

Chromite deposits in the John Day District, Grant County, contain mostly high-alumina chromite with as much as 27 pct Al_2O_3 (*29*). The three most significant deposits were explored by trenching and shallow diamond drilling by the Bureau in the 1940's. The deposits contain lenses of heavily disseminated to massive chromite enclosed by serpentized dunite. Bureau estimates are 113,000 mt averaging 23 pct Cr_2O_3 with a 1.8 Cr-Fe ratio for the Chambers Mine, 68,000 mt averaging 22 pct Cr_2O_3 for the Iron King Mine, and 7,500 mt averaging 20 pct for the Dry Camp Mine (*12*).

LATERITE DEPOSITS

Laterite resources in Oregon are estimated at 2,323,000 mt Cr_2O_3 contained within 92,922,000 mt of lateritic soil. The bulk of these resources were delineated between 1976 and 1979 during the Bureau's field program.

PLACER DEPOSITS

Black sand deposits occur on raised marine terraces along the southern coast in Coos and Curry Counties. Concentrations of black sands are found as lenses and layers that range from a few centimeters to more than 12 m thick (*8*). Detailed investigations, including drilling, were initiated in the 1940's and have continued intermittently through 1980. Drilling by the Bureau during the 1970's totaled more than 100 holes.

Production of chromite from the higher grade deposits occurred during World War II and the Korean War, during which time 1,844,800 mt of sands averaging 3.8 pct Cr_2O_3 were mined and concentrated. Not all of the material mined was concentrated to a final product. Total shipped concentrates were 48,600 mt averaging 39.3 pct Cr_2O_3 with a 1.5 Cr-Fe ratio.

Resources estimates for individual deposits were derived from published U.S. Geological Survey and Bureau reports, and from reasonable extensions based on the Bureau's drilling in the 1970's. This resource is estimated to contain 384,500 mt Cr_2O_3 in 8,068,700 mt of black sands. The source of these estimates is described in table 7.

Additional resources are probably vast; however, additional drilling would be required to determine the full potential. Drilling to date in the vicinity of the Seven Devils and Whiskey Run terraces suggests the presence of at least 2 million mt Cr_2O_3 contained in 200 million mt of black sands.

TABLE 7.—Southwest Oregon beach sand deposits

Deposit	Ore, mt	Cr_2O_3 grade, pct	Contained Cr_2O_3, mt
South slough	1,995,800	3.25	64,900
Section 33	1,274,000	3.93	50,200
Section 4	719,600	5.02	36,100
Seven Devils	1,236,200	5.85	72,300
Seven Devils area ...	144,200	7.80	11,200
Whiskey Run area ...	99,000	6.20	6,100
Shepard Mine	257,500	7.04	18,100
Shepard Extension ..	1,436,000	3.35	48,100
Pioneer-Eagle	470,000	8.80	41,400
Butler Mine	62,200	8.70	5,400
The Lagoons	124,200	10.60	13,200
Madden	100,000	10.00	10,000
Others	150,000	5.00	7,500
Total	8,068,700	4.77	384,500

Source: Reference 8 and Bureau estimates (1978).

WASHINGTON

Estimated resources in Washington State total 30,700 mt of low-iron Cr_2O_3. Additional resources present in iron ore deposits total 221,700 mt Cr_2O_3.

PODIFORM DEPOSITS

Low-Fe chromite in Washington occurs as lenses, pods, and disseminated crystals in the Twin Sisters area of Whatcom and Skagit Counties.

The Twin Sisters area contains a mass of dunite 11 km long and 5 km wide that is a major source of olivine for foundry sand. Chromite deposits on the south summit of the Twin Sisters Range consist of small lenses and pods estimated to contain 30,700 mt Cr_2O_3 in 470,000 mt of chromite-bearing material (*16*). The potential for large tonnages of lower grade resources in a dunite of this size is exceedingly high, and investigation of the area is warranted.

OTHER OCCURRENCES

Chromium contained in iron ore deposits in the Blewett Pass and Cle Elum areas may provide a future source of domestic chromite. The Cle Elum deposit consists of irregular lenses of iron ore in a serpentized peridotite. Extensive diamond drilling by the Bureau delineated a total resource of 7,520,000 mt averaging 2.6 pct Cr_2O_3, 42 pct Fe, and 0.93 pct Ni. The principal iron minerals are magnetite, hematite, and limonite that occur intermixed with serpentine and olivine.

The Blewett Pass deposit is similar to the Cle Elum, but smaller and lower in grade; however, additional resource is contained in the conglomerate that overlies the deposit. The total resource consists of 41,900 mt of iron ore averaging 2.48 pct Cr_2O_3, 32.5 pct Fe, and 0.88 pct Ni, and 3,029,400 mt of conglomerate averaging 0.88 pct Cr_2O_3, 11.5 pct Fe, and 0.4 pct Ni (*21*).

WYOMING

The only significant occurrence of chromite in Wyoming is the Casper Mountain deposit located in Natrona County. The deposit, a high-Fe, chromite-bearing, actinolite-talc schist, was investigated by the U.S. Geological Survey as early as 1934 and drilled by the Bureau in 1939. The Bureau program included 1,105 m of drilling and 24 surface trenches (*10*). This work delineated two schist bodies containing a total of 3,774,900 mt averaging 2.5 pct Cr_2O_3, including higher grade resources of 521,500 mt averaging 8.7 pct Cr_2O_3 (*10*).

These resources were calculated to a depth of 30 m, and drilling indicates that additional resources may persist to a depth of 150 m.

APPALACHIAN STATES

Estimates of chromite resources in the Appalachian States are restricted to placer deposits in the State Line district of Pennsylvania and Maryland and smaller areas in North Carolina and Georgia. Although the State Line district produced at least 254,000 mt of high-Fe (Cr-Fe ratios averaging 1.6) chromite from podiform deposits prior to 1900, little work has been done to determine if additional resources remain. However, resource estimates were made by the Bureau of Mines for 18 placer deposits derived from weathering of the podiform deposits. Past production from these deposits was estimated to total 19,000 mt concentrates (*16*).

Resource estimates for 9 deposits in Maryland, 5 in Pennsylvania, 3 in North Carolina, and 1 in Georgia total 1,247,000 mt averaging 1.4 pct Cr_2O_3 for the 18 deposits.

SUMMARY

The total available chromite in the conterminous United States is estimated at 21,554,100 mt Cr_2O_3 (fig. 2).

The known low-Fe Cr resources in the conterminous United States are in the California, Oregon, and Washington podiform deposits, and the majority of the total 1.6 million mt Cr_2O_3 is contained in the lower grade (5 to 20 pct Cr_2O_3) disseminated deposits (95 pct) associated with the more massive smaller pods and lenses exploited in the past (fig. 3). Additional low-Fe resources similar to those identified in Siskiyou and Del Norte Counties, CA, and the Chrome Ridge area of Josephine County, OR, may be developed by detailed mapping and sampling of deposits in San Luis Obispo County, CA, Curry County, OR, and the Twin Sisters area of Whatcom and Skagit Counties, WA.

The primary source for high-Fe Cr is the Stillwater Complex, MT. Approximately 75 pct of the total 12.4 million mt Cr_2O_3 estimated is contained in Stillwater stratiform deposits (fig. 3). Other major sources of high-Fe Cr are large low-grade (3 to 5 pct Cr_2O_3) podiform deposits in the Western States such as the Pilliken deposit in El Dorado County, CA, or the black sand deposits of Coos and Curry Counties, OR. Additional high-Fe resources may be developed by continued exploration of the black sand deposits in Oregon and northwest area podiform deposits.

Domestic sources of high-alumina refractory chromite are located principally in the John Day area of Grant County, OR. For this study, these deposits are combined with the high-Fe resource. Other sources of refractory-quality chromite have been found associated with podiform deposits elsewhere in Oregon and California; however, most deposits are small.

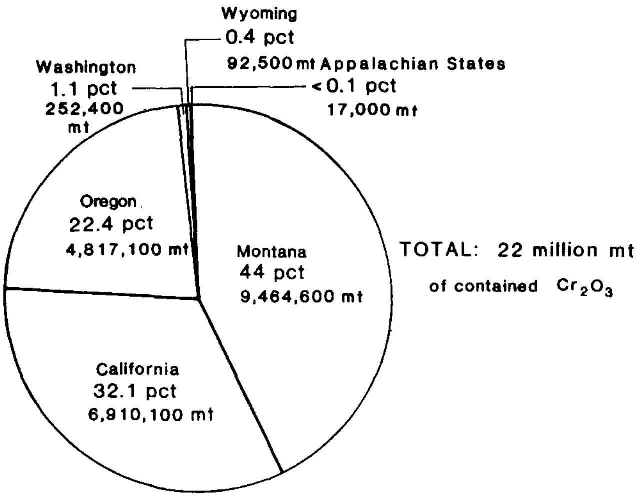


FIGURE 2.—Total estimated resources by State.

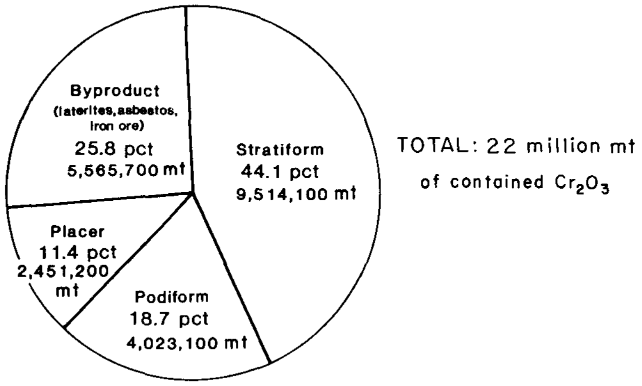


FIGURE 3.—Total estimated resources by type.

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EXTRACTIVE METALLURGY SESSION

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COPRODUCT CHROMITE FROM NICKEL—BEARING LATERITES

By Donald E. Kirby[1] and Donald R. George[2]

ABSTRACT

The Bureau of Mines developed a process to recover chromite from nickel-bearing laterites in the Western United States. The laterite deposits are extensive but low grade, and their value as a resource is dependent on recovery of contained Ni and Co in addition to the chromite. In the present investigation, emphasis was placed on recovering chromite from the residues remaining after Ni and Co extraction. Both the unprocessed laterites and the laterite residues responded to standard ore dressing methods, but Cr recovery was generally below 50 pct and concentrate grades were 29 to 40 pct Cr_2O_3. The low yields and grades resulted from fine particle size of the chromite and the gangue.

PACIFIC COAST LATERITES

Laterites of southwestern Oregon and northern California are the largest secondary deposit of chromium in the United States (*1*). These laterites are soils – the product of chemical weathering of peridotite rocks exposed to tropical or subtropical climates. In the laterization process the Ca, Mg, and SiO_2 constituents of the rock are dissolved and leached away. The Co, Cr, Fe, and Ni resist leaching and become enriched in the lateritic residual soils.

Laterite mineralogy is variable; it includes primary minerals of the original peridotite and secondary minerals resulting from its weathering. The predominant mineral is goethite, a hydrated iron oxide, FeO(OH), which contains most of the nickel. A wadlike manganese oxide mineral (asbolite) contains most of the cobalt. Other minerals are commonly found in smaller amounts: massive and fibrous serpentine, chlorite, quartz, talc, hematite, tremolite, and enstatite. Chromite and magnetite present in the original rock resist weathering; they are found in the laterites chemically unchanged, but concentrated by removal of the other constituents.

Mineral particles in the chromite-bearing laterites are very fine grained. The average particle diameter is about 8 µm. The chromite in laterite has an average particle diameter between 100 and 200 µm, and it is usually present as a high-Fe spinel containing a maximum of 50 pct Cr_2O_3 and having a Cr-Fe ratio of 1.9.

The typical laterites processed in this study contain 2.8 to 4.1 pct chromite. It is doubtful that such a low-grade Cr resource could be used were it not for its size and the presence of other valuable constituents (Ni and Co). Laterites containing significant Ni and Co values and appreciable Cr cover a sizable area of northern California and southwestern Oregon, as shown in figure 1. It is estimated that this laterite resource exceeds 217 million st (*2*), and there are additional Ni-bearing laterites located farther south in California; e.g., in Mendocino County. The laterites examined contain 0.7 to 1.1 pct Ni and 0.06 to 0.10 pct Co in addition to 1.9 to 2.8 pct Cr_2O_3.

The Bureau of Mines developed a hydrometallurgical process to recover Ni and Co from laterites. This four-step process includes (1) low-temperature selective reduction, (2) extraction by ammonia-ammonium sulfate solution under oxidation conditions, (3) separation and concentration of the values by liquid ion exchange, and (4) recovery of Ni and Co as pure metals by electrowinning (*3*).

The residue from this process is finer than the original laterite. Its color is changed from reddish orange to black as its Fe content is partly reduced. Although nearly all the Ni and Co content of the laterite is removed and recovered, the chromite is unchanged during processing except for a slight size reduction.

Abbreviations Used in This Paper

µm	micrometer
pct	weight percent
st	short ton
st/d	short ton per day

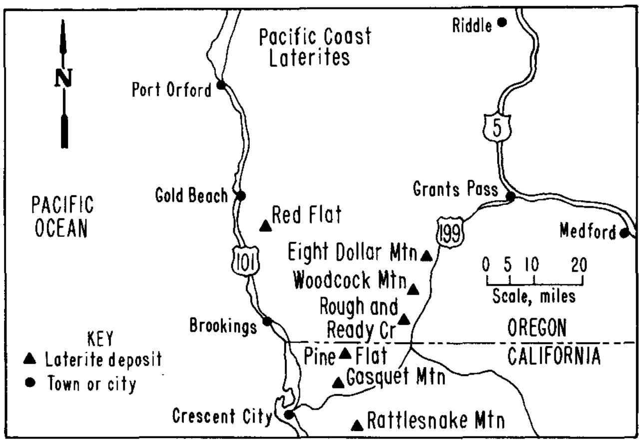

FIGURE 1.—Pacific coast laterites.

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CHROMITE BENEFICIATION

FLOWSHEET DEVELOPMENT AND RESULTS

The low grade and fine size of chromite would make the laterite materials a very questionable Cr resource were it not for the accompanying Ni and Co values. For laterite to be considered a Cr resource, it must be appraised primarily for the recovery of the Ni and Co values and secondarily for the coproduction of the Cr values.

In this study, the primary efforts to recover chromite from laterite were directed toward processing the residues following Ni and Co extraction. The low Cr values in the residue suggested a low-cost approach using physical ore dressing methods, although both the residues and unprocessed laterites were finer than appropriate for many of these processing methods. Methods investigated included gravity concentration, flotation, low- and high-intensity magnetic separation, electrostatic separation, sizing, and combinations of these.

Examination and characterization of a variety of laterites and laterite residues indicated that the coarsest fractions were predominantly serpentine, low in chromite content, and the finest fractions were either goethite or partly reduced goethite and also low in chromite content (*4*). As a result of these findings the general processing flowsheet shown in figure 2 was developed, taking advantage of differences in mineral size, specific gravity, and magnetic properties. Using this flowsheet, sizing rejected more than three-quarters of the total feed weight, but less than half of the chromite. Screening removed the coarse waste, and hydrocycloning removed the fine waste. The chromite that is lost to the finest fraction was unrecoverable by any known methods. Among methods used to attempt scavenging chromite from the slimes were flotation, elutriation, and sizing with smaller hydrocyclones to produce finer cuts.

The intermediate product, finer than minus 65 mesh and coarser than 10 μm, was then treated by two stages of low-intensity magnetic separation to reject the bulk of the naturally occurring magnetite and some of the partly reduced goethite, although the latter was too fine to respond well to magnetic separation.

The nonmagnetic fraction, enriched in chromite, was classified further at about 200-mesh equivalent size prior to feeding it to two parallel gravity circuits, one processing the coarser fraction and the other the finer fraction. A shaking table, shown in figure 3, was used in the two gravity circuits. Both circuits used a rougher step followed by a second tabling step in which the rougher middlings were retreated. About 80 pct of the chromite contained in the minus 65- plus 200-mesh sands reported to the concentrate. However, only about 35 pct of the chromite was recovered from the minus 200-mesh fraction in dual tabling. The table middlings from this operation were essentially a fine, liberated mixture of chromite and enstatite, $MgSiO_3$, a pyroxene mineral. A two-stage treatment of these middlings on a Bartles-Mozley[3] separator, a gravity concentrator designed to scavenge and recover heavy minerals fines from slimes, increased recovery in the chromite slime circuit by 8 to 18 pct. Results shown in table 1 are typical of the chromite grade and Cr recovery values, both with and without scavening, that might be expected from beneficiating laterite residues. In this case, processing results are shown for Red Flat and Rough and Ready Creek materials. Both deposits are located in southwest Oregon.

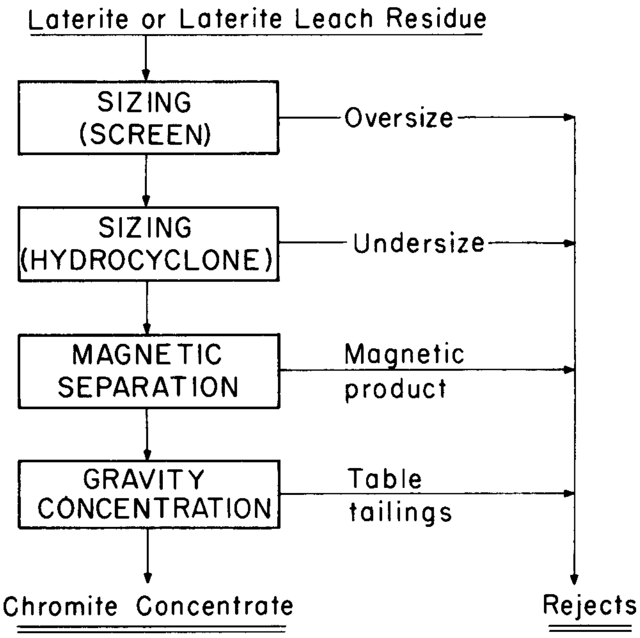

FIGURE 2.—Chromite from laterite or laterite leach residue.

FIGURE 3.—Table concentration of chromite from laterite.

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[3] Reference to specific products does not imply endorsement by the Bureau of Mines.

Most of the developmental work on the benefication system for recovering chromite from laterite was done using leach residue from the ¼-st/d, Ni-Co extraction miniplant operated at the Bureau's Albany Research Center. As an alternative to processing residues after hydrometallurgical treatment, untreated laterite was studied as a feed to the chromite benefication circuit. Raw laterite from the Rough and Ready Creek deposit was chosen for these studies as it represented a fairly typical laterite material. Results of these benefication tests are summarized in table 1. Recovery from the untreated laterite was comparable to that from residues, but the grade was somewhat lower. This is the result of improved mineral liberation in the extraction process residue. As can be seen, the Cr content of the benefication concentrates from either untreated laterites or residues is much lower than that of either commercial lump ore or concentrates. Values for the latter typically range between 40 and 50 pct Cr_2O_3. Chromium recoveries are low when compared to those from most beneficiation processes, in which overall recovery of values normally ranges from 70 to 95 pct. Grade and recovery are usually a trade-off – increase one and the other decreases. In chromite recovery from laterite, both grade and recovery are low – the result of attempting to recover a very fine concentrate from an extremely fine, slimy gangue by methods better suited to treating coarser materials.

TABLE 1.—Miniplant beneficiation of laterite and laterite leach residue

Beneficiation feed	Cr_2O_3 recovery, pct	Concentrate	
		Cr_2O_3 grade, pct	Cr-Fe ratio
Red Flats residue:			
Without scavenging	35	34	1.6
With scavenging	53	33	1.6
Rough and Ready Creek residue:			
Without scavenging[1]	36	29	1.9
Without scavenging[2]	26	37	1.6
With scavenging	44	29	1.6
Rough and Ready Creek untreated laterite:			
With scavenging	40	25	1.4

[1] Beneficiation for Cr recovery.
[2] Beneficiation for Cr grade.

PILOT PLANT OPERATIONS

The Bureau's successful development of processing technology for the Oregon and California laterite materials and the operation of Ni-Co extraction and chromite beneficiation miniplants encouraged further work on a larger, continuous scale. A contract was let by the Bureau of Mines to the Mineral Sciences Division of UOP Inc. to undertake the research effort. A 5-st/d hydrometallurgical pilot plant for extracting and recovering Ni and Co from laterite materials was assembled and operated at Tucson, AZ (*5*). During the operation of the Ni-Co pilot plant, a beneficiation circuit was operated for recovering chromite from the residues.

The chromite beneficiation circuit at Tucson was incomplete. Coarse screening (65 mesh), hydrocycloning, rougher-sand tabling, and magnetic separation operations were performed at Tucson. The nonmagnetic products from low-intensity magnetic separators and the screening and tabling products were shipped to the Albany Research Center, where beneficiation was completed. The flowsheet for the entire benefication circuit is shown in figure 4. Product analyses and distributions are shown in table 2. These analyses and recovery figures reflect the operating performance of both the pilot plant in Tucson and the Bureau's miniplant. It was determined that an overall Cr recovery of 46 pct as a concentrate containing 40 pct Cr_2O_3 with a 1.8 Cr-Fe ratio is achievable. The concentrate was used successfully to prepare a ferrochromium alloy and water-soluble Cr salts. These results are described elsewhere in this publication.

TABLE 2.—Product stream analyses and distributions from pilot plant beneficiation of Rough and Ready Creek laterite leach residue

Stream No.	Stream name	Analysis, pct					Distribution, pct		
		Cr_2O_3	Fe	SiO_2	MgO	Al_2O_3	Cr	Fe	Weight
1	Rough and Ready Creek residue	3.6	32.8	19.4	11.8	7.0	100.0	100.0	100.0
2	Screen oversize	1.2	12.3	36.7	24.3	4.1	3.2	2.9	7.0
3	Screen undersize	3.8	34.2	18.2	10.5	7.2	96.8	97.1	93.0
4	Hydrocyclone overflow	2.0	38.4	15.8	8.1	6.8	41.0	86.5	73.8
5	Hydrocyclone underflow	10.5	18.2	27.4	19.8	8.6	55.8	10.6	19.2
6	Magnetic product	5.5	54.1	5.8	3.4	6.0	4.8	4.9	3.0
7	Nonmagnetic product	11.4	11.6	31.3	22.9	9.1	51.0	5.7	16.2
8	Classifier sands	12.7	9.4	32.1	24.3	8.7	27.9	2.3	8.0
	Rougher sand table:								
9	Concentrate	41.0	15.1	4.2	14.4	21.3	18.0	.7	1.6
10	Tailings	1.9	7.2	42.8	28.2	2.7	3.0	1.3	5.8
11	Middlings	17.4	9.5	31.1	26.0	13.8	9.1	.6	1.9
	Scavenger sand table:								
12	Middlings	6.1	6.9	43.8	31.8	5.1	2.2	.3	1.3
13	Concentrate	41.8	15.1	3.6	13.6	21.9	6.9	.3	.6
14	Classifier slimes	10.2	13.9	30.6	21.5	9.5	23.1	3.4	8.2
	Rougher slime table:								
15	Concentrate	41.4	16.1	1.7	12.4	22.3	4.5	.2	.4
16	Tailings	2.3	12.4	41.5	26.9	4.6	.4	.2	.6
17	Middlings	10.5	13.9	31.3	21.6	9.2	18.2	3.0	7.2
	Scavenger slime:								
18	Tailings	.9	13.4	41.2	24.2	4.6	1.4	2.1	5.6
19	Concentrate	18.7	11.7	17.0	15.0	13.4	25.6	3.0	5.0
20	Cleaner slime tailings (recycle)	9.4	14.0	25.2	15.4	8.1	8.8	2.1	3.4
21	Cleaner slime concentrate	38.8	15.5	3.8	14.2	22.1	16.8	.9	1.6
22	Combined concentrate (9 + 13 + 15 + 21)	40.3	15.4	3.7	14.0	21.8	46.2	2.1	4.2

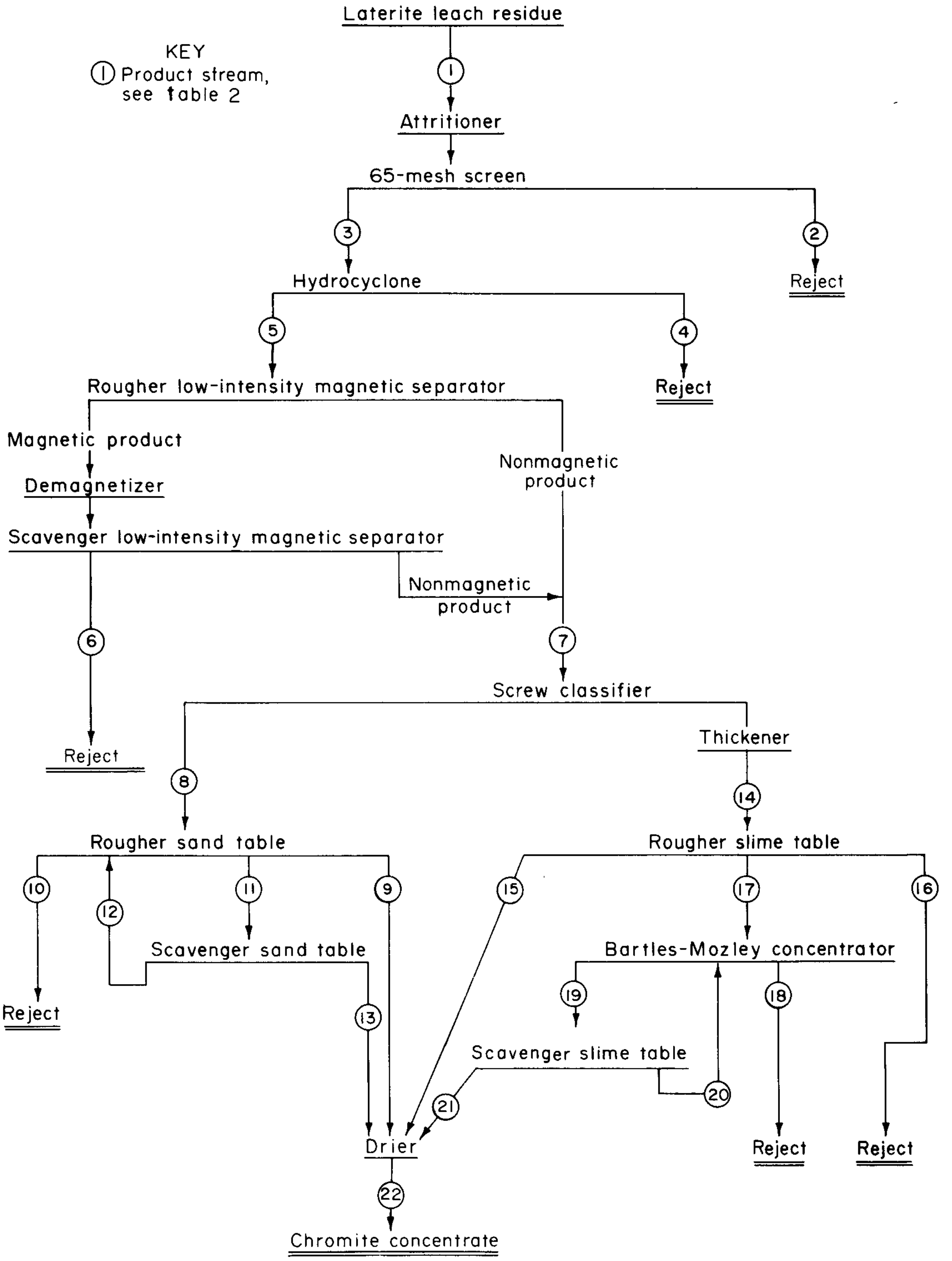

FIGURE 4.—Chromite from pilot plant leach residues.

SUMMARY AND CONCLUSION

Southern Oregon and northern California laterites are potentially a significant domestic resource of Ni, Co, and Cr. Recovery of the Ni and Co by a hydrometallurgical process developed by the Bureau was successfully demonstrated at several operating scales. In an attempt to recover the Cr values from the laterite, a scheme was devised and perfected for capturing chromite from either the hydrometallurgical residue or the untreated laterite by standard mineral dressing procedures. The preferred beneficiation feed is the residue after Ni and Co have been removed, because it is already ground and in a slurry form that is readily transported to the chromite beneficiation circuit.

Recoveries of up to 50 pct and concentrate grades of 35 to 40 pct Cr_2O_3 can be expected from a simple beneficiation procedure, which includes sizing plus magnetic and gravity separation. The low recovery and the low grade of concentrates can be attributed to the fine particle size of both the chromite and the gangue. The chromite contained in many of the laterite deposits has a relatively low Cr_2O_3 content and Cr-Fe ratio; this is a limiting factor in concentrate grades.

Chromite concentrates recovered from laterites by the Bureau processing technology have been used in research on developing technology for pyrometallurgical preparation of ferrochromium and for fusion-leaching as a path to Cr chemicals or high-purity metal. The fine size of the recovered chromite concentrate makes it particularly suitable for preparation of Cr chemicals. Research on both of these processing approaches is described in detail later in this publication.

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CHARACTERIZATION AND BENEFICIATION OF DOMESTIC CHROMITE-BEARING MATERIALS

By Lawrence L. Brown[1]

ABSTRACT

The Bureau of Mines performed characterization and beneficiation studies on materials from domestic chromite-bearing deposits in order to more completely evaluate potential resources of this critical and strategic mineral. In cooperation with the Bureau's Field Operations Centers, which performed reconnaissance studies on deposits, bulk samples were obtained for mineralogical, physical, chemical, and concentration studies at the Albany Research Center to properly characterize the deposits.

Representative specimens were selected from the samples for mineralogical studies including polished surface, optical and scanning electron microscopy, electron microprobe examination, magnetic separation, and liberation determination. A beneficiation procedure that included grinding, sizing, and gravity concentration was developed to produce chromite concentrates. Beneficiation characteristics, grade, general recovery, and classification of the chromite concentrate were determined.

Chromite is not a simple mineral but a series of mineral varieties within a larger grouping of minerals called spinels. The Cr_2O_3 content of "chromite" has been found to range from 15 to 64 pct. The traditional classification system based on usage (metallurgical, chemical, and refractory grades) for rating quality specifications is no longer adequate, and a more suitable terminology has been proposed and used: high-Cr, high-Fe, and high-Al chromites. Two new categories, marginal and submarginal chromite, are presented for rating chromite concentrates.

INTRODUCTION

Chromites in domestic deposits were characterized by mineralogical and benefication studies in an effort to facilitate possible utilization of this critical and stragetic mineral now or at some future date. In cooperative efforts with the Bureau's Alaska Field Operations Center (AFOC) and Western Field Operations Center (WFOC), bulk samples were selected from chromite-bearing areas in the field and forwarded to the Albany Research Center (ALRC) for these studies. Additional sample materials were obtained from State and private sources as the opportunity arose.

Field office personnel conducted reconnaissance investigations, studied and analyzed the geologic nature of the chromite-bearing deposits, and evaluated deposits from a resource standpoint including estimates of the potential tonnage of chromite available. Mineralogical and beneficiation information is a very important part of these evaluations in that the mineralogical, chemical, and physical character and the crushing, liberation, and recovery characteristics bear strongly on deposit evaluation.

In the last 6 years the Bureau has focused on studies of chromite resources in Alaska and has completed six reports (*1-6*). The publications describe chromite occurrences in Alaska and, except for possible new discoveries, represent a significant contribution to the Bureau's studies of chromite deposits in that State. A comprehensive summary report is being compiled.

The studies are, of necessity, not overly detailed in either geology or characterization, as the degree of detail required for such studies is beyond the scope of the Bureau's program. The amount of data provided will, however, give the Nation's decision and policy makers a realistic view of the resources available and of the nature of the chromite in Alaskan deposits, and enable more rapid future development of the deposits in time of possible national need.

Abbreviations Used in This Paper

°C	degree Celsius
ft	foot
in	inch
lb	pound
µm	micrometer
pct	weight percent

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CHROMITE: THE MINERAL

The theoretical composition of chromite, a spinel group mineral, is $Fe^{2+}Cr_2O_4$. This composition is only approached in chromite found in meteorites. Chromite is more accurately referred to as an isomorphous solid solution of continuously variable composition $(Fe^{2+},Mg)(Cr,Al,Fe^{3+})_2O_4$. This wide compositional variation can best be illustrated by the fact that the chromium oxide (Cr_2O_3) content in "chromite" has been found to range from 15 to 64 pct. (Theoretical chromite would contain 67.9 pct.) Consequently, the physical and chemical properties of "chromite" from different deposits and even within single deposits may vary widely. This is the major reason for the differences in the mineral's response to beneficiation and metallurgical processing and, ultimately, in its end use.

A discussion of the spinel group is in order to help clarify the wide compositional variations noted in chromite. The group consists of three series of minerals with the general formula AB_2X_4 (where A = Mg, Fe^{2+}, Zn, Mn, Ni; B = Al, Cr, Fe^{3+}, Mn^{3+}, V, Ti; X = O)–the spinels $[(Mg, Fe^{2+}, Zn, Mn)(Al, Fe^{3+}, Cr, Mn^{3+}, V, Ti)_2O_4]$, the magnetites $[(Fe^{2+}, Mg, Zn, Ni)(Fe^{3+}, Al, Cr, Mn^{3+}, V)_2O_4]$, and the chromites $[(Fe^{2+}, Mg)(Cr, Al, Fe^{3+})_2O_4]$–with each of the minerals containing a number of well-defined mineral varieties. There is complete miscibility of components within series but much less between series. Pure end members are rarely found. The spinels do not commonly show wide variations in the B part of the formula. The series is incompatible with quartz. Mineral specie names are designated by the predominant divalent and trivalent atoms, and the substitutional varieties by the next most common constituent in order. Historic names also prevail. For example, the spinel hercynite ($FeAl_2O_4$), with significant amounts of Mg and Cr substituted for Fe and Al, respectively, may be termed a magnesian chromohercynite. The Cr-bearing spinel-group minerals and mineral varieties of particular concern follow:

Spinel ($MgAl_2O_4$).–Forms a continuous replacement series with hercynite ($FeAl_2O_4$) and with *magnesiochromite* ($MgCr_2O_4$). Chromian spinel, containing a large proportion of Cr substituting for Al, has been called *picotite*, but picotite is now restricted to an intermediate variety, $(Mg,Fe^{2+})(Al,Cr)_2O_4$, with Al greater than Cr and with an Fe-Mg ratio of 3.

Chromite ($Fe^{2+}Cr_2O_4$).–Forms a series with magnesiochromite ($MgCr_2O_4$) and hercynite ($FeAl_2O_4$). Ordinary magnesiochromite usually contains some Fe^{2+} substituting for Mg. With additional substitution it grades to *ferroan magnesiochromite*, the most common variety, and then to chromite. *Aluminian magnesiochromite* has Al substituting for Cr with a usual increase in Mg content. Additionally, Fe^{3+} can substitute for Cr, giving a *ferrian magnesiochromite*. It has been suggested that, since the majority of the members of the chromite series have $Mg > Fe^{2+}$, the Mg-bearing variety is the normal chromite and that the end member $Fe^{2+}Cr_2O_4$ should be called ferrochromite.

Magnetite ($Fe^{2+}Fe^{3+}{}_2O_4$).–There is no Cr-bearing series to magnetite. However, Cr can substitute for Fe^{3+} in magnetite in generally small amounts. Relatively large amounts of Cr in magnetite indicate admixed chromite mineral.

Most Cr-bearing spinels also contain small amounts of SiO_2 and traces of other components such as Mn, Ti, and Ca. It has been found that there is generally a relationship between the composition of a chromite and that of its enclosing rock.

In the above discussion, considerable use has been made of volume 2 of Dana's System of Mineralogy, 7th Edition (*7*), and of volume 5 of Rock Forming Minerals (*8*). The reader is referred to these publications for further detailed information.

The three traditional end use varieties or general grades of chromite have been metallurgical, chemical, and refractory grades. However, technological advances during the last decade or so are now allowing considerable interchangeability among these grades. Thus, the current, more definitive chromite classification that is preferred is–

High-Cr chromite–A minimum of 46 pct Cr_2O_3 with Cr-Fe ratio 2 (metallurgical grade).
High-Fe chromite–40 to 46 pct Cr_2O_3 with Cr-Fe ratio 1.5 to 2.0 (chemical grade).
High-Al chromite–More than 20 pct Al_2O_3 and more than 60 pct Al_2O_3 + Cr_2O_3 (refractory grade).

Continued advances in chromite-use technology and improvements in ore beneficiation and chromite upgrading science will undoubtedly lead to additional classification and specification changes. In the current characterization studies, two classifications were added to those listed above for evaluation and rating of chromite concentrates obtained from samples during the studies:

Marginal chromite.–Material that meets either the grade or Cr-Fe ratio requirements for one of the above classifications and very nearly meets the other.

Submarginal chromite.–Material that fails to meet the above classifications.

These materials could be upgraded by developing technology to meet one or more of the preferred grade specifications; otherwise, industrial developers could provide new markets to utilize these materials.

For more detailed information on chromium and a general overview of the commodity, the reader is referred to recent Bureau of Mines publications (*9-10*).

MINERALOGICAL CHARACTERIZATION

The geological occurrence of chromite is almost entirely limited to igneous rock types high in Mg and Fe that are referred to as ultramafic rocks, mafic rocks, basic igneous rocks, or perioditites, and the serpentine and basic metamorphic rocks that have been derived from them. Sedimentary rocks and alteration materials derived from these rocks often contain significant amounts of weathering-resistant chromite.

Ultramafic rocks originate in the mantle or deep in the earth's crust and are rare in the upper crust. They generally are found at or near continental margins in the vicinity of plate-tectonic subduction zones and deep-seated interplate fractures. The Bushveldt Complex in Africa, an area of mafic rocks, is an exception. It is in a stable area of very old rocks and contains the bulk of the world's chromite reserves.

Ultramafic rocks and peridotites contain less than about 45 pct SiO_2, are generally dark colored, and have a high specific gravity. They are rather simple mineralogically, being composed primarily of olivine [$(Fe,Mg)_2SiO_4$] and the pyroxene minerals enstatite ($Mg_2Si_2O_6$) and diopside ($CaMgSi_2O_6$). The percentage of each mineral in any rock may vary from one extreme to the other. Small to large amounts of serpentine, other pyroxene minerals, amphibole minerals, and their alteration products chlorite, talc, and iron oxide minerals also may be present. Sulfides of Fe, Cu, and Ni also may be present in small to locally large amounts, along with trace to very minor amounts of the platinum-group minerals (PGM's). Chromite generally occurs in rock types high in olivine or in serpentine that has been derived from olivine.

Chromite and magnetite are found in minor to abundant amounts in ultramafic rocks as very fine to coarse grained disseminations and intergrowths and locally as coalescent streaks and small to large lenses. Also, small to very large pods and continuous layers up to several feet thick of essentially pure chromite are found. Most domestic chromite production has come from larger pods and continuous layer deposits.

SAMPLE MATERIALS

In order to collect bulk samples with a chromite content sufficient for metallurgical testing, high-grade rock samples were intentionally selected from surface exposures, or specimens were collected from high-grade portions of sampling channels by personnel from AFOC and WFOC. At ALRC representative specimens were selected from each sample for mineralogical examination and characterization. The rest of the sample was reduced in size in a series of crushing steps to pass 1/4 in, and a head sample and samples for beneficiation tests were prepared. The head sample was pulverized and subjected to chemical analysis.

The representative specimens were examined under a binocular microscope for preliminary description and mineral identification. Portions were selected for encapsulation in plastic resin for polished surface preparation so that studies by reflected light microscopy, scanning electron microscopy (SEM), and electron microprobe could be made.

Detailed mineralogical examinations and liberation studies were made on samples split from sized fractions prepared from benefication feed and product materials. The sized products were separated on a laboratory-model isodynamic magnetic separator, and the resulting fractions were studied critically by petrographic methods. Mineral percentages based on weight were estimated, and high-purity chromite concentrates that best represented the chromite in the sample were prepared from gravity concentrates by carefully controlled magnetic separation and then subjected to analysis.

Composition of individual chromite grains was determined by SEM and electron microprobe examination of polished surfaces. Associated mineral varieties were also analyzed, and the sample was scanned for lesser but important elements such as Ni, Cu, Au, and the PGM's. It has been observed that chromite from a particular locality usually has about the same character and chemical composition and that the composition changes little across a grain.

Compositional zoning in the chromite is seen, but is not common. Quite frequently, chromite will show late-stage magnetite that crystallized later than chromite from the magma; this magnetite is intimately associated on outer surfaces and penetrates fractures in the chromite crystals. Where the crystals are highly fractured and separated, the magnetite may penetrate throughout the grain. An example of such crystallization is shown in figure 1, which displays electron microprobe micrographs and element distribution maps of typical grains from a magnetic product of a minus 65-mesh chromite gravity concentrate. The sample is from Miners Point on Kodiak Island, Alaska. The central grain contains a core of chromite with a magnetite overgrowth and with olivine gangue attached. Other similar grains will be observed, as will the presence of intergrown, fine-grained magnetite in the gangue minerals. Liberation is not complete. The variable brightness that the element displays is an indication of the relative amounts of the element present.

Examination of all the chromite-bearing products in this sample showed that most, if not all, chromite grains have magnetite overgrown on their surfaces and that the thickness of the overgrowth varies considerably from grain to grain, but the total amount of magnetite is not large. the Fe and Cr contents of the chromite are relatively uniform within grains and from grain to grain. Composition is about 45 pct Cr_2O_3, 19 pct FeO, 15 pct Al_2O_3, and 13 pct MgO.

Another interesting example of complicated mineralogical association is shown in figure 2, which displays SEM micrographs at two different magnifications of a polished surface specimen of chromite. The sample is from Dust Mountain in the Tonsina District, southern Alaska. SEM examination revealed that this sample's "chromite" is a magnesian chromohercynite containing a relatively large amount of exsolved chromian magnetite within grains and along grain boundaries. The white phase is the chromian magnetite. The hercynite contains about 25 pct Cr_2O_3, 35 pct FeO, 28 pct Al_2O_3, and 10 pct MgO. The magnetite phase contains 75 pct Fe_3O_4, 18 pct Cr_2O_3, 3 pct Al_2O_3, 2.5 pct TiO_2, and 1.5 pct MgO. In the system magnetite-hercynite, a complete solid solution exists above 858° C.

The rock sample from which the above material came also contained massive magnetite and massive chromite; however, the chromite was borderline (marginal chromite) in grade with a high-purity concentrate containing only 40 pct Cr_2O_3. The head sample contained 17.7 pct Cr_2O_3, and a minus 65-mesh magnetic concentrate contained 22.9 pct Cr_2O_3.

Specimen Chromium

Magnesium Iron

Silicon Aluminum

FIGURE 1.—Electron microprobe micrographs and element distribution maps showing magnetite overgrowth on chromite grains. Grids are 33 μm square.

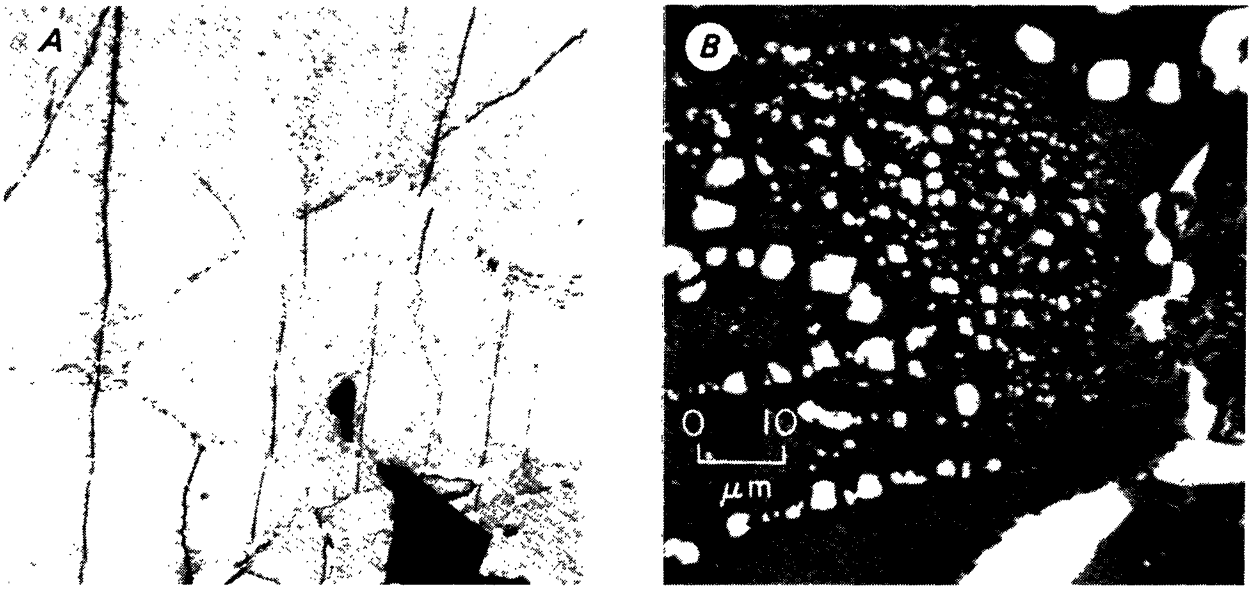

FIGURE 2.—SEM micrographs showing chromian magnetite (light gray) exolved from chromian hercynite (dark gray) within grains and along grain boundaries. *A*, × 90; *B*, × 1,000.

BENEFICIATION

The bulk samples contained fragments up to 12 in. in the largest dimension; as described earlier, each sample was crushed in a series of crushing operations to pass 1/4 in, and then a head sample and 20-lb sample splits for beneficiation tests were prepared. Care was required in crushing and milling because chromite, by nature, is brittle and will reduce in size rather rapidly. In addition, both the chromite and the gangue minerals, especially olivine, usually are highly fractured, as observed under the microscope, and therefore will crush rather easily. Without care and control, excessive amounts of slime-sized particles are produced. The general beneficiation procedure developed to concentrate the chromite from the samples is shown in figure 3. The procedure was modified to suit individual samples.

In preparation for beneficiation studies, a presplit 20-lb sample was sized at 28 and 65 mesh. The plus 28-mesh fraction was stage-ground dry to pass 28 mesh and sized on a 65-mesh screen. The minus 28- plus 65-mesh fraction was beneficiated on a sand deck of a 2- by 4-ft laboratory shaking table to produce a clean gravity concentrate and tailings. The tailings were dried and then stage-ground to minus 65 mesh, combined with the minus 65-mesh material from the initial grinding and screening, and beneficiated on a slime deck. A high-grade concentrate, middlings, coarse tailings (those that settled and banded on the table), and slime tailings (those that washed off the deck before they had a chance to settle) were collected. A scavenger tabling operation was done on the middling product to improve chromite recovery. Commonly, on high-grade samples, there was an overlap between the middlings and course tailings, and substantial amounts of chromite were observed intermixed with the coarse tailings in overlapping bands on the table. When this happened, the products were combined and given a scavenger tabling. When the samples contained fine-grained chromite or were very low grade, the entire sample was ground to minus 65 mesh and rougher and cleaner tabling was done rather than the rougher-scavenger sequence. All of the concentrates produced were classified according to the system presented earlier.

Examples of beneficiation results on bulk sample materials collected from three widely separated areas in Alaska are presented below. The results show the variability of chromite and the variability of results that may be expected from deposits in any one area. Thirty-five samples were collected from chromite deposits along the Border

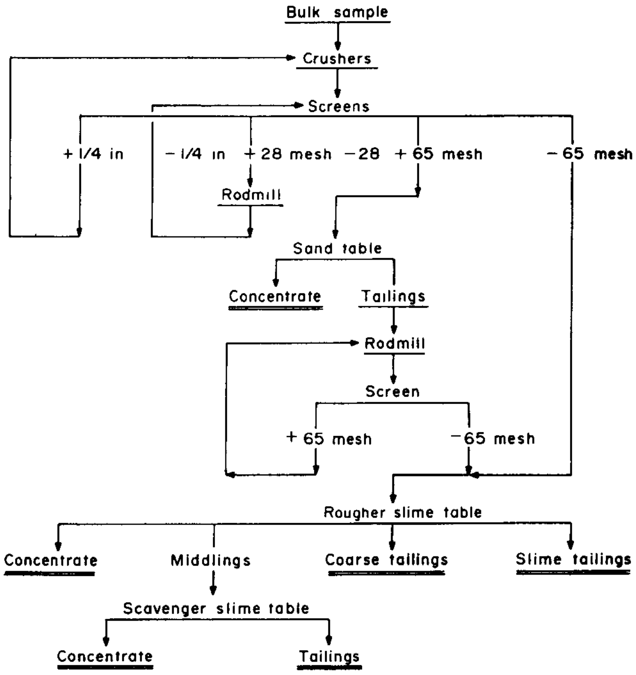

FIGURE 3.—General beneficiation procedure used to concentrate chromite from rock samples.

Ranges Fault in southern Alaska. Concentrates produced from these samples gave 24 high-Cr or marginal high-Cr concentrates, 6 high-Fe or marginal high-Fe concentrates, and 5 submarginal chromites. Chromite recoveries ranged from 37 to 95 pct, with Cr-Fe ratios ranging from 0.6 to 3.1.

The highest grade concentrate contains 57.8 pct Cr_2O_3, and 17 concentrates have grades in excess of 50 pct Cr_2O_3. The highest Cr-Fe ratio obtained was 3.1, and 11 concentrates have ratios of 2.5 or better. The five submarginal concentrates were of low grade and low Cr-Fe ratio and could not be improved by further beneficiation.

In a second example, 10 samples collected from low-grade deposits in the western Brooks Range, northwestern Alaska, were all high-Cr chromites. Concentrate grades produced ranged from 49 to 59.5 pct Cr_2O_3 with Cr-Fe ratios from 2.3 to 3.3. Recoveries ranged from 72 to 99 pct.

As a third example, 11 samples were collected from low-grade deposits in the Caribou Mountain and lower Kanuti River areas in central Alaska. Three samples produced high-Cr chromite concentrates, two produced high-Fe Concentrates, and one produced a high-Al chromite concentrate. Three other samples produced marginal concentrates, and two produced submarginal concentrates. Chromite recoveries ranged from 54 to 92 pct with Cr-Fe ratios ranging from 0.8 to 2.4. The highest grade concentrate contained 53.8 pct Cr_2O_3 with a Cr-Fe ratio of 2.4.

Magnetic separation as a beneficiation step was considered and may be suggested by sample mineralogy, but generally improved Cr grade and Cr-Fe ratio would be at the expense of chromite recovery. High-Fe chromites are more magnetic than high-Cr chromites. Likewise, electrodynamic separation was considered, and while good products could be recovered, the process is time consuming and throughput rate is slow.

Other steps such as flotation or the closer sizing of gravity separation feed materials could have been taken to possibly improve grade, Cr-Fe ratio, and recovery, but such steps were beyond the scope of these studies.

SUMMARY AND CONCLUSIONS

In cooperation with Bureau of Mines Field Operations Centers, State departments of geology, and others, bulk samples of chromite-bearing materials were received from domestic deposits in Alaska and the Northwest. The samples were subjected to characterization and beneficiation studies to provide data for more complete resource evaluation for this strategic and critical mineral.

The mineralogical nature of "chromite" was discussed. Chromite is not a simple mineral but a series of mineral varieties within a larger grouping of minerals called spinels. The material referred to as chromite has a wide compositional variation in Cr_2O_3 content ranging from 15 to 64 pct, although the mineral from a single deposit is usually of uniform composition. The classification scheme used to rate quality specifications for chromite usage was discussed, and, as promoted by many experts in the field, a more appropriate terminology for classification of high-Cr, high-Fe, and high-Al chromite is favored. Two new classifications, marginal and submarginal chromite, were suggested for addition to the above ratings for evaluation and rating of chromite concentrates.

The geological occurrence and mineralogical content of chromite-bearing rock were discussed. Representative specimens were selected for various mineralogical studies including polished surface preparation, optical and scanning electron microscopy, electron microprobe examination, magnetic separation, and liberation determination. Mineral content percentage estimates were made, and chemical analyses were performed. Examples of the mineralogical character of selected chromite variations were discussed and illustrated.

A beneficiation process that included grinding, sizing, and gravity concentration was developed to produce chromite concentrates from the samples. Other beneficiation procedures were examined and evaluated, but they generally were less successful than the scheme designed in recovering chromite from the sample materials studied. The studies described were not designed to determine optimum chromite recovery of any one particular sample, but rather to determine beneficiation character, grade, general recovery, and classification of the chromite minerals producible from the deposits. Examples are given on samples from three different areas in Alaska.

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FLOTATION BENEFICIATION OF CHROMITE FROM LOW-GRADE DEPOSITS

By J. L. Huiatt[1]

ABSTRACT

The Bureau of Mines investigated conventional flotation techniques for upgrading chromite samples from the Mouat and Benbow Mines in the Stillwater Complex, Nye, MT, and in low-grade California chromite samples. A newly devised column flotation technique was also investigated.

Deslimed Mouat samples were upgraded satisfactorily by conventional flotation with HF depressant and oleic acid collector but were not upgraded satisfactorily when floated with a primary amine collector. The poor upgrading was attributed to the presence of olivine, which floated with chromite. Deslimed Benbow samples responded favorably to both flotation techniques; however, amine flotation produced higher recoveries. Flotation of undeslimed Benbow samples with carboxymethylcellulose and tall oil, or with an oil emulsion, produced acceptable-grade chromite concentrates but at reduced recoveries. Beneficiation of low-grade California chromite samples by these four procedures was not satisfactory.

A column flotation apparatus, which can use either coarse or fine air bubbles for frothing, was constructed and evaluated using the amine flotation technique. Results demonstrated that column flotation was superior to conventional flotation for beneficiating either deslimed or undeslimed Benbow chromite ore samples.

INTRODUCTION

Gravity separation techniques have been quite effective in beneficiating domestic chromite resources. For example, from 1952 to 1961 the American Chrome Co. used tabling to upgrade ore from the Mouat and Benbow Mines in the Stillwater Complex, Nye, MT, from about 22 to 41 pct Cr_2O_3. Nearly 1 million st of chromite concentrate having a Cr-Fe ratio of 1.7 was produced (*1*). Tabling was also used to concentrate chromite at the Pilliken Mine near Auburn, CA, and the Grey Eagle Mine in Glenn County, CA. The Humphreys spiral is also quite effective in beneficiating chromite ores, although tabling may produce somewhat higher grades and recoveries.

Particle size limits the use of gravity separation techniques such as tabling and Humphreys spiral separation. The lower particle size limit is approximately 100 mesh. However, smaller particle sizes can be beneficiated on tables with slime decks or on a Bartles-Mozley cross-belt separator; these techniques have lower production capacities. Many domestic chromite deposits are low grade and finely disseminated; consequently, liberation of the bulk of the mineral values may require grinding through 100 mesh, often precluding gravity beneficiation.

Froth flotation offers an alternative technique for beneficiating lower grade deposits where fine grinding is necessary for liberation. Flotation can be used in concert with gravity methods or by itself. Generally flotation is effective in upgrading mineral values ranging from minus 35 mesh to about 20 µm in size. Occasionally the flotation technique can be modified to treat feed materials that are slightly coarser and slightly finer than the above size range. Flotation has found limited commercial use for upgrading domestic chromite ores. The most recent commercial use of chromite flotation was at the Butler Estates property near Coalinga, CA; however, the mine was closed in 1976 because of economic factors.

Considerable work has been performed by the Bureau of Mines and other laboratories to investigate chromite flotation behavior and to devise flotation techniques for low-grade domestic ores (*2–8*). The techniques were designed to overcome problems inherent to a particular ore body. Collectively, the problems include (1) need of fine grinding to liberate chromite values, (2) presence of abundant minus 20-µm slimes, (3) aging of chromite and gangue minerals, and (4) nonselectivity due to natural or induced activation of gangue and chromite mineral values.

Slimes present chronic problems with most domestic chromite ores. These ores are low grade and finely disseminated and require considerable grinding to liberate chromite minerals; consequently, excessive slimes are generated. The slimes are detrimental to froth flotation because they may (1) form a fine coating on the mineral particles, preventing selective reagent adsorption and hence depressing flotation or decreasing mineral selectivity, (2) consume excessive quantities of reagents, and (3) decrease the flotation rate by increasing pulp viscosity. The most expedient method for resolving the slimes problem is to deslime prior to flotation; however, the desliming results in significant chromite losses.

Abbreviations Used in This Paper

ft	foot
in	inch
lb/st	pound per short ton
min	minute
µm	micrometer
pct	weight percent
st	short ton

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A variety of gangue minerals are associated with chromite ores including quartz, olivine, serpentine, diopside, hedenbergite, chlorite, labradorite, biotite, enstatite, calcite, magnetite, bronzite, epidote, and hematite. Fibrous minerals may also be present. The presence and relative abundance of the minerals varies markedly with the ore body. Many factors influence the floatability, or nonfloatability, of gangue minerals as well as the chromite minerals. These factors include, but are not limited to, pulp pH, mineral solubility, presence of metallic ions in flotation water, types of reagents added, and the history of the ore being treated (*9–11*).

In a fundamental study, Smith (*11*) determined that floatability of naturally occurring chromite depended on whether the mineral was aged in air and whether the mineral had been heated. The observed effects were attributed to oxidation and reduction reactions involving surface chromium and iron species. Acid washing removed easily soluble surface material; thus, after washing, the mineral behaved like a simple oxide and was floatable with anionic or cationic collectors, depending on pH.

Smith also reported that among the gangue minerals studied (olivine, diopside, hedenbergite, and bronzite), olivine appeared to be the most readily floated and was the mineral most likely to cause problems in the chromite flotation system. All minerals appeared to be affected in their electrokinetic, adsorption, and flotation behavior by metal ions that dissolve naturally from chromite ore. Aging of stockpiled ore will probably change its flotation characteristics.

Metallic ions, whether originating from the chromite mineral or present naturally in the flotation water, are likely to affect chromite and gangue mineral flotation. The theoretical composition of chromite is $FeO \cdot Cr_2O_3$, but in nature Mg^{++} is substituted for Fe^{++}, while Fe^{+++} and Al^{+++} are substituted for Cr^{+++}. Fuerstenau and Palmer (*9*) reported that the composition has a direct effect on the electrokinetic properties of the mineral surface. For example, points of zero charge (PZC) at pH 4.4 to 9.6 have been measured for chromites of various compositions. The electrokinetic behavior is attributed to the presence of hydroxy ion species; i.e., $Mg(OH)^+$ and $Fe(OH)^+$ at pH 11 and 8, respectively. These are the pH values where zeta potential reversal occurs and where the hydroxy complexes are present in significant amounts. Fuerstenau and Palmer also reported that aluminum and chromium hydroxy species are not involved in chromite flotation.

The flotation behaviors of chromite ores from several locations have been evaluated by the Bureau using several techniques. A basic flotation method was developed by Havens (*3*). The Havens method consisted of treating deslimed pulp with sodium fluoride (NaF) and sulfuric acid (H_2SO_4), followed by chromite flotation with oleic acid collector and Emulsol X-1 dispersant. Samples of the Stillwater Complex ore (Mouat Mine), beach sands, and minus 200-mesh chromite slime tailings were reported to be amenable to this procedure. Flotation produced substantial upgrading at fair recoveries of the Mouat and beach sand samples. The slime tailings upgraded fourfold, but recovery was only 44.6 pct. Desliming of all three samples at 10-μm particle size was necessary to achieve the metallurgy reported. Reagent consumptions were high. For example, oleic acid consumption ranged from 1.1 to 5.8 lb/st, Emulsol X-1 from 0.2 to 1.2 lb/st, H_2SO_4 from 12.4 to 17.7 lb/st, and NaF from 6.4 to 16.5 lb/st.

Because of high reagent consumptions and marginal grades and recoveries achieved using available flotation technology, the Bureau performed research to evaluate available technology and to devise new and improved methods for testing domestic chromite ores. This report summarizes work accomplished between fiscal years 1978 and 1980 and current work.

MATERIALS

Principally, one Mouat and two Benbow Mine samples from the Stillwater Complex were used in the research. The samples were collected from ore piles at the mine sites. Table 1 lists the partial chemical analyses of these ore samples. The mineralogy of the two Benbow samples was similar. The most abundant silicate minerals were serpentine and enstatite; subordinate amounts of olivine and diopside were present. The Mouat sample contained abundant olivine and enstatite with small amounts of serpentine, diopside, chlorite, labradorite, and biotite. The chromite mineral from the Stillwater Complex contained about 46 pct Cr_2O_3 with a Cr-Fe ratio of less than 2. Liberation size was estimated, petrographically, to be about minus 48 mesh; however, finer grinding was necessary to achieve optimum flotation.

TABLE 1.—Chemical analyses of Stillwater Complex samples, percent

Analysis	Benbow 1	Benbow 2	Mouat
Cr_2O_3	16.3	20.4	23.4
Fe	11.6	12.2	16.8
SiO_2	20.8	21.0	17.0
MgO	23.0	17.0	16.0
Al_2O_3	12.8	11.6	10.6

Samples ranging from 0.5 to 3.6 pct Cr_2O_3 were obtained from deposits near Auburn, Seiad Creek, and Crescent City, CA. Collectively, the California samples contained olivine, antigorite serpentine, tremolite, epidote, enstatite, and chlorite. Liberation size was minus 48 mesh. The Cr_2O_3 contents of the chromite minerals ranged from 46 to 55 pct. The Cr-Fe ratio was not determined.

CONVENTIONAL FLOTATION TECHNIQUES

Chromite flotation separation from either deslimed or undeslimed Stillwater Complex samples was investigated using four flotation reagent schemes. Conventional laboratory flotation cells were used in the separations. A modified version of the Havens oleic acid-NaF method (in which HF was used instead of NaF) (*3*) and an amine method devised and patented by the Bureau (*5-6*) were used to beneficiate deslimed samples. Preliminary testing demonstrated that chromite samples were not amenable to the oleic acid-HF or the amine flotation procedures. Consequently, an oil emulsion method and a carboxymethylcellulose (CMC)-tall oil method (*12*) were used to beneficiate undeslimed samples. Flotation screening tests were also performed on low-grade chromite samples from northern California to determine their amenability to the preceding flotation methods.

FLOTATION PROCEDURES

Petrographic analyses indicated that chromite in the Benbow and Mouat samples was liberated at minus 48 mesh; however, optimum flotation occurred at screen sizes of minus 65 mesh or finer. Chromite in the California samples was liberated at minus 65 mesh; best flotation occurred at this grind size.

Oleic acid-HF.—Minus 65-mesh Benbow 1 sample (16.3 pct Cr_2O_3) was deslimed by sedimentation and decantation according to Stoke's Law at 30-μm particle size, conditioned at 25 pct solids with 3.0 lb/st HF, and floated at pH 4 in three 5-min rougher stages using 5.0 lb/st oleic acid total. Minus 100-mesh Benbow 2 (20.4 pct Cr_2O_3) and Mouat (23.4 pct Cr_2O_3) chromite samples were deslimed at 20 μm particle size, conditioned at 25 pct solids with 2.0 lb/st HF, and floated at pH 4 in three rougher stages using 2.0 lb/st oleic acid total. Sulfuric acid was used to adjust pH.

Amine.—Minus 65-mesh Benbow 1 sample was deslimed at 20-μm particle size and conditioned at 25 pct solids with H_2SO_4 and primary coco-amine (Armac C). The pulp was floated in three 5-min rougher stages. Total reagent consumption was 33 lb/st H_2SO_4 and 0.6 lb/st Armac C; flotation pH was 2.

Minus 100-mesh Benbow 2 sample was deslimed at 20-μm particle size, conditioned at 25 pct solids with H_2SO_4 and amine, and floated in two 5-min rougher and one 5-min cleaner stages. Total reagent consumption was 34 lb/st H_2SO_4 and 1.0 lb/st Armac C. Flotation pH was 2.

Minus 65-mesh Mouat samples was deslimed at 20-μm particle size and conditioned at 25 pct solids with H_2SO_4 and Armac C. The pulp was floated in two 5-min rougher stages and one 5-min cleaner stage. Total reagent consumption was 56 lb/st H_2SO_4 and 0.8 lb/st Armac C. Flotation pH was 2.

Oil emulsion.—Minus 65-mesh Benbow 2 sample was conditioned (without prior desliming) at 60 pct solids and pH 8 for 40 min with an oleic acid-diesel oil emulsion. The pulp was diluted to 25 pct solids and floated in one rougher and one cleaner stage. Total reagent addition was 4.0 lb/st oleic acid and 40 lb/st No. 2 diesel oil. Flotation time was 5 min per stage. Pulp was maintained at pH 8.

CMC-tall oil.—Minus 65-mesh Benbow 2 sample was conditioned (without prior desliming) at 25 pct solids and pH 11.3 with 1.0 lb/st dispersant [3 parts Na_2SiO_3 to 1 part $(NaPO_3)_6$], 0.5 lb/st CMC, and 2.5 lb/st tall oil. The pulp was floated for 7 min. The rougher concentrate was further upgraded in a 9-min cleaner flotation stage using an additional 0.5 lb/st CMC and 2.5 lb/st tall oil; flotation pH was maintained at 11.3.

The minus 65-mesh samples from the California deposits were deslimed and treated by the four flotation methods described above. Conditions were similar, except reagent dosages were higher.

CONVENTIONAL FLOTATION RESULTS

Flotation results for the Benbow and Mouat samples are listed in table 2. Both Benbow samples responded well to the amine flotation method. Rougher flotation upgraded the 16.3-pct-Cr_2O_3 sample to 38.4 pct Cr_2O_3 at 84-pct recovery. Rougher flotation followed by cleaner flotation upgraded the 20.4-pct-Cr_2O_3 sample to 43.6 pct Cr_2O_3 at 86-pct recovery. Rougher flotation using HF and oleic acid upgraded the 16.3- and 20.4-pct-Cr_2O_3 materials to 40.1 and 40.3 pct Cr_2O_3, respectively. However, chromite recoveries were only 75 pct and 60 pct, respectively.

The HF-oleic acid method upgraded the 23.4-pct-grade Mouat sample to 39.6 pct Cr_2O_3 at a rougher flotation recovery of 82 pct. Amine flotation recovered 94 pct of the chromite in rougher flotation and 84 pct in a cleaner flotation; however, only a 31.8-pct-Cr_2O_3 concentrate was obtained even with cleaner flotation.

The Mouat sample was not as amenable to amine flotation as the Benbow 2 sample. The main gangue mineral in the Mouat sample was olivine, which readily floated with the amine collector. The main gangue mineral in the Benbow sample was serpentine, which does not float readily with amine collector. The difference in gangue mineral constituents probably accounts for the poor selectivity when floating Mouat chromite by the amine method.

The CMC-tall oil and the oil emulsion methods, in which desliming was not done prior to flotation, produced 85- and 83-pct-chromite rougher flotation recoveries, respectively, from the Benbow 2 sample; however, rougher concentrate grades were only 33 pct Cr_2O_3. The gangue mineral slimes present in the ore sample were not completely depressed, resulting in poor selectivity. Cleaner flotation of the rougher concentrates produced acceptable chromite grades of 38.6 and 41.4 pct Cr_2O_3, but chromite recoveries were reduced significantly. Total reagent consumptions were reasonable for the CMC-tall oil method but excessive for the oil emulsion method.

Flotation of low-grade samples from Auburn, Seiad Creek, and Crescent City, CA, using the four flotation techniques achieved only limited success (table 3). The best response occurred when floating a deslimed Auburn sample using the HF-oleic acid reagent scheme; chromite was upgraded from 3.6 to 15 pct Cr_2O_3 at 62-pct recovery. Oleic acid-HF flotation of the other samples containing less than 3.6 pct Cr_2O_3 consistently yielded poor-grade concentrates

TABLE 2.—Chromite flotation from Benbow and Mouat samples, percent

Sample and flotation method	Rougher conc		Cleaner conc	
	Cr_2O_3 grade	Distribution	Cr_2O_3 grade	Distribution
Benbow 1:				
HF-oleic acid	40.1	74.6	NA	NA
Amine	38.4	84.4	NA	NA
Benbow 2:				
HF-oleic acid	40.3	60.3	NA	NA
Amine	40.8	89.1	43.6	85.7
CMC-tall oil	32.5	84.6	38.6	77.0
Oil emulsion	32.9	83.2	41.4	68.8
Mouat:				
HF-oleic acid	39.6	82.3	NA	NA
Amine	28.8	94.0	31.8	84.1

NA Not analyzed.

TABLE 3.—Oleic acid-HF flotation of low-grade California samples, percent

Sample	Cr_2O_3		Distribution
	Head assay	Conc grade	
Auburn (1)	3.6	15.0	62.0
Auburn (2)	.5	1.5	24.2
Crescent City	2.8	5.5	50.3
Seiad	1.0	1.4	61.7

(1.5 to 5.5 pct Cr_2O_3) at low recoveries (24 to 61 pct). Excessive amounts of reagent were required (6 to 16 lb/st oleic acid). Beneficiation of the samples using amine, oil emulsion, or CMC-tall oil reagent schemes was unsuccessful. The poor flotation response was attributed to slime particles, complex chromite mineralization, and nonselective reagent adsorption. Beneficiation of these samples could be achieved by gravity and magnetic separation techniques (*13*).

NEW FLOTATION TECHNOLOGY

The Bureau's Salt Lake City Research Center has been performing research on oxide mineral beneficiation. Initial efforts were directed toward devising reagent schemes for conventional flotation of oxide minerals. Flotation is difficult because of complex mineralogy and abundant fine particles. Satisfactory conventional methods, which produce acceptable grades and recoveries with low reagent consumptions, have not been developed; consequently, an investigation of new flotation devices was initiated. As a result of this work, a flotation column was designed which utilizes coarse or fine bubbles to produce a mineralized froth.

EQUIPMENT AND PROCEDURE

The experimental column (fig. 1) is 2½ in ID by 18 ft tall and is constructed of clear plexiglass tubing with ¼-in wall thickness. The column is equipped with injection and sampling ports located along its entire length. Coarse air bubbles are introduced through fritted glass tubes mounted at the bottom and middle of the column. Fine air bubbles are produced extrinsically in a dissolved air generator and injected through a slotted jet at the bottom of the column. Pulp conditioning is accomplished in a modified Denver cell; the pulp is then transported through tubing by gravity to an injection port located about 10 ft from the column bottom. Makeup water and wash water can be added at the column top or at any port along the column. Froth is collected in an annular launder at the top. Tailings can be recycled in the column or pumped to a scavenger column.

Delimed and undeslimed Benbow 2 chromite samples were beneficiated in the column and by conventional flotation using the Bureau's amine flotation method. Minus 65-mesh sample was conditioned for 10 min at pH 2.0 with 2.0 lb/st Armac C. If appropriate, the ore was deslimed prior to conditioning at minus 20-μm particle size, using up to 4.0 lb/st Na_2SiO_3 dispersant. For deslimed samples, collector addition was reduced to 1.0 lb/st Armac C. The column was partially filled with aerated water, to which 0.2 lb/st Dowfroth 400 was added, and the conditioned pulp was introduced. When the pulp contacted the aerated water, a mineralized froth immediately developed. The froth moved up the column and was discharged. The tailings were recycled until all the chromite concentrate was collected. Flotation time was 4 to 6 min. Fine or coarse bubbles were used to develop froth.

COLUMN FLOTATION RESULTS

Table 4 compares results obtained by (1) conventional flotation in a Denver laboratory cell (conventional flotation results reported are those obtained concurrently with column flotation results), (2) coarse bubble column flotation, and (3) fine bubble column flotation. Recovery results were based on analysis of samples as received. Conventional flotation of deslimed material recovered 77 pct of the chromite in a rougher concentrate containing 43.5 pct Cr_2O_3. Column flotation significantly improved chromite recovery and grade. For example, coarse bubble flotation

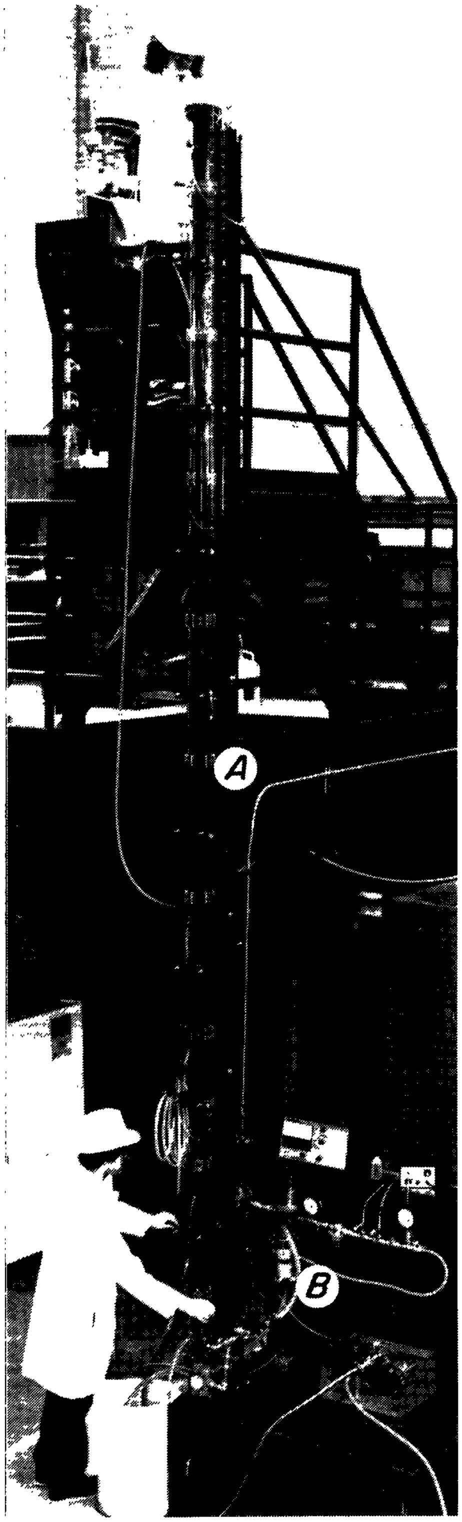

FIGURE 1.—Flotation column (*A*) and bubble generator (*B*).

TABLE 4.—Amine rougher flotation of deslimed and undeslimed Benbow 2 chromite using conventional flotation equipment and flotation columns, percent

Flotation method	Cr_2O_3 grade		Distribution	
	Deslimed	Undeslimed	Deslimed	Undeslimed
Conventional	43.5	35.6	77.0	86.5
Column:				
Coarse bubble ..	43.8	41.6	85.0	94.3
Fine bubble	44.7	41.5	87.1	94.9

recovered 85 pct of the chromite in a rougher concentrate of 43.8 pct Cr_2O_3, and fine bubble flotation recovered 87 pct of the chromite in a rougher concentrate of 44.7 pct Cr_2O_3. Fine bubble column flotation appeared to be slightly better than flotation with coarse bubbles.

Conventional flotation of undeslimed chromite was not satisfactory; the maximum grade was only 35.6 pct Cr_2O_3, and overall recovery was 87 pct. However, a marked improvement in grade and recovery was achieved when beneficiating the material by column flotation using either coarse or fine bubbles. A 9-pct increase in recovery was attributed to flotation of chromite mineral in the slime fraction. Mineral particle separation occurred primarily in the pulp slurry rather than in the froth column; consequently, less gangue was occluded in the chromite froth, and higher grades were achieved.

The advantages of using column flotation for beneficiating Benbow chromite sample with amine collector follow: (1) Desliming prior to flotation is not required; (2) flotation kinetics are improved; (3) extra cleaning steps are unnecessary; and (4) improved grades and recoveries are obtained. From a commercial consideration, flotation columns (1) require less space, e.g., one column has been used to replace two banks of conventional cleaner-flotation cells, (2) have fewer moving parts so that less maintenance is required, (3) can be automated easily, and (4) have lower equipment and installation costs.

SUMMARY AND CONCLUSIONS

Four conventional flotation techniques were evaluated using Mouat and Benbow samples from the Stillwater Complex, Nye, MT, and low-grade samples from California chromite deposits. The techniques used oleic-HF, oil emulsion, CMC-tall oil, and amine flotation reagent schemes.

The Mouat sample (23.4 pct Cr_2O_3) upgraded satisfactorily by flotation using HF depressant and oleic acid collector; however, it did not upgrade significantly using amine collector at acid pH, though recovery was high. For example, chromite upgraded to 39.6 pct Cr_2O_3 at 82-pct recovery with HF-oleic acid scheme; amine flotation recovered 94 pct of the chromite in a rougher concentrate containing 28.8 pct Cr_2O_3. The low grade obtained using the amine collector was attributed to the presence of olivine, which cofloated with chromite.

Both Benbow samples responded favorably to HF-oleic acid flotation and to amine flotation. Generally higher recoveries were achieved using the latter reagent scheme.

Flotation of undeslimed Benbow 2 sample (20.4 pct Cr_2O_3) using CMC-tall oil or oil emulsion collectors produced rougher concentrates containing only 32.5 and 32.9 pct Cr_2O_3 at recoveries of 85 and 83 pct, respectively. Flotation cleaning improved concentrate grade at significantly reduced recoveries. Overall, amine flotation produced better chromite upgrading.

A low-grade sample from Auburn, CA, upgraded from 3.6 to 15.0 pct Cr_2O_3 at 62-pct recovery using the HF-oleic acid method but did not respond favorably to the amine, oil emulsion, or CMC-tall oil flotation methods. Other low-grade samples, which contained less than 3.6 pct Cr_2O_3, did not respond favorably to any of the conventional flotation schemes.

Column flotation of the Benbow 2 sample using coarse or fine air bubbles was investigated and compared with conventional flotation methods using a similar reagent scheme (Armac C collector). Results demonstrated that column flotation produced superior chromite concentrate grades and recoveries. Flotation kinetics was also improved. For example, in a single pass, column flotation of deslimed samples using coarse and fine bubbles produced concentrates containing 43.8 and 44.7 pct Cr_2O_3 at 85- and 87-pct recoveries, respectively. Column flotation of undeslimed samples produced concentrates containing nearly 42 pct Cr_2O_3 at 94-pct recovery. Conventional flotation produced significantly lower grades and recoveries.

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A CHEMICAL METHOD FOR RECOVERING CHROMIUM FROM DOMESTIC CHROMITES

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ABSTRACT

The Bureau of Mines has devised a procedure to recover Cr chemicals from low-grade domestic chromites. These domestic chromites contain Si and Al impurities at levels that are too high to permit processing by present industrial processes. The Bureau procedure consists of reacting chromite with molten NaOH under oxidizing conditions to form sodium chromate (Na_2CrO_4). The reaction product is leached with methanol to recover the majority of the unreacted NaOH, and then with water to remove the Na_2CrO_4 and the remainder of the NaOH. The Na_2CrO_4 product is recovered by evaporative crystallization from the aqueous solution.

This report presents laboratory results of studies to determine the optimum fusion and leaching conditions and the Cr extractions obtained for several domestic chromite concentrates. Preliminary results on solution purification and crystallization are also included. The concentrates are from a variety of sources including the Stillwater Complex in Montana, Red Bluff Bay and the Kenai Peninsula in Alaska, and an Ni-Co laterite from southern Oregon. All of these concentrates were successfully treated by this procedure. The best Cr extraction obtained for each of these materials ranged from 92.5 to 98.9 pct.

INTRODUCTION

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

Commercial processes presently used to chemically treat chromite concentrates include an oxidizing roast of the chromite with Na_2CO_3 and lime in a rotary kiln at around 1,100° to 1,150° C. The amount of reagents and a diluent are controlled so that the reaction mixture remains as a solid phase in the kiln (*2*). Concentrates produced from domestic chromite deposits contain too much Si to be processed by this method. The Si forms molten, sticky reaction products with the Na_2CO_3, which cause balls or rings of material to form in the kiln, hindering its operation. the Al content in domestic resources is also high, resulting in an excess consumption of reagents (*3*).

A simplified flowsheet for the Bureau of Mines procedure to recover Cr chemicals from low-grade domestic chromites is shown in figure 1. Briefly, the procedure consists of reacting the chromite at 550° to 650° C with an excess of molten NaOH under oxidizing conditions to produce Na_2CrO_4. The product from the fusion reaction is solidified, crushed, and leached with methanol in a countercurrent procedure. The methanol leach removes the majority of the excess NaOH while removing only a trace of the Na_2CrO_4. This separation can be accomplished because of the large difference in solubility of the two compounds in methanol. For example, the solubility of Na_2CrO_4 in a methanol solution containing 10 pct NaOH is only 0.013 pct (*4*). The methanol solution is then evaporated to recover the NaOH, which is recycled to the fusion reactor.

The residue from the methanol leach is water-leached to recover the remainder of the NaOH and the Na_2CrO_4 product. This solution is purified of Si and Al compounds by sparging with CO_2 to reduce the pH so that the Al and Si compounds precipitate. The carbonate ion formed during the CO_2 sparge is removed by adding lime to the solution to precipitate $CaCO_3$. The final Na_2CrO_4 product is recovered from the aqueous solution by evaporative crystallization. The mother liquor exiting the crystallizer is evaporated, and the solids are recycled to the fusion reactor. The Na_2CrO_4 product from this procedure is a basic chemical used industrially and can be used to produce the other common Cr compounds in commerical use.

The general equation for the fusion reaction of the chromite with the NaOH is

$$FeO \cdot Cr_2O_3 + 4NaOH + 7/4\ O_2 \rightarrow 2Na_2CrO_4 + 1/2Fe_2O_3 + 2H_2O$$

Abbreviations Used in This Paper

°C	degree Celsius
cm	centimeter
g	gram
g/L	gram per liter
h	hour
mL	milliliter
mm	millimeter
min	minute
pct	weight percent
ppm	part per million

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Previous work by Chandra (*5*) showed that an excess of NaOH must be used to maintain a fluid reaction mixture. An NaOH-to-chromite weight ratio of ~4 (22.4 mole ratio) is typically necessary to maintain fluidity and to obtain good conversion of the Cr in the chromite to Na2CrO$_4$. Reaction products build up on the surface of the chromite particles, preventing further reaction, so the mixture must be kept well agitated to remove these surface products. Chandra used a small ball-mill-type reactor in his studies, but this type of reactor proved to be unworkable in larger sizes. A stirred-pot-type reactor was used in the present work. Studies are also being conducted in Japan on a similar procedure using $NaNO_3$ as the oxidizing medium rather than air as used in the Bureau method (*6-7*).

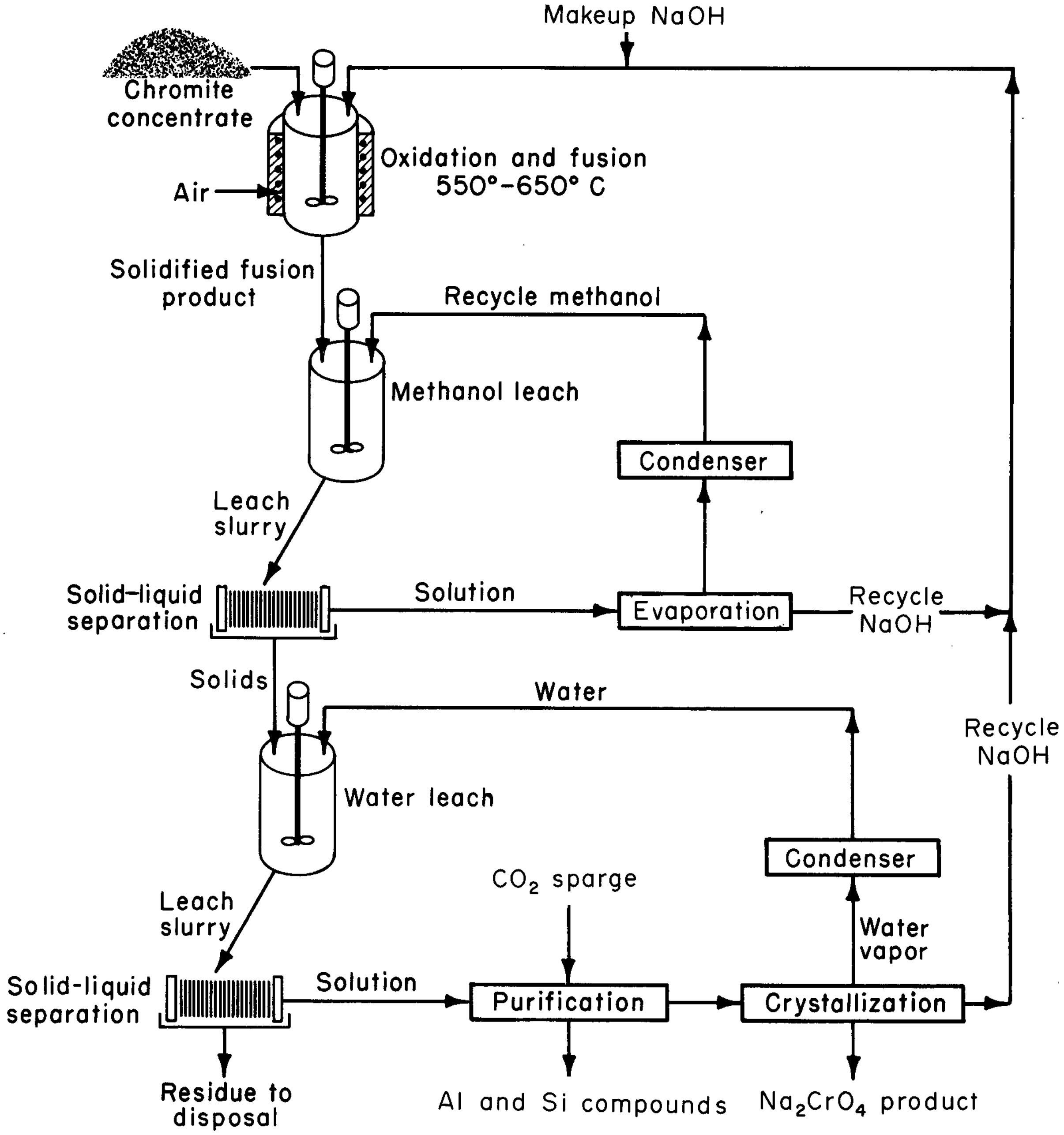

FIGURE 1.—Flowsheet for chemical processing of chromites.

RAW MATERIALS

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

1. High-Cr (metallurgical-grade) chromite that contained a minimum of 46 pct Cr_2O_3 with a Cr-Fe ratio $>2.0{:}1$.
2. High-Fe (chemical-grade) chromite that contained 40 to 46 pct Cr_2O_3 with a Cr-Fe ratio of 1.5 to 2.0.
3. Marginal chromite that met either the grade or Cr-Fe ratio requirements for one of the classifications above and very nearly met the other.
4. Submarginal chromite that failed to meet the above classifications.

These classifications were obtained from Dahlin (*8*). Four of the concentrates tested are listed in table 1 with their origin, composition, and classification of quality. The results of 10 additional samples are presented in Report of Investigations 8977 (*9*).

Test results for two concentrates from Alaska are reported in this paper. One sample from Red Mountain was a high-Cr concentrate containing 56.4 pct Cr_2O_3 with a Cr-Fe ratio of 2.8 (*10*). The Si impurity was 1.4 pct SiO_2. The other sample from Alaska was from Red Bluff Bay (*10*). This was a high-Fe concentrate containing 41.7 pct Cr_2O_3 with a Cr-Fe ratio of 2.0. The Si impurity was 8.0 pct SiO_2.

A concentrate from southern Oregon was derived from an Ni-Co laterite leach residue. This material was the residue remaining after processing in the Bureau's roast-leach procedure for recovering Ni and Co. Beneficiation of this residue resulted in a high-Fe chromite concentrate containing 41.5 pct Cr_2O_3 with a Cr-Fe ratio of 1.8 (*11*). The SiO_2 content of this concentrate was 1.7 pct.

A concentrate from the Mouat Mine in the Stillwater Complex in Montana was also tested. This was also a low-grade high-Fe material having a Cr-Fe ratio of 1.5 and a high Si content of 8.5 pct SiO_2.

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

The chromite mineral is a spinel structure theoretically represented by the formula $FeO \cdot Cr_2O_3$. Magnesium can substitute for the Fe^{2+}, and Al^{3+} and Fe^{3+} can substitute for the Cr^{3+} in the crystal lattice, giving the formula $(Mg,Fe)O \cdot (Al,Fe,Cr)_2O_3$. In addition to the lattice impurities, additional Fe in the form of magnetite (Fe_3O_4) is also commonly associated with the chromite grains.

TABLE 1.—Head analyses of chromite concentrates

Location	Sample	Analysis, pct					Cr-Fe ratio	Quality classification
		Cr_2O_3	Fe	MgO	Al_2O_3	SiO_2		
Alaska:								
Kenai Peninsula	Red Mountain	56.4	13.7	15.2	8.8	1.4	2.8	High-Cr.
Baronof Island	Red Bluff Bay	41.7	14.3	16.9	9.2	8.0	2.0	High-Fe.
Southern Oregon	Eight Dollar Mtn. laterite.	41.5	16.1	12.4	22.3	1.7	1.8	Do.
Montana:								
Stillwater Complex.	Mouat	36.1	16.7	16.3	15.0	8.5	1.5	Marginal.

ALKALI FUSION

EQUIPMENT AND EXPERIMENTAL PROCEDURES

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

A larger reactor was also constructed for use in preparing larger samples for the countercurrent leaching studies and for comparing the Cr extractions obtained in the two different-sized reactors. The larger reactor measured 15 cm in diam by 31 cm deep.

The metal extractions in the fusion reaction are defined as the amount of the various metals in the chromite converted to a water-soluble form. The reactor product was leached with water at 15 pct solids for 2 h to determine the soluble metal content. The resulting leach solutions were analyzed for Cr, Al, Si, Na, and NaOH. The residue from the leach step was analyzed for Cr. The Cr extraction was determined by a material balance between the Cr in the feed material, the Cr in the leach solution, and the Cr in the insoluble residue remaining after water leaching. A material balance was not normally determined for the Al and Si. Their extractions were determined by comparing the amount of metal in solution with the amount in the chromite feed. The Cr extraction values represent the amount of Cr in the chromite converted to soluble Na_2CrO_4 and are not necessarily the overall maximum recovery that could be attained in a process.

The variables studied in the fusion tests were reaction time, temperature, and NaOH-to-chromite ratio. The NaOH-to-chromite rato was based on the chromite content of the concentrate, not on its total weight. Such variables as stirring rate, particle size of the chromite, and airflow rate were not studied. The agitation rate and airflow were kept the same for all tests. Early testing showed that as long as the product was well stirred and sufficient airflow was maintained, these variables did not affect the results. The concentrates were generally minus 65 mesh, although the laterite concentrate was minus 200 mesh. The particle size of the concentrates was the size necessary for liberation of the chromite mineral in the beneficiation studies. No additional grinding or sizing of the chromite particles was performed.

EXPERIMENTAL RESULTS AND DISCUSSION

The Red Mountain concentrate is a high-grade, high-Cr material containing 1.4 pct SiO_2. A limited amount of this concentrate was available, so extensive testing was not performed. However, all conditions tested with this material resulted in Cr extractions in excess of 90 pct (table 2). Relatively mild reaction conditions (2-h fusion time at 550° C with a NaOH-to-chromite ratio of 2) resulted in a Cr extraction of 94.9 pct. More severe conditions (4-h fusion time at 650° C with an NaOH-to-chromite ratio of 4) resulted in extractions as high as 98.8 pct. This material also stayed very fluid under all reaction conditions.

The Red Bluff Bay chromite is a high-Fe chromite that contains 8.0 pct SiO_2. The effect of time on the Cr extraction was not very significant with this chromite; the NaOH-to-chromite ratio was much more important (figs. 2-3, table 3). This material reacted quite rapidly with a Cr extraction of 91.7 pct obtained after 1 h and a 94.4-pct extraction obtained after a 4-h reaction time at 650° C. Changing the NaOH-to-chromite ratio from 2 to 4 increased the Cr extraction from 81.7 to 94.4 pct. This material also became less viscous as the NaOH content was increased. A ratio of 3 was the minimum practical amount with this concentrate, because at a ratio of 2 the reaction mixture was very viscous and would not pour out of the reactor. Data points are shown for a temperature of 550° C at NaOH-to-chromite ratios of 2 and 4 for comparison purposes, but no curve is drawn through the two points.

TABLE 2.—Results of chromite fusion tests, Red Mountain concentrate

NAOH-chromite, wt ratio	Temp, °C	Time, h	Extraction, pct		
			Cr	Al	Si
2:1	550	2	94.9	81.8	53.8
	650	2	92.6	79.4	50.8
	550	4	95.5	81.3	72.3
	650	4	92.6	65.0	27.7
4:1	550	2	94.8	80.6	77.6
	650	2	95.2	88.9	71.4
	550	4	98.0	75.7	71.4
	650	4	98.8	87.1	65.3

TABLE 3.—Results of chromite fusion tests, Red Bluff Bay concentrate

(Small reactor unless otherwise indicated)

NaOH-chromite, wt ratio	Temp, °C	Time, h	Extraction, pct		
			Cr	Al	Si
1:1	650	0.1	7.9	11.3	11.8
2:1	650	2	81.7	43.5	20.9
	550	4	79.8	37.7	26.8
3:1	650	4	93.0	60.7	31.6
4:1	550	4	88.6	70.8	68.4
	650	4	94.4	65.9	55.0
	650	1	91.7	80.0	67.8
	650	2	92.8	77.9	56.4
	650	3	95.0	69.5	55.9
	650	4	94.4	65.9	55.0
4:1[1]	650	4	96.9	90.8	63.3

[1] Large reactor.

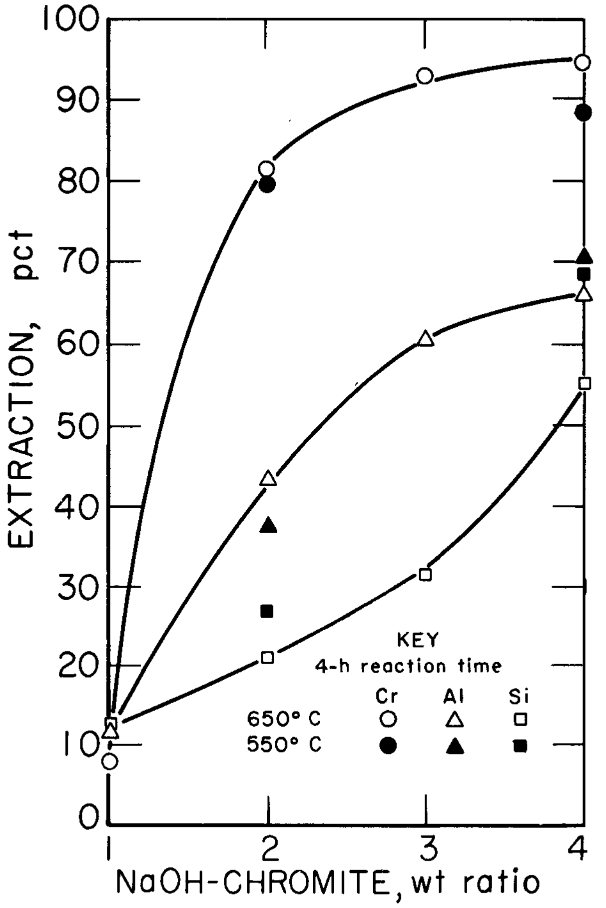

FIGURE 2.—Effect of NaOH-chromite weight ratio on metal extraction—Red Bluff Bay chromite.

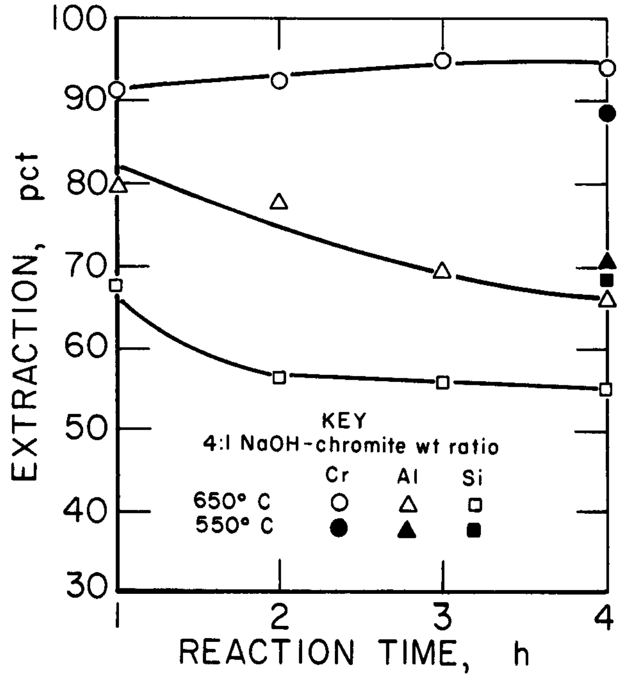

FIGURE 3.—Effect of reaction time on metal extraction—Red Bluff Bay chromite.

The chromite concentrate obtained from the Eight Dollar Mountain laterite leach residue is a high-Fe chromite containing only 1.7 pct SiO_2. The maximum Cr extraction obtained from this material in the small reactor was 93.5 pct at 650° C, a reaction time of 4 h, and an NaOH-to-chromite ratio of 4. The NaOH-to-chromite ratio had very little effect on the Cr extraction (fig. 4, table 4), and the reaction mixture remained very fluid under all conditions tested. The effects of time and temperature on Cr extraction were more pronounced, as shown in figure 5 and table 4. The Cr extraction increased from 71.4 to 93.5 pct as the reaction time was increased from 1 h to 4 h at 650° C. At 550° C, the Cr extraction increased from 51.2 pct to 80.1 pct as the reaction time was increased from 1 h to 4 h.

The Mouat concentrate from Montana was tested under a variety of conditions. Reaction times from 1 to 4 h were used at temperatures of 650° and 550° C, and the NaOH-to-chromite ratio was varied from 2 to 6. Ratios below 4 were totally unsuccessful because the mixture became too viscous to stir. As indicated in table 5 and figure 6, the best extractions obtained with this material averaged 92.5 pct at an NaOH-to-chromite ratio of 4 and 91.7 pct at a ratio of 6. An NaOH-to-chromite ratio of 6 would be necessary in a large-scale operation, however, to obtain a product that will flow

TABLE 4.—Results of chromite fusion tests, Eight Dollar Mountain laterite

(Small reactor unless otherwise indicated)

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

[1] Large reactor.

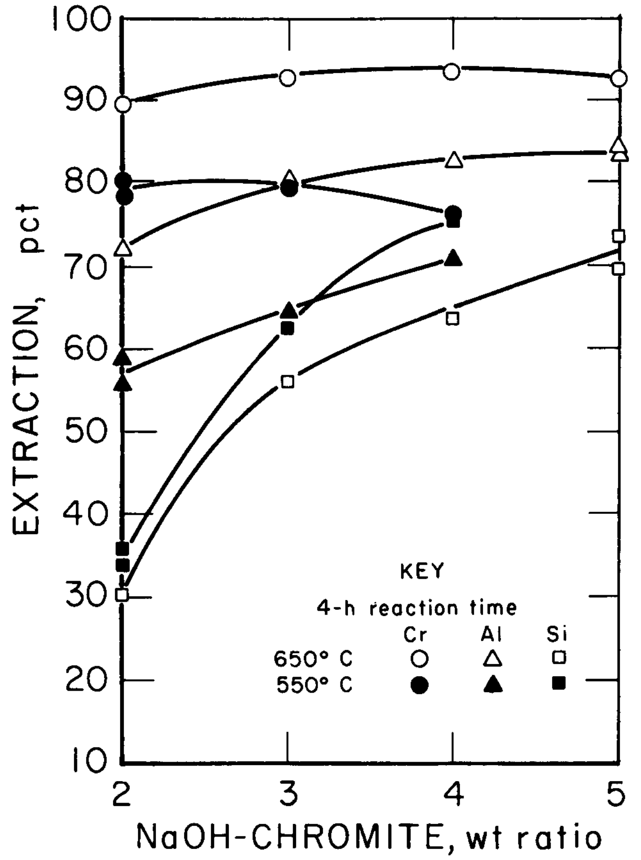

FIGURE 4.—Effect of NaOH-chromite weight ratio on metal extraction—Eight Dollar Mountain laterite.

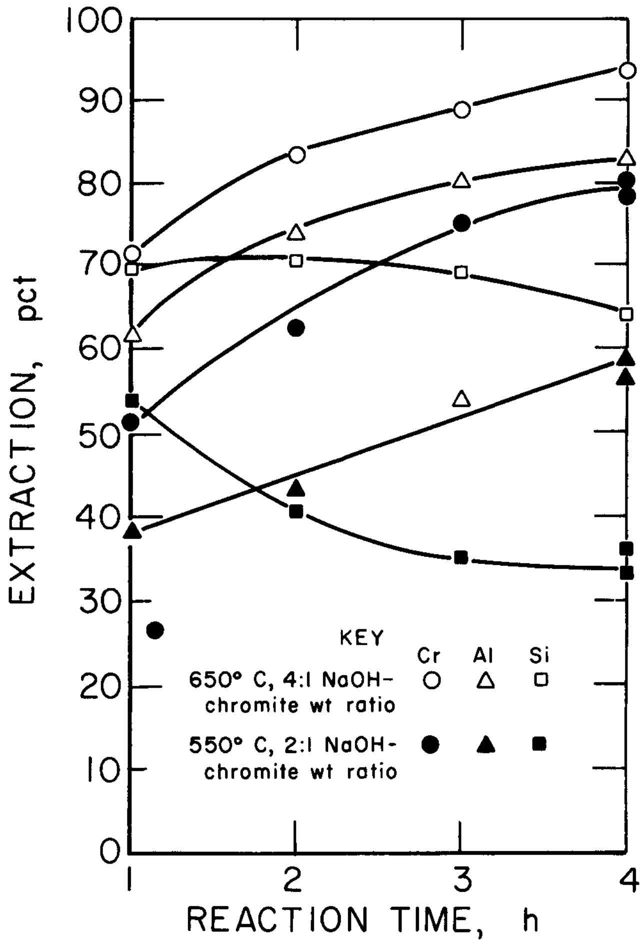

FIGURE 5.—Effect of reaction time on metal extraction—Eight Dollar Mountain laterite.

out of a reactor. The mixture prepared at a 4:1 ratio is too viscous to pour, and even at the 6:1 ratio the mixture is fairly thick and does not flow readily. The data also indicate that a reaction time greater than 2 h does not greatly increase the Cr extraction at 650° C but has a greater effect at 550° C (fig. 7). A curve was not shown for the 550° C results because only two data points are available. The data are shown for comparison purposes.

Chromium extractions in the large reactor were generally slightly higher than those obtained in the small reactor. This is shown in the results in tables 3-5.

As mentioned earlier, limited testing was performed on 10 other chromite concentrates with compositions ranging from high-Cr concentrates to submarginal concentrates. The poor-grade materials typically resulted in Cr extractions in the 50- to 78-pct range, while the high-grade materials resulted in extractions in the 92- to 99-pct range.

The viscosity of the fused reaction mixture ranged from almost waterlike to a pastelike consistency that would not flow out of the reactor. The lower grade chromites containing high Fe or a combination of high Si + Al generally resulted in higher viscosity reaction products. Operating conditions resulting in very high viscosities also tended to result in somewhat lower Cr extractions. Moderate viscosity reaction products could still result in Cr extractions in the 90-pct area, however.

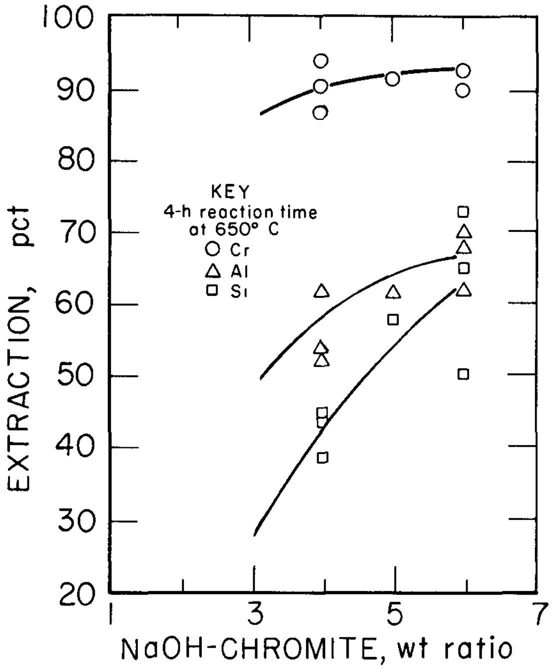

FIGURE 6.—Effect of NaOH-chromite weight ratio on metal extraction—Mouat chromite.

TABLE 5.—Results of chromite fusion tests, Mouat concentrate

(Small reactor unless otherwise indicated)

NaOH-chromite, wt ratio	Temp, °C	Time, h	Extraction, pct		
			Cr	Al	Si
6:1	650	4	90.0	61.7	50.1
	650	4	92.4	67.8	72.9
	650	4	92.6	69.9	64.9
	550	4	77.9	62.6	83.0
	550	4	85.2	64.8	92.2
	650	2	88.9	67.1	81.0
	550	2	82.2	55.1	86.5
5:1	650	4	91.7	61.3	57.6
	550	4	81.3	49.2	71.2
4:1	650	4	90.5	52.0	45.2
	650	4	94.3	61.5	38.6
	650	3	88.0	51.8	53.3
	650	2	85.1	50.8	54.3
	650	1	80.9	50.8	54.8
	550	4	87.0	48.1	48.5
	550	2	63.3	34.6	73.8
6:1[1]	650	4	95.4	70.6	77.9
	650	4	94.3	81.5	80.5

[1] Large reactor.

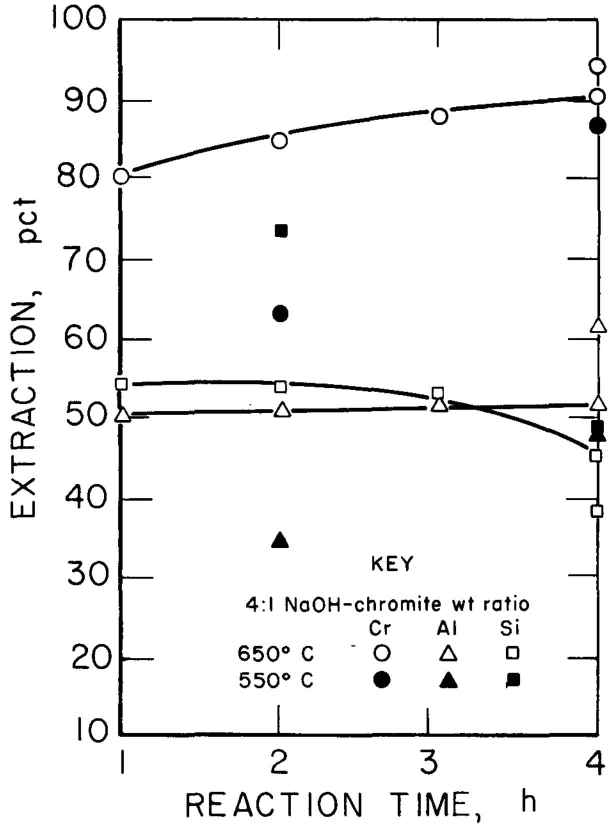

FIGURE 7.—Effect of reaction time on metal extraction—Mouat chromite.

COUNTERCURRENT LEACHING

EQUIPMENT AND PROCEDURE

The solidified fusion product from the first step of the process was crushed and ground to minus 20 mesh. All grinding and screening operations were performed in a dry box to prevent the absorption of moisture by the material. Single-stage batch leach tests were conducted on this material to determine the appropriate conditions to use in countercurrent leach tests. These showed that the solids-to-liquid ratio and the amount of water in the methanol were important factors. In particular, the water in the methanol solvent had to be limited to 5 pct or less to prevent solubilization of Na_2CrO_4.

Countercurrent leach tests were performed in a stepwise manner using the Shanks system to simulate steady state conditions (*12*). Each leach stage was performed in a 250-mL sample bottle using a small, three-bladed propellor for mixing. After leaching, the solid-liquid separation step was conducted by centrifuging the sample bottles. The liquid was decanted off and added to the next appropriate stage. The solids and the bottle were advanced to the next stage. In this manner, the solids remained in the same bottle for all three leach stages and did not have to be removed, minimizing handling losses.

Fusion products from all four concentrates reported in the previous section were studied in countercurrent leach tests. These materials were leached in three countercurrent stages with methanol; then the residue from the methanol leach was leached with water in three countercurrent stages (fig. 8) in the equipment previously described. All the leach tests except one were conducted with 30 pct solids in the leach slurry. The other test was conducted at 15 pct solids. The 30-pct-solids value was chosen in order to produce methanol leach solutions that were nearly saturated with NaOH. This is necessary to minimize the energy required to evaporate the solution so the NaOH can be recycled. Leach time was 30 min in the methanol leach step and 10 min in the water leach. A particle size of minus 20 plus 32 mesh was used in most of the tests in the methanol step. The water leach step used the particle size resulting from the methanol leach, which was quite fine because the particles were broken down as the methanol removed the NaOH. A concentration of 95 pct methanol and 5 pct water was used in all tests.

RESULTS AND DISCUSSION

The results indicate that methanol leaching removes 88 to 94 pct of the unreacted NaOH. The higher extraction is obtained from fusion products containing a higher ratio of NaOH to chromite. As shown in table 6, only a trace of the Cr is found in the methanol solution. The aqueous solution contains the remainder of the NaOH and 90 to 99 pct of the soluble Cr. The remainder of the Cr and a trace of the NaOH are found in the residue from the water leach. These results are for three countercurrent stages. In the case of the Mouat concentrate, where 10 pct of the soluble Cr remains in the leach residue, an additional stage would be necessary to remove this material. The NaOH concentration in the methanol solution ranged from 146 g/L for the Red Mountain fusion product to 224 g/L for the Mouat material. A saturated NaOH solution in methanol is approximately 240 g/L NaOH. The Cr concentration in the aqueous solution was 80 to 90 g/L, and the NaOH was 35 to 80 g/L. A saturated solution at 25° C would contain approximately 170 g/L Cr and 150 g/L NaOH.

TABLE 6.—Results of two-step, three-stage countercurrent leach tests

Concentrate	NaOH-chromite, wt ratio in fusion	Solids in leach, pct	Methanol leach		Water leach		Residue	
			NaOH ext, pct	Cr ext, pct	NaOH ext, pct	Cr ext, pct	NaOH, pct	Cr, pct
Red Mountain	2:1	30	88.8	Tr	11.1	98.7	0.1	1.2
Red Bluff Bay	4:1	30	87.9	Tr	7.7	96.5	4.4	3.5
Eight Dollar Mountain	4:1	30	84.0	Tr	15.6	96.8	.4	3.2
Mouat	6:1	30	94.3	Tr	5.5	90.0	.2	10.0
	6:1	15	92.7	Tr	7.2	98.6	.1	.4

ext Extraction. Tr Trace.

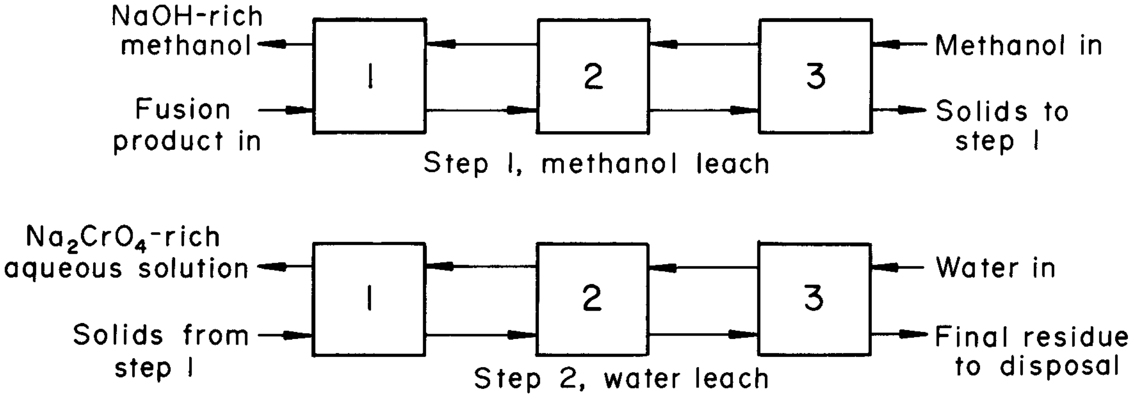

FIGURE 8.—Two-step three-stage countercurrent leach.

SOLUTION PURIFICATION

No significant amount of impurities were found in the methanol solution. Aluminum and silicon were found in the 10- to 50-ppm range.

The major impurities that were solubilized in the aqueous solution by the fusion reaction were Si and Al. A minor amount of ferrous iron (Fe^{2+}) was also soluble but oxidized on exposure to air and precipitated from solution. Magnesium was a major impurity in the chromite concentrates but did not become soluble to any extent. Solution concentrations were typically 1 ppm Mg or less. As shown in tables 2-5 and figures 2-6, the Al extraction generally tended to follow the same trend as the Cr extraction. This would be expected because the Al substitutes for Cr in the chromite lattice. As the Cr was reacted, the Al would also be exposed and react with the NaOH.

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

The total amount of Si found in the aqueous solution after countercurrent leaching ranged from 1.6 to 13 pct of the total Si content in the chromite. The Al content in the solutions ranged from 32 to 71 pct of the total amount in the chromite. These values are considerably lower than was obtained in single-stage leaching of the fusion product. The amount of Si extracted into the aqueous solution is particularly reduced in the countercurrent leaching.

The Si and Al compounds can be removed from solution by sparging with CO_2. The pH of the solution was reduced from 12-13 to 9.5, and the compounds were precipitated. The carbonate ion formed during the CO_2 sparge is removed from the solution by the addition of lime.

CRYSTALLIZATION

Only preliminary crystallization work has been conducted. A batch crystallizer was constructed and operated for short periods with varying mother liquor compositions. The crystals that were formed were removed, washed, and analyzed for Na_2CrO_4 and NaOH. The corresponding mother liquor composition was also determined. The crystal size resulting from this procedure was very small, and the crystals were difficult to wash free of the mother liquor. Testing was conducted at 65° and 90° C. Preliminary results from these tests indicated that Na_2CrO_4 crystals containing less than 0.1 pct NaOH can be produced from mother liquors containing an NaOH-to-chromate ratio of as high as 10. Concentration of NaOH was aproximately 57 pct (860 g/L). A semicontinuous crystallizer has been constructed and is presently being operated. Crystals with a much larger size, minus 16 plus 32 mesh, have been produced with this equipment and again show NaOH contents of less than 0.1 pct.

SUMMARY AND CONCLUSIONS

Laboratory-scale testing showed that low-grade domestic chromites that are not sutiable for chemical processing by present commercial methods can be treated successfully by a procedure devised by the Bureau of Mines. The procedure involved reacting the chromites with fused NaOH under oxidizing conditions to form Na_2CrO_4. The Na_2CrO_4 was then recovered by leaching and crystallization. Chromium extractions as high as 98.9 pct were obtained in the fusion step from high-Cr concentrates. Marginal high-Fe concentrates resulted in Cr extractions in the 90- to 94-pct range.

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PYROMETALLURGICAL PROCESSING OF DOMESTIC CHROMIUM RESOURCES

By R. H. Nafziger[1]

ABSTRACT

This paper reviews pyrometallurgical research conducted by the Bureau of Mines to prepare ferrochromium and other products. Emphasis is placed on the problems encountered in using domestic chromite sources. Advantages and disadvantages of each process are addressed.

The Bureau demonstrated that a wide variety of domestic Cr resources can be used to prepare suitable ferrochromium by electric arc smelting. At first, open-bath conditions were used; later, submerged-arc operations proved more feasible and required less energy.

More recently, basic research by the Bureau delineated the conditions under which domestic Cr concentrates can be prereduced in the solid state prior to melting. Domestic materials were prereduced satisfactorily in a batch rotary kiln and melted to produce ferrochromium. The results also delineated the advantages and disadvantages of prereduction and melting compared with direct-smelting techniques. Successful scrap recycling techniques also were demonstrated.

INTRODUCTION

Over 75 pct of domestic Cr consumption was used in the metal industry in 1981 (*1*). Increased hardness, increased creep and impact strengths, and increased resistance to corrosion or oxidation are among the attributes that make Cr an essential additive to iron, steel, and nonferrous alloys. Chromium is typically added as ferrochromium to these metals. This product must be produced from chromites using some form of pyrometallurgical processing. Ferrochromium accounts for nearly 55 pct of total domestic Cr consumption (*2*).

Traditionally, pyrometallurgical techniques are used to convert Cr ores or concentrates to ferrochromium. Fluxes and reductants are added to these ores or concentrates, and the mixture is smelted in a three-phase ac electric arc furnace. Chromium metal also can be produced by pyrometallurgical processing. A typical process involves the reduction of pure chromia (Cr_2O_3) by finely divided Al metal.

Conventional electric arc furnace techniques have been used to smelt Cr concentrates to produce ferrochromium for many years. Ideally, the charge should be lumpy to minimize both the loss of Cr contained in fines and segregation with resultant nonreduction during smelting. Unfortunately, supplies of hard, lumpy ore are decreasing and are becoming more costly. Pelletizing or briquetting the feed is an alternative, but these processes require fine grinding, addition of binders for agglomeration, and sintering, all of which are labor and energy intensive. Relatively high electrode consumption and slag burden contribute to the disadvantages of conventional smelting processes.

Prereduction of Cr ores and concentrates prior to melting promises some advantages over direct smelting. Among these are (1) more readily available carbonaceous reductants can be used for partial reduction so that electrical energy is not required to reduce the entire charge, (2) less C is required during melting, resulting in easier operational control with fewer impurities introduced into the system, (3) increased productivity can be realized, (4) higher quality slags could be prepared, (5) more O_2 and volatiles are removed prior to smelting, (6) lower electrode consumption can be obtained, (7) higher recoveries can be realized, (8) smoother melting operation is possible, and (9) the heat generated in the prereduction process can be used.

More recently, plasma processing of Cr resources has attracted considerable attention owing to numerous stated advantages (*3*). Although it has conducted no experimental work in this field, the Bureau of Mines is monitoring developments closely.

For many decades, the Bureau of Mines was engaged in research directed toward the more efficient pyrometallurgical processing and recycling of Cr resources and toward a decrease in U.S. dependence on imports. Roasting studies to more efficiently use domestic deposits began in Bureau laboratories nearly 60 years ago. Smelting research on the Montana Cr concentrates in the Stillwater Complex started in 1936, and work on many Cr materials continued through 1982. Prereduction and melting studies were conducted intermittently from 1963 through 1980.

The objective of this paper is to review Bureau research in the pyrometallurgical processing and recycling of Cr resources, including roasting, smelting, and prereduction and melting, with emphasis on domestic deposits.

Abbreviations Used in This Paper

°C	degree Celsius
h	hour
kg	kilogram
kg/h	kilogram per hour
kg/min	kilogram per minute
kg/mt	kilogram per metric ton
kW	kilowatt
kW•h/mt	kilowatt hour per metric ton
min	minute
mt	metric ton
pct	weight percent

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SMELTING

OPEN-BATH TESTS

The Bureau has conducted extensive smelting studies on unreduced lower grade Cr concentrates over the past several decades. Most of the earlier research that was begun in 1948 was conducted using open-bath (or open-arc) conditions wherein the molten bath is not covered either with an unmelted charge or with a reductant such as woodchips. Under these conditions, excessive heat losses, electrode consumption, and refractory wear can be expected.

Stillwater Concentrates

A majority of the open-bath experiments were accomplished on concentrates from the Mouat Mine in the Stillwater Complex in Montana. Wessel and Rasmussen (*4-5*) smelted Mouat material in a basic magnesite-lined, single-phase, 227-kg-capacity electric arc furnace using a subbituminous coal or a char made from this coal. A C-Cr ratio of 1.02 in the charge yielded a ferrochromium with a typical Cr-Fe ratio of 1.36. Chromium and iron recoveries in the metal were usually 97 and 94 pct, respectively. Silicon and carbon contents were inversely related and ranged from 0.2 to 5 pct and from 4 to 7 pct, respectively. Decreases in the C-Cr ratio in the charge from 1.02 to 0.41 resulted in lower Cr and Fe recoveries in the metal (down to 16 pct and as low as 55 pct, respectively) and hence poorer metal. Tests in an acid-lined furnace produced metal having a higher Si content (from 7 to 14 pct) and Cr-Fe ratio (up to 1.53) than tests in a furnace with a basic lining. Recoveries for Cr and Fe were 84 to 95 pct and 76 to 90 pct, respectively. One test in a three-phase furnace using a magnesite lining resulted in a ferrochromium with an average Cr-Fe ratio of 1.46 and demonstrated the feasibility of this technique for producing a satisfactory product.

Hunter (*6*) conducted smelting tests in a 23-kg-capacity, single-phase electric arc furnace on the high-Fe Cr concentrates characteristic of the Stillwater materials to selectively reduce the iron, thereby increasing the Cr-Fe ratio. Carbon additions in the form of coke to the charges ranged from 40 to 100 pct of the stoichiometric requirements, and acid to neutral slags were used. The Fe was readily separated from the Cr, and 89-pct-Cr recovery was realized in the slag. The slag subsequently was reduced to produce a satisfactory ferrochromium.

More recent research involved open-bath smelting of selected Stillwater concentrates in a single-phase, 100-kg-capacity electric arc furnace to provide baseline data for comparison with prereduction and melting tests (*7-8*). Open-bath tests required at least a neutral slag to achieve Cr-Fe levels of 1.5 and Cr recoveries of only 60 pct in the ferrochromium. A more basic slag was deemed preferable for better Cr recoveries and higher Cr-Fe ratios.

Northern California Ore

A chromium ore having a Cr-Fe ratio of nearly 3 occurs in northern California in widely disseminated podiform deposits. Some of this material was smelted under open-bath conditions with coal char (115 pct of the stoichiometric requirement) in a single-phase, 100-kg-capacity electric arc furnace (*7-8*). A satisfactory ASTM grade C ferrochromium[2] was produced with a slightly acid slag.

South-Central California Concentrates

A metallurgical-grade Cr concentrate from south-central California having a Cr-Fe ratio of 1.9 was smelted in the same furnace under open-bath conditions (*7-8*). A satisfactory ASTM grade A ferrochromium was produced using a basic slag.

This material also was used to prepare a very-high-C ferrochromium for use in a fusion-welding process for hard-facing. Open-bath conditions were used to prepare the material both in a 100-kg, single-phase, ac electric arc furnace and in a 1-mt, three-phase ac furnace (*9*). Approximately 110 pct of the stoichiometric C requirement was used with a basic slag. The resulting ferrochromium contained 59 to 64 pct Cr and 25 to 31 pct Fe. Carbon levels in the metal from all tests were greater than 9 pct. Hard facings applied by a fusion-welding process using the produced ferrochromium demonstrated acceptable properties in subsequent tests. Smelting to produce a high-C ferrochromium required a basic slag with an Al_2O_3-MgO ratio of 1.

SUBMERGED-ARC TESTS

In addition to open-bath tests, the Bureau devised techniques for smelting a wide variety of unreduced Cr materials using submerged-arc conditions. Typically, these techniques involved establishing a small molten pool and then maintaining the furnace full of unmelted charge materials during smelting. A majority of the reductant was present as uniform woodchips or hogged fuel (waste wood products such as edgings, trimmings, and splinters processed through a machine known as a hog). The arcs were submerged beneath the unmelted material throughout the test. The "dry-top" cover conserved heat, minimized the need for agglomeration, and decreased refractory erosion and electrode consumption.

Stillwater Concentrates

In 1952, the Bureau resumed smelting research on domestic Cr materials. Early results demonstrated that finely divided concentrates could be smelted directly in a dry-top operation without agglomeration or mixing with lumpy ores when hogged fuel was used (*5*). This lower density charge material facilitated metal-slag separation without the use of high temperatures. Further experiments showed that useful ferroalloys could be produced from high-Fe chromites typical of those found in the Stillwater Complex (*10*).

These tests failed to improve the Cr-Fe ratio, but high-C ferrochromium was produced under acid smelting conditions. From 132 to 141 pct of the stoichiometric C requirement, approximately 100 kg of concentrate, and an acid slag

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[2] For high-C ferrochromium, ASTM grade A has, in weight percent, 52-58 Cr, 6-8 C, 6 max Si, 0.040 max S, and 0.030 max P. Grade B has 55-64 Cr, 4-6 C, 8-14 Si, 0.040 max S, and 0.030 max P. Grade C has 62-72 Cr, 4-9.5 C, 3.0 max Si, 0.060 max S, and 0.030 max P.

appeared optimum. Other alloys such as ferrochromium-silicon, low-C ferrochromium, and Cr-Mn-Si were successfully produced and tested (*10*).

Stockpile concentrates from the Stillwater Complex were nodularized in later tests in a rotary kiln with fluxing constituents (quartz, limestone, and fluorspar) and smelted using coal and/or coal char. In addition, high-C ferrochromium was successfully prepared from these stockpile concentrates using hogged fuel as the major reductant. Chromium and iron recoveries ranged from 87 to 93 pct. Silicon levels in the ferrochromium were inversely proportional to slag basicity and C content (*11*).

More recent tests using woodchips to provide approximately 75 pct of the desired C requirements (*7-8*). Six different reductants (charcoal, coke breeze, coal char, coal, metallurgical coke, and petroleum coke) were evaluated. Coal char was the most reactive of these and provided the highest Cr recovery, lowest energy consumption, and highest metal weight. An ASTM grade A, high-C ferrochromium[3] was produced when 110 to 120 pct of the stoichiometric C requirement was used, with 60 pct of the C present as woodchips and an initial slag basicity of 1.1

Central Oregon Chromium Ore

Early Bureau research included a few tests on a refractory ore from Grant County, OR (*12-13*). Energy consumption was comparable to that when Cr concentrates were smelted, and Cr recovery was only 5 pct lower than that obtained when smelting the concentrates (approximately 93 pct). Low-C ferrochromium-silicon was judged to be an especially desirable product to make from these central Oregon ores.

Oregon Beach Sands

Concentrates from the southern Oregon coast with similar Cr-Fe ratios of 1.4 also were smelted by the Bureau (*10*). Results were similar to those obtained with Stillwater materials described previously (*10*).

Northern California Chromium Ore

Different ores from northern California having Cr-Fe ratios ranging from 1.3 to 1.5 could not be smelted to produce satisfactory commercial alloys using submerged-arc techniques owing to high energy requirements (2,000 kW•h/mt Cr produced) and low Cr recoveries (78.5 pct). Coke and hogged fuel were used as reductants (*14*). However, beneficiation prior to smelting increased the production rate 1.8 times, the electrical energy consumption decreased 39 pct, less flux was required to yield a fluid slag, and the Cr content of the alloy increased nearly 30 pct (to 59 pct) (*14*).

Additional smelting tests on mixtures of lump ore and concentrates from northern California and southern Oregon demonstrated that submerged-arc conditions could produce a satisfactory high-C ferrochromium containing 60 pct Cr, with a Cr recovery of 93 pct in the metal (*15*). Energy consumption was relatively low (4,365 kW•h/mt alloy).

More recent submerged-arc smelting experiments on a northern California metallurgical-grade ore using 115 pct of the stoichiometric C requirements showed that a more acid slag yielded more metal and Cr recovery was higher (up to 96 pct). Both ASTM grades B and C high-C ferrochromium[4] were prepared from this ore (*7-8*).

South-Central California Chromium Concentrate

A metallurgical-grade Cr concentrate from south-central California was smelted using the aforementioned six reductants and from 100 to 110 pct of the stoichiometric C requirements. Coal char provided the most satisfactory overall submerged-arc smelting operation, followed by charcoal and metallurgical coke. An ASTM grade C high-C ferrochromium[5] was produced when coal char was used (*7-8*). In this case, a more basic slag was desirable.

Laterites

The most recent Bureau Cr smelting research involved the use of a concentrate derived from residues generated by the processing of Ni and Co from domestic laterites. (*16*). These concentrates contained approximately the same amount of Cr and less Fe than other offgrade Cr concentrates smelted previously (*6-8, 11*). With respect to fluxing constituents, Al_2O_3 was higher, but MgO and SiO_2 levels were comparable. Results of submerged-arc smelting tests showed that metallurgical-grade coke provided the best quality ferrochromium when 120 pct of the stoichiometric C requirement was used. A high-C ferrochromium was smelted satisfactorily from the concentrate in a 100-kg-capacity furnace, provided that suitable flux additions were made and that the P and S contents can be decreased during the steelmaking process. Agglomeration of the charge materials was not required.

COMPARISON OF OPEN-BATH AND SUBMERGED-ARC SMELTING

In general, submerged-arc smelting of Cr ores and concentrates is preferred over open-bath smelting. However, the latter technique often results in higher Cr contents in the metal. Results throughout the years of Bureau research support this conclusion. Noteworthy are the higher productivity and lower apparent electrical energy and electrode consumption for submerged-arc smelting. In submerged-arc operations, furnace operation was smoother and refractory wear was less, particularly at the slag level. Examples are given in table 1 (*7-8*).

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[3] See footnote 2.

[4],[5] See footnote 2.

TABLE 1.—Comparison of open-bath and submerged-arc smelting tests on various domestic chromites

	Stillwater concentrate		Northern California ore		South-central California concentrate	
	Submerged arc	Open bath	Submerged arc	Open bath	Submerged arc	Open bath
Metal:						
Cr ....pct..	44	48	60	66	63	56
Cr-Fe ratio	1.17	1.15	2.60	2.75	2.59	1.86
Cr recovery ....pct..	97	60	96	77	95	45
Slag:						
Cr ....pct..	.35	9.01	3.87	6.83	1.57	11.4
Fe ....pct..	1.53	1.98	2.07	4.17	1.77	3.49
Metal in conc. ....kg/mt..	609	331	503	430	464	226
Slag-metal wt ratio	1.16	3.66	1.91	1.64	2.42	5.25

PREREDUCTION AND MELTING

BASIC RESEARCH

The Bureau has engaged in considerable basic research to ascertain the mechanism of solid-state chromite reduction, as well as the effects of variables such as temperature, composition, and reductant on chromite reduction. Hunter (*17*) reduced Stillwater Complex Cr concentrate with graphite in Ar at 1,030° to 1,630° C. Significant reduction occurred above 1,100° C. Results indicated that the reduction of Fe and Cr oxides occurred concurrently. The temperature of reduction significantly affected the reduction behavior, as shown in table 2 (*17*).

Nafziger (*18*) studied the reduction of a Cr concentrate from the Stillwater Complex and an ore from northern California using four reductants (coke breeze, coal char, metallurgical coke, petroleum coke) to determine optimum reductants and other variables such as temperature and reduction time for the solid-state prereduction of chromites prior to melting. With respect to the degree of reduction and metallization, coal char generally was the preferred reductant in laboratory experiments in Ar between 1,100° and 1,500° C. The degree of reduction or metallization was proportional to the time and/or temperature used. The rate of reduction was greatest during the first 15 min. The Stillwater concentrate was more easily reduced than the northern California ore, especially at the higher temperatures. Simple kinetic equations could not adequately describe the reduction mechanisms for both Cr materials. The reduction may be nucleation controlled, especially under conditions of interest in commercial operations, where total metallizations as high as possible (80 to 90 pct) are desired.

TABLE 2.—Carbothermic reduction of Mount chromium concentrate

Temp, °C	*Reduction, pct*
1,033	1.6
1,192	18.2
1,205	15.7
1,283	30.0
1,367	63.1
1,517	89.2

PREREDUCTION EXPERIMENTS

The aforementioned fundamental data were used by the Bureau as a basis for preparing four prereduced Cr materials in a gas-fired, 500-kg batch rotary kiln prior to melting (*7-8*). The Cr materials were pelletized with coal char, dried, and charged with more readily available coke breeze into the kiln. Reduction was accomplished between 1,100° and 1,375° C. The prereduced pellets were discharged into an Ar-filled hopper and covered with coal char to prevent reoxidation. Results are tabulated in table 3.

TABLE 3.—Results of prereducing four domestic chromium materials

	Stillwater chromium concentrates		Northern California ore	South-central California concentrate
	Mouat	Benbow		
Total (Fe + Cr) metallization ....pct..	60	67	78	62
Temperature, °C:				
Start of reduction	1,150	1,150	1,150	1,150
End of reduction	1,350	1,325	>1,400	ND
Reduction complete ....h..	3	2	3	3
Product, pct:				
Cr	26	26	32	32
Fe	17	16	12	12

ND Not determined.

MELTING TESTS ON PREREDUCED MATERIALS

Prereduced Cr materials from the four aforementioned sources were melted in a 100-kg-capacity, single-phase ac electric arc furnace, and the results were compared with those obtained on unreduced materials. The prereduced Cr materials were mixed with fluxing constituents and coal char and/or other reductants (where necessary) and melted. For the materials from the Stillwater Complex and from south-central California, slag basicities of 1.1 and 110 pct of the stoichiometric C requirements were used. Melting tests for the northern California ore used a slag basicity of 1.2 and 150 pct of the stoichiometric C requirement (*7-8*). Results are shown in table 4.

COMPARISONS BETWEEN PREREDUCTION—MELTING AND DIRECT SMELTING

Metal quality, as reflected in the compositions, was similar in material derived from direct smelting and from melting of prereduced feed. Metal melted from prereduced material generally possessed greater S levels owing to relatively high levels in the reductants used for prereduction. Phosphorus contents also were higher. With the exception of the Cr concentrate from south-central California, prereduction yielded more C and generally less Si in the metal after melting (*7-8*).

As shown in table 4, prereduction generally resulted in higher productivity and lower electrical energy consumption, with the exception of the Mouat material, which showed no significant advantages in prereduction other than metal Cr content (*7-8*).

ADVANTAGES AND DISADVANTAGES OF PREREDUCTION

The research conducted by the Bureau on Cr materials indicates that many of the advantages of prereduction enumerated earlier in this paper could be realized. However, it was not proven that higher quality slags were more easily attainable or that lower electrode consumption was obtainable. One disadvantage of prereduction may be increased metal S, which would require refining during or after the melting operation. Total energy consumption may not be improved significantly as a result of prereduction. Other disadvantages include the necessity for fine grinding and close temperature control to prevent excessive sintering during prereduction.

TABLE 4.—Results of prereduction and melting of four domestic chromium materials compared with smelting unreduced materials

	Stillwater chromium concentrates				Northern California ore		South-central California concentrate	
	Mouat		Benbow					
	Unreduced	Prereduced[1]	Unreduced	Prereduced[1]	Unreduced	Prereduced[2]	Unreduced	Prereduced[3]
Melt rate ....kg/min..	1.0	0.8	0.9	0.8	1.0	1.3	0.9	0.9
Electrical energy consumption ....kW•h/mt metal..	4,540	4,410	6,230	4,940	6,420	3,400	5,920	3,975
Electrode consumption ...kg/mt metal..	58.0	58.7	50.8	50.4	54.4	44.8	53.9	51.4
Metal:								
Cr-Fe ratio	1.17	1.59	1.73	1.55	2.64	2.21	2.59	2.54
Cr ....pct..	44.3	53.3	52.8	52.9	57.6	56.7	60.3	63.1
Cr recovery ....pct..	99	82	93	77	83	62	76	71
Slag, pct:								
Cr	0.35	4.41	0.72	0.52	2.06	0.31	1.57	1.58
Fe	1.53	3.04	0.57	1.02	0.95	2.80	1.77	2.07
Slag-metal wt ratio	1.16	1.79	2.61	2.02	1.91	1.94	2.42	2.44
Productivity ....kg/h metal..	16.0	16.2	11.0	14.8	11.1	19.2	9.6	13.9

[1] Average of 3 tests. [2] Average of 2 tests. [3] Average of 4 tests.

SCRAP PROCESSING

It has long been recognized that a significant domestic resource for Cr is alloy scrap. Accordingly, the Bureau contracted with several outside organizations to devise a process for recovering Cr from superalloy scrap. A pyrometallurgical oxidation-reduction approach was chosen (*19*). Superalloy scrap was melted in 20- and 50-kW induction furnaces. Oxidizing gases were introduced to separate the Cr into a slag phase. Chromium removal exceeding 99 pct could be achieved. In this step, a metal fraction rich in Ni and Co was obtained. The Cr-bearing slag was reduced with FeSi (75 pct Si) to produce a suitable ferrochromium (containing 65 pct Cr) with a Cr yield over 85 pct with up to 95 pct recovery. Aluminum and carbon also could be used as reducing agents (*19*). An alternative process involves melting and partly oxidizing a blended scrap charge, followed by careful sulfidation to form a partial matte (17 to 25 pct S) of Ni_3S_2, Cr_2S_3, and an Ni-rich metal phase. Mineral processing techniques were used to separate metals and sulfides. The Cr_2S_3 containing some Ni can be roasted in a fluidized bed to decrease S to 0.02 pct and aluminothermically reduced to produce a metal with 0.033 pct S (*20*). Satisfactory Cr recoveries (85 pct) were realized.

CONCLUSIONS

Extensive pyrometallurigcal experiments by the Bureau of Mines have shown that it is possible to prepare satisfactory ferrochromium from a wide variety of lower grade domestic Cr materials. For smelting unreduced materials, submerged-arc techniques generally provide better results than open-bath methods, with respect to both furnace operations and product quality. Byproduct hogged fuel or woodchips can be used effectively as reductants.

Prereduction and melting offer an alternative processing technique for Cr materials. However, advantages of this method over direct smelting have not been clearly established. A pyrometallurgical oxidation-reduction technique also was used successfully to recover Cr from superalloy scrap.

It is evident from this review that more research is required to evaluate the efficiencies of present processes and to propose new processes (*21*). A better understanding of physical properties and reaction mechanisms applicable to reduction and smelting is needed. Thermochemical and kinetic investigations are required, as is a more thorough knowledge of relevant crystal structures to increase the effectiveness of the pyrometallurgical processing of Cr. Emerging technologies such as prereduction and plasma arc melting for Cr should be evaluated further.

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CARBONYL PROCESS TO UPGRADE CHROMITE CONCENTRATES

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ABSTRACT

The Bureau of Mines has upgraded domestic chromite concentrates by carbonyl processing. The concentrates are first solid-state-reduced with H_2 or CO to render the contained Fe responsive to carbonylation with CO under pressure. The carbonyl reaction occurs in two regimes, depending on whether only Fe or Fe and Cr are metallized in the reduction step. When only Fe is metallized during reduction, the subsequent conversion of Fe to $Fe(CO)_5$ is rapid, and nearly all of the metallized Fe is converted. When Cr is metallized along with Fe during reduction, carbonyl conversion decreases rapidly with increasing Cr metallization. This decrease is attributed to Fe-Cr alloying by intermetallic diffusion during reduction. Controlling the chromite concentrate metallization level during solid-state reduction allows production of upgraded chromite concentrates with diverse Cr_2O_3 content and Cr-Fe ratios. Chromite concentrate response to carbonylation is presented as a function of Fe and Cr metallization levels. Results of a Bureau of Mines cost evaluation to upgrade an available Montana high-Fe concentrate from 42.9 pct Cr_2O_3 and 1.6:1 Cr-Fe ratio to 51.0 pct Cr_2O_3 and 4:1 Cr-Fe ratio are summarized.

INTRODUCTION

Metals in periodic table groups VIB, VIIB, and VIII react with CO under certain conditions to form a series of volatile carbonyls with properties potentially suitable for extractive metallurgy. A number of extractive processes based on the formation of metal carbonyls have been investigated or used. Example include commercial production of high-purity Ni (*6*), recovery of Fe and Ni from lateritic ores (*3*), recovery of Fe from flotation tailings or iron oxides (*1, 4-5, 7*), production of synthetic rutile from ilmenite (*9*), and production of upgraded chromite concentrates (*10-11*). In the latter case, reduced chromite concentrates is reacted with CO to form volatile $Fe(CO)_5$ according to the reaction

$$Fe \cdot Cr_2O_3 + 5(CO)(g) \rightarrow Cr_2O_3 + Fe(CO)_5(g).$$

Removal of some of the Fe from the concentrate increases the product Cr_2O_3 content and Cr-Fe ratio.

Common to all the carbonyl processes is the need to catalyze or promote the reaction. Sulfur or sulfur compounds have been favored for this, and were in not for the increase in reaction rate effected by them, commercial extraction of Ni and Fe as carbonyls from reduced metals probably would not be practical (*6*). Although the mechanism by which sulfide ions activate the metal surface and make it reactive is not precisely known, there is evidence that no more than a monolayer of the metal surface is involved. One proposed mechanism is that up to a monolayer the metal surface is composed of the metal and sulfide ions approximating the crystal habit and stoichiometry of the most stable sulfide. Activation is the result of interference with normal bonds existing on a clean metal, thereby producing atoms that are nearly free. In the presence of absorbed CO, such atoms form an activated metal-CO complex which then builds up into the metal carbonyl. The surface remains uniformly active by continuously remaking the sulfide-metal bonds ruptured when metal carbonyl is removed from the surface by volatilization (*6*). The other mechanism proposes that a set of intermediate metal carbonyl sulfides is formed that lowers the apparent activation energy of carbonyl formation (*2*). In either case, a very small amount of S is required, and excess S hinders the reaction.

Abbreviations Used in This Paper

atm	atmosphere, standard
°C	degree Celsius
g	gram
h	hour
min	minute
pct	weight percent
psig	pounds (force) per square inch gauge
st	short ton
st/d	short ton per day
SLM	standard liter per minute

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[1] Research physicist.

[2] Supervisory metallurgist.

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EXPERIMENTAL PROCEDURE

The six chromite concentrates investigated in this study ranged from high-Cr through high-Fe to submarginal and consisted of five particle size groups, as summarized in table 1.

Equipment, procedures, and conditions used to solid-state-reduce and carbonylate the chromite concentrates, and the optimum CO pressure, temperature, promoter trends, and other factors enhancing $Fe(CO)_5$ formation have been previously reported (*10–11*). Modifications to the previous procedures include multiple-charge solid-state reductions at different temperature zones in the small hydrogen reduction furnace to produce a variety of Fe metallization levels in the chromite concentrates. Carbonylation of reduced chromite concentrates was modified by concurrently treating 1-g-size multiple charges in individual boats in the reactor. Promoter additions were based on total concentrate treated in the reactor.

TABLE 1.—Characteristics of domestic chromite concentrate before reduction and carbonylation

Concentrate		Particle size, pct			Analysis, pct					Cr-Fe ratio
Name	Designation	Plus 100 mesh	Minus 100 plus 200 mesh	Minus 200 mesh	Cr_2O_3	Fe	MgO	Al_2O_3	SiO_2	
Montana high-Fe	A	99.4	0.6	0	42.9	18.7	11.8	16.9	1.3	1.6
	B	4.4	23.4	72.2	42.9	18.7	11.8	16.9	1.3	1.6
	C	87.6	10.2	2.2	38.2	15.1	13.3	16.5	4.5	1.7
	D	5.4	23.4	71.2	38.2	15.5	13.3	16.5	4.5	1.7
California high-Fe	E	0	0	100	42.8	19.5	12.8	23.0	1.6	1.5
Alaska high-Fe	F	0	100	0	51.0	20.7	10.2	8.3	2.0	1.7
Alaska high-Cr	G	0	100	0	55.0	15.6	12.4	10.1	3.2	2.4
Alaska submarginal	H	0	100	0	26.3	22.6	15.1	23.0	2.0	.8

RESULTS AND DISCUSSION

SOLID-STATE CHROMITE REDUCTION

All chromite concentrates required a reductive roast to make them respond to carbonylation. Both H_2 and CO solid-state reductions were effective; but during CO reduction, the charge could not be cooled below 1,000° C under CO because of carbide formation in and carbon formation around the concentrate. Cooling the CO-reduced charge under He from the reduction temperature eliminated this problem.

The chromite concentrates were reduced to various degrees of metallization, as summarized in table 2. The data

TABLE 2.—Domestic chromite concentrate solid-state reduction

(Heated to 400° C under He, 400° C through roast back to 400° C and H_2, and 400° C to ambient under He; or heated to 400° C under He, 400° C through roast under CO, and roast to ambient under He. 250-g charges reduced in large furnace, and 25-g charges reduced in small furnace)

Concentrate[1]	Reduction					Equivalent Fe metallization, pct
	Reducing gas	Temp, ° C	Time, h	Furnace	Weight loss, pct	
A	H_2	1,100	4	Large	0.64	11.2
B	H_2	1,100	4	..do	2.15	40.1
		1,150	4	..do	2.74	51.1
		1,150	16	..do	3.35	62.5
		1,200	4	..do	2.79	52.1
		1,200	16	..do	4.26	79.5
		1,235	16	..do	5.10	95.2
		1,120	16	Small	5.89	109.9
		1,155	16	..do	6.43	120.0
		1,185	16	..do	7.05	131.6
		1,180	24	..do	7.29	136.1
		1,185	40	..do	8.53	159.2
C	CO	1,045	16	..do	2.36	53.3
		1,130	16	..do	3.49	78.6
		1,230	16	..do	4.97	111.9
D	H_2	1,200	16	Large	3.77	84.4
	CO	1,045	16	Small	4.21	94.8
		1,130	16	..do	5.06	117.1
	H_2	1,145	16	..do	5.32	119.8
	CO	1,230	16	..do	6.17	138.9
	H_2	1,185	16	..do	6.74	151.7
		1,250	40	..do	9.43	212.3
E	H_2	1,200	16	Large	3.19	57.1
		1,235	16	Small	6.65	119.1
	CO	1,300	20	..do	6.90	123.5
F	H_2	1,200	16	Large	5.77	97.3
	CO	1,300	20	Small	9.05	152.6
	H_2	1,290	16	..do	9.21	157.5
G	H_2	1,200	16	Large	4.65	104.0
		1,235	16	Small	7.75	173.5
H	H_2	1,200	16	Large	6.61	102.1
		1,250	16	Small	7.49	115.6
	CO	1,300	20	..do	9.09	140.4

[1] Designations from table 1.

represent a large number of individual reduction roasts and are presented to show a number of trends associated with precarbonylation preparation of the chromite concentrates. The weight lost by each concentrate is due to Fe and Cr oxides reduction, with the reduction of Fe oxides preceding the reduction of Cr oxides. In a study of reduction behavior of chromite, Searle (*8*) found 80 pct Fe metallization before any significant Cr metallization. The equivalent Fe metallization values are derived from weight loss on the assumption that the Fe is present as FeO since the Fe_2O_3 contributes only up to 25 pct of the total Fe and is reduced to FeO before any Fe metallization takes place. Metallization values in excess of 100 pct indicate definite Cr metallization.

The data in table 2 show an expected increase in metallization with increase in roast time and temperature. Also evident in comparing data from concentrates A and B, and from CO-reduced concentrates C and D, is the increased metallization in the finer particle size concentrates in comparison to the larger particle size concentrates. This increased metallization is attributed to shorter Fe diffusion distances in the smaller grains.

Figure 1 shows four chromite concentrate photomicrographs. The natural concentrate B (fig. 1*A*) has the predominantly smooth, gray reflectivity of chromite. After H_2 reduction to 51.1-pct equivalent Fe metallization (*B*) and to 79.5-pct equivalent Fe metallization (*C*), metallic Fe agglomeration is evidenced by the appearance of the high-reflectivity white specks and coating on the periphery of the chromite grains. Concentrate D, reduced to 212.3-pct equivalent Fe metallization, is shown in figure 1*D*. The photomicrographs show that coalescence of Fe on the surface increases with metallization, while the unreacted central regions (light shade in fig. 1*B*) decrease in volume. Metallization begins at the surface and moves inward, with the Fe diffusing to the surface. As Fe metallizes and diffuses to the surface, the grain interiors become enriched in Cr_2O_3. The chromium oxide begins to metallize and diffuse to the surface when the FeO metallization is nearly complete. The larger agglomerated particles in figure 1*D* are due to both Fe and Cr metallization. Photomicrographs of concentrates E, F, and H before and after solid-state reduction reveal similar relationships, but the larger grain concentrates, F and H, show more agglomeration in central regions along cracks and voids than along the periphery.

CARBONYLATION OF REDUCED CHROMITE CONCENTRATES

Research reported previously (*10-11*) established that metallized Fe in chromite concentrates reacts readily with CO to form the volatile $Fe(CO)_5$. The optimum rate of Fe conversion to $Fe(CO)_5$ occurred at 140° C under 1,500 psig CO with the addition of small quantities of H_2S as a promoter. The Cr_2O_3 level and Cr-Fe ratio of the upgraded product were shown to be controlled by the degree of reduction in the precarbonylation roast, duration of the carbonyl treatment, and mineralogy of the starting concentrate. The results reported here supplement and expand on the previous findings.

A primary reason for continued interest in carbonylation of chromite concentrates was to determine if Cr metal could be extracted by metallizing the Fe and Cr, converting both to the respective carbonyls, and separating the two by fractional distillation. Chromium carbonyl, $Cr(CO)_6$, had been produced in small quantities along with $Fe(CO)_5$ from stainless steel powders, and it was surmised that it could be produced from chromite concentrates with sufficient Cr metallization. Instead, a pronounced decrease in carbonyl formation was observed in concentrates reduced to a level of complete Fe metallization and the beginning of Cr metallization. Further increase in Cr metallization only decreased the chromite concentrate response to carbonylation. As a result of these findings, Fe extraction from chromite concentrates was further investigated, primarily as a function of Fe and Cr metallization in the concentrates.

Table 3 illustrates this by comparing the carbonylation weight loss and Fe extraction percentages of concentrate B and D at partial Fe and no Cr metallization levels (<100 pct equivalent Fe metallization) to those of total Fe and partial Cr metallization levels (>100 pct equivalent Fe metallization). The results show that during 2-h carbonylation, the Fe extraction passes through a maximum at about 110-pct metallization for concentrate B and at about 120 pct for concentrate D. During 24-h carbonylation, Fe extraction appears to improve somewhat for the higher metallization levels.

The appearance of chromite concentrates shown in figure 1 after carbonyl processing is illustrated in figure 2. The natural concentrate B carbonylated without solid-state reduction (panel *A*) shows no marked difference in appearance. When concentrate B was reduced to 51.1-pct equivalent Fe metallization, Fe agglomeration along the grain peripheries disappeared; regions of unreacted chromite were still apparent as lighter shaded interior grain areas (*B*). After 79.5-pct equivalent Fe metallization, concentrate B, showed no Fe or distinguished regions of unreacted chromite (*C*). Concentrate D, reduced to 212.3-pct equivalent Fe metallization, shows dense, large metal particle agglomeration (*D*). In the latter case, Fe extraction was less than 5 pct. The agglomeration of Fe and Cr into large spherical particles in the more highly reduced chromite may be another factor, in addition to Fe and Cr alloying by intermetallic diffusion during reduction, that contributes to decrease in the carbonyl reaction rate due to less available metal surface area. Chromite concentrates E, F, and G revealed similar characteristics after carbonylation, with voids replacing Fe in the central regions of large-grain concentrates F and G.

Based on observation of decreased carbonyl conversion with increasing combined Fe and Cr metallization in tests performed to study the feasibility of extracting Cr by carbonyl processing, the relationship between chromite concentrate metallization and carbonyl conversion was further investigated. Results of these studies are summarized in figure 3 and table 4. The studies were performed on coarse- and fine-particle chromites listed in table 1, reduced with H_2 and CO to a wide selection of metallization levels, and carbonylated for periods ranging from 2 to 72 h.

Figure 3 summarizes carbonylation results on concentrate B reduced up to 160-pct equivalent Fe metallization. Data are presented as percent of total Fe extracted from the concentrate for 1-g charges carbonylated for 2, 24, and 72 h. The results show that for metallization levels up to approximately 110 pct, the conversion of Fe to $Fe(CO)_5$ is practically the same for all the carbonylation times and increases linearly with increasing metallization. Above 110-pct metallization, conversion decreases rapidly for the 2-h treatment; Fe extracted becomes less than 5 pct at 160-pct metallization. Concentrates carbonylated for 24 and 72 h reach maximum conversion at 120- and 130-pct metallization, respectively, and then decrease at higher levels. At these higher metallization levels, there is a marked decrease in carbonyl formation rate.

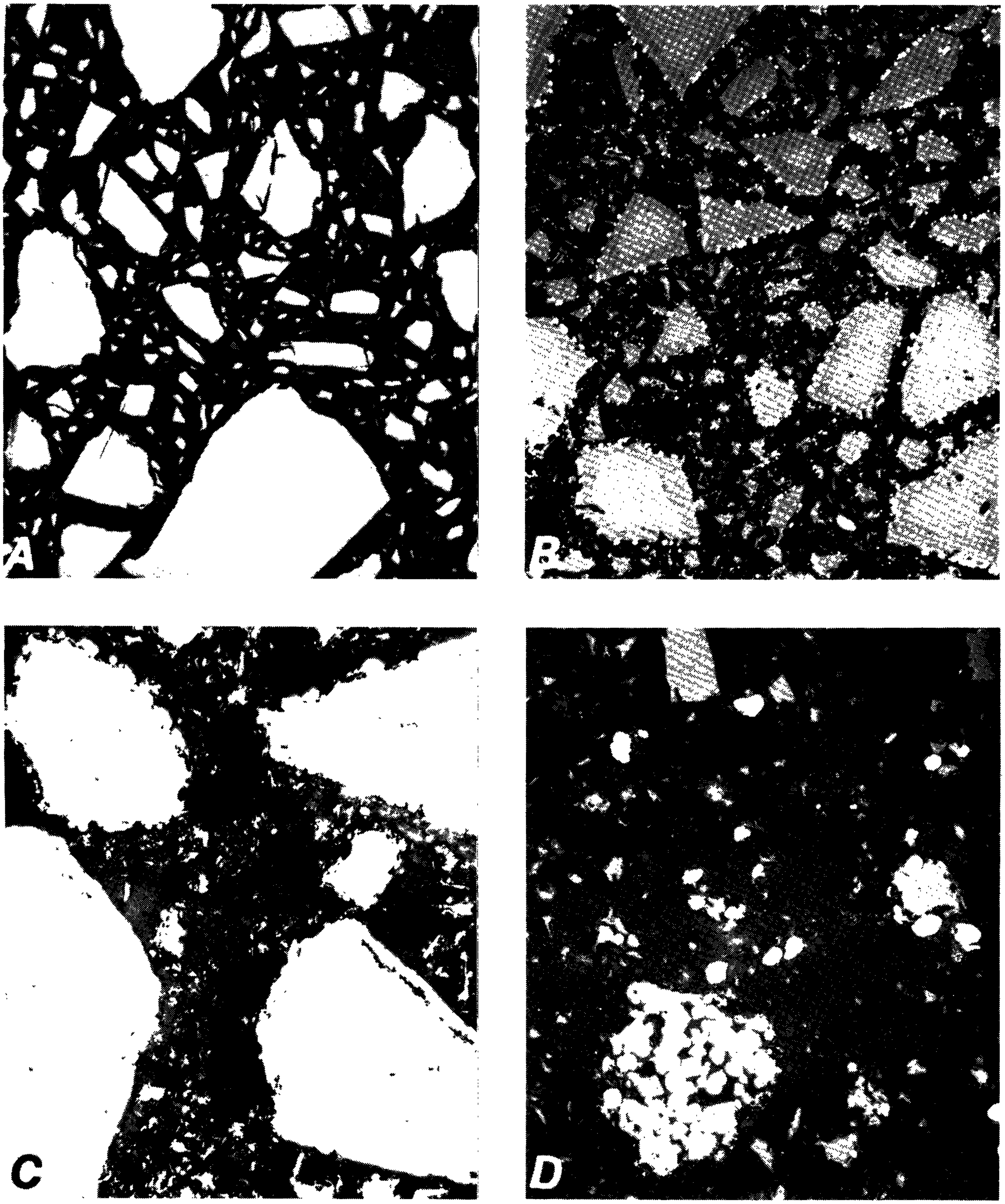

FIGURE 1.—Micrographs of Montana high-Fe chromite concentrate before and after solid-state reduction (X 500). *A*, Natural concentrate B, shows a predominantly smooth gray reflectivity of the chromite grains; *B*, after H_2 solid-state reduction to 51.1-pct equivalent Fe metallization, metallic Fe is evident by appearance of white specks along the periphery of the grains, and the unreduced central regions are indicated by the lighter shade; *C*, after reduction to 79.5-pct metallization, metallic Fe is evident as a coating, and central region appears reduced; and *D*, concentrate D reduced to 212.3-pct metallization shows agglomeration of large metal particles.

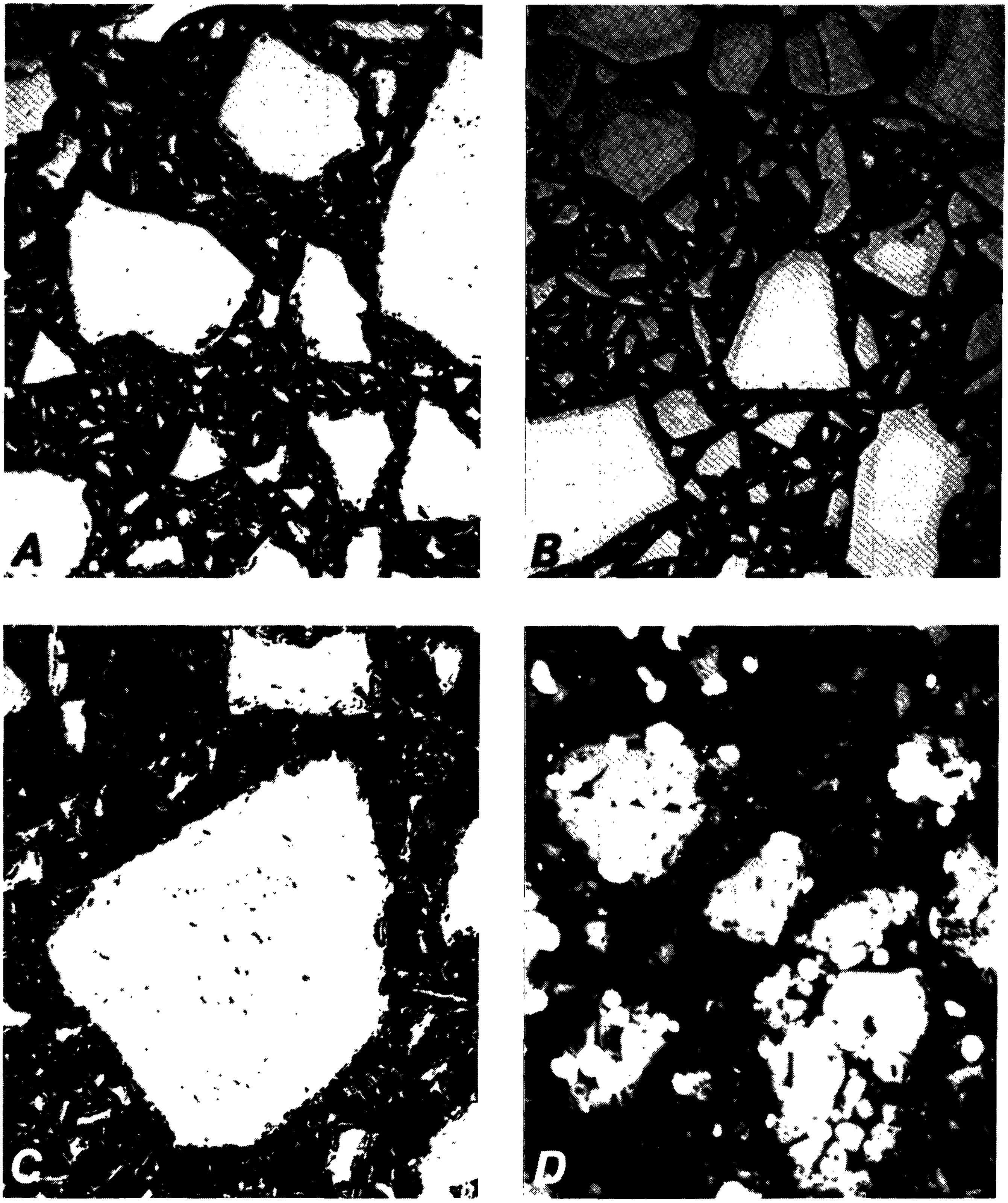

FIGURE 2.—Micrographs of Montana high-Fe chromite concentrate after carbonylation (X 500). *A*, Natural concentrate B carbonylated without solid-state reduction shows no structure change; *B*, carbonylated after reduction to 51.1-pct equivalent Fe metallization, concentrate B shows no metallic Fe but still an unreduced central region; *C*, carbonylated after reduction to 79.5-pct metallization, concentrate B shows no metallic Fe but a reduced central region; and *D*, concentrate D carbonylated after reduction to 212.3-pct metallization shows large agglomerated metal particles.

TABLE 3.—Dependence of chromite concentrate Fe extraction by carbonyl processing on equivalent Fe metallization in solid-state H_2 reduction

(10-g charge, 1,500-psig CO pressure, 0.15-SLM CO flow, 140° C, 17:1 contained Fe-H_2S promoter mole ratio, and He purge)

Concentrate[1]	Equivalent Fe metallization, pct	Carbonylation		Analysis, pct		Iron extracted, pct	Cr-Fe ratio
		Time, h	Weight loss, pct	Cr	Fe		
B	40.1	2	4.41	31.4	15.4	23.1	2.0
	62.5	2	8.30	33.1	12.0	42.9	2.7
	79.5	2	11.83	34.8	8.74	60.6	4.0
	82.9	2	12.51	35.1	8.07	63.9	4.4
	109.6	2	15.25	36.8	5.45	76.8	6.8
	119.6	2	12.38	35.8	8.67	62.0	4.1
	131.0	2	7.47	34.1	13.7	37.1	2.5
	136.1	2	4.94	33.3	16.0	24.5	2.1
	159.2	2	.31	32.2	20.2	1.5	1.6
D	47.4	2	5.79	28.3	10.7	36.6	2.7
	70.2	2	7.08	29.0	9.60	44.3	3.0
	97.3	2	11.50	30.9	5.31	71.0	5.8
	111.3	2	13.20	31.7	3.58	81.0	8.9
	120.5	2	14.85	32.4	1.79	90.7	18.1
	123.2	2	14.63	32.4	2.07	89.2	15.7
	136.3	2	13.30	32.1	3.69	80.6	8.7
	151.7	2	7.95	30.4	9.41	47.8	3.2
	210.8	2	.19	28.9	16.9	1.1	1.7
B	40.1	24	4.84	35.1	15.0	25.3	2.1
	95.2	24	14.16	36.0	6.46	71.7	5.6
	136.1	24	9.81	31.5	11.5	48.6	3.1
D	111.3	24	13.87	31.9	2.83	85.1	11.3
	119.8	24	15.06	32.5	1.54	92.0	21.1
	151.7	24	14.36	32.4	2.64	86.4	12.4
	163.9	24	.77	28.4	16.1	4.6	1.8
	212.3	24	.74	29.1	16.5	4.3	1.8

[1] Designations from table 1.

TABLE 4.—Dependence of chromite concentrate Fe extraction by carbonyl processing on equivalent Fe metallization in solid-state reduction

(1-g multiple charges, 1,500-psig CO pressure, 0.15-SLM CO flow, 140° C, 17:1 contained Fe-H_2S promoter mole ratio, and He purge)

Concentrate[1]	Reduction			Iron extracted by carbonylation, pct		
	Reducing gas	Weight loss, pct	Equivalent Fe metallization, pct	2 h	24 h	72 h
D	H_2	2.11	47.6	22.7	29.8	24.0
		3.75	84.4	56.6	60.6	59.7
		4.32	97.4	68.9	71.0	74.2
		4.94	111.2	79.9	84.2	85.2
		5.36	120.6	86.0	92.3	92.3
		6.09	137.2	91.1	95.2	99.5
		6.74	151.7	72.7	96.5	99.9
		9.43	212.3	0	8.5	24.0
C	CO	.19	4.2	1.0	.5	ND
		1.37	30.8	16.7	18.3	ND
		2.08	46.8	27.0	29.1	ND
		3.49	78.6	51.7	55.2	ND
		4.97	111.9	61.5	71.0	ND
		5.44	122.5	19.3	72.6	ND
		5.65	127.2	7.9	65.2	ND
D	CO	.69	15.5	12.0	11.4	ND
		4.21	94.7	68.8	71.8	ND
		5.20	117.1	84.0	84.4	ND
		6.17	138.9	92.1	94.3	ND
		7.15	161.0	10.7	77.3	ND
		7.42	167.1	14.4	47.1	ND
E	H_2	1.67	29.9	14.8	15.2	19.8
		3.67	65.6	35.7	40.2	41.3
		4.26	76.2	42.4	52.2	51.8
		5.40	96.6	37.6	61.6	62.2
		6.49	116.1	15.0	53.1	59.7
F	H_2	2.69	45.4	14.5	10.4	16.2
		6.02	101.5	54.0	53.3	59.3
		7.68	129.5	56.6	78.1	82.3
		9.34	157.5	15.5	68.6	67.7
G	H_2	3.83	85.8	24.0	30.4	32.8
		4.94	110.5	28.5	43.2	51.7
		7.75	173.5	9.5	75.6	80.7
H	H_2	5.26	81.3	51.2	55.7	56.3
		5.83	90.1	57.8	58.2	62.6
		7.49	115.6	71.5	74.8	78.8

ND Not determined. [1] Designations from table 1.

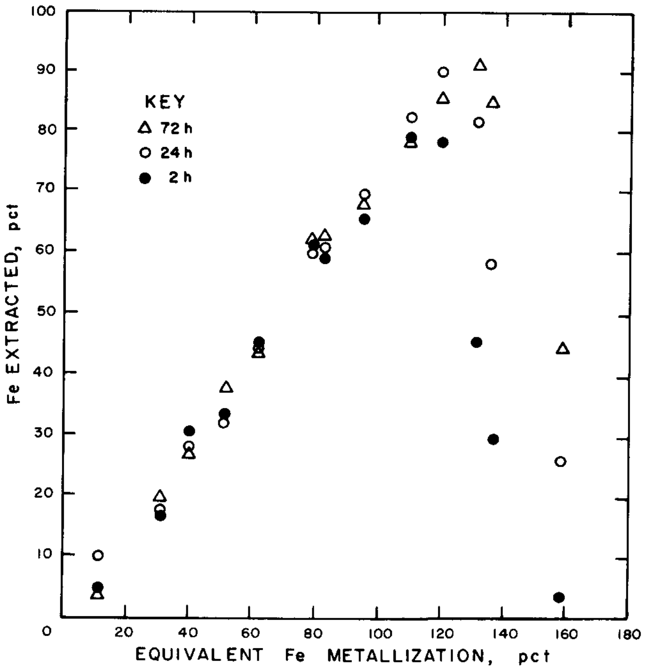

FIGURE 3.—Iron extraction as a function of equivalent Fe metallization, H_2-reduced Montana high-Fe chromite concentrate B. One-gram multiple charges, 1,500-psig CO pressure, 0.15-SLM CO flow, 140° C, 17:1 contained Fe-H_2S promoter mole ratio, and He purge.

Table 4 summarizes the Fe extraction results for concentrates C through H. All concentrates exhibit the same general pattern of carbonylation response graphically depicted in figure 3. The CO-reduced coarse concentrate C shows a decline in conversion for both 2- and 24-h carbonylations at a lower metallization level than the CO-reduced fine concentrate D. Carbonylation response of the California high-Fe chromite concentrate, E, shows more scatter in data, and the maximum conversion takes place at lower metallization levels. This concentrate required high temperature to achieve even 120-pct metallization, even though it was minus 200 mesh. Carbonylation response data for the concentrates F, G, and H are limited, but the overall pattern is in agreement with that evident on other, more thoroughly investigated chromite concentrates.

The Fe-to-$Fe(CO)_5$ conversion characteristics of the above reduced chromite concentrates indicate that carbonylation occurs in two regimes, depending on the degree of Fe and Cr metallization. The carbonyl reaction rate is rapid when only Fe is metallized, and almost all of the Fe converts to $Fe(CO)_5$. Rapid and nearly complete Fe conversion is maintained until start of Cr metallization after approximately 80 pct or more of the Fe is metallized. As Cr metallization begins and increases, carbonyl conversion exhibits a strong direct dependence on time of treatment and an inverse dependence on Cr metallization. This decrease in carbonyl reaction rate is attributed to Fe and Cr alloying by intermetallic diffusion during the reduction step. The alloying effect becomes more pronounced owing to the increased diffusion rates at the higher roast temperatures necessary for more complete Cr metallization; this, in turn, inhibits carbonyl formation during the subsequent carbonyl treatment. Controlling the metallization pretreatment permits removal of some or nearly all of the Fe from chromite concentrates. Thus, the Cr-Fe ratio can be adjusted to any practical value, or a product that is nearly free of Fe can be produced. An adverse implication is that the recovery of Cr metal from chromite by carbonyl technology may not be practical owing to the decrease in reaction rate as Cr metallizes and alloys with Fe.

COST EVALUATION

The Bureau of Mines Process Evaluation Group completed an economic evaluation of the carbonyl process for upgrading chromite concentrate. The evaluation was performed specifically for concentrate B, solid-state-reduced to 80-pct equivalent Fe metallization. During processing, 60 pct of the contained Fe is extracted, producing an upgraded product that analyzes approximately 51.0 pct Cr_2O_3 and 8.7 pct Fe and has a 4:1 Cr-Fe ratio.

The estimated operating cost and amount required to yield a 15-pct rate of return on investment after taxes, without credit for recovered Fe, is $127/st upgraded chromite concentrate for a plant designed to process 1,000 st/d of concentrate feed. If the Fe is recovered and briquetted, it yields a credit of $13/st upgraded concentrate. The corresponding credit for Fe recovered as powder is $79. Some processing equipment is eliminated when Fe is recovered as powder, and this reduces the operating cost and 15-pct rate of return to $32/st of upgraded chromite. Cost estimates are based on an M and S equipment cost index of 781.7. The report concludes that (1) to maximize the economic potential of the process, research should be concentrated on the recovery of an Fe powder byproduct suitable for use in powder metallurgy, and (2) since no individual cost item dominates the process operating cost, only a major process modification will be likely to have a significant effect on process economics.

CONCLUSIONS

Results of this study have demonstrated that chromite concentrates with diverse Cr-Fe ratios, Cr_2O_3 content, particle size, mineralogy, and accessory mineral content can be upgraded by carbonyl processing. The concentrates must first be solid-state-reduced with H_2 or CO. The degree of Fe and Cr metallization achieved in reduction controls the subsequent carbonylation response of the concentrate. For Fe-only metallization, the carbonyl reaction rate is rapid and conversion of metallized Fe to $Fe(CO)_5$ is nearly complete. As Cr metallization begins and increases, the carbonyl reaction rate decreases rapidly owing to Fe and Cr alloying by intermetallic diffusion during reduction. The product Cr-Fe ratio can be closely controlled by controlling the Fe metallization in reduction. Recovery of Cr from chromite by carbonyl technology may not be practical owing to the decrease in reaction rate at the required Cr metallization levels. Finer-particle-size chromite concentrates respond more readily to solid-state reduction, but the finer particle size does not improve reduced concentrate response to carbonylation at the low and medium Fe metallization levels.

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IN-PLANT RECYCLING OF CHROMIUM-BEARING SPECIALTY STEELMAKING WASTES

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ABSTRACT

Significant amounts of Cr, Ni, and other metals are contained in furnace dusts, mill scale, and swarfs produced annually by the domestic specialty steelmaking industry. Little progress has been made toward in-plant recycling of these wastes. Bureau of Mines research has led to development of a process for the in-plant recovery of about 90 pct of the Cr and Mo and well over 90 pct of the Ni and Fe from stainless steelmaking electric furnace dusts, AOD vessel dusts, mill scale, and oily swarf. In the process, the mixed wastes are blended with coke breeze reductant and binder, pelletized, and furnace-smelted to recover the contained metals. All-pellet heats can be smelted, but the recommended procedure is to charge the pellets to the production electric arc furnace to replace up to 20 pct of the scrap charge. A number of industrial-sized (19-st) commercial heats have been successfully made with pelletized wastes representing 14 to 19 pct of the furnace charge. Cost evaluation indicates the process is economically attractive.

INTRODUCTION

The scrap market, for technical and economic reasons, has traditionally concentrated on metallic materials, with the low-grade dusts, fumes, solutions, and sludges being normally destined for landfills or other available means of disposal. Producers of such wastes have had little incentive to treat them for metals recovery.

In the domestic specialty steelmaking industry, for instance, it is estimated that well over 20 million lb Cr and 8 million lb Ni, plus other valuable metals, are contained in flue dusts, mill scale, and grinding swarfs in a typical year.

Traditional waste handling and disposition has undergone a significant change over the past decade as a result of the passage in 1976 of the Resource Conservation and Recovery Act (RCRA), which is concerned with the "cradle-to-grave" generation, transportation, and disposal of hazardous waste. Chromium-bearing electric arc furnace dust has been categorized by the U.S. Environmental Protection Agency (EPA) as a hazardous waste. Other particulates are deemed hazardous if they fail the EPA's Extraction Procedure (EP) toxicity test (*14*). Companies that generate hazardous wastes are faced with much-increased costs of complying with regulatory standards for storing, transporting, and disposing of the wastes.

One alternative to disaposal of such wastes is to develop improved recovery and recycling technology, which can augment domestic supplies of critical metals such as Cr and Ni, as well as associated metals such as Fe and Mo.

Research on steelmaking and other wastes has been conducted over a number of years by the Bureau of Mines. Much of the research (*2-3, 6-7*) involved various schemes to remove Zn and Pb from carbon steelmaking furnace dusts, using combinations of techniques such as sulfation, pelletization, reduction roasting, and specialized furnacing.

Bureau recycling research (*13*) was also conducted on stainless steelmaking baghouse dusts, mill scale, and grinding swarf. Physical separation and leaching tests proved impractical for segregating the metal values. The constituents were too intimately mixed for beneficiation separations and too refractory and complex for selective leaching. Acid-soluble constituents resulted in a high acid consumption. The only method showing promise involved pelletizing the wastes with coke breeze reductant and smelting to produce a master alloy. Encouraging laboratory results in this earlier research led to the making of a 1-st trial heat in an industrial plant (*1*).

All of these earlier heats involved all-pellet charges and production of master alloy ingot. Overall metal recoveries were deemed promising, with Cr recoveries being consistently somewhat lower than the recoveries of Ni and Fe. A preliminary economic evaluation was favorable. Further research involved initial tests of adding the pelletized wastes to the electric furnace in lieu of part of the conventional scrap charge (*5, 8*).

Abbreviations Used in This Paper

d/wk	day per week
° F	degree Fahrenheit
h	hour
in	inch
kW•h	kilowatt hour
kW•h/lb	kilowatt hour per pound
lb	pound
min	minute
pct	weight percent
st	short ton
st/d	short ton per day
yr	year

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In addition to in-plant recycling, a master alloy can be produced by a centralized waste processing facility. An example of this type of facility is the Inmetco plant of the International Nickel Co. (INCO), which has for the past several years been processing part of the stainless steelmaking dusts, mill scale, and grinding swarf being generated (*11*). The treated and smelted compositions are adjusted with higher grade materials to produce recyclable Fe-Cr-Ni ingot.

Fosnacht (*4*) has recently compiled a comprehensive bibliography of the state-of-the-art of the processing of particulate steelmaking wastes.

The results reported herein represent the more recent efforts of Bureau research to find technically and economically viable recycling technology for specialty steelmaking wastes – to permit the return of otherwise lost metal values to the steelmaking circuit. An in-plant reduction technique has been developed that results in the consistent recovery of about 90 pct of the Cr and Mo and well over 90 pct of the Ni and Fe from particulate stainless steel wastes. Description is given of the work, which began with small laboratory arc furnace melts, as it progressed through ~ 19-st demonstration heats at Joslyn Stainless Steels, Ft. Wayne, IN, under a Bureau-industry cooperative effort. Discussion of a cost evaluation is included.

PROCEDURE AND RESULTS

RAW MATERIALS

The waste products evaluated in the research included electric furnace (EF) baghouse dust, argon-oxygen decarburization (AOD) vessel baghouse dust, oily grinding swarf, and mill scale. The majority of the material was supplied by Joslyn Stainless Steels, and partial representative analyses are shown in table 1. Samples of baghouse dust and mill scale were also obtained from several other companies. Variations noted in composition of the wastes reflect variations in the feed to the furnaces, operating procedures, waste collection, and product mix.

The arc furnace and AOD vessel baghouse dusts are typically about 90 pct minus 400 mesh and consist essentially of complex oxides involving metals such as Fe, Cr, Ni, Mo, Mn, and Zn, with numerous other constituents such as reactive Ca, Mg, K, Na, S, Si, C, etc. Mill scale, which is accrued from blooming of heated billets, is also composed principally of metal oxides. Mill scale is mostly powder, but it is typically much coarser in particle size than baghouse dusts. Some larger chunks of mill scale will commonly be present.

Swarfs result from the surface grinding of billets, slabs, and bars. Some of the dry swarf generated during billet grinding, which is less oxidized than baghouse dusts and mill scale, is recycled directly back to the electric furnace. The oily swarf used in these experiments was specifically from the centerless grinding of various-sized rods. It consisted of many small, partly oxidized fragments. It also contained oxide and carbide particles from the grinding wheels and was often still wet from cutting oils used as a coolant during grinding. The particle size of swarf is typically somewhat coarser than the finer fractions of mill scale.

The coke breeze obtained from a steel plant ranged downward in size from about 1/4 in; it contained about 85 pct C. The portland cement used as binder typically has a very fine particle size.

LABORATORY EXPERIMENTS

Laboratory experiments have been conducted for various waste mixtures using pelletizing agglomeration with coke breeze reductant, followed by smelting of approximately 100-lb charges in an arc furnace.

Pelletizing

Pelletizing was selected as the most practical and economic means for agglomeration of the wastes. The four steelmaking wastes (table 1), in proportion consistent with their rate of generation, were mixed with coke breeze reductant and cement binder and blended into a composite mixture. For a plant that is collecting all four wastes, this composition might typically represent some 15 pct AOD dust, 15 to 25 pct each EF dust and mill scale, and about 40 pct grinding swarf. Substantial variation can, of course, be expected. Coke breeze, added as about 10 pct to this waste blend, was selected as a logical C reductant because it is largely in a powdered condition and is an accessible source of C in the steelmaking industry. With a wide particle-size range for steelmaking wastes, a binder may be necessary, particularly if proportions of coarser sizes are relatively high. An addition of about 4 pct cement was found to be an effective binder for the waste mixes evaluated; the fine particle size of the cement aids pellet formation prior to the hardening reaction.

When raw coke breeze is used, it is necessary to dry it and crush it to pass an intermediate size screen, such as 35 mesh, before adding it to the mixture. All mill scale was likewise dried, then passed through crushing rolls until > 70 pct passed a 35-mesh screen – usually two passes through the rolls. Only the minus 35-mesh fraction was blended into the pellet mix used in smelting tests; the oversize fraction was saved and added with the pellets as furnace charge. A flow diagram of this procedure is presented in figure 1.

TABLE 1.—Partial chemical analyses of typical stainless steelmaking waste products, percent

Waste material	Fe	Cr	Ni	Mo	Mn	Pb	Zn
Electric furnace dust	27.8	9.3	2.2	1.1	3.6	0.8	4.9
AOD vessel dust	40.5	11.1	3.8	.7	5.5	.6	.8
Grinding swarf	61.6	11.7	6.8	1.2	1.0	.1	<.1
Mill scale	54.8	8.6	3.9	.5	.8	.1	<.1

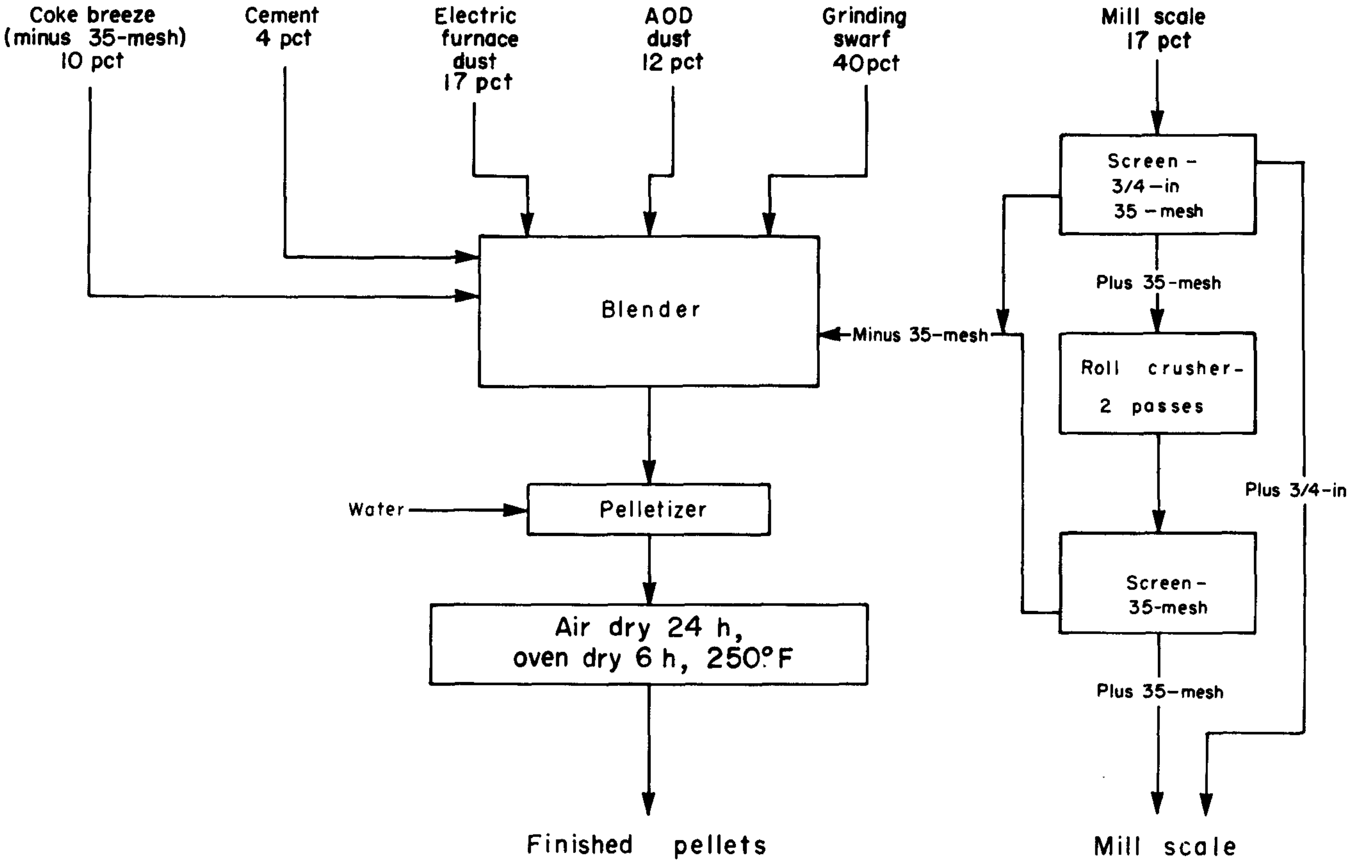

FIGURE 1.—Flow diagram for laboratory agglomeration of four stainless steelmaking wastes by pelletizing with coke breeze reductant and cement binder. Pellets of somewhat reduced but generally adequate strength can also be produced by air drying only.

Pellets of the four-waste mixture were made in a 36-in-diam drum pelletizer and required the addition of about 12 pct water to the blended mix in order to form 3/8- to 3/4-in-diam pellets. The pellets were first air-dried for 24 h, then oven-dried at 250° F for 6 h. Drying at higher temperatures tended to result in spalling. The pellets had 5- to 30-lb crushing strength, which was sufficient for the limited amount of handling required. When the wastes listed in table 1 were mixed in the indicated proportion and pelletized, the resultant pellets plus oversize mill scale analyzed roughly 10 pct Cr, 4 pct Ni, and 1 pct Mo.

Experience has shown that it is not always necessary to oven-dry the pelletized waste mix. Most of the laboratory heats made in the latter part of the testing program were made using pellets that were air-dried only. The experiments included adding pellets to the furnace that were only 2 h old and very wet. These were rolled at a uniform rate down a conveyor and dropped through the furnace top onto the melt surface. As much as 13 pct of the melt charge (the most tried) was added in this manner without problem.

Other efforts were made to simplify the pelletizing procedure. For some trials, the cement binder was eliminated from the pellet mix to decrease slag volume. No difficulty was encountered in making pellets; however, after storage for several weeks, the pellets tended to spall and powder. For extended storage, some binder appears necessary. Adding 1 to 2 pct bentonite resulted in acceptable pellets that were stable for longer periods than when no cement was added. It was found that the mill scale could be crushed and screened through 20-mesh or even 10-mesh (rather than 35-mesh) screens with no apparent effect on pellet properties.

Arc Furnace Smelting of Stainless Steelmaking Wastes

Earlier tests in an induction furnace (*13*) indicated that numerous combinations of pellet compositions could be smelted, with the C in the coke breeze reducing essentially all the oxides of Fe and Ni and about half of the Cr oxide. It was observed that ferrosilicon could then be added to the molten bath to scavenge much of the remaining Cr from the slag.

The procedure for the 100-lb arc furnace melts began with preheating the furnace refractories for 1 h, followed by charging 90 to 95 lb of pellets over a 45-min period. The 5- to 10-lb portion of loose (plus 35-mesh) mill scale was then added, and the furnace temperature was brought to at least 2,950° F. At this point, 3.0 pct Si, as ferrosilicon (75 pct Si), was added to the melt and stirred vigorously to enhance mixing and effect additional reduction of Cr oxide from the slag. The melt was allowed to reach 2,950° to 3,100° F before tapping. The ingots accounted for about a 60-pct metal yield from the wastes charged. The slag represented some 10 to 15 pct of the original charge weight.

Further laboratory testing indicated that 0.3 pct Al (as a percentage of charge weight), added as shot, accomplished roughly the same amount of reduction as 3.0 pct Si. Table 2 shows results of tests comparing the use of Fe-Si, Fe-Si-Al, and Al. Other heats were made without Si or Al reductants; the melts were held similarly for 20 to 30 min before tapping, within the range 2,850° to 3,050°F. Only those held 30 min at 3,050°F showed improved Cr recovery relative to that for the lower temperatures. The reduction of the Cr oxide is related to time and temperature, as well as the type and amount of reductant.

Some stainless producers had indicated that they had been stockpiling mill scale. Samples were obtained from five companies. Partial analyses are shown in table 3. The scale from company C originated from ferritic stainless production; the others were from austenitic stainless production. The mill scales were mixed with other wastes and pelletized in two approximate compositions, as shown in table 4.

The values are arbitrary, but those for the "low" scale composition are intended to represent an approximate generation rate in a plant producing and segregating all four wastes. The "high" scale composition reflects a situation wherein stockpiled mill scale would be used up at a faster-than-generated rate. Small-scale pelletizing tests indicated that pellets containing as much as 55 pct mill scale could be made, but 35 pct was a more practical value from the standpoint of a higher proportion of fines present and better pellet formation and strength.

The mixtures were prepared, blended to the compositions shown for low and high mill scale, and arc-furnace-melted as described previously. The slag was reduced with ferrosilicon. The results obtained from the group representing "low" mill scale (17.4 pct) pellets are shown in table 5.

It should be noted that laboratory smelting tests involved a charge consisting of 90 to 95 pct pellets and 5 to 10 pct loose mill scale. Some producers might have furnace capacity available to intermittently melt all-pellet charges for metering of hot metal to production heats. This method could also help reduce large backlogs of wastes. However, in normal industrial practice, it is anticipated that only 10 to 20 pct of the furnace charge would consist of pelletized wastes, to replace a portion of the scrap charge. This is the most economical and least energy-intensive approach and can readily match or exceed waste generation rates. Excess reductant normally available in production heats can also assist metal recoveries from the wastes. Under these circumstances, the slag generation would not be as much as indicated for the heats in table 5 but should be near to, although perhaps toward the high end of, normal ranges.

The experiments with pelletized mill scale indicated that 82 to 92 pct of the Cr could be readily recovered. Additional reductant and/or additional heating would increase the recoveries. Nickel recovery was, as expected, much higher. The results of the melting trials on "high" mill scale (35.0 pct) mixtures indicated a Cr recovery 5 to 10 pct lower than for "low" (17.4 pct) mill scale mixtures. This was due, at least in part, to the fact that the higher mill scale content resulted in a somewhat greater slag volume; that is, even with the same Cr slag solubility per unit volume, more total Cr partitioned to the higher volume slag.

With other factors being equal, the Cr solubility in slag decreases with increased slag basicity (*12*), with slag basicity being defined as the ratio of percentage CaO plus MgO to SiO_2. The increased slag volume and weight brought about by the increased lime addition needed to increase the basicity may, however, offset any gain in reduced Cr solubility when considering the total Cr in the slag.

TABLE 2.—Recovery of Fe, Cr, and Ni from pelletized wastes after the smelting addition of various reductants[1]

Reductant added, pct	Ingot analysis, pct				Recovery, pct			Metal recovered pct of charge
	Fe	Cr	Ni	Si	Fe	Cr	Ni	
3 Si[2]	61.9	14.2	7.1	6.9	85.3	91.5	99.3	64.6
0.6 Si, 0.3 Al[3]	69.6	15.1	6.9	2.3	97.1	84.7	90.5	58.2
0.3 Al[4]	69.9	15.5	7.1	.7	99.9	93.4	97.8	61.8

[1] In addition to the 10 pct coke breeze reductant in pellets.
[2] As ferrosilicon (75 pct Si)
[3] As Al-containing ferrosilicon (20 Al-40 Fe-40 Si).
[4] As Al shot.

TABLE 3.—Partial analyses of stainless steel mill scale samples, percent

Company designation	Fe	Cr	Ni	Mo
A	54.8	8.6	3.9	0.48
B	51.9	11.2	7.0	.47
C	62.7	7.6	.5	.22
D	49.4	8.4	3.7	.16
E	56.2	9.1	3.0	.66

TABLE 4.—Composition of pellets with low and high mill scale content, percent

Component	Low mill scale	High mill scale
Mill scale	17.4	35.0
EF dust	17.4	12.6
AOD dust	13.0	9.5
Grinding swarf	39.1	28.0
Coke breeze	8.7	10.5
Cement	4.4	4.4
Total	100.0	100.0

TABLE 5.—Results of smelting pelletized waste mixtures containing mill scale[1] obtained from five stainless steel producers

Company designation	Ingot analysis, pct			Recovery, pct			Ingot as pct of charge	Slag as pct of charge
	Cr	Ni	Mo	Cr	Ni	Mo		
A	16.0	7.2	1.00	92.6	100.0	74.5	60.0	14.0
B	16.1	7.7	.80	87.7	90.7	91.9	47.9	13.0
C	14.5	5.9	.79	86.1	97.9	91.5	56.9	16.9
D	14.9	7.1	.83	82.3	93.2	63.6	55.9	19.3
E	14.9	6.2	.92	93.0	99.0	100.0	63.4	19.0

[1] 17.4 pct mill scale in the pellets; other ingredients were (in pct) 17.4 EF dust, 13.0 AOD dust, 39.1 grinding swarf, 8.7 coke breeze, and 4.4 cement.

It remains to be conclusively demonstrated to what extent some of the minor metals such as Zn and Pb in the electric furnace dust will build up in the baghouse dust with repeated pelletizing and refurnacing. The longer term concentration of minor elements (rate and extent) in recycled furnace dust will not be clarified until results are reported for campaigns extending over a substantial number of heats, with careful analysis of all charge and product materials.

Some extended campaigns have been made to recycle baghouse dusts to the furnace without added C or other reductant, with the main objective being to dispose of hazardous waste by slagging as an alternative to landfilling, rather than gaining metal recovery. One firm has been recycling pelletized minimill carbon steelmaking furnace dust in this manner (*10*). Even without reductant added with the pellets, some increased Fe yield has apparently been realized in these instances, evidently by supplying some "equilibrium" slag Fe oxide requirements from the furnace dust rather than by Fe oxidation from the melt. Some limited reduction may be expected from excess reductant (Si and C) present in the melt. For further information on the composition and nature of carbon and stainless steelmaking furnace dusts, the reader is directed to the comprehensive arc furnace dust program conducted by Lehigh University and the Bureau of Mines, with U.S. Department of Commerce funding, under AISI collaboration and coordination (*9*).

LARGE-SCALE DEMONSTRATION HEATS

All-Pellet Heats

The procedures derived in the laboratory experiments were tried on a larger scale in the form of a 1-st heat of the pelletized waste mixture (*1*), which was made by Union Carbide Corp., Niagara Falls, NY. When it was evident that recoveries from this heat were sufficiently good, plans were formulated for substantially larger scale industrial trials.

The first of these large-scale demonstration trials was an all-pellet heat of approximately 12.5 st made in the production plant of Joslyn Stainless Steels. The wastes, generated during normal operations at Joslyn, were pelletized by a contractor in accordance with specifications developed at the Bureau's Rolla Research Center. The pellets ranged from 3/8- to 1-in diam and represented the mixture indicated earlier as "low" (17.4 pct) mill scale. The pellets analyzed 42.5 pct Fe, 9.6 pct Cr, 4.0 pct Ni, and 0.7 pct Mo.

The charge to the furnace consisted of approximately 20,900 lb pellets and 1,100 lb oversize mill scale along with 0.5 st lime. Several hundred pounds of steel punchings had been added at the outset to help strike an arc. When the charge was fully molten, the melt was sampled over a 30-min period. An addition of 1,320 lb ferrosilicon (50 pct Si) was made to reduce Cr oxide remaining in the slag. Improved contact between the ferrosilicon and slag was achieved by stirring with an argon lance. The melt was tapped through the slag into a ladle from which it was poured into 14- by 14-in molds. The master alloy ingot produced weighed 12,300 lb and analyzed, in pct, 76.7 Fe, 11.8 Cr, 6.5 Ni, 0.8 Mo, 0.9 Mn, 4.3 Si, and 3.2 C. These values represented recoveries of (in pct) 86.1 Fe, 68.7 Cr, and 92.0 Ni. As shown in table 6, power consumption was 1.05 kW•h/lb of metal tapped.

The Cr recovery was lower than that experienced in smaller scale tests but was considered good for a "one-shot" experiment. Temperature was probably responsible for the lower recovery. After the ferrosilicon addition, the bath temperature of 2,750° F was some 200° F below the temperature of most of the laboratory heats. Nevertheless, Ni, the metal of highest total value, reported to the ingot as expected.

An 8,000-lb portion of the master alloy ingot from the all-pellet heat was incorporated into a commercial 19-st heat (heat 2, table 6) of type 316 stainless steel. The master alloy was completely compatible with the balance of the charge, principally stainless scrap. The heat was completed within the expected time, power consumed was normal, and there were no problems in either the arc furnace melting or AOD refining. The remainder of the ingot material was used in another commercial heat with equally good results.

Pellet-Plus-Scrap Heats

At this point, rather than optimizing the making of all-pellet heats, it was decided to go directly to the overall simpler and more economical introduction of waste pellets into the production arc furnace in lieu of part of the normal scrap charge. It was judged that the advantages of this approach would be (1) lower energy consumption, (2) simpler processing without intermediate master alloy ingot requiring remelting, and (3) variation of the quantity and composition of waste pellets as dictated by needs. It was realized that careful attention would have to be given to the furnace charge to accommodate the pellet waste ingredients and their products. However, since the makeup of furnace charges is commonly computer calculated, programs can be readily adjusted to account for this unconventional raw material.

Two heats were made with the remaining pellets from the Joslyn all-pellet heat and are hereafter referred to as "low-scale" pellets. Tonnage quantities of pellets also were produced by a contractor with substantially augmented percentage of mill scale. This "high-scale" composition was

TABLE 6.—Comparison of charge weight, metal tapped, and energy requirements for Joselyn demonstration heats 1 (all pellet) and 2 (master alloy)

Heat	Type of heat	Charge, lb		Waste, pct	Metal tapped, lb	Power consumption,[1]
		Total	Waste			
1	All pellet	25,385	22,010	86.7	12,320	1.05
2	Scrap plus heat 1 master alloy	42,025	7,980	19.0	39,700	.254

[1] Per pound of metal tapped.

TABLE 7.—Comparison of charge weight, metal tapped, and energy requirements for Joslyn demonstration heats 3 to 7 (pellets partly replace scrap)

Heat	Type of heat	Charge, lb		Waste, pct	Metal tapped, lb	Power consumption,[1] kW·h	Tap temp, °F
		Total	Waste				
3	Scrap plus "low-scale" pellets ..	41,790	5,970	14.3	38,500	0.244	2,920
4	..do..........................	41,600	7,870	18.9	36,500	.260	2,960
5	Scrap plus "high-scale" pellets .	41,940	6,300	15.0	38,000	.263	3,000
6	..do..........................	43,490	6,250	14.4	36,600	.259	2,950
7	..do	42,900	8,200	19.0	36,300	.261	2,940

[1]Per pound of metal tapped.

TABLE 8.—Recovery of Cr, Ni, and Mo from commercial pellet-plus-scrap heats 3 to 7, percent

Heat	Type of heat	Cr	Ni	Mo
3	Scrap plus 14 pct "low-scale" pellets ..	93.0	99.7	99.9
4	Scrap plus 19 pct "low-scale" pellets ..	93.7	89.7	95.0
5	Scrap plus 15 pct "high-scale" pellets .	97.3	99.1	93.2
6	Scrap plus 14 pct "high-scale" pellets .	90.8	91.9	82.8
7	Scrap plus 19 pct "high-scale" pellets .	91.4	92.3	84.5

tested to simulate consumption of substantial quantities of stockpiled mill scale. The makeup of the "high-scale" pellets follows:

	Pct
Mill scale	30
EF dust	13
AOD dust	9
Grinding swarf	33
Coke breeze	11
Cement	4

The pellet composition (including oversize mill scale) was, in pct, 39.2 Fe, 8.9 Cr, 3.7 Ni, and 0.5 Mo.

Five type 316 stainless steel heats were made in a 19-st production furnace, in which pelletized wastes constituted 14 to 19 pct of the nominal charge. The pellets were added to the arc furnace concurrently with the stainless scrap, making it unnecessary to backcharge. In all heats, only that quantity of ferrosilicon normally added to "quiet" such scrap melts was added. This ranged from 0 to 300 lb. The slag volume in each case was considered within the normal range for production heats. (With an extended campaign, some increased slag volume can be expected when partly replacing relatively clean scrap with pelletized wastes, other factors being equal.) Pertinent statistics from the five heats are presented in table 7. All heats met required specifications after processing through the AOD vessel and were marketed as commercial bar, rod, or forging ingot. Table 8 gives the recoveries of Cr, Ni, and Mo, which, on the average, were considered equivalent to the customary values for all-scrap heats. Iron recoveries were consistently substantially >90 pct.

Metal Value of Pelletized Wastes

Technically and mechanically, this recycling scheme has been shown to work well. The question naturally arises as to whether it is also economical. The Bureau completed internal studies of capital and operating costs for a plant addition producing pellets from wastes such as flue dusts, mill scale, and/or oily swarf. The cost for a 15-st/d pelletizing capacity was estimated at $1,004,000 for oven drying of pellets and $554,000 for air drying. Estimated operating cost based on 1-shift-per-day, 5-d/wk operation (20-yr life) was estimated at about $122/st for oven drying and $46/st for air drying.

This can be contrasted to the contained value of the Cr, Ni, and Mo in the pellets. The value depends on the current price of ferroalloys or of appropriate scrap, particularly stainless steel (18 Cr-8 Ni) scrap. A charge is sometimes added for iron units, but this has not been the case with the recent relatively depressed scrap market. On the basis of only Cr, Ni, and Mo for a waste mixture similar to that employed in the trials at Joslyn Stainless Steels (low mill scale), with approximate contained metal values of $0.42/lb for Cr, $3.18/lb for Ni, and $4.60/lb for Mo (mid-1984 ferroalloy contained-metal values), the pellets would have a value of over $390/st. Deducting the net operating cost of some $122/st for oven drying or $46/st for air drying indicates a net gain of some $0.13 or $0.17/lb, respectively–a significant economic potential.

CONCLUSIONS

It has been shown that stainless steelmaking wastes such as flue dusts, mill scale, and grinding swarf can be pelletized and reduced in the arc furnace as a means of recovering the contained scarce and valuable metals, while coincidentally solving problems of storage and waste disposal. The recovery procedure utilizes the reduction of metal oxides with C during the arc furnace melting, followed by a scavenging slag reduction of additional Cr oxide with ferrosilicon or Al.

One variation of the processing involves preparation of all-pellet smelting heats to produce master alloy ingot for recycle. This may be appropriate if furnace capacity is available in slack periods and large waste backlogs exist.

Alternatively, and recommended as being more economical, the waste-bearing pellets can be added directly to the arc furnace as some 10 to 20 pct of the total charge for production heats in lieu of part of the usual scrap or alloy charge required. The addition rate will depend on factors such as the rate of waste generation, waste backlog accumulation, and alloy product mix at a particular plant.

The dusts, scale, and swarf can be mixed and pelletized with little difficulty, providing both a means for adding C to the mix and a vehicle for charging to the furnace. Numerous varied combinations of pellet mix have been shown to be possible. Only conventional equipment is needed for agglomeration.

Usual recoveries of substantially greater than 90 pct of the Ni and Fe have been attained, and some 90 pct of the Cr and Mo appear consistently recoverable with proper control of variables. Other metals such as Mn are coincidentally recovered. Conventional arc furnaces were used throughout the testing.

The fact that this technology is readily transferable to an industrial scale was shown by the successful making of a number of demonstration heats ranging in size from 12.5 st for an all-pellet heat to about 19 st for a series of pellet-plus-scrap heats. The master alloy ingot from the all-pellet demonstration heat was used to make commercial stainless steel products without difficulty. No problems were encountered in the commerical stainless production heats to which up to 19 pct pellets were added in lieu of the normal scrap charge.

When the particular waste combination outlined in this report is pelletized for recycle as a scrap substitute charge material, the pellets have a net value of more than $0.13/lb for oven drying or $0.17/lb for air drying, which implies an economically viable process.

Test results also indicate that a wide compositional variation of specialty steelmaking wastes can be incorporated into pellets for furnace charging.

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MATERIALS SESSION

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AN OVERVIEW OF CHROMIUM NEEDS AND USES

By Howard W. Leavenworth, Jr.[1]

ABSTRACT

The importance of maintaining viable ferrochromium and stainless steel industries in the United States is stressed, as is the need for developing substitute materials for those containing large quantities of Cr, including superalloys, refractories, and coatings as well as stainless steels. The availability of Cr-free substitutes for superalloys would make the United States stronger, but the most urgent need is for improvements in scrap identification and recycling and in near-net-shape technology. The need to make Cr-bearing materials last longer in service through research on wear and corrosion also is emphasized.

INTRODUCTION

One purpose of this presentation is to provide an overview of the many uses for Cr. Another purpose is to serve as an introduction to the materials session that deals with Cr as an alloying element either in coatings or in new alloys that contain less Cr than do the materials they are designed to replace in the event of a disruption of Cr supplies.

Topics in the session will also include Cr usage in wear-resistant materials and in refractories. Wear represents more than $100 billion annual loss to our economy, and it is an especially serious problem in the mining industry, where strategic metals, such as Cr, are used in large machinery. Figure 1 shows worn-out cone crushers near a mine in Colorado. The stack of cones shown here represents less than a 1-yr supply. They also represent a loss of strategic metals unless that material is recycled. Dr. Blickensderfer will have much to say to us on the subject of wear.

Mr. Arthur Petty will talk to us about refractories. Of the Cr ore that was imported into this country from 1979 to 1983, 17 pct (*1*) was used for making refractories. Mr. Petty's research deals with lowering the Cr content of refractories, used mainly for making refractory brick to line metallurgical furnaces.

Abbreviations Used in This Paper

lb	pound
mt	metric ton
pct	weight percent
st	short ton
yr	year

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FIGURE 1.—Worn cone crusher liners.

CHROMIUM USAGE

As discussed earlier by Dr. John Papp, the chromium commodity specialist for the Bureau of Mines, Cr has a wide range of uses in three primary consumer groups: refractories, chemicals, and metals and alloys.

In 1978, the National Academy of Sciences published an NMAB report entitled "Contingency Plans for Chromium Utilization" (*2*). Table 1 in that report summarized the potential savings of Cr by substitution and an estimate of the time to conduct necessary research and development activities. Particularly interesting is the amount of Cr that was identified as "irreplaceable," 35 pct of the total or 40 pct of that used in metallic alloys. The conclusion that this much Cr is irreplaceable was based on "current state of knowledge." The NMAB publication was invaluable, and it still is today, but this conference will supplement that report by showing that more Cr can be saved through substitution than was realized 7 yr ago.

The most critical use of Cr from a national defense point of view is in the making of superalloys for airplane engines (or in actuality, for making scrap). The weight of semifinished superalloy products shipped is only one-third of the weight of the alloy melted (*3*). In fact, some complex machined components may have a final product yield of less than 10 pct. The 14,030 lb of materials that go into making an engine for a modern fighter plane are listed in the caption of figure 2. This engine weighs only about 3,000 lb,[2] so it is evident that much of the Cr and other strategic alloying elements are not utilized efficiently. Therefore, if the Cr that goes into making airplane engines is to be conserved, not only should the technology of recycling superalloy scrap be continually updated, but it would be more productive to concentrate on lowering the production of scrap. The latter can be done by near-net-shape technology.

As is well known, the Bureau of Mines has conducted research on recycling for many years. Mr. Leander Neumeier will talk about recycling stainless steel making wastes. As far as superalloys are concerned, the Bureau contracted for studies on them several years ago (*4-5*), and now scientists at the Bureau's Avondale (MD) Research Center are working on various scrap identification techniques, including one based on specific characteristics of sparks emitted by a simple grinding procedure.

The use of Cr for making the superalloys that go into airplanes is obviously important, but that is not the greatest usage for this critical and strategic metal. Stainless steels typically account for 70 pct of the metallurgical-grade Cr imported into the United States (*6*).

The consumption of Cr ferroalloys, metal, and other Cr-containing materials by end use follows: stainless and heat-resisting steel, 81 pct; full-alloy steel, 9 pct; superalloys, 3 pct; and other alloys, 7 pct. In 1984, estimated Cr contained in purchased stainless steel scrap amounted to 18 pct of Cr demand (*7*). This shows that some progress is being made in recycling Cr-containing materials, because only 9 pct was recycled in 1980 (*8*). Nevertheless, improved recycling technology is needed, particularly for obsolete and contaminated special alloy scrap and waste.

Stainless steels are made from scrap and ferrochromium, not Cr metal. In 1960, 92 pct of all ferroalloys consumed in the United States were domestically produced. By 1970, that figure was down to 86 pct; by 1980, it was down to 55 pct; by 1981, it was down to 45 pct; and by 1982, it was at 35 pct (*7*). The point is, the United States has not been importing chromite ore; domestic steel plants have been importing ferroalloys. Domestic smelters have not been able to compete with modern smelters located close to Cr ore fields. Ferrochromium production costs, which include power, labor, and transportation, are lower in countries where Cr ore is mined than they are in the United States (*9*). Also, national policies in the producer countries often provide economic incentives for local processing of ferroalloys. But these advantages are not insurmountable, and they may not last much longer.

The growing need to blend together ores that have different chemical and physical properites means that all producers will need to import ores. Eventually all producers will pay the additional cost of transporting ore (*10*). Labor

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[2] Discussion between the author and engineers at Pratt and Whitney Aircraft Co., East Hartford, CT.

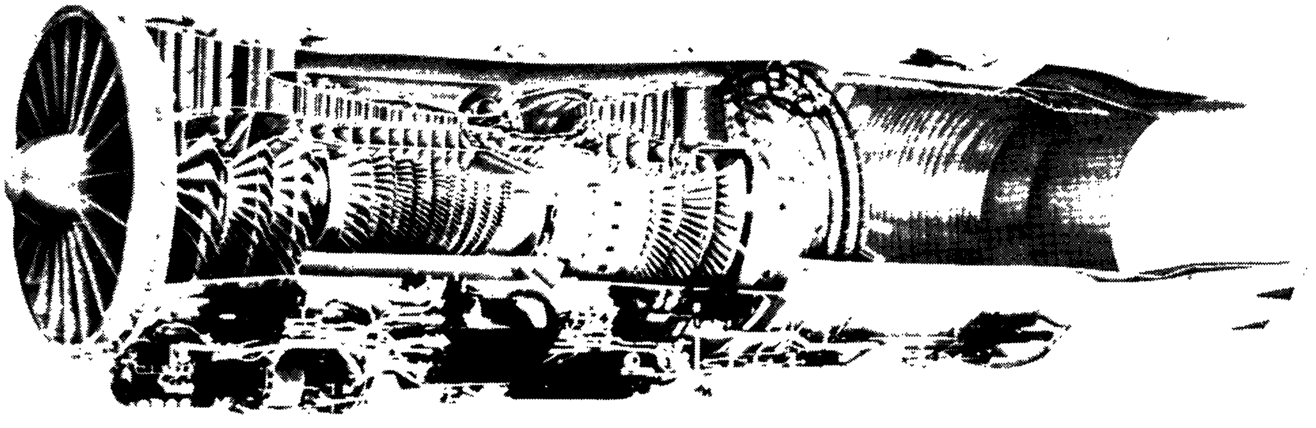

FIGURE 2.—The metals that go into making an engine for a modern fighter plane include 5,366 lb Ti, 5,204 lb Ni, 1,656 lb Cr, 910 lb Co, 720 lb Al, 171 lb Cb, and 3 lb Ta. Most of these materials are lost during machining.

rates in many producer countries are low now, but are likely to increase rapidly, thereby narrowing the cost advantages of foreign labor. If U.S. industry can improve its furnaces to reduce energy consumption and automate our processing, there is a good chance to revitalize the ferrochromium industry in this country.

Evidently the Federal Government does not want to lose this vital industry. In 1982, domestic ferrochromium producers were given the opportunity to process up to half of the General Services Administration (GSA) chrome ore stockpile over a 10-yr period (*10*). In 1984, the Undersecretary of Defense for Research and Engineering, Richard DeLauen, signed a Government procurement policy requiring defense contractors to buy high-C ferrochromium only from U.S. producers even though there was no ongoing domestic production at the time of signing. Mr. DeLauen emphasized that ferrochromium "is our most critical material–period." He noted that the national defense stockpile held nearly 2.5 million st Cr ore "which would be worthless in an emergency situation if there were no way to convert it to ferrochromium, an essential ingredient in special grades of steel" (*11*). More recently, the GSA proposed a "Buy America" clause in the Federal Government's procurement code, requiring that all purchases of Cr for stockpile purposes be made from the domestic industry(*12*).

On the suject of ferrochromium, an unusual trend has started in Japan and Europe. The Ministry of International Trade of Japan (MITI) is requiring that ferrochromium manufacturers reduce capacity by 10 pct by 1988 (*13*). This MITI action is a departure from the traditional Japanese trade position of importing raw materials and exporting finished goods.

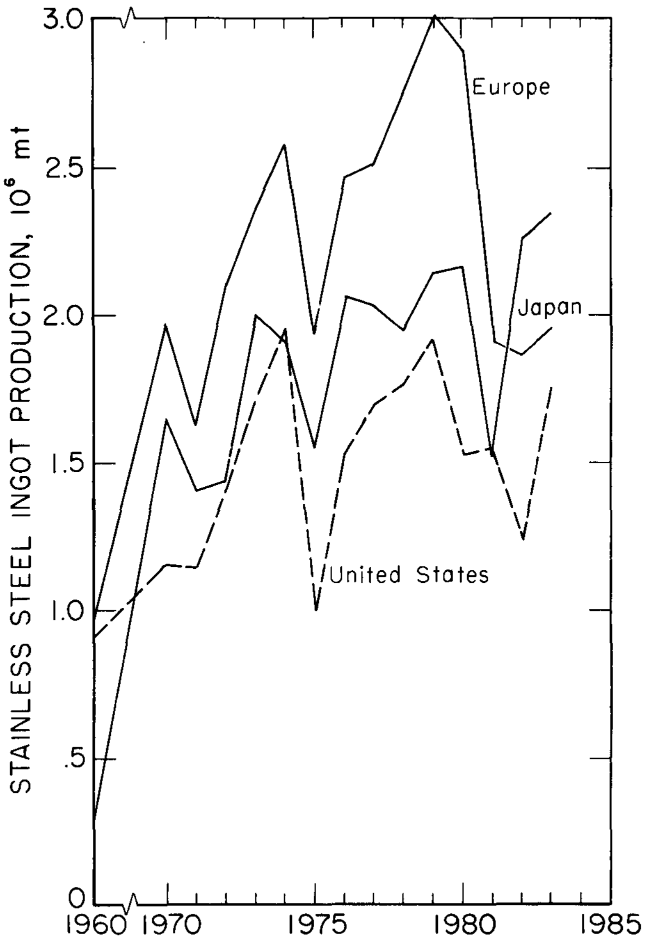

FIGURE 3.—Stainless steel ingot production by the United States, Japan, and the European Economic Community.

Shutdowns have been common in the ferrochromium industry, but what about the steel industry? The capacity of the United States to produce stainless steel ingots from scrap and ferrochromium is about 2 million mt. That maximum capacity was almost reached in 1974 and 1979, as shown in figure 3. However, note that both Japan and the European Economic Community (EEC) exceed domestic capacity. Japan has reduced its steel exports, and most steel exports from the EEC are being restrained by a 1982 agreement. Actually, these restraining agreements only increased imports from Canada and from developing countries such as Korea, Mexico, and Brazil. The point being made here is that the United States has actually gone beyond the point of importing ferrochromium and is now increasing its imports of stainless steels. Everyone at this conference knows what this means in terms of jobs, reduced salaries, mergers, plant closures, and even bankruptcy for some. Potential substitutes for Cr in stainless steels and other products will be discussed during this seminar, but we should be aware of what is happening to one of our basic industries that has served this country well over the years. Good substitute materials are being developed, as we shall learn today and tomorrow, but let's not forget that we need the capacity to make them.

The next speaker will be Mr. Gerald Smith of the Bureau's Avondale Research Center, who will talk about a technique for conserving Cr by electroplating a wide range of Fe-Ni-Cr alloy compositions. Thus, to conserve Cr, a complex shape can be cast or forged out of plain carbon steel, for example, and its surface protected against corrosion by electrodepositing a stainless-steel-type coating on all exposed surfaces. In a similar manner, strip material can be protected from corrosion by cladding. Cladding research was done here at the Albany Research Center, and if anyone is interested, a publication on this subject (*14*) is available.

Casting research also is being done here. Following Mr. Smith's paper on coatings will be a presentation by Mr. Jeffrey Hansen on new casting techniques that conserve Cr in equipment used by the mining industry. Be sure to note the unique use of styrofoam patterns when Mr. Hansen describes this casting technique.

After these two talks, the one on coatings and the one on castings, the behavior of new materials that could substitute for some of the high-Cr alloys being used today will be discussed. Dr. David Flinn of the Avondale Research Center will talk about new surfacing techniques such as laser glazing, sputtering, and nitriding. Dr. Flinn's interest is in understanding the basic surface properties of materials made by these techniques. He also will talk about conserving Cr during the many pickling operations that are used between passes when stainless steel is rolled into sheet or plate.

Following Dr. Flinn's presentation, Dr. John Dunning will tell us about new alloys being developed at the Albany Research Center. Dr. Dunning's current interest is in the oxidation behavior of these materials, but he also will discuss sulfidation and aqueous corrosion.

CONCLUSION

All of these presentations represent more than just opportunities for learning about techniques for conserving Cr. They also represent opportunities for an exchange of ideas. We in the Bureau of Mines hope that each one of you will take back with you at least one idea that will help our Nation's basic industries that depend on uninterrupted supplies of Cr, whether it be for chemicals, refractories, or metals and alloys.

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CHROMIUM ALLOY COATINGS—A NEW METHOD OF PREPARATION

By G. R. Smith,[1] J. E. Allison, Jr.,[2] and W. J. Kolodrubetz[3]

ABSTRACT

As part of a research program on conservation of critical metals, a modified aqueous electrodeposition method for preparing stainless-steel-type alloy coatings has been studied. This method involved mechanically suspending Cr powder (av 2-μm diam) in a ferrous-nickelous sulfate electroplating bath and occluding the Cr particles in the electrodeposited Fe-Ni alloy matrix. Subsequent heat treatment of the resulting composite coating formed the ternary alloy. The occlusion process was affected by the quantity of Cr powder suspended as well as by the microstructure and composition of the electrodeposited matrix. The largest quantity of Cr was occluded when the electrodeposited matrix exhibited a dual-phase γ(Ni,Fe)-α(Fe,Ni) microstructure. Coatings with up to 21 pct Cr have been deposited from an electrolyte containing 20 vol pct suspended Cr powder. Heat treatment at 1,100° C for 8 h effectively homogenized the composite coating. A 55 Fe-29Ni-16Cr alloy produced by this method corroded at a rate of only 0.7 mm/yr during 240 h of exposure to boiling 65-pct HNO_3. Applicability of this method to the preparation of electroforms has also been demonstrated.

INTRODUCTION

It has been known for many years that insoluble particles present in a electrolyte during plating can be occluded in the electrodeposited metal. In recent years, occlusion has been used advantageously to produce electrodeposited composite coatings called cermets (*1-12*). These composites contain a variety of ceramic particles including oxides, nitrides, and carbides that serve to improve the oxidation or wear resistance of the electrodeposit. A possible extension of the use of the occlusion method is in the production of composite coatings containing metal particles. Subsequent heat treatment can yield alloy coatings, such as stainless steels, that would be very difficult to prepare by conventional aqueous electrolysis methods. Although two reports have suggested that the occlusion method could be used to produce stainless steel coatings (*13-14*), they did not give specific details of the method or evidence of its feasibility. Initital research results obtained by the Bureau of Mines (*15*) provided experimental evidence of the feasibility of this method.

The present paper presents further results of experiments conducted to produce stainless-steel-type Fe-Ni-Cr alloy coatings using the particle occlusion heat-treatment method. It addresses the effects of current density, electrodeposit composition and microstructure, and concentration of suspended Cr powder on the quantity of Cr particles occluded in the composite coatings, and includes a discussion of the heat treatment required to homogenize the composite coatings as well as an evaluation of the corrosion resistance exhibited by the resulting ternary alloy.

Abbreviations Used in This Paper

A/dm²	ampere per decimeter squared
°C	degree Celsius
°C/h	degree Celsius per hour
dm²	decimeter squared
h	hour
mm	millimeter
mm/yr	millimeter per year
μm	micrometer
mol/L	mole per liter
mol pct	mole percent
pct	weight percent
rpm	revolution per minute
vol pct	volume percent

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EXPERIMENTAL WORK

ELECTROLYTIC CELL

A polymethylmethacrylate plating cell, 100 mm diam by 135 mm high (fig. 1), was used to prepare the composite coatings. Two electrolytically pure Ni anodes and two 99.6-pct-pure Fe anodes were placed opposite each other and positioned 30 mm from a cold-drawn AISI 1020 steel rod cathode. The diameter of the cathode was 10 mm, and the effective plating area was 0.13 dm^2. The quantity of current passing through each set of anodes was controlled by two dc power supplies connected in parallel to the cell. This permitted accurate control of the dissolution and deposition rates. Total charge passed through the cell was measured using an ampere-hour meter.

The composition of the electrolyte used in the preparation of the composite coatings is listed in table 1. Although the total metal ion concentration was maintained at 1.78 mol/L, the relative ratio of Fe^{2+} and Ni^{2+} in the electrolyte was varied in order to change the composition of Fe and Ni in the electrodeposit. Sodium saccharin was added to relieve internal stresses in the electrodeposit.

TABLE 1.—Electrolyte composition

Constituent	*Conc, mol/L*
Total metal ion (Fe^{2+}, Ni^{2+})	1.78
Sulfate ion	1.70
Chloride ion	.18
Boric acid	.65
Sodium saccharin	.04

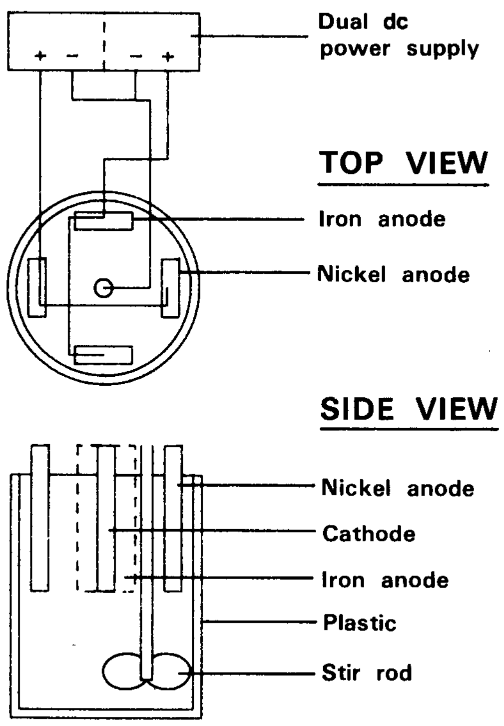

FIGURE 1.—Schematic of electroplating assembly.

Chromium powder was suspended in the electrolyte by a motor-driven, 50-mm-diam, polypropylene propeller, positioned near the base of the cell. A rotation speed of 360 rpm was employed in this study.

Commercially available Cr powder (99.86 pct Cr) was used in the preparation of the composite coatings. The particle size was ~ 2μm (fig. 2) as determined by image analysis methods using the transmission electron microscope. The Cr particles have been observed to have a predominantly spherical shape.

EVALUATION OF COMPOSITE COATINGS

The composition of the composite coatings was determined by dissolving the Fe-Ni alloy matrix in 10-pct HNO_3 and recovering the insoluble Cr particles by filtration. Dissolution of the coating was carried out after mechanical removal from the cathode. The concentration of the dissolved Ni was determined by atomic absorption. The Fe concentration was calculated by difference. X-ray diffraction methods were used to elucidate the microstructure of the composites. Scanning electron microscopy (SEM) and energy-dispersive X-ray analysis (EDAX) were used to examine the distribution characteristics of the Cr powder within the electrodeposited matrix.

HEAT TREATMENT OF COMPOSITE COATINGS

Heat treatment was carried out at 1,100° C in an Astro vacuum furnace,[4] model 1100 V, using a heating rate of 60° to 120° C/h. After heat treatment, the samples were allowed to cool in the furnace at a typical rate of ~ 1,000° C/h. Each sample was then reheated to 1,100° C under an N atmosphere and quenched in water to prevent segregation of carbides and possible formation of sigma (σ) phase.

EVALUATION OF HEAT-TREATED COATINGS

Two types of samples were prepared for post-heat-treatment evaluation of the Fe-Ni-Cr alloy coatings. The first type had been removed from the substrate prior to heat treatment. This provided a means for evaluating the alloy independent of any effects related to substrate-coating interdiffusion. Evaluation consisted of exposing the alloys to boiling 65-pct HNO_3 in five 48-h stages (Huey test for stainless steels). Comparison of the corrosion rates of coatings with different heat treatments was then made. In the second type of sample the coating and substrate remained an integral unit during heat treatment. This type of sample provided a means for determining the extent of substrate-coating interdiffusion during heat treatment and the corresponding capability of an Ni barrier coating to limit this interdiffusion. Prior to deposition of the Ni barrier coating from a standard Watts Ni electrolyte, the substrate was acid-cleaned in a 10-pct HNO_3 solution, then in a 25-pct HCl solution, followed by a water rinse.

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[4] Reference to specific products does not imply endorsement by the Bureau of Mines.

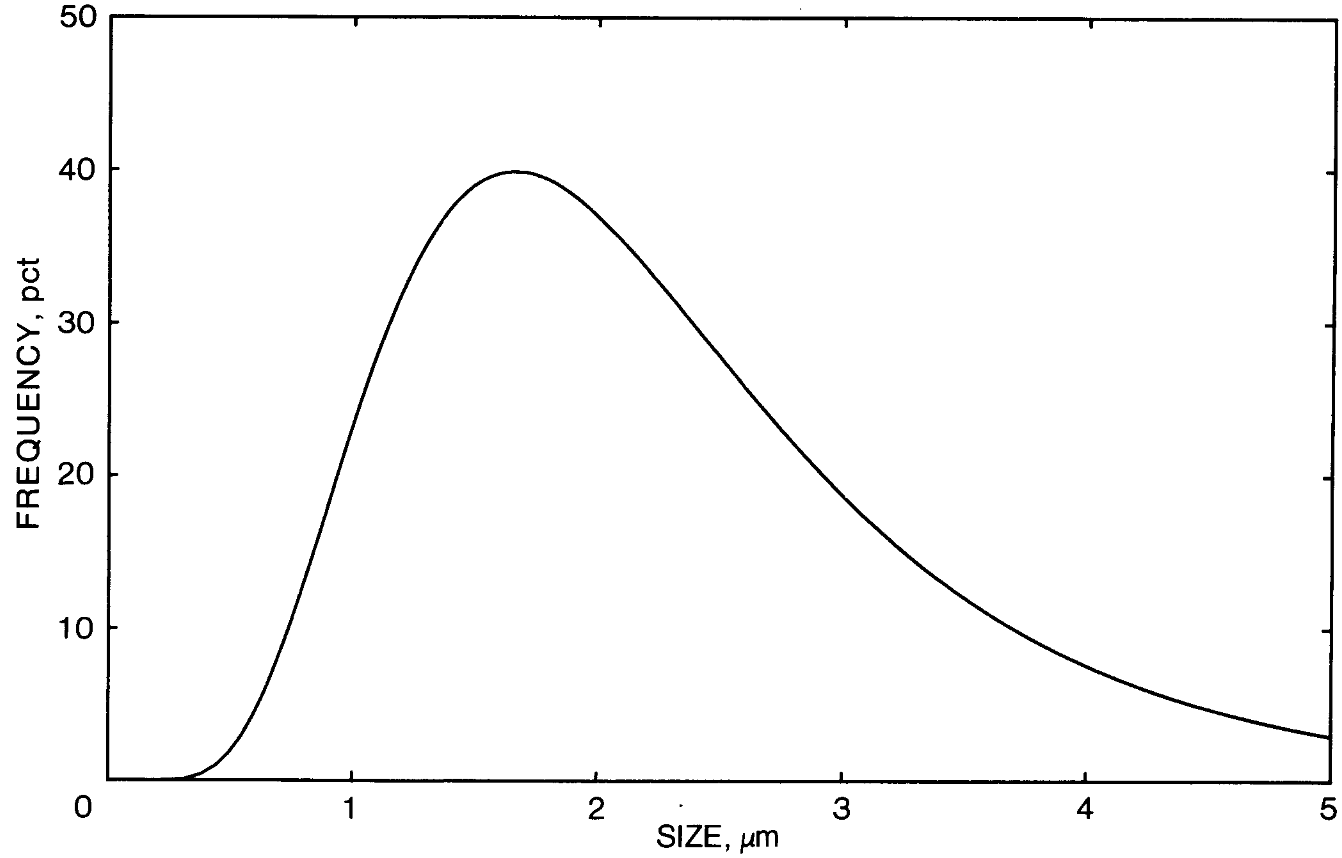


FIGURE 2.—Particle-size distribution of Cr powder.

RESULTS AND DISCUSSION

PREPARATION OF COMPOSITE COATINGS

Powder Suspension Effects

To determine the effect of Cr powder concentration on the quantity of particles occluded, the Cr suspension was varied from 0.3 to 30 vol pct for a series of electrodeposits prepared at 2.5 A/dm^2. The Cr was occluded into an 86Fe-14 Ni electrodeposited alloy matrix using an electrolyte containing 60 mol pct Fe^{2+} and 40 mol pct Ni^{2+}.

Figure 3 shows that the Cr content in the composite coatings increased significantly as the concentration of suspended Cr powder was increased above 1 or 2 vol pct. These data are consistent with a model proposed by and experimentally confirmed by Guglielmi (*12*) for the occlusion of ceramic particles in an electrodeposited Ni matrix. The model was further confirmed by Celis and Roos (*16*) in their investigation of the occlusion of Al_2O_3 in an electrodeposited Cu matrix. A schematic of this model is shown in figure 4. The model consists of a two-step mechanism in which loosely adsorbed particles on the cathode are in equilibrium with the positively charged suspended particles. The adsorbed particles are then irreversibly occluded into the electrodeposit. The mathematical expression for this model relates a Langmuir adsorption isotherm constant to the reversible adsorption step and the metal deposition parameters to the occlusion step.

Matrix Composition and Microstructure Effects

The quantity of Cr particles occluded varied significantly as the composition and microstructure of the matrix changed. Using a 20-vol-pct suspension to ensure a sufficient quantity of Cr particles, electrolysis results were obtained at current densities of 2, 5, and 10 A/dm^2 over the full range of matrix composition (fig. 5). These results showed that (1) the quantity of Cr particles occluded increased as the Fe in the γ(Ni-Fe) matrix increased and (2) the largest quantities of Cr particles were occluded when electrolysis conditions yielded a mixed γ(Ni-Fe)-α(Fe-Ni) or an α(Fe-Ni) microstructure. This relationship between Cr particle occlusion and matrix composition and microstructure may be associated with the compatibility of the particle and matrix lattice structures. Specifically, both Cr and α(Fe-Ni) exhibit a body-centered cubic lattice structure, whereas γ(Ni-Fe) exhibits a face-centered cubic lattice structure. The quantity of Cr particles occluded in an electrodeposited matrix composed only of α-Fe was 12 times higher than that in a matrix containing only γ-Ni. In general, the quantity of chromium occluded at any matrix composition increased as the current density was increased.

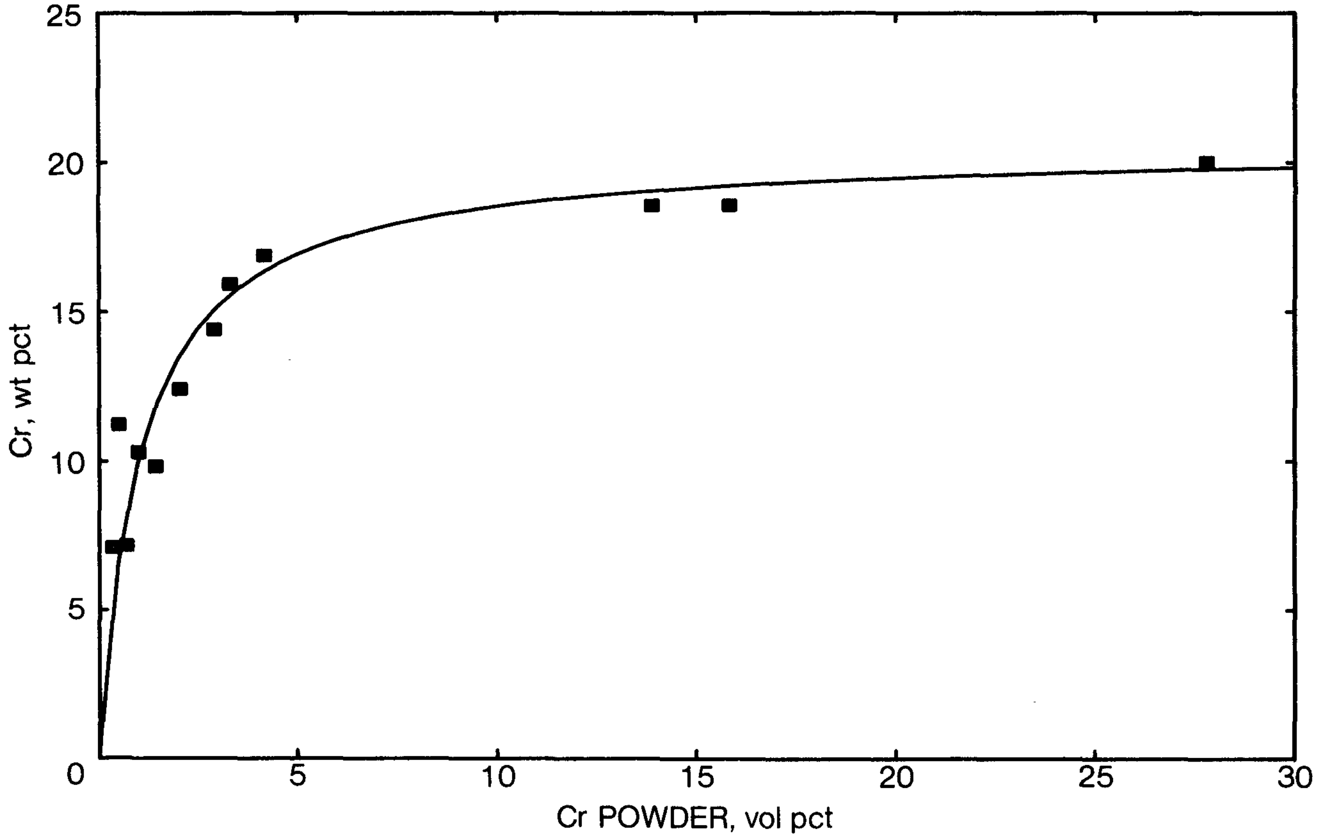


FIGURE 3.—Relationship between Cr powder suspended and occluded.

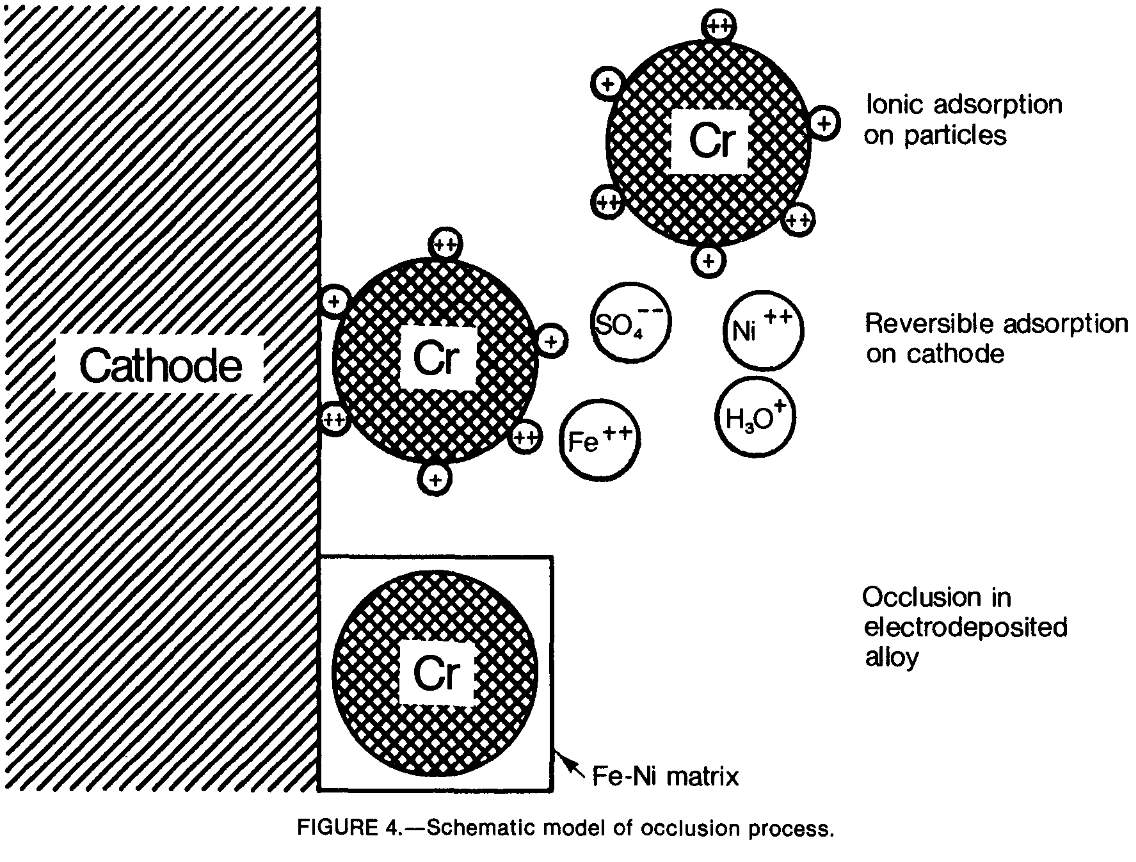


FIGURE 4.—Schematic model of occlusion process.

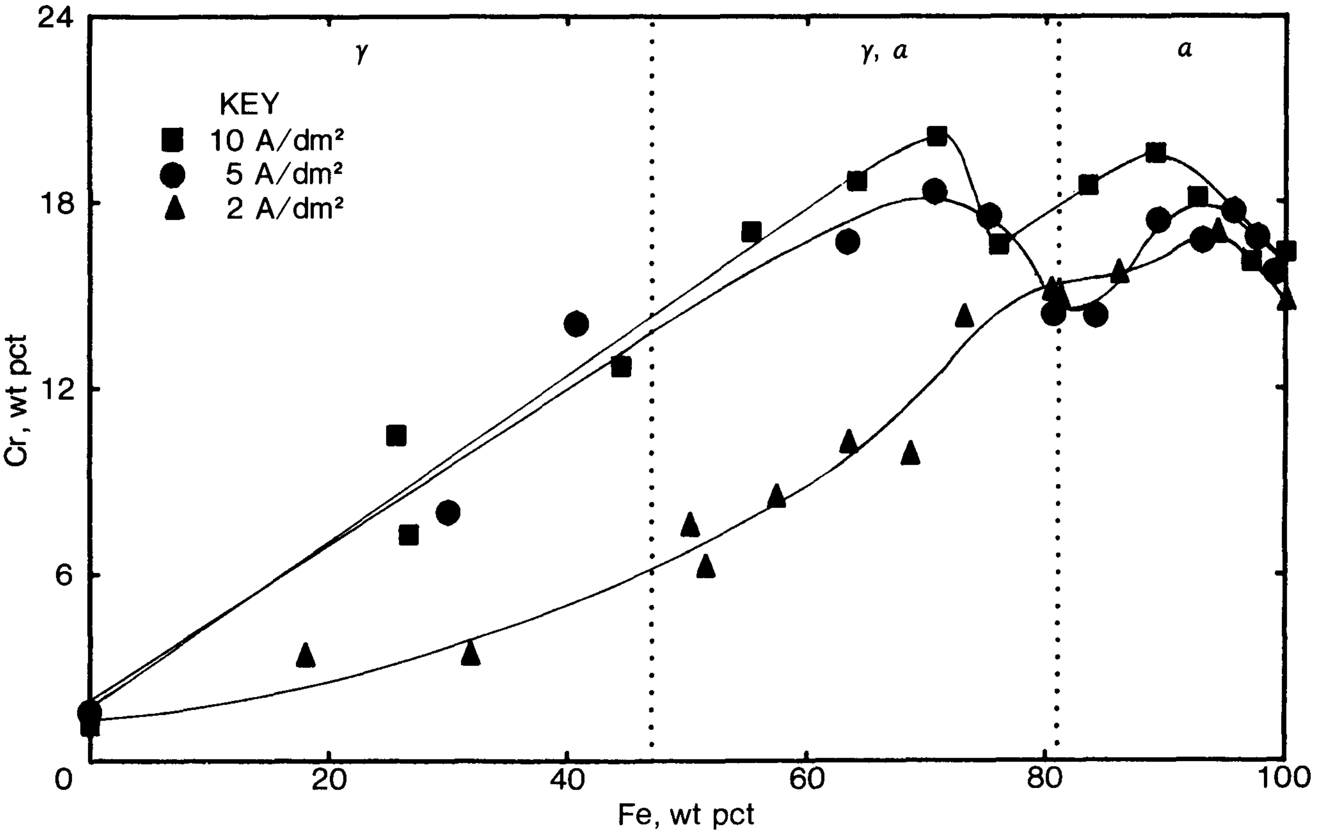


FIGURE 5.—Effects of Fe-Ni matrix composition and microstructure on occlusion of Cr.

HEAT TREATMENT OF COMPOSITE COATINGS

The extent of coating homogenization was determined for heat-treated coatings containing 78Fe-10Ni-12Cr. Cross sections of these coatings before and after heat treatment at 1,100° C for 1 h are shown in figure 6. The SEM photo of the unhomogenized composite shows discrete Cr particles distributed uniformly throughout the Fe-Ni alloy matrix. An EDAX map at the same location shows the occluded Cr appearing as bright areas. After heat treatment, significant Cr diffusion was evident. Individual 2-μm particles could not be distinguished in the matrix. The corresponding EDAX map substantiates this result. During heat treatment of these samples, some interdiffusion of the coating and the 1020 AISI steel substrate occurred. The relative intensities of Cr and Ni near the coating-substrate interface, as determined by EDAX, showed that a coating 125 μm thick exhibits a diffusion zone ~80 μm wide after heat treatment.

An important factor that had to be considered in evaluating the effects of coating-substrate interdiffusion was the control of the quantity of carbon migrating from the substrate to the coating. In the presence of >0.02 pct C, the chromium carbide (Cr_3C_2) phase is likely to precipitate at the Fe-Ni-Cr alloy grain boundaries (sensitization). This is detrimental to the corrosion resistance of the alloy because of accelerated attack at the grain boundaries. A 50-μm-thick electrodeposited Ni undercoat effectively decreased the diffusion of carbon from substrate to coating during heat treatment at 1,100° C for 1 h. Micrographic examination of the Ni-substrate interface (fig. 7) showed a significant concentration of carbides (right photo, dark areas) associated with carbon that had been blocked from entering the coating. Without the Ni undercoat (left photo), the region of the 1020 steel substrate adjacent to the coating was decreased from the normal 0.2 pct C in this steel to <0.02 pct C, and carbides were evident in the coating. On the basis of these results, the possibility of preparing a protective Fe-Ni-Cr alloy coating on an inexpensive substrate appears promising.

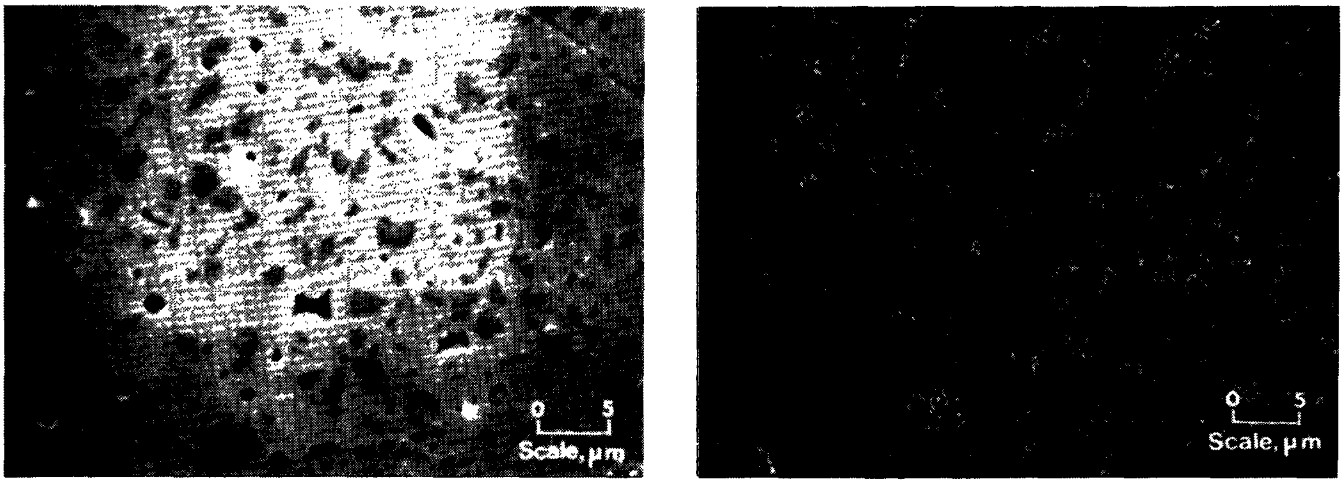
To effectively determine the heat-treatment conditions required to homogenize the Fe-Ni-Cr powder composites, that is, produce a corrosion-resistant alloy, the coatings were mechanically removed from the substrate prior to heat treatment. This made possible an evaluation of the heat-treatment process independent of effects related to substrate-coating interdiffusion or coating porosity. Subsequent corrosion rate data then served to establish the effectiveness of the heat-treatment procedure.

Effect of Heat-Treatment Pressure on Corrosion Rate

The corrosion rate data for composite coatings heat-treated at three pressures are shown in table 2. Each of these 250-μm-thick composites contained ~55 pct Fe, 29 pct Ni, and 16 pct Cr and was heat-treated for 8 h at 1,100° C.

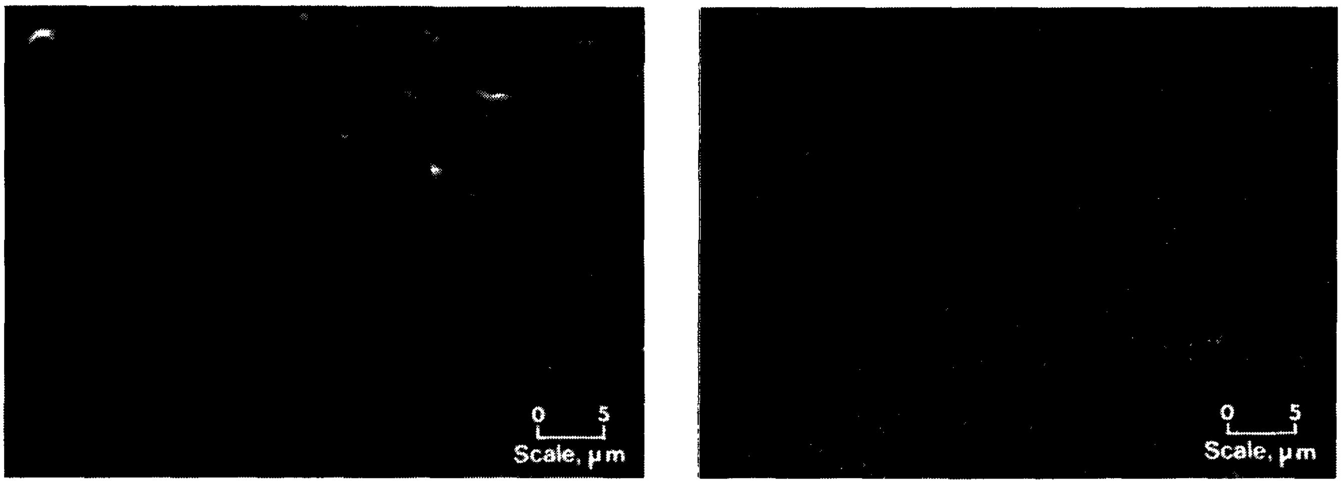
TABLE 2.—Effect of pressure during heat treatment (8 h, 1,100°C) upon corrosion rate of a 55Fe-29Ni-16Cr alloy

Pressure, torr	Corrosion rate, mm/yr
1×10^{-6}	1.3
1×10^{-4}	.9
1×10^{0}	.7



Composite coating

EDAX of composite coating



Heat-treated coating

EDAX of heat-treated coating

FIGURE 6.—Photomicrographs and EDAX (for Cr) before and after heat treatment.

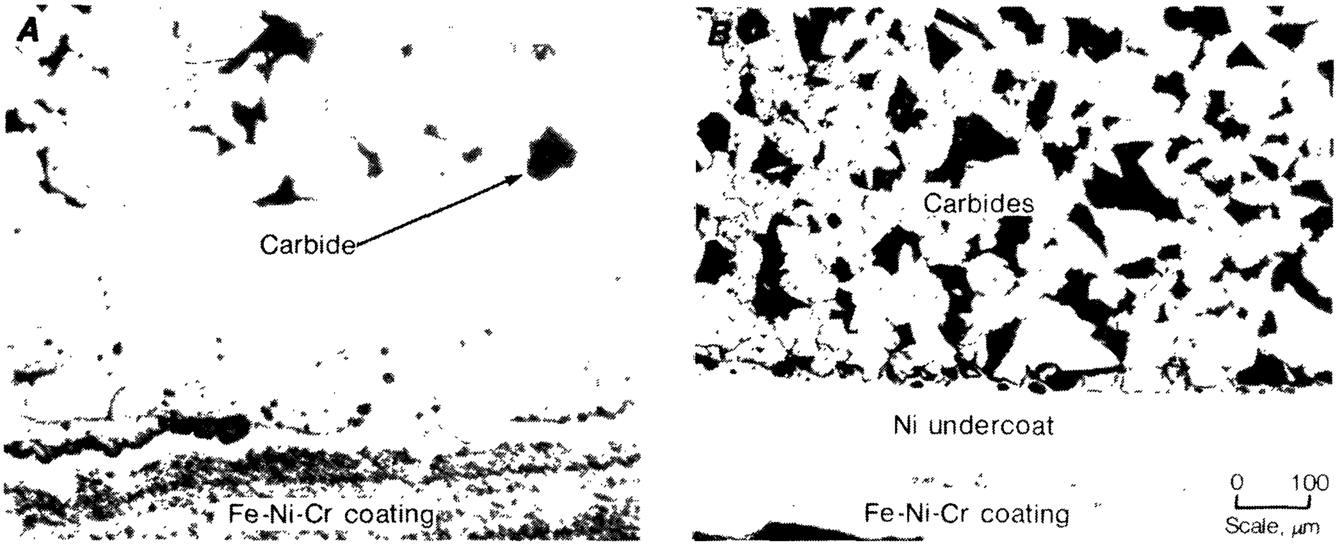


FIGURE 7.—Effect of an Ni undercoat on carbon diffusion from the carbon-steel substrate into the Fe-Ni-Cr alloy coating. *A*, Carbide-free zone near the substrate-coating interface associated with carbon diffusion into the coating; *B*, use of an Ni undercoat retards this diffusion.

The composite heat-treated at 1 Torr exhibited the lowest corrosion rate during 240 h of exposure to boiling 65 pct HNO_3. A comparison with the corrosion rate of a commercial 304 stainless steel shows that, in this corrosive environment, the Fe-Ni-Cr alloy was approaching the 0.2-mm/yr corrosion rate of the stainless steel.

Effect of Heat-Treatment Time on Corrosion Rate

The improved corrosion resistance at the highest pressure is consistent with other results showing better corrosion resistance when the heat-treatment time was decreased from 16 h to 8 h using 1×10^{-6} Torr pressure (table 3). There is assumed to be an excessive loss of Cr through sublimation at the lower pressures and the longer heat-treatment times. When only 4 h of heat treatment was employed, the higher corrosion rates were indicative of incomplete homogenization.

TABLE 3.—Effect of duration of heat treatment (1,100° C, 1×10^{-6} Torr) upon corrosion rate of a 55Fe-29Ni-16Cr alloy

Heat treatment, h	*Corrosion rate, mm/yr*
4	3.7
8	1.3
16	2.5

ELECTROFORMING

Practical application of the alloy coating method for the preparation of small electroforms has been demonstrated. Figure 8 shows three examples of these electroforms, prepared at 5 A/dm^2 in an electrolyte having a 3:1 Ni^{2+}-Fe^{2+} ratio and containing 20 vol pct suspended Cr powder. The electroformed cylinder (right) was prepared by electrodepositing the Fe-Ni-Cr powder composite on a 1020 steel rod, heat-treating at 1,100° C for 4 h, and subsequently dissolving the rod (mandrel) with HNO_3. The other two electroforms were prepared using a more practical mandrel material. A polyethylene wax mandrel plated with a thin electroless Ni coating and a 25-μm-thick electrodeposited Ni coating served as the base upon which an Fe-Ni-Cr electroform, 750 μm thick, was deposited. After deposition the form was removed from the mandrel by heating the wax to its melting point of 110° C. A cylindrical, 12-mm-diam, 38-mm-high beaker (left) and a rectangular container, 12 mm square and 32 mm high, with a round base (center) thus resulted. Each of the electroforms was then heat-treated at 1,100° C for 8 h to homogenize the composite into a ternary alloy. A uniform composition was achieved throughout the rectangular form as indicated by the analytical results shown in table 4. Chromium and nickel values were obtained by X-ray techniques. Corresponding values for Fe were determined by difference.

TABLE 4.—Composition of rectangular electroform, percent

Side	Fe	Ni	Cr
1	45.7	34.3	20.0
2	45.2	34.6	20.2
3	44.0	36.9	19.1
4	44.6	35.2	20.2

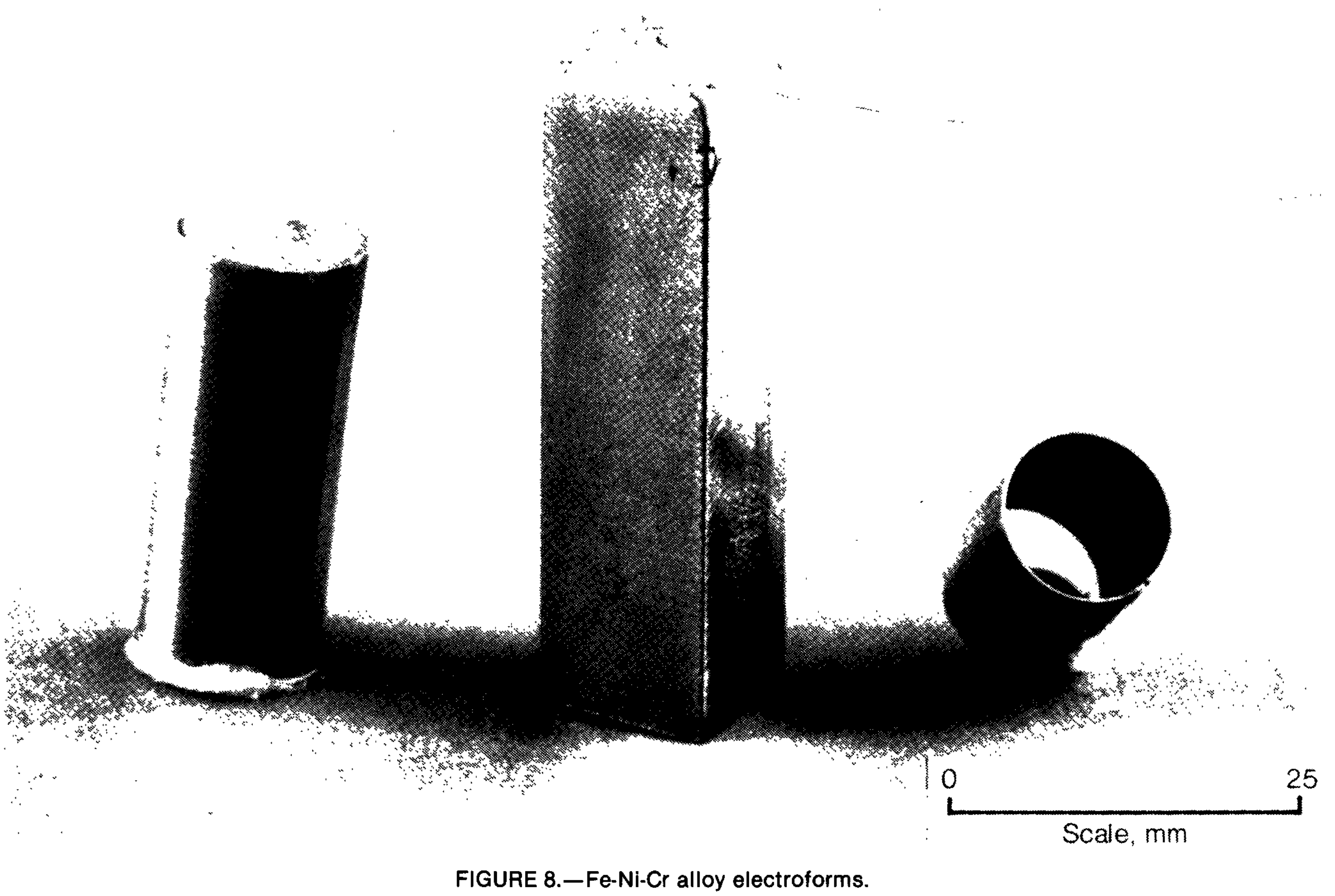


FIGURE 8.—Fe-Ni-Cr alloy electroforms.

CONCLUSIONS

Coatings of Fe-Ni-Cr alloy up to 750 μm thick have been prepared by a method employing occlusion of Cr particles in an electrodeposited Fe-Ni alloy. A uniform Cr distribution has been achieved, and a wide range of alloy compositions can be produced. Heat treatment at 1,100° C homogenizes the Fe-Ni-Cr alloy, and an Ni precoat effectively decreases the quantity of detrimental carbon diffusing from the 1020 steel substrate to the coating during heat treatment. Corrosion rates as low as 0.7mm/yr have been observed for the alloy when exposed to boiling 65-pct HNO_3. Under similar conditions, a commercial 304 stainless steel corrodes at 0.2 mm/yr. Possible application of the coatings process to the preparation of small electroforms has been shown, and the ability to prepare a protective Fe-Ni-Cr alloy coating on an inexpensive carbon steel substrate appears promising.

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WEAR PROTECTION OF IRON-BASE CASTINGS BY CAST-ON HARD SURFACING

By Jeffrey S. Hansen[1]

ABSTRACT

To reduce wear and maintain toughness in Fe-base castings, the Bureau of Mines has investigated a process to bond hard surfacings to cast parts while the part is being cast. Wear-resistant material in powdered form is applied on a polystyrene pattern, the pattern is embedded in a mold of unbonded sand, and the wear-resistant material is transferred to a casting surface at the time of pouring. The process eliminates the labor involved in applying conventional hard surfacings, reduces the danger of surfacing warpage and heat cracking, allows concurrent heat treatment of the part and hard surfacing, and produces a metallurgical bond between the hard surfacing and casting. In field tests, bucket-wheel excavator teeth and plowshares with cast-on hard surfacings had wear lives that were equal to or longer than those of similar parts with conventional hard facings. Surfacings composed of chromium white irons, tungsten carbide (WC), and WC with titanium carbide (TiC) have been applied successfully.

INTRODUCTION

The Bureau of Mines is investigating methods to reduce the need for imported metals, such as Mn, Cr, and Ni, in Fe-base alloys in order to minimize the Nation's dependency on foreign sources of these critical materials. Applications of hard surfaces to areas of cast parts that are subject to wear is an effective means of conserving wear-reducing alloying metals because the necessity for alloying the entire casting is eliminated. Surfacing operations also are effective because the enhancement of wear resistance is not accomplished at the expense of toughness. These two properties are mutually desirable in many applications, and particularly in mining and metallurgical processing equipment.

Commercially, hard surfacings have been applied to a variety of parts by weld overlaying and by flame and detonation-gun spraying. However, greater usage of such methods has been impeded by a number of difficulties. Weld overlaying can be prohibitively expensive; the heat generated during welding can cause distortion or cracking and loss of heat-treated properties, and weld overlays are sometimes brittle and susceptible to shock. Flame and detonation-gun hard surfacings suffer from these same faults and, in addition, generally have weak bonds and less than theoretical density.

The Bureau has investigated a new method for applying hard surfacings. The method, called cast-on surfacing, eliminates most of the drawbacks that arise from other surfacing methods. Hard surfaces applied by the cast-on process are thick, heat-treatable, and metallurgically bonded. When compared with conventional surfacing processes, cast-on surfacing eliminates several steps and greatly reduces the dangers of warpage and heat cracking.

Abbreviations Used in This Paper

DPH	diamond pyramid hardness
h	hour
in	inch
lb	pound
mg/m	milligram per meter
mm^3	cubic millimeter
pct	weight percent

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BACKGROUND

Cast-on surfacing is a method whereby powdered, wear-resistant material that has been applied to a polystyrene pattern is transferred and fused, with the assistance of vacuum, to the surface of a casting during pouring. The concept of cast-on surfacing as developed by the Bureau is a unique combination of two technologies, neither of which is new.

The first technology, that of transferring a dissimilar metal to a casting during pouring, dates back to 1913 (*1*). Since then, a variety of techniques have been tried to accomplish the same result. Liquid metals have been centrifugally cast against other liquids (*2*) and also against solids that have been heated to a point sufficient to promote fusion (*3-4*). These techniques generally are limited to simple geometries and narrow composition limits.

Other researchers have attempted to cast metals into molds containing sintered powder compacts that are attached to mold walls (*5-7*). Most recently, loose powders have been pasted in molds or held in place by vacuum (*8-9*). Generally, however, consistency and predictability have not been achieved. In addition, most researchers have encountered problems with erosion, shrink voids, excessive dilution, poor infiltration, uneven thickness, poor surface finish, and porosity.

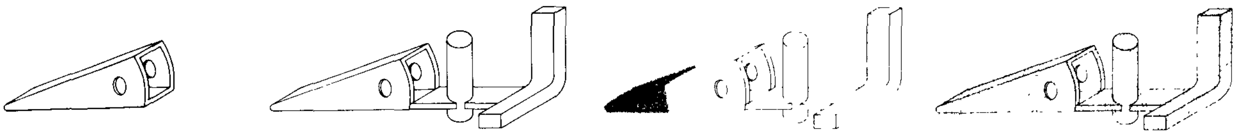
The second technology used in the Bureau cast-on surfacing process involves a novel casting process in which an expendable polystyrene pattern is consumed during each cast (*10-11*). The pattern, which is embedded in a flask of unbonded sand, is vaporized as it is replaced by liquid metal. As with previous attempts to cast-on surfacings, the polystyrene pattern casting technique has not been universally accepted. However, new advances are continually being made, and one market research firm predicts that by 1995, polystyrene pattern casting will account for 15 pct of total ferrous casting tonnage (*12*).

THE PROCESS OF CAST-ON SURFACING

Initially, the polystyrene pattern technique was thought to be the best way to avoid the difficulties that had plagued earlier researchers of cast-on surfacing. Foremost among its advantages is that a pattern can be oriented in a sand mold in any one of several positions. Because of this positioning flexibility, an orientation can be selected that is least likely to disturb powdered surfacing material during pouring. In addition, lightweight polystyrene patterns can be coated with powdered surfacing materials, thoroughly dried, and stored until needed.

Use of vacuum was seen as necessary to draw off gases generated by vaporizing the pattern and to assist in drawing the molten casting metal into the powdered surfacing. It seemed a relatively simple task to combine the use of vacuum with existing polystyrene pattern technology. As the research progressed, this assumption was proved valid.

Figure 1 shows the Bureau's polystyrene pattern cast-on surfacing process. The first step entails making a pattern from polystyrene either by molding pre-expanded beads or by cutting and machining parts from a solid polystyrene

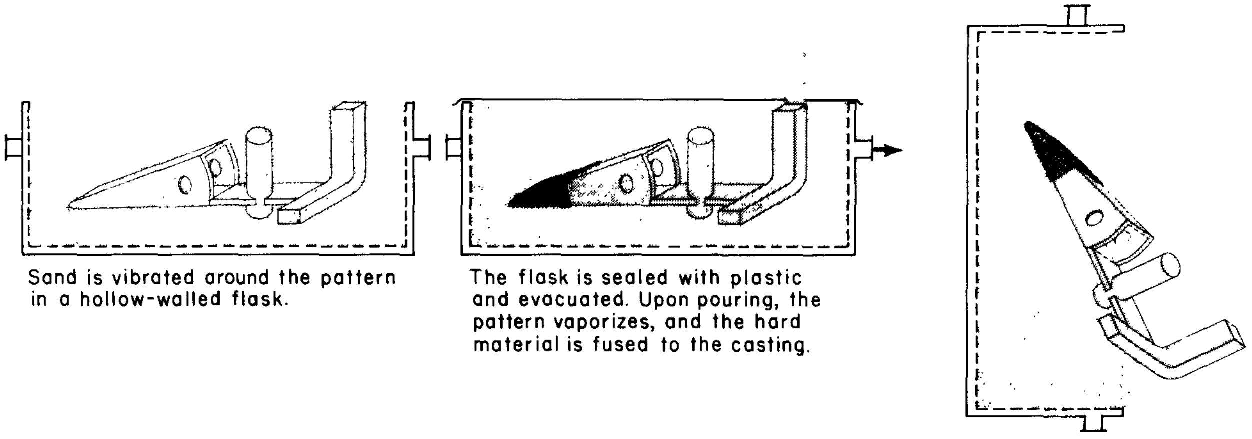


A polystyrene pattern is made.

Gates and risers are attached.

Powdered hard material paste is applied to wear-prone surfaces.

A refractory coating is sprayed on the entire pattern.



Sand is vibrated around the pattern in a hollow-walled flask.

The flask is sealed with plastic and evacuated. Upon pouring, the pattern vaporizes, and the hard material is fused to the casting.

The vacuum is released and the casting drops away.

FIGURE 1.—Process steps for applying cast-on surfacings to polystyrene pattern castings.

block. To minimize gassing, the polystyrene density must be lower than the density of similar polystyrene that is used to make household items. Sprues and gates to direct metal to the pattern are attached. Risers must also be attached to provide a source of liquid metal to the solidifying casting and prevent shrinkage. Joints must be filled if necessary, and appropriate fillets used in corners.

The next step involves the placement of the surfacing material in powdered form onto the pattern. Surfacing materials that have been applied successfully include ferrochrome, white iron compositions, tungsten carbide (WC), and mixtures of WC and titanium carbide (TiC). Two application methods have been used. With one method, the surfacing powder with a binder and carrier is trowled on patterns in thicknesses up to ¼ in. In the second method, the binder and carrier are sprayed onto the pattern, and the pattern is dusted with the surfacing powder. The excess powder is shaken off, and additional layers are similarly applied until the desired thickness is obtained. Once applied, the surfacing powder is thoroughly dried to drive off the carrier and to form an adherent layer. Figure 2 shows a ripper tooth pattern with hard-surfacing material applied to a wear-prone surface.

After the surfacing powders are placed and dried, the entire pattern, including the gating system, is sprayed with a commercially available refractory coating containing zircon in alcohol. The refractory coating provides an effective barrier to interference from the molding sand that is subsequently added. The refractory barrier also is needed to prevent burn-on defects and localized, massive sand drop. Like the hard surfacing, the refractory is thoroughly dried to prevent gassing when the part is cast.

Next, the pattern is placed in a vacuum flask that has double walls (fig. 3). The inside walls are screened to allow the passage of pattern gas into the space between the walls. The outside walls are welded steel. Unbonded sand is filled in around the pattern to the flask top.

With the sand and pattern in place, the flask is vibrated to increase the bulk density of the sand and fill all cavities. The flask is covered with a sheet of 0.003-in polyethylene. The assembly can be easily stored or transported. Prior to and during pouring, vacuum is applied to the flask to draw off gases, aiding contact of the metal with the powdered surfacing material and maintaining the mold shape.

Steel coastings are poured at conventional pouring temperatures. The heat from the metal at these temperatures is sufficient to either melt the surfacing, as in the case of white iron powders, or allow the casting metal to infiltrate around the powder grains. Sand that adheres to the casting and does not pop off upon cooling to room tempature can be removed by shot-blasting or other conventional procedures.

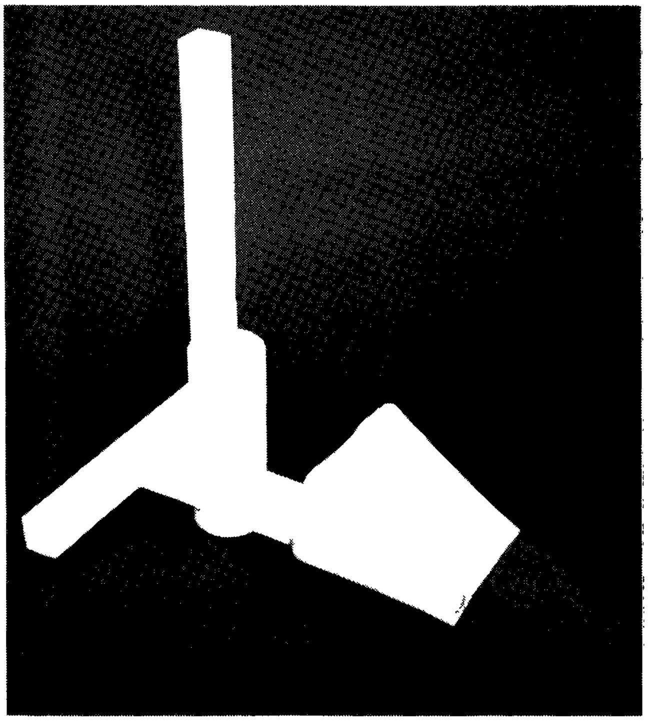


FIGURE 2.—Hard-surfacing material powder applied to the tip of a ripper tooth pattern.

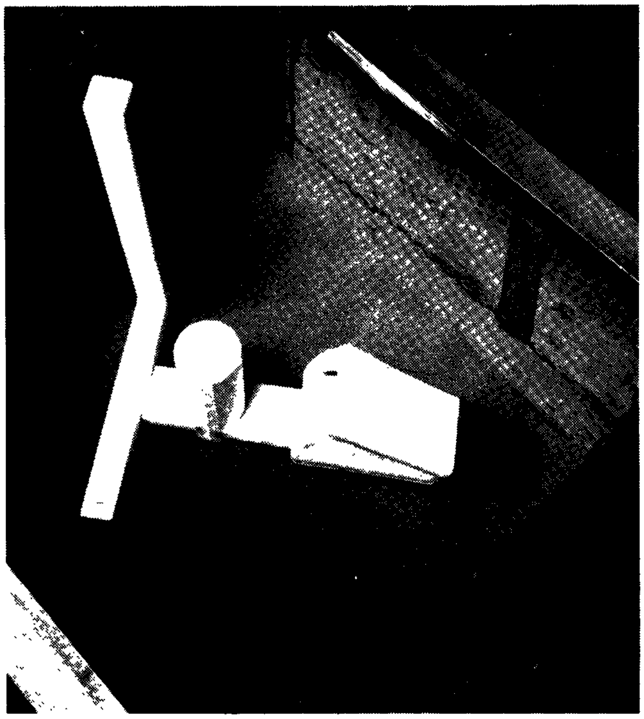


FIGURE 3.—Ripper tooth (without refractory coating) placed in unbonded sand in a double-walled vacuum flask.

LABORATORY TESTING AND EVALUATION

Several experiences and studies reported in the literature showed that a system combining cast-on surfacing techniques with polystyrene pattern casting methods would contain many variables. Consequently, statistically designed 2- and 3-level factorial experiments were used to evaluate 17 individual and combined effects of several variables. The following is a list of the most important variables:

Independent Variables	*Dependent Variables*
Binder type	Surfacing porosity
Binder level	Casting porosity
Surfacing particle size	Internal porsity
Surfacing thickness	Surfacing roughness
Casting thickness	Surfacing contour
Pouring temperature	Proportion of unmelted surfacing
Vacuum level	Proportion of dendrites in surfacing
Powder application technique	Proportion of carbides in surfacing
	Wear resistance

A casting was designed that allowed three separate samples to be cast simultaneously (fig. 4). After casting, each defect type on each sample was given a ranking from 1 to 5 by three independent observers. The rankings were averaged to provide a numerical assessment of the defect severity. The averaged rankings of the defects and other variables were compared with independent variables by computer analysis. Surprisingly, good surfacings generally were obtained under a wide variety of conditions.

One variable that deserves special mention because it influenced surfacing quality most was surfacing thickness. Especially in ferrochrome and white-iron-based surfacings, thickness dictated the microstructure, which in turn determined wear resistance. At a 1/16-in thickness, white iron surfacings were diluted substantially by steel from the casting, which resulted in a microstructure with few carbides (fig. 5*A*). At a thickness of 3/16 in, the dendritic structure disappeared entirely, and a substantial increase in carbides was obtained (fig. 5*B*). Because these carbides have a microhardness of about 1,600 DPH, wear protection is afforded against siliceous minerals, for example, which have a hardness of about 800 to 900 DPH.

In addition to microstructural analysis, most surfacings were subjected to one or both of two types of wear tests. The first test simulates so-called low-stress abrasion in which the abrasive particle does not break down. A 1- by 3-in sample is pressed against a rotating rubber-tired wheel while a measured amount of silica sand is dropped between the two. The action produces a wear scar in the sample. The scar is measured and compared with the wear scars of standards and other materials. The test conforms to ASTM Standard G65-81 *(13)*.

The second test uses a rotating drum that is covered with garnet sandpaper. A weighted pin of the surfaced material is pressed against the drum as it rotates. The stress is considerably higher and sufficient to break the abrasive grains. The wear is measured similarly to the wear of dry-sand test specimens. There is no standard for the test.

The results show that excellent wear resistance can be obtained with cast-on surfaces. Based upon the results obtained from commerical weld-rod hard facings, values of 11 mm^3 for the dry-sand test and 3.0 mg/m for the pin-on-drum test have been arbitrarily selected as benchmarks. The first two entries in table 1 indicate the increase in wear resistance that is obtained by increasing surfacing thickness. In the case of commercial ferrochrome, the volume loss sustained by a 3/16-in-thick specimen was 8.3 mm^3 in the dry-sand test; this is about one-third the volume loss of 21.6 mm^3 sustained by a similar specimen that was only 1/16 in thick. Specimens with values lower than these numbers are considered very good. The table also shows test results for a custom-made 9-pct-C ferrochrome, two white irons, and a WC-TiC mix. For comparison, the results for a commonly used WC-containing, commercial hard-facing alloy are shown at the bottom of table 1.

TABLE 1.—Dry-sand rubber-wheel and pin-on-drum abrasion test results on cast-on surfacings

Surfacing material	Dry-sand test vol loss, mm^3	Pin-on-drum test wt loss, mg/m
Commercial FeCr (1/16-in)	21.6	Not tested
Commercial FeCr (3/16-in)	8.3	1.68
No. 2 custom FeCr (9 pct C)	8.4	.87
5C-21Cr-8.5Cb-9Mo white iron ...	11.7	3.14
9C-22Cr-2Mo-1Ni white iron	10.4	2.51
83WC-17TiC	9.3	.15
FeMo plus carbon	12.0	2.54
NiHard IV (solid)	13.2	.40
Weld-applied WC hard facing ...	11.3	.15

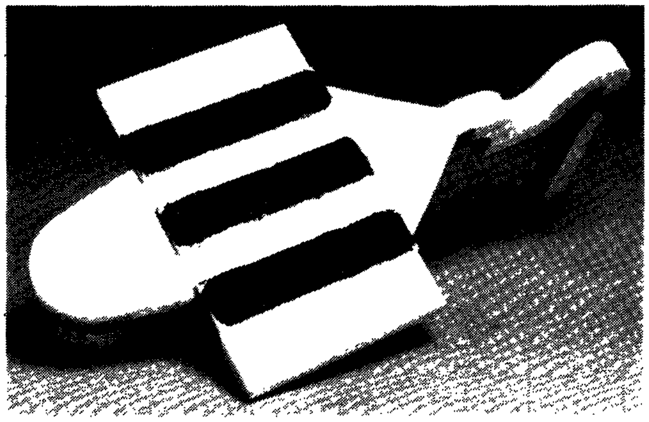


FIGURE 4.—Three-sample pattern with powdered surfacings for determining the effect of variables upon defect occurrence.

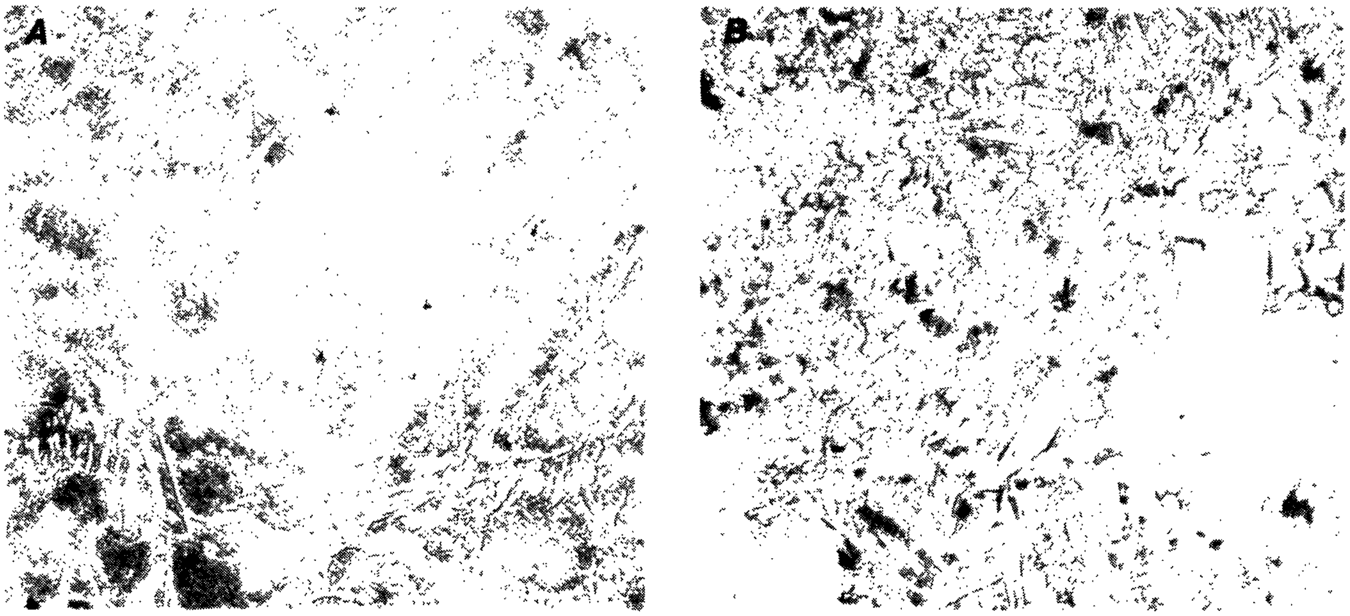


FIGURE 5.—Microstructure of (*A*) 1/16-in-thick and (*B*) 3/16-in-thick white iron surfacings (X 200).

While the wear tests are valuable for screening purposes, they often do not correlate with real-life conditions. It is important, therefore, to test materials under field conditions before judging their worth. Cast-on surfaces have been subjected to two field environments.

The first field trial was accomplished on a bucket-wheel excavator (fig. 6) that is used to remove claylike overburden at a coal mine. Without surfacing protection, the teeth on the buckets wear out in about four 8-h shifts. With weld-rod hard surfacing, the teeth may last 48 shifts.

The entire outside surfaces of two teeth were cast-on-surfaced with the 9-pct-C custom ferrochrome and the 5C-21Cr-8.5Cb-9Mo white iron alloy seen in table 1. The teeth were run for 31 shifts on separate buckets but at identical corner positions on the buckets. The mine supplied two weld-rod, hard-surfaced control teeth that were run for comparison. The wear of each tooth was assessed by noting the loss in length (fig. 7). The white-iron-surfaced tooth lost 1/2 in. In comparison, the control teeth lost 1¼ in and 1½ in. In terms of length then, the white-iron, cast-on-surfaced tooth registered a 60-pct improvement over the best control tooth. The 9-pct-C ferrochrome-surfaced tooth was not as good. Since the test, porosity has been reduced, and the wear resistance of surfacings has been improved. Additional tests are planned to obtain statistical significance.

In the second field trial, plowshares were cast-on-surfaced along the share wear edges and used to plow about 140 acres of sandy, abrasive river bottom soil. Although plowshares normally are made of wrought steel and most likely will never be cast, the abrasion that occurs in plowing is similar to the abrasion that occurs in many other environments. The sandy soil at the test farm caused unsurfaced blades to wear out after 25 acres or less. Weld-rod hard surfacing allowed the farmer to plow over 150 acres without replacing the plowshares.

Plowshares are affixed to the bottoms of each of five blade assemblies similar to the one shown in figure 8. The shares make the initial contact with the soil and protect the remainder of the blade. Two field trials were conducted. The shares were located at several positions on the plow, as noted in table 2, because the outside shares (positions 1 and 5) are subject to greater abrasion and typically wear more. As table 2 shows, the cast-on-surfaced shares performed admirably. The ferrochrome and WC cast-on-surfaced shares lost about the same weight as equally placed weld-rod-surfaced shares. However, the 5C-21Cr-8.5Cb-9Mo white iron alloy that perfomed best in the bucket-wheel excavator test did somewhat worse than the weld-rod-surfaced shares. Figure 9 shows two shares after the field tests. In addition to showing good wearability, the tests demonstrated that cast-on surfaces can be successfully applied to thin section castings.

TABLE 2.—Plowshare field trial results

Surfacing material	Plow position[1]	Wt loss, lb
Commercial ferrochrome	5	1.0
	4	1.0
5C-21Cr-8.5Cb-9Mo white iron	5	1.3
WC	4	.8
Weld-applied hard surfacing	3	.7
	1	1.0
	3	.8

[1] Plowshares numbered 1 and 5 are located in outside positions; 2 through 4 are located in inside positions.

FIGURE 6.—One of eight buckets belonging to a bucket-wheel excavator at a coal mine. Nine teeth are fitted on the edge.

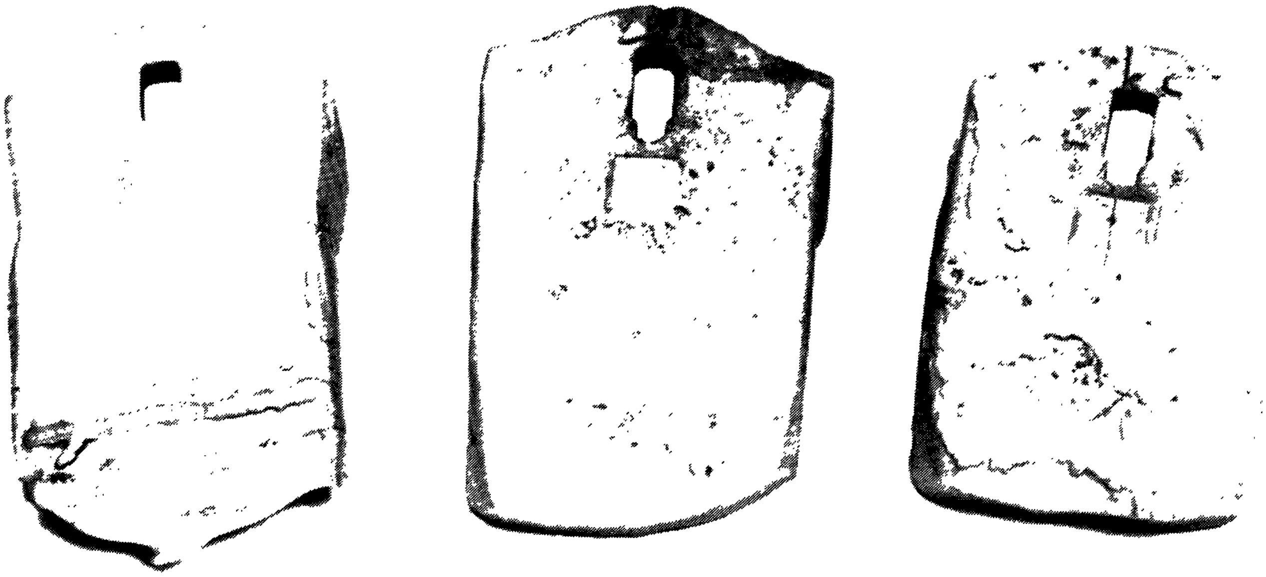


FIGURE 7.—Bucket-wheel excavator teeth after return from field trials. Left, weld-rod hard-surfaced control tooth; middle, Fe-5C-21Cr-8.5Cb-9Mo composition white iron alloy cast-on-surfaced tooth; right, custom-melted ferrochrome cast-on-surfaced tooth.

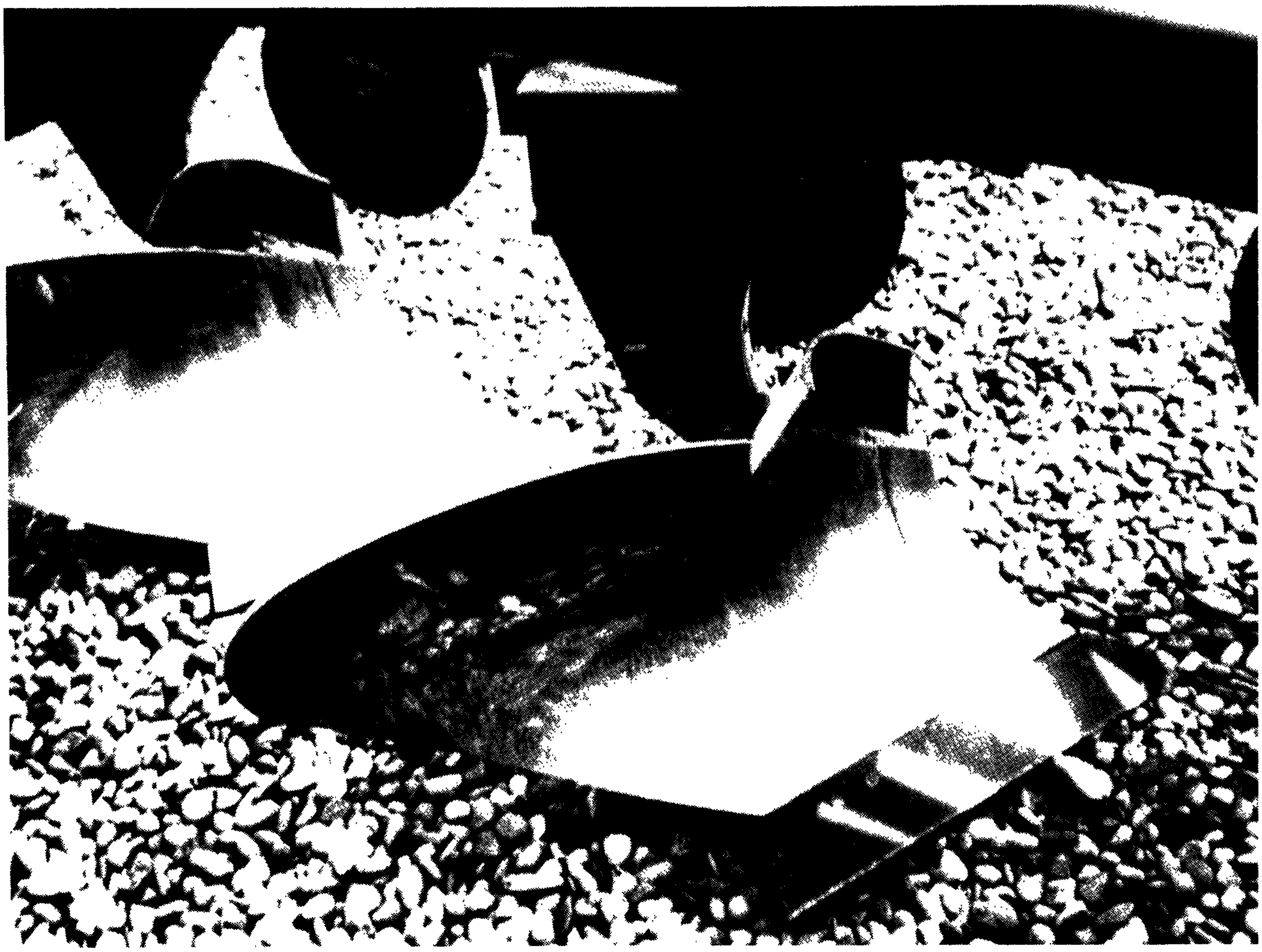


FIGURE 8.—Plowshares affixed to the lower portion of plow blade assemblies.

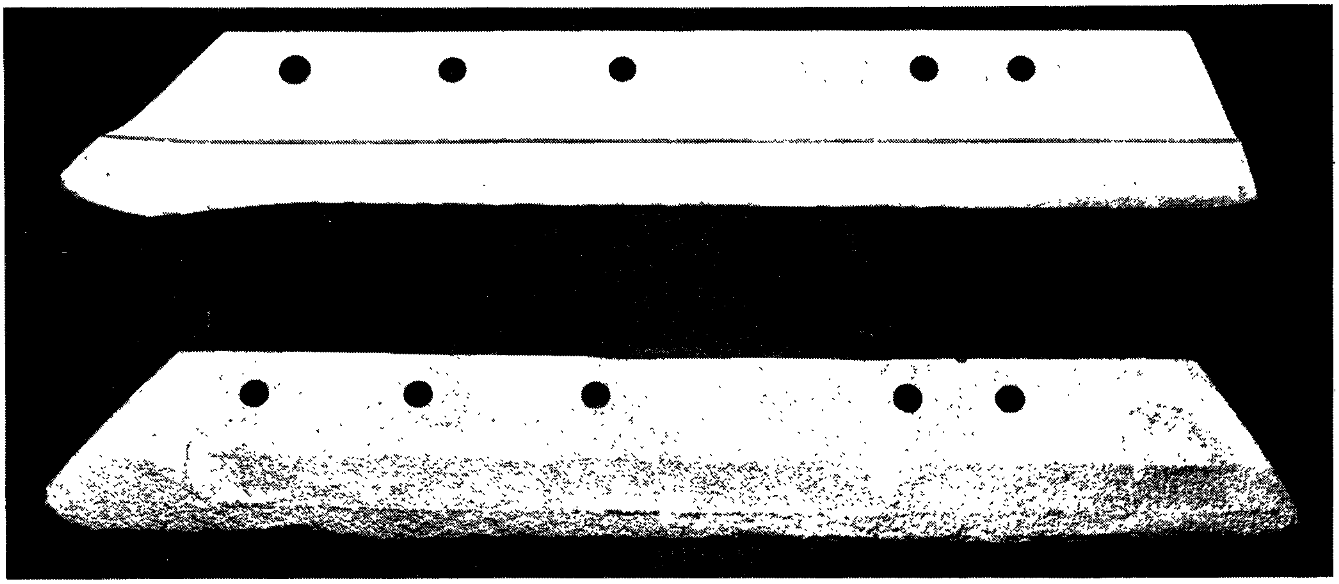


FIGURE 9.—Weld-rod hard-surfaced control plowshare (upper) and ferrochrome cast-on-surfaced plowshare (lower) after field trials.

CONCLUSIONS

Cast-on surfacing using polystyrene patterns has the potential to become a viable surfacing technique. It eliminates the harmful localized heating that is associated with other surfacing processes and forms a composite structure that will safely respond to heat treatment to develop good surface and casting properties. Strong metallurgical bonds are formed between the hard surfacing and casting, thereby increasing impact resistance and widening the field of surfacing applications. Wear resistance is substantially improved, and more importantly, critical materials are conserved.

The polystyrene pattern casting technique is ideally suited to cast-on surfacing. Because parting surfaces can be ignored, patterns can be optimally oriented within a molding flask with respect to the surfaces intended for hard material application. Patterns can be prepared well in advance of use and can be stored without tying up flasks and vacuum equipment for long periods prior to pouring.

The potential of cast-on surfacings to replace weld-rod hard facings has been demonstrated in field tests on bucket-wheel excavator teeth and plowshares. Currently, other applications are being sought, and additional field tests are underway to statistically strengthen the results.

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OPTIMIZATION OF MATERIALS SELECTION THROUGH CORROSION SCIENCE

By D. R. Flinn[1]

ABSTRACT

The cost of corrosion to the U.S. economy is very large. It includes accelerated maintenance or replacement or other mitigation methods, as well as the importation of critical metals, including Cr, for use in alloys that have been shown to be resistant to corrosion in many environments. Reduction of these costs depends on an improved fundamental understanding of corrosion processes as well as wide dissemination of this information. The approach of the Bureau of Mines to understanding corrosion phenomena through both fundamental and applied studies is discussed, and examples of the techniques used and results attained are given.

INTRODUCTION

The cost of metallic corrosion to the U.S. economy was estimated to be $70 billion in 1975 (*1*). This figure represented 4.2 pct of the gross national product for that year, a figure that agrees well with studies from other countries. In the same study (*1*), it was estimated that $10 billion of this cost could have been avoided by use of currently available technology. Logically, decisions should be made to implement corrosion control procedures when the economics are favorable or where health and safety factors are involved. Unfortunately, even when these conditions exist, there may be insufficient knowledge about material performance in a given environment to make cost-effective choices; or, in some cases, no commercially available material may be able to provide the required service life.

For many years the Bureau of Mines has conducted research to expand the information base on corrosion properties of new materials and to determine cost-effective materials for use in mineral and material processing environments. In the early 1930's, Bureau scientists at what was then the Bureau of Mines Eastern Experiment Station in College Park, MD (it later became the College Park Research Center and then the Avondale Research Center) studied the corrosion and embrittlement of boiler steels. This work resulted in numerous publications, including a bulletin (*2*). In the 1940's and 1950's, the corrosion properties of Zr (*3*), Ti (*3*), and V (*4*) were studied extensively. These studies contributed greatly to the acceptance of these new materials. A bulletin (*5*) on the corrosion properties of Ti is still frequently cited.

Between 1972 and 1981, the Bureau conducted extensive research to determine suitable materials for use in construction of geothermal energy and mineral recovery plants. This work resulted in 28 technical publications. Data from these studies comprise a large section of a Department of Energy publication, "Materials Selection Guidelines for Geothermal Energy Utilization" (*6*), which is the only compiled sourcebook for use by design engineers for material selection for these environments.

Corrosion studies to determine suitable materials for use of specific environments and evaluation of new materials remain an important area of Bureau research. Most of this research is directed at long-range, high-risk areas, where an improved fundamental understanding of the factors leading to corrosive degradation of materials will impact a wide range of problems. This understanding ultimately should permit the increased use of domestic mineral resources and a concurrent decrease in the demand for Cr and other imported metals. These fundamental studies have required the development or adaptation of numerous analysis and characterization techniques, which are described in following sections.[2] Because of the nature of the corrosion process, many of those techniques involve alteration and/or analysis of the near-surface region.

In the "Applications" section, two examples are given of current research where it is demonstrated that the optimum solution to a corrision problem will depend on improvements in our basic understanding of the corrosion process.

Abbreviations Used in This Paper

°C	degree Celsius
K	kelvin
M	molar (concentration)
m	molal (concentration)
min	minute
µm	micrometer
N	normal (concentration)
nm	nanometer
pct	weight percent
ppm	parts per million
ppt	parts per thousand
V	volt
yr	year

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[2] All citations to the experimental work described in the following sections refer to research conducted by the Corrosion and Surface Science research group at the Avondale Research Center. These citations are intended to describe our approach to developing an understanding of important corrosion processes.

MATERIAL CHARACTERIZATION

In the early 1970's research was conducted on the use of a high-energy ion beam incident on the metal surface (clean or corroded) to produce X-rays characteristic of the elements present in the first few thousand angstroms of the material (*7*). This technique, known as particle-induced X-ray emission analysis (PIXE), is very appropriate for the study of corrosion films and has proven very useful in numerous studies. (See references *8-10* for examples.) A second technique, Auger electron spectroscopy (AES), which can detect elements present in only the first few atomic layers of a material, has been utilized in numerous studies of corrosion and oxidation on metals (*11-12*). When combined with argon ion bombardment that removes atoms from the surface, both the PIXE and the AES techniques can provide a depth profile of a material. An example will be shown later in which a depth profile of a corrosion film permitted an understanding of the role of the various alloying elements in forming a very protective corrosion film.

In addition to PIXE and AES, many other analytical techniques are utilized to develop an understanding of the corrosion process. Optical metallography, X-ray diffraction, scanning electron microscopy (SEM), and scanning transmission electron microscopy (STEM) and its associated electron diffraction capabilities are available at Avondale and are used routinely in these studies. An X-ray photoelectron spectrometer (ESCA) that was recently installed will be used to determine the chemical bonding and/or oxidation state(s) of elements in the corrosion films. Other techniques, such as secondary ion mass spectrometry (SIMS) and ion-scattering spectrometry (ISS), available through private service companies, and the electron microprobe at the Bureau's Albany Research Center, also have provided very useful information. In most cases, no single analytical technique can provide the required information; the techniques are usually complementary. When combined with the various electrochemical and corrosion tests, it is possible to develop an understanding of the roles of the environment and the components of a material in the corrosion process.

FUNDAMENTAL CORROSION REACTIONS

Chromium-containing iron-base alloys comprise the largest class of corrosion-resistant metallic materials. Although much is known about the performance of these alloys in a wide range of environments, the roles of important chemical species in the corrosion process on these alloys are still not well understood. For example, depending on the solution pH and the amount of O_2 present, the overall cathodic process in the corrosion reaction can be due to either reduction of H^+ or O_2. Intermediates in the fundamental reactions, H atoms and oxide or hydroxide ions, can interact with the corroding metal surface to influence the corrosion behavior. Previous electrochemical corrosion research (*13*) on an Fe-Cr alloy (Fe-18Cr) in ultra-high-purity dilute H_2SO_4 showed that, in the presence of H_2, the alloy did not corrode, but attained a potential near that of the reversible hydrogen electrode. By a cathodic polarization of the alloy surface it was possible to induce active corrosion. A mechanism was proposed (*13*) that involved the formation of Cr-H species on the surface that controlled the evolution of H_2 and the dissolution of the alloy. A more recent study (*14*) showed that the bonding strength of H atoms to the alloy surface was a strong function of potential, and that the rate of the cathodic process at the corrosion potential was controlled by the electrochemical-desorption step, $H^+ + e + H \rightarrow H_2$.

In many oxidizing environments it has been shown that stainless steels exhibit low corrosion rates because of the presence of a Cr-rich passivating oxide film. If the steel is used in the presence of chloride ions, this passive film can be disrupted and serious pitting corrosion will occur. In a recent study (*15*), it was shown that the resistance of this passivating film to degradation by chloride ions can be improved by prepassivating the steel in a chloride-free H_2SO_4 solution prior to exposure to chloride ions. The rate of breakdown of the passive film, as expected, increased with increasing chloride ion concentration. The relationship between time before breakdown occurred, potential, and chloride ion concentration is shown in figure 1 for a Fe-18Cr alloy in 1*N* H_2SO_4 solution. The induction time represents the interval between addition of the chrlorde ion and the breakdown of the films as evidenced by the open circuit potential decaying to the corrosion potential. Similar results were observed for 430 stainless steel.

The understanding that has been gained through these fundamental studies and the experimental techniques that have been developed are proving useful in many areas of current corrosion research. One area of research where insufficient knowledge exists is that of the mechanism of action of various corrosion inhibitors. Studies are underway to determine the effect of both inorganic and organic inhibitors on the important corrosion reactions, including H^+ and O_2 reduction and metal dissolution. The understanding gained from these studies should lead to improved, more environmentally acceptable inhibitors that will extend the lifetime of materials and permit the use of alloys containing less Cr in corrosive environments.

FUNDAMENTAL MATERIALS STUDIES

A small, but important, portion of our research has been to demonstrate that coatings and other surface modification techniques can be used to protect materials from corrosion or wear and thereby reduce the requirements for certain critical materials. A more important use of these techniques is to prepare model alloys that either would be very expensive if made by conventional metallurgical procedures or cannot be prepared by other techniques. These alloys permit us to study the roles of composition and structure of an alloy in improving the corrosion properties.

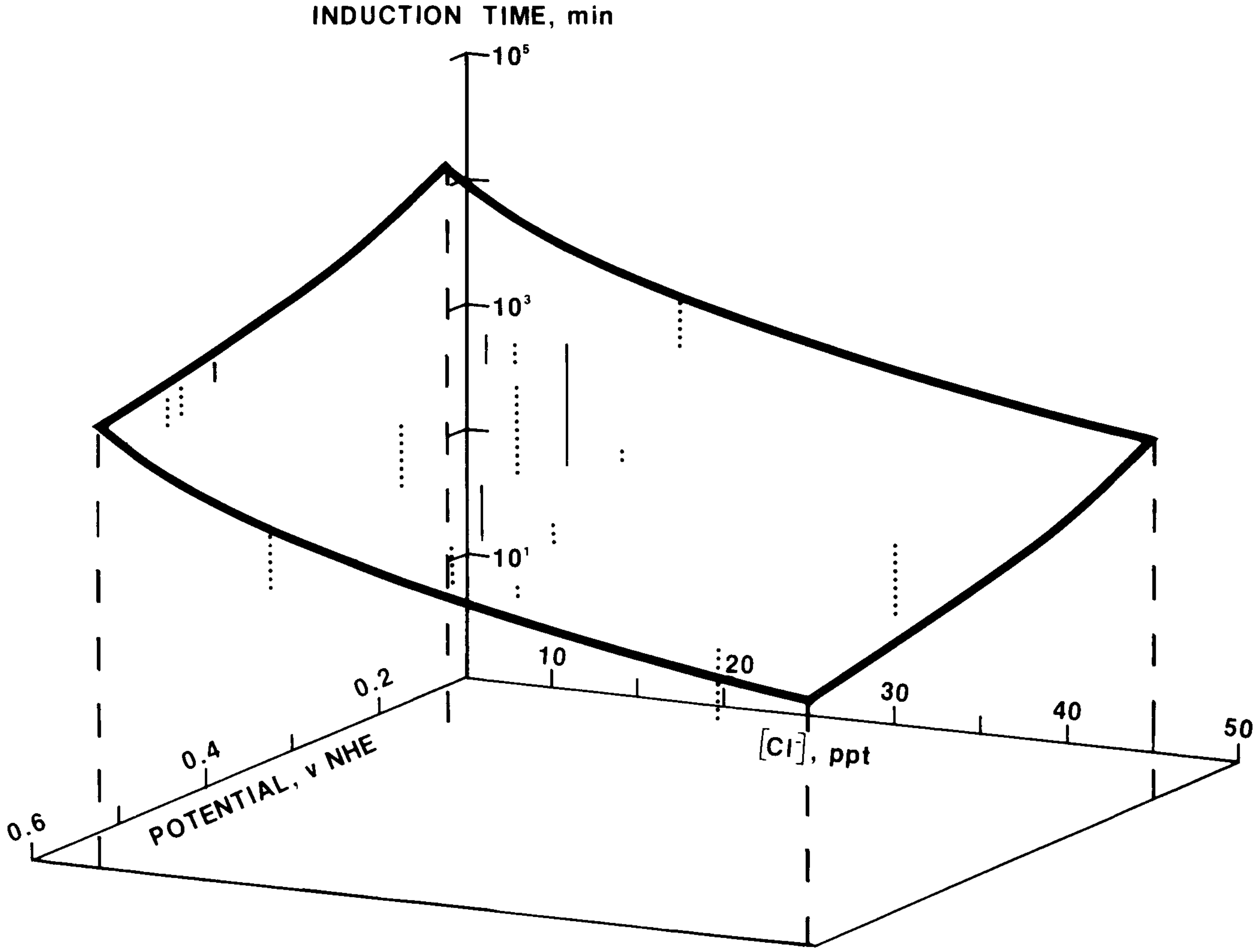

FIGURE 1.—Effect of chloride ion concentration and open circuit potential on time required for breakdown of the passive film on Fe-18Cr (*15*).

Research on the preparation of platinum-group-metal (PGM) coatings (*16-19*) demonstrated that these coatings on high-temperature alloys such as Mo can be used in place of bulk Pt shapes. Research on nitrided low-alloy steels showed that these steels exhibited corrosion properties equivalent or superior to those of stainless steels in aerated chloride-containing solutions (*20*).

The use of ion beams (ion implantation) to prepare a very thin corrosion-resistant region by implantation of ions such as Cr and Ni into a less corrosion resistant material was demonstrated in the early to mid 1970's (*21-22*). In later studies, ion implantation was used as a tool to study such factors as the role of Cr in reducing the oxidation of Fe (*23-24*), the effect of Ti, Mo, or Ta on the corrosion fatigue behavior of Fe in 0.1*N* H_2SO_4 (*25*), and the effect of Si, N, or Ar on the stress corrosion cracking (SCC) of 316 stainless steel in boiling $MgCl_2$ (*26*). While Mo and Ta did not affect the corrosion fatigue behavior of Fe, Ti reduced the fatigue lifetime due to the formation of an imperfect amorphous surface layer (*25*). Nitrogen and argon implantation increased the likelihood of SCC failure of 316 stainless steel, apparently as a result of ion damage and gas coalescence, but Si improved the SCC resistance, apparently due to the formation of a thin, resilient protective film (*26*).

Although it no longer uses this research tool, the Bureau is recognized as one of the pioneers in this field (*27*). A wide range of direct applications of ion implantation are underway at other laboratories to reduce corrosion and wear and to increase the durability of ceramics (*27*).

Another technique that can be used to prepare experimental alloys with controlled composition and microstructure is the use of a laser to melt and mix a surface coating with a thin layer (generally < 100 μm) of a substrate material. As shown in figure 2, a thin, apparently uniform alloy layer, in this case an Fe-Cr alloy, can be produced by this method. The electrochemically determined corrosion properties of a series of Fe-Cr alloys prepared by this laser mixing technique indicate that there may be unexpected spatial nonuniformities in the composition. A STEM study of the laser-processed region for these alloys is in progress in order to determine if composition and/or structure fluctuations are present that would explain the corrosion properties.

Another technique for alloy preparation, vapor quenching, has proven to be particularly useful in our studies to determine how alloy composition and structure affect corrosion properties. This technique involves sputtering a target material by energetic inert gas ions. The target contains the

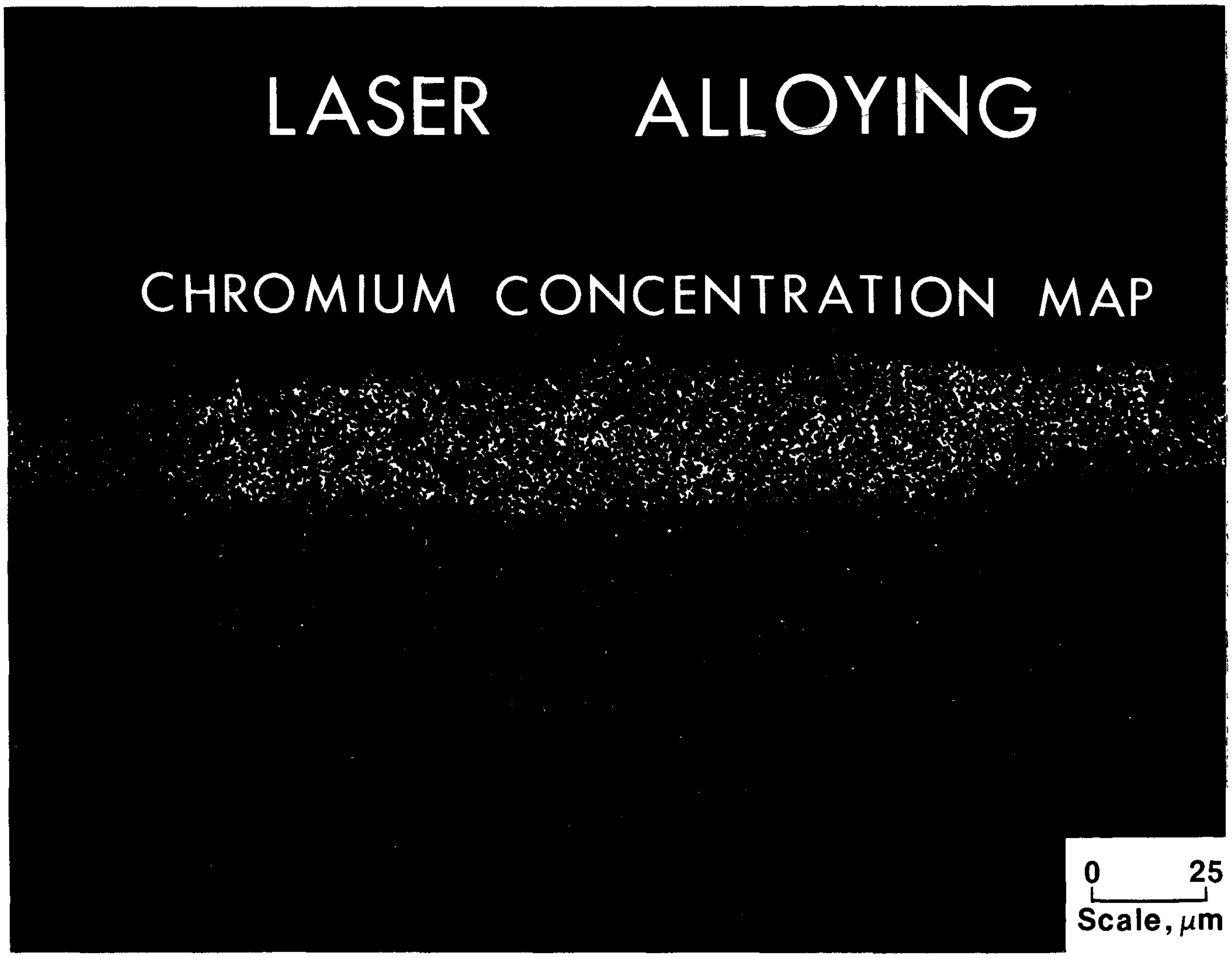

FIGURE 2.—Energy-dispersive X-ray map showing Cr in the cross section of Fe-5Cr substrate with an initial 3-mm-Cr coating after laser processing. Alloyed region is 25 to 30 mm thick with an average composition equivalent to Fe-15Cr.

components of interest either as a metallurgical alloy or as a compressed pellet composed of a mixture of the components in the proper ratio for the alloy being prepared. The sputtered target atoms are quenched onto the desired substrate. The alloy produced may be either crystalline or amorphous, depending on such factors as the nature of the substrate, the substrate temperature, the rate of deposition, and the surface and/or solid state mobilities of the alloy components.

An example of an alloy prepared by vapor quenching that demonstrates the role of structure in determining corrosion properties is Fe-Zr (*28*). The Fe-Zr vapor-quenched alloys[3] were found to be amorphous over the range of compositions from $Fe_{90}Zr_{10}$ to $Fe_{33}Zr_{67}$ (*28*). Electrochemical anodic polarization studies (*28*) showed the $Fe_{90}Zr_{10}$ alloy to be approximately as corrosion resistant as an Fe-18Cr alloy and the $Fe_{33}Zr_{67}$ alloy to be equivalent to pure Zr. All of the alloys exhibited a region of reduced anodic current ("passive region") over a range of potentials similar to that observed for many common stainless steels. A depth profile (fig. 3)

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[3] These alloys were prepared by Dr. C. L. Chien, Department of Physics, Johns Hopkins University, Baltimore, MD 21218.

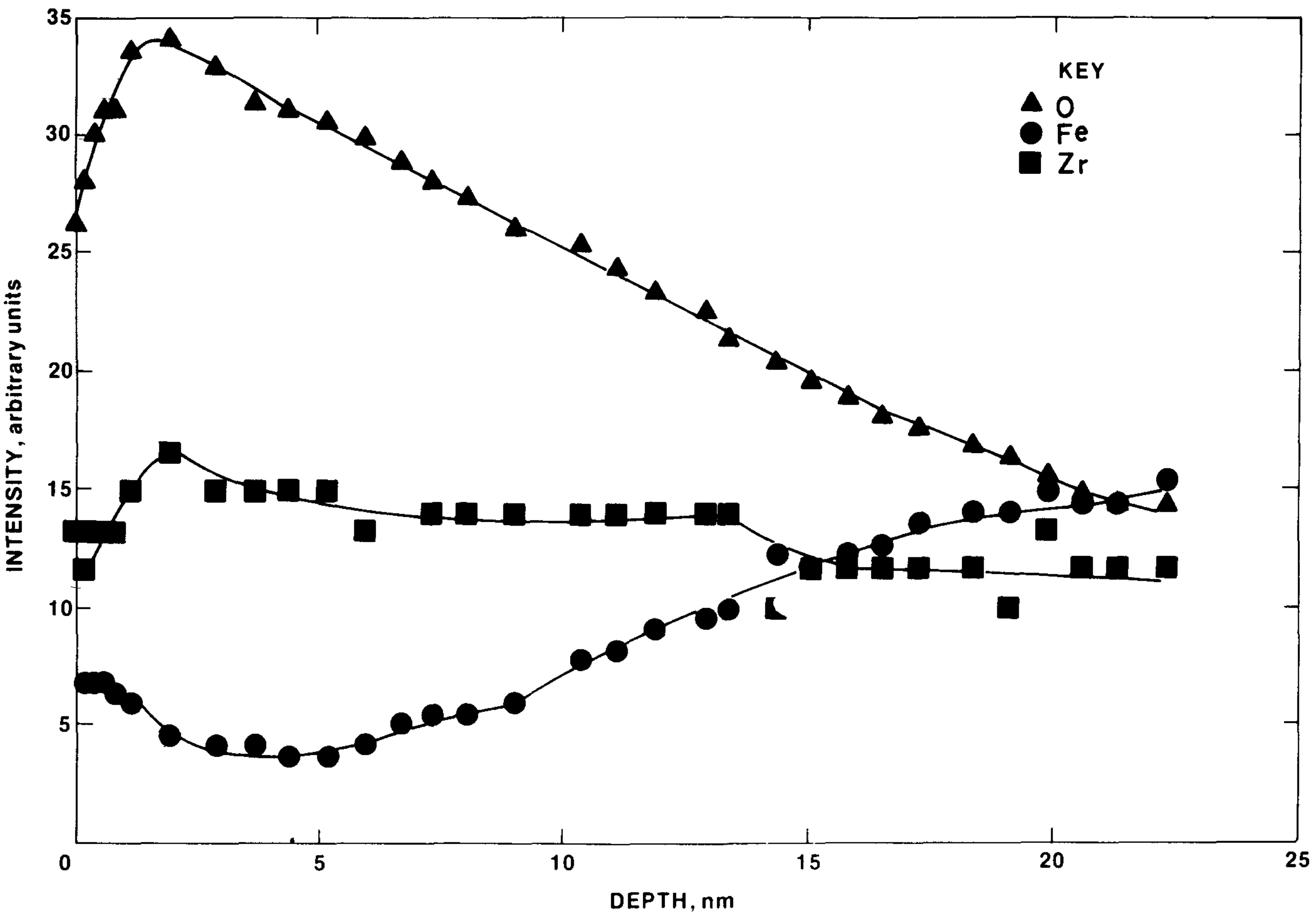

FIGURE 3.—Auger electron spectroscopy depth profile of $Fe_{60}Zr_{40}$ amorphous alloy after passivation in 1*N* H_2SO_4.

obtained by AES-ion sputtering of the $Fe_{60}Zr_{40}$ alloy following formation of the passive film in a 1*N* H_2SO_4 solution showed the passive film to be predominantly composed of Zr and O, with the Fe being significantly depleted in the first 10 nm of the corrosion film.

It is thus apparent that these alloys behave in a manner similar to that of pure Zr because of the formation of a Zr-enriched oxide film that resists the acidic environment. This behavior is equivalent to that of stainless steels, where the passive oxide film is highly enriched in Cr. Also, the lack of crystallinity seems to greatly improve the corrosion properties compared to what would be expected for a multiphase, crystalline alloy over this composition range.

A vapor-quenched alloy having the composition of commercial 304 stainless steel also has been prepared. This alloy was found to have a body-centered cubic crystalline microstructure rather than the face-centered cubic structure of the conventionally prepared 304 alloy (*29*). No amorphous phases were detected for this vapor-quenched alloy. Both intergranular and intragranular microvoids, ranging from 10 nm to 40 nm in size, were observed in the vapor-quenched 304 alloy. These voids, whose population decreased with increasing deposition (substrate) temperature, were mostly localized near the substrate (*29*) and are not expected to influence the corrosion properties. A transmission electron microscope micrograph of a typical alloy exhibiting intergranular voids is shown in figure 4.

The capabilities to characterize metallic materials and surface corrosion films and to prepare materials of desired composition and structure have improved dramatically during this decade. The ability to make optimum material selection depends on understanding how material composition and structure affect performance.

FIGURE 4.—Bright-field transmission electron micrograph of a vapor-quenched (at 77 K) 304 stainless steel film exhibiting intergranular voids and small grains. Picture is overfocused to show voids (*29*).

APPLICATIONS

A large number of commercial alloys were evaluated in high-temperature geothermal environments typical of western hydrothermal resources. These alloys included stainless steels (*30-36*), carbon and alloy steels (*30-34, 36*), Ni alloys (*30-34, 37*), Cu alloys (*31, 33, 38*), Ti alloys (*30-31, 33-34, 38*), Al alloys (*31, 34, 38*), and Cb and Mo alloys (*31, 33, 38*). Figure 5 shows the effect of Cr concentration on the general corrosion of a wide variety of commercially available steels in geothermal wellhead brine containing 115,000 ppm Cl^- (about 25 pct total dissolved solids) at pH 5.3 and 215° C. The measurements were made by linear polarization on "scale-free" surfaces and correspond to an upper limit on the rate one would observe in this environment. (Cramer (*39-40*) has described the design and techniques used in the linear polarization experiments.) An analysis of the linear polarization data showed that corrosion rates vary over more than two orders of magnitude. The solid curve represents the behavior of Fe-Cr alloys without other alloying elements; the cross-hatched area represents stainless steels with various additions of Mo and Ni and smaller amounts of other elements. Two regions exist where there are appreciable benefits from Cr additions. Small additions (2 to 4 pct) markedly reduce the corrosion rate compared to that of the mild steels. Further additions, up to 12 pct Cr, result in only marginal improvements, and there is no effect from the addition of other elements such as Mo, Ni, and Cu. On the other hand, very substantial reductions in corrosion rate are realized in the range of 18 to 29 pct Cr, and these reductions are markedly enhanced by the presence of small amounts of Mo and Ni. Longer exposures in this environment showed that a number of these alloys, particularly Fe-29Cr-4Mo and Fe-29Cr-4Mo-2Ni, have excellent resistance to general corrosion, crevice and pitting corrosion, and stress corrosion cracking and are recommended for use in severely corrosive geothermal environments.

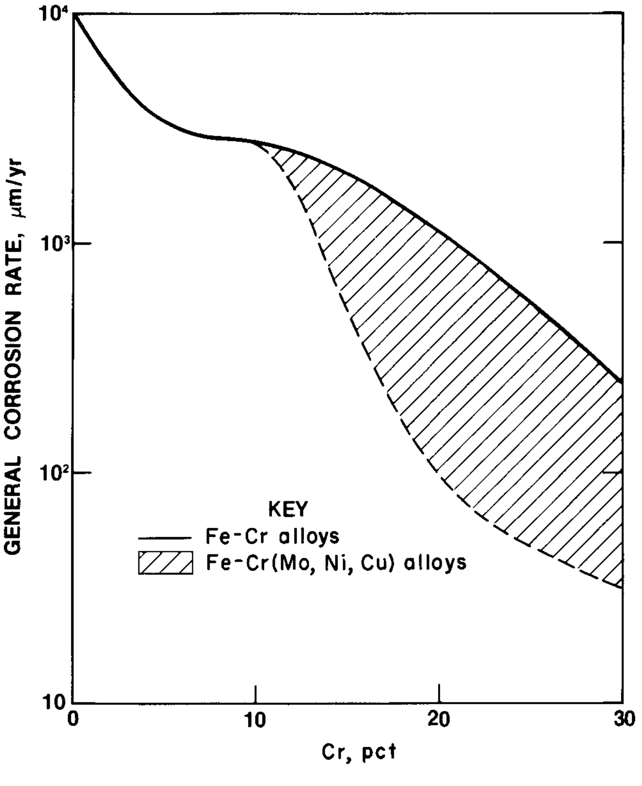

FIGURE 5.—Dependence of corrosion rate on Cr concentration and added Mo, Ni, and Cu for alloys in contact with geothermal brine containing 115,000 ppm Cl^- at pH 5.3 and 215° C.

The expertise developed in the material studies in geothermal environments has proved very useful in a new fundamental study of the behavior of metallic materials in high-temperature environments of interest in minerals processing. Hydrometallurgical and pressure hydrometallurgical processes for extraction, purification, and recovery of mineral and metal values frequently use acid sulfate environments. Typical processes of interest include H_2SO_4 pressure leaching of Ni-Cu and Ni-Co matte, acid pressure oxidation of ZnS concentrates, and H_2 pressure reduction of Cu from acidic solutions. These acid sulfate solutions are corrosive at ambient temperature and even more so at the temperatures encountered in pressure hydrometallurgical processes.

Stainless steels have been shown in Bureau research to exhibit widely varying corrosion resistance in acid sulfate environments at 50° to 250° C and pH 1 to 3. In pH 1, 0.9*m* Na_2SO_4, the ferritic stainless steels 430, Fe-18Cr, and Fe-18Cr-2Mo exhibit high corrosion rates at all temperatures. However, the austenitic stainless steels 304 and 316L, the duplex stainless steel Sandvik 3RE60, and ferritic stainless steels containing 25 to 30 pct Cr show a uniform increase in corrosion rate with temperature up to approximately 180° C, and then a decrease at higher temperatures. In the case of the ferritic stainless steels, the decrease is dramatic; corrosion rates are an order of magnitude lower at 250° C than at 180° C. This unexpected corrosion maximum correlates with a change in the composition and structure of the corrosion film from a mixed Fe-Cr oxide to one that is basically an oxide of Cr.

Figure 6 shows the alloy surface after the removal of the corrosion film for three ferritic stainless steels exposed 15 days to the pH 1 sulfate solution at 180° and 250° C. All of the SEM photomicrographs represent the same magnification. The rapidly corroding Fe-18Cr shows no evidence that metal dissolution has been altered by the corrosion film. Other than a slight roughening and the absence of crystallographic etch pits, the grains corrode as freely at 250° C as at 180° C. This is not the case for the other two alloys. Both alloys exhibit severe intergranular corrosion and localized attack on the grains at 180° C. These forms of attack are eliminated at 250° C. Both alloys are only lightly attacked. In the case of the Fe-26Cr-3Mo-2Ni, the grain boundaries actually appear more resistant to attack than the grains themselves. The attack on the Fe-29Cr-4Mo-2Ni is even more mild, and no crystallographic features are evident. As our understanding of the compositional, structural, and thermodynamic factors that govern the formation of stable, protective corrosion film in high-temperature solutions improves, applications of that technology are possible to lower Cr containing alloys, to lower and higher temperatures, and to erosive conditions.

In cooperation with the American Iron and Steel Institute, research is being conducted to determine the effects of the mixed acid bath variables on the pickling of commercial stainless steels. Acid pickling is widely used in the metal industry for cleaning annealed and hot-worked stainless steel (*41*). Compositions of pickling solutions are generally

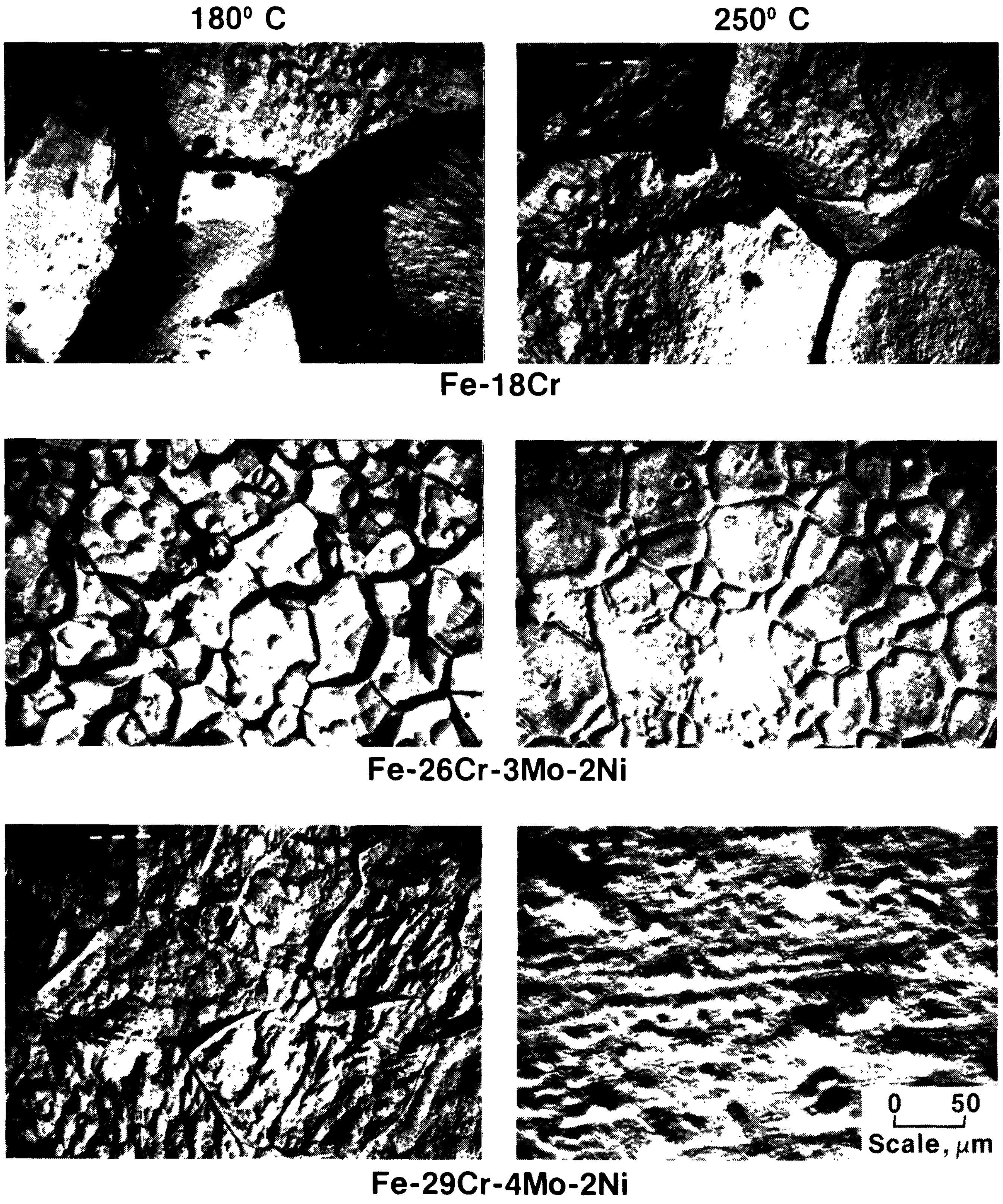

FIGURE 6.—Scanning electron micrographs following removal of corrosion film for three Cr alloys exposed at 180° C or 250° C to deaerated 0.9*m* Na_2SO_4 at pH 1.

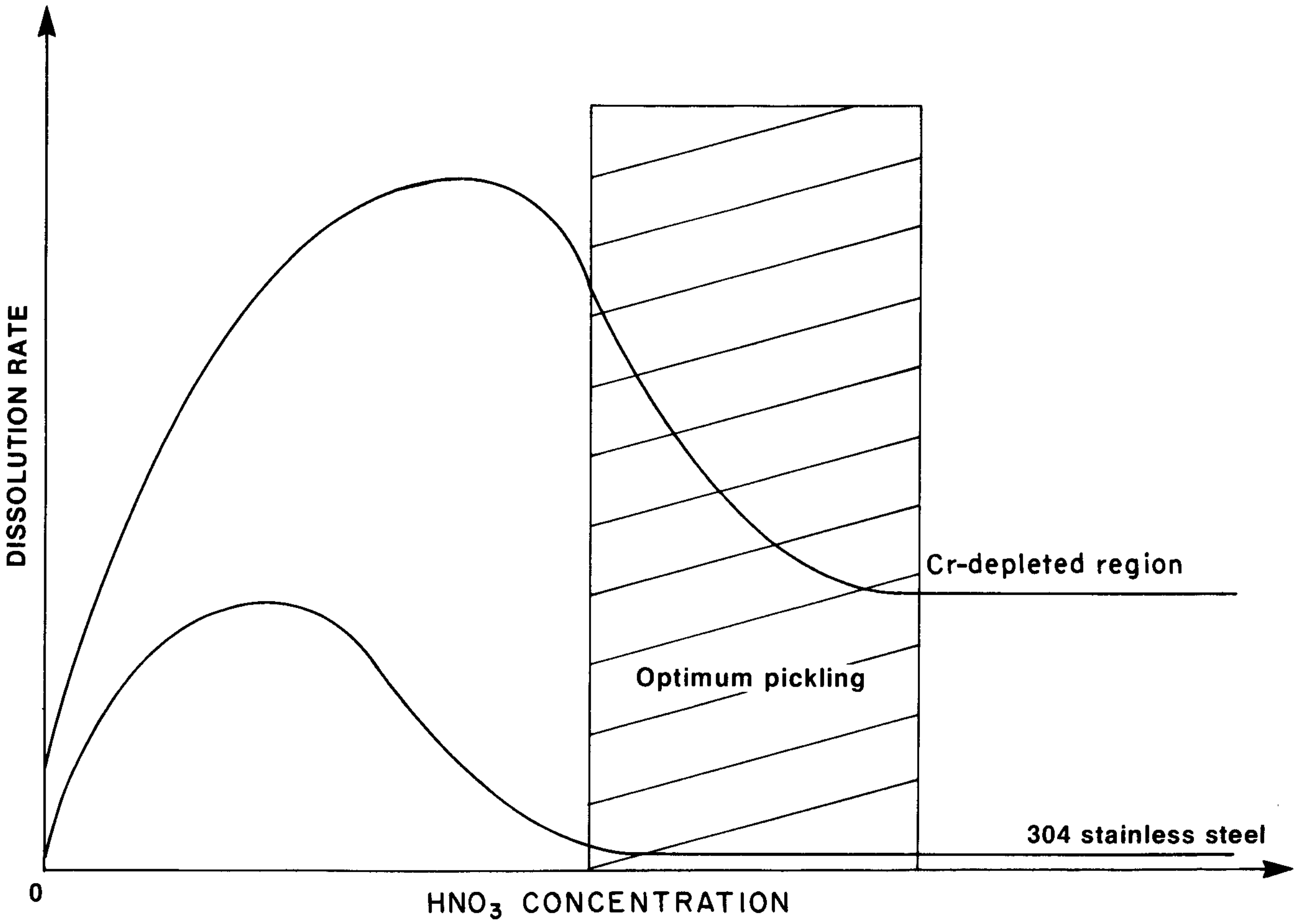

FIGURE 7.—Dependence of dissolution rate on HNO$_3$ concentration for 304 stainless steel and for Cr-depleted region. Hatched region indicates conditions where most efficient pickling would occur.

chosen for their ability to remove mill scale and alloy-depleted surfaces, and to provide an acceptable surface appearance. The most frequently used solution, HNO$_3$-HF, operates by undermining the scale and thus causing it to fall off. Simultaneously, the alloy-depleted surface layers (reduced Cr concentration compared with that of the bulk) are dissolved. These surface cleaning reactions result in annual losses amounting to several thousand tons of Fe, Cr, and Ni and create a sizable disposal problem. The dissolution products also interfere with the operation of the pickling bath. The effects of important parameters such as temperature, concentration of HNO$_3$ and HF, bath chemical complex formation, scale and alloy composition, agitation, aeration, immersion time, alloy cold work, and dissolved metal concentrations are being investigated. The objective is to select a set of operating conditions that yields improved surface quality of the stainless steels, reduces corrosion loss of critical elements, lessens the disposal problem, and extends bath life.

For the two steels currently being studied, alloys 304 and 430, corrosion and surface analysis studies have shown that the alloy dissolution rate increases with increasing HF concentration and that, for a given concentration of HF, for example, 0.5*M* HF, the dissolution rate exhibits a maximum at approximately 1*M* HNO$_3$. The Cr-depleted region dissolves at a much higher rate than the bulk alloy. A diagrammatic representation of these experimental observations is shown in figure 7. The obvious conclusion that can be drawn from this figure is that a region exists where optimum pickling will occur. Such information will enable the industry to improve the economics of pickling and to reduce the loss of Cr and other important alloying elements.

CONCLUSIONS

The selection of the most appropriate alloy for use in a given environment can only be made when performance, cost, and availability are known. As new environments are encountered, efficient techniques are required to determine and understand material performance. A fundamental understanding of the roles of alloy composition and structure in material performance is necessary in order to predict service life with respect to material loss by general corrosion or more localized forms of corrosion, such as pitting or stress corrosion cracking. Modern surface- and electroanalytical techniques and innovative material preparation methods permit the determination of mechanisms of corrosive material loss and of material protection, and allow for optimal use of our material resources.

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SUBSTITUTES FOR CHROMIUM IN CORROSION- AND OXIDATION-RESISTANT STAINLESS STEELS

By J. S. Dunning[1]

ABSTRACT

Bureau of Mines research into substitutes for Cr in stainless steels is reviewed. In less severe, low-temperature environments, steel containing 9 pct Cr with additions of Mo, Cu, and V provided aqueous corrosion resistance comparable to that afforded by 18-8 grades of stainless steels. In high-temperature, oxidation-resistant applications, Al and Si have demonstrated potential for replacing significant amounts of Cr. Additions of up to 5 pct Si or Al can replace significant amounts of Cr while retaining or even enhancing oxidation resistance. Basic studies to determine the role of Cr, Si, and Al in providing oxidation protection also are surveyed.

INTRODUCTION

The production of stainless steels accounts for approximately 70 pct of the Cr imported for the metals industry in the United States. A sizable portion of this is used for AISI 300 series grades, type 304 in particular. These steels withstand a greater variety of service environments than any other commercial metal alloys. This versatility stems from resistance to corrosion and oxidation, room-temperature and high-temperature strength, excellent ductility and formability, machinability, weldability, appearance, and ease of maintenance. Alloys that do not possess this rare versatility are not likely to substitute for stainless steels in a significant range of applications.

The development of new alloys is a slow process, and certification of these alloys in critical applications takes years of testing after the alloy compositions have been finalized. However, the development of alloy substitutes that in the event of a Cr supply disruption could be used in the less demanding applications of stainless steel could be important. Very large tonnages of Cr are used in the less demanding applications. Stockpile and recycled Cr could be used for critical defense and high-technology process requirements. Since Cr is currently cheap and readily available, there is little incentive for private industry to develop substitute alloys, and the responsibility has fallen largely to federally funded research. In addition to the development of versatile low-Cr substitute alloys, basic research on the principles controlling oxidation-corrosion behavior in Fe-base alloys is necessary to advance the state-of-the-art in developing low-Cr or non-Cr alloys that can function effectively in severe environments.

Abbreviations Used in This Paper

°C	degree Celsius
h	hour
N	normal (concentration)
pct	weight percent
ppm	parts per million

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BUREAU OF MINES RESEARCH ON SUBSTITUTES FOR CHROMIUM IN STAINLESS STEELS

Reduced dependence on imported Cr can best be realized by finding substitutes for Cr in stainless steel alloys. Technical opportunities for reaching this goal are outlined below.

A. *Conservation*
    Rycycling
    Improved service life of parts
    Improved processing
B. *Partial Replacement*
    Performance needs related to application
C. *Complete Substitution*

Bureau research has indicated that, in terms of new alloys, complete substitution for Cr is unlikely; partial substitution has therefore been the most fruitful research approach.

As stated above, the stainless steels are versatile materials. A substitute alloy will have to possess the same versatile traits outlined as follows:

A. Cost.
B. Workability.
C. Weldability.
D. Machinability.
E. Corrosion or oxidation resistance.
F. Room and/or high-temperature mechanical properties.

Any alloy that falls short in one or more of these requirements may find only limited use as a substitute material. Since large tonnages of stainless steel are used in such a broad array of applications, it is extremely difficult to categorize end uses. Figure 1 is a qualitative representation of the tonnages of stainless steel used at various temperatures combined with a qualitative representation of the criticality of the application to the economic and military well-being of the United States. Very large tonnages of stainless steels are used at low temperatures in corrosion-resistant applications where plain carbon steels or low-alloy steels will not suffice. Typical examples are found in the food and transportation industries. At intermediate temperatures, lower tonnages are used, but the applications are more demanding in terms of properties. These applications are at the heart of high-technology industry such as the chemical process and power generating industries. At the high end of the temperature spectrum, the quantity of Cr used is much less, but uses are critical high-technology and military applications, such as turbines and jet engines. Stainless steels and high-Cr, Fe-base alloys are currently used over this wide temperature spectrum. It is unlikely that a universal substitute alloy will be developed that will find application over this entire temperature range. Bureau research has shown that alloying additions that can substitute for Cr to provide corrosion resistance at ambient temperature are generally of little help for oxidation resistance at elevated temperature, and vice versa (*1*). Thus, technically there is little justification for developing a universal substitute. Bureau research is aimed at two categories: (1) low-temperature, corrosion-resistant applications, and (2) high-temperature, oxidation-resistant applications.

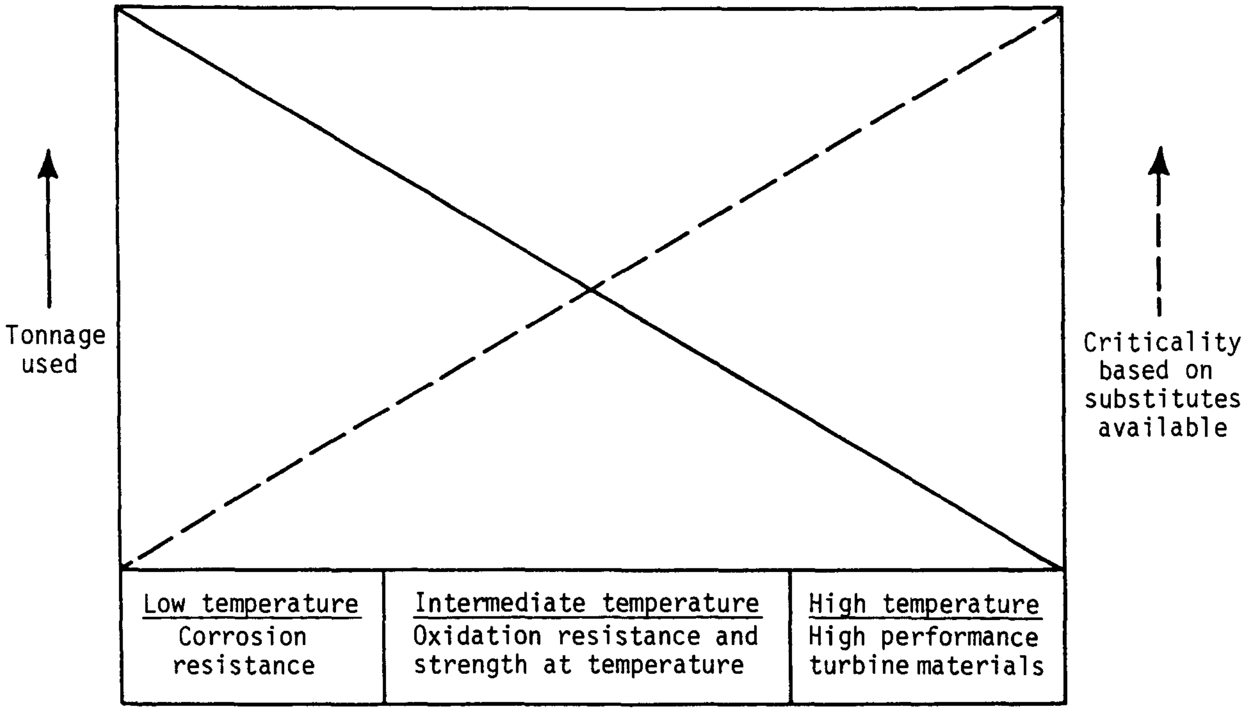

FIGURE 1.—Qualitative representation of tonnages of stainless and high-temperature steels.

SUBSTITUTE OPTIONS FOR CORROSION RESISTANCE

Low-temperature, corrosion-resistant applications consume large tonnages of stainless steel and thus present a large potential for Cr conservation. For example, if the average Cr content could be reduced from 18 pct to 12 pct for these applications, several million pounds of Cr could be saved annually.

The literature on alloying elements that modify the corrosion behavior of Fe-Cr and Fe-Cr-Ni stainless steels has been recently summarized (*2*). Taking the elements that have a beneficial effect on corrosion and/or pitting corrosion resistance of austenitic stainless steels and eliminating Cd, Be, Ag, Re, and Zn on the basis of either toxicity, cost, or adverse effect on other properties, we have for consideration Mo, Ni, Si, Cu, V, and N (*1, 3*).

Bureau-sponsored contract research conducted by International Nickel Co. showed that a stainless steel containing 9 pct Cr, with additions of Mo and possibly Cu and V, could provide comparable ambient temperature corrosion properties to 18-8 grades of stainless steel in less severe environments such as 1*N* H_2SO_4, marine environments, and 10,000 ppm Cl^- solutions. Mechanical properties, workability, and weldability of these austenitic alloys are all acceptable.

The fact that these alloys are suitable for less severe environments should not be taken as an indication of limited potential. Large tonnages of stainless steel are used in just such applications. Thus, the reduction from 18 pct Cr to 9 pct Cr is indeed significant.

Typical additions in the 9-pct-Cr alloys range from 2 to 5 pct Mo with 2 pct V and 2 pct Cu. Nickel additions in the range of 12 to 16 pct are required to maintain an austenitic microstructure (*4*), although Ni requirements can be reduced through minor additions of Mn and/or C.

SUBSTITUTE OPTIONS FOR OXIDATION RESISTANCE

The effect of alloying additions on the resistance of stainless steels to oxidation has been well documented (*2, 5*). Additions of Al and Si are of primary interest. These two elements have the potential for replacing substantial amounts of Cr in high-temperature applications. Furthermore, minor additions of Y, Ca, Ce, and N can be considered as candidates to enhance oxidation resistance, but it is not likely that any of the four, by itself, can replace a great deal of Cr.

Relatively small additions of Si and Al (up to 5 pct) can replace significant quantities of Cr while retaining or even improving on the oxidation resistance of 18-pct-Cr steels. Aluminum in combination with lower Cr additions also can result in enhanced resistance to high-temperature corrosion in sulfur-containing environments (*6*).

Silicon additions in the range of 3.5 to 4.5 pct with or without an Al addition of 1 to 2 pct provides excellent oxidation resistance in 8- to 10-pct-Cr alloys.

Aluminum additions to 4 pct with or without Si additions of 1 pct provide excellent oxidation resistance in 8- to 10-pct-Cr alloys. Aluminum additions above 4 pct can adversely affect ductility and workability (*7*).

A combination of Al and Si performs better than either alloying element by itself.

Additions of Ni, Mn, and C are necessary to retain an austenitic microstructure. Chromium is a ferrite stabilizer, and Ni, Mn, and C stabilize austenite. The potential Cr substitutes–Al and Si–are potent ferrite stabilizers. Therefore, to control alloy structure, substitution is usually done in terms of the Cr and Ni equivalents:

$$\text{Cr equivalent} = \text{pct Cr} + 2(\text{pct Si}) + 5.5(\text{pct Al})$$
$$\text{Ni equivalent} = \text{pct Ni} + 30(\text{pct C}) + 0.5(\text{pct Mn}).$$

Thus, if Cr is replaced one-for-one by Al or Si, Cr-equivalent values will be higher than they are for conventional 18-pct-Cr stainless steels, and Ni-equivalent values would have to be raised accordingly to maintain an austenitic structure.

In addition, as Cr is lowered progressively, the austenitic structure becomes more unstable in relation to the thermally induced and strain-induced martensite transformation. Therefore, there are limits on how far the Cr content can be reduced without significantly raising the Ni content (and cost) to retain a stable austenitic microstructure. Manganese can be added to reduce the required Ni, but Bureau research has shown that large Mn additions compromise the oxidation properties of these alloys and increase work-hardening rates (*8*). However, small Mn additions (1 to 2 pct) help in stabilizing the austenitic microstructure and improve workability.

Typical compositions currently being studied for high-temperature use include Fe-8Cr-14Ni-3.5Si-1Al-1Mn for oxidation resistance and Fe-10Cr-14Ni-2Mn-4Al for a combination of oxidation and sulfidation resistance.

BASIC STUDIES OF OXIDATION

While oxidation rates and mechanisms of many pure metals and simple alloys have been determined in controlled environments, we have not learned to predict the behavior of more complex alloys from first principles. As a practical example, it is not possible to lower the Cr content of commercial stainless steels and, either from theory or empirically derived relationships, select the concentrations and combinations of Al and Si that will maintain the same oxidation protection.

After a survey of lower Cr (< 10 pct), Fe-base compositions with Al (0 to 4 pct) and Si (0 to 6 pct) additions, an alloy was selected with Al and Si additions in the midrange of the above compositions and with oxidation and fabrication properties similar to those of AISI 300 series stainless steels.

An Fe-8Cr-14Ni-3.5Si-1Al-1Mn composition was studied to determine the role of Cr, Si, and Al in providing oxidation protection (*9*). Scanning electron microscopy, X-ray diffraction, microprobe analysis, and Auger spectrometry were used to determine the composition and structure of the oxide formed on the alloy as a function of temperature and time. The alloy was oxidized in air at 700° to 1,000° C for 1 to 1,000 h. The initial protection was derived from an Al-based Fe and Cr spinel. Later oxide protection came from the development of a chromium oxide (Cr_2O_3) layer next to the base metal surface. An outer oxide layer also formed which was a mixed composition spinel of Cr and Mn ($MnO{\cdot}Cr_2O_3$). The aluminum that was part of the original protective layer eventually (after 100 h) formed a pure Al_2O_3 precipitate in the base metal. Aluminum in this original oxide structure eventually was dispersed into the base metal. Later oxidation protection came from development of a Cr_2O_3 layer next to the base metal surface.

Nickel had little effect on the oxidation process, but Si played a role in controlling diffusion rates. The rate of oxidation appeared to be controlled by the diffusion of Cr and Mn into the metal-oxide interface. The rate of diffusion may be controlled by the formation of a thin layer of SiO_2 at this interface.

CONCLUSIONS

1. Elements that provide low-temperature corrosion resistance in low-Cr stainless steel substitutes do not necessarily provide high-temperature oxidation resistance. The most effective research strategy is to study separate alloys for low- and high-temperature application.
2. To duplicate the versatility of the austenitic stainless steels, it is desirable to maintain an austenitic microstructure for both low- and high-temperature alloys.
3. Stainless steels containing 9 pct Cr, with additions of Mo and possibly of Co and V, can provide low-temperature corrosion properties comparable to 18Cr-8Ni grades of stainless steels in less severe environments, such as 1*N* H_2SO_4, marine environments, and 10,000 ppm Cl^- solutions.
4. In high-temperature applications, additions of Si and/or Al of up to 5 pct can replace significant quantities of Cr while retaining or enhancing the oxidation resistance typical of 18-pct-Cr stainless steels. Good combinations of properties have been demonstrated in alloys with 8 to 10 pct Cr, and the potential for further reduction in the Cr content has been demonstrated.
5. Basic studies of oxidation kinetics have been successful in defining the unique characteristics of Si and Al in combination with Cr in providing oxidation resistance.
6. Studies of sulfidation mechanisms have shown that Al additions in combination with Cr can drastically improve sulfidation resistance at elevated temperatures.

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WEAR-RESISTANT ALLOYS—REDUCING CHROMIUM CONTENT AND IMPROVING WEAR RESISTANCE

By Robert Blickensderfer[1]

ABSTRACT

This report reviews Bureau of Mines research toward reducing the wear losses of strategic and critical materials. Research on low-alloy steels showed that the Cr in the steel does not enhance wear resistance; therefore, Cr may be reduced in many applications. In high-Cr white cast irons, the spalling wear resistance was improved 24 times over the as-cast condition by heat treatment. Welded hard facings in the Fe-Mo-Ni-Si system are being investigated in an attempt to acquire adequate wear resistance in alloys that are free of Co and Cr. Plasma-sprayed coatings, using TiB_2 to impart wear resistance, are being developed to replace hard facings high in Cr, Co, and Ni. Research on grinding ore in phosphoric acid waste water showed that Cr is not necessarily effective in reducing wear under erosion-corrosion conditions.

INTRODUCTION

Chromium is an important alloying element for imparting wear resistance to numerous steel alloys, white cast irons, and weld hard facings. The so-called abrasion-resistant steels typically contain 0.5 to 2 pct Cr. The abrasion-resistant, alloyed white cast irons contain 2 to 28 pct Cr, and as much or more is used in welded hard-facing alloys.

The Bureau of Mines is particularly concerned about the tremendous wear losses that occur in mining and mineral processing equipment. Power shovels, excavators, scoops, bucket teeth, and other kinds of earth-penetrating equipment suffer greatly from wear. Some parts wear out completely after several weeks or even days of use. The greatest tonnages of wear losses, however, occur in crushing and grinding equipment. Typically, about 400,000 st of rods, balls, and mill liners are consumed annually in the United States just for mineral grinding (*1*).

The thrust of the Bureau's wear research is toward improving wear resistance without increasing the Cr content of alloys and toward reducing the Cr content of other alloys without sacrificing wear resistance. Such results would not only conserve Cr but would also reduce operator costs and downtime.

Abbreviations Used in This Paper

cm	centimeter
°F	degree Fahrenheit
in	inch
kg	kilogram
m	meter
m/g	meter per gram
mm^3	cubic millimeter
µm	micrometer
mm/yr	millimeter per year
N	Newton
pct	weight percent
st	short ton

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WEAR TEST FACILITIES

The Bureau's laboratories have a total of 12 wear test rigs in use; 10 are for abrasive (including erosive) wear tests, and 2 are for repeated impact-spalling wear tests. Ten of the units are located at the Albany Research Center, one is at the Rolla Research Center, and one is at the Salt Lake City Research Center. The wear tests, fully described by Blickensderfer (*2*), include dry-sand, rubber-wheel abrasive wear; Taber Abraser; abrasion resistance of refractory materials; dry-particle erosive wear; elevated-temperature dry-particle erosive wear; low-angle slurry wear; jaw crusher gouging wear; ball mill wear; pin-on-drum abrasive wear; and high-speed impact gouging. The two repetitive impact tests include a ball-on-block impact-spalling test and a ball-on-ball impact-spalling test.

The wear research has several aspects. One is the evaluation of existing commercial alloys by laboratory wear testing. These data give baseline wear values for future comparison and provide unbiased wear values for industry. Another part of the research effort is to determine the basis of various wear processes in order that wear might be reduced through better understanding and more controlled application. The third part, which also is the basis for the previous two, is to reduce the consumption of Cr. The effect of Cr content on the wear of commerical alloys, as well as experimental alloys, is studied. This requires the melting, casting, fabricating, and heat treating of alloys. A battery of analytical methods is used to support this work.

RESULTS

LOW-ALLOY STEELS

The question arose as to whether the Cr used in low-alloy steels actually contributes to wear resistance. In previous investigations, Haworth (*3*) and Moore (*4*) found that C was important in providing wear resistance in steels. Grinberg (*5*) found that Cr, W, and V in ferrite did not increase the wear resistance.

The 41 different steels that were evaluated by the Bureau ranged from pure iron to about 2 pct Cr, Mn, Ni, Si, and/or Al, 1.07 pct C, and lesser amounts of Mo, Cu, and S. With several different heat treatments, a total of 80 test specimens were evaluted by the ASTM dry-sand, rubber-wheel abrasive wear test. The results, as reported by Tylczak (*6*), showed that Cr was not effective in providing wear resistance to the steels, and furthermore, may even be slightly detrimental. Because wear resistance of a given alloy composition normally increases with hardness, Cr may be useful in thick sections by increasing the depth of hardening (hardenability). Carbon, on the other hand, was the most potent addition for wear resistance.

The above results are based on a multiple-linear-regression program that considered various functional relationships and included hardness and the effect of nine elements. A simplification of the results for Cr is shown in figure 1 for two narrow ranges of C and hardness. Although the effect of other alloying elements, such as Mn and Si, cannot be shown in this figure, the graph does show that Cr does not improve wear resistance.

The detailed analyses resulted in two equations that relate wear, in cubic millimeters, to composition. For hardened steels,

$$\text{wear} = 14\left(1+\frac{1}{C}\right), \text{ or wear resistance} = \frac{1}{\text{wear}} = \frac{C}{14(1+C)}; \quad (1)$$

and for unhardened steels,

$$\text{wear} = 190 - 130\sqrt{C} - 25(\text{Mn}) + 110(\text{Mo}), \quad (2)$$

where the elements are in percent.

To get the best abrasive wear resistance from a low-alloy steel, (1) make the steel as hard as practical, (2) use a high carbon level, at least 0.7 to 0.8 pct, (3) use up to 2 pct Mn, and (4) add other alloying elements as required, for example, Ni for toughness and Cr or Mo for hardenability.

ALLOYED WHITE CAST IRONS

Wear of alloyed white cast irons accounts for significant losses of Cr. Although the white cast irons are very abrasion resistant, wear by spalling is considerable, and their brittleness limits them to low-impact applications, as reviewed by Dodd (*7*). To reduce the brittleness compared with that of the older NiHard 4 white cast iron, the high-Cr white cast irons, containing 15 to 26 pct Cr, were developed. Spalling of the high-Cr white cast irons, however, continued to be a problem in repeated-impact situations, such as those encountered in ore crushing and grinding equipment. Although much was learned by experience and from the ball-on-block experiments of Dixon (*8*), basic causes of spalling were not understood. The development of the repeated impact spalling test by Blickensderfer and Tylczak (*9*) allowed systematic studies of impact spalling under controlled laboratory conditions.

The first approach by the Bureau's research was to determine whether heat treatments could be found that would make white cast irons more resistant to spalling. Figure 2 shows the effect of heat treatment on the spalling life of a commercial white cast iron containing 17 pct Cr. It

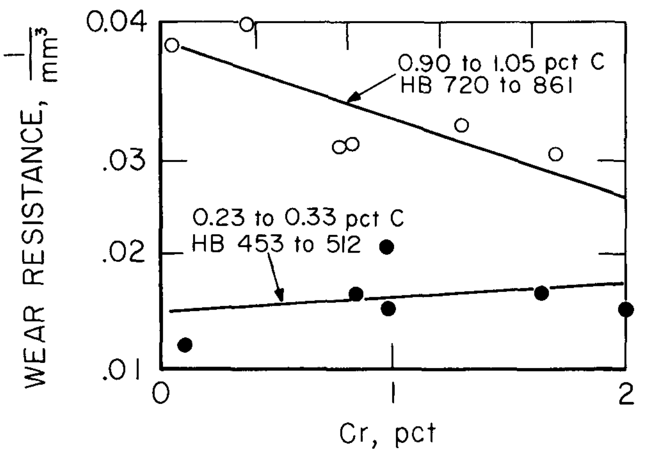

FIGURE 1.—Effect of Cr on wear resistance of hardened low-alloy steels. Three-body, dry-sand, rubber-wheel abrasive wear, 133-N load, 1,436-m wear path.

is typical of the results for other high-Cr white cast irons studied. The balls in the as-cast condition had the shortest spalling life, or least spalling resistance, less than 10,000 impacts. The subcritical heat treatments at 1,100° and 1,200° F produced excellent spalling resistance, with lives of about 200,000 impacts. The reaustenized balls were intermediate in spalling. Thus, for only 11 different heat treatments, the spalling rate differed by a factor of 24. But how did the heat treatments affect abrasive wear?

The abrasion resistance was affected much less by heat treatment, but still by a factor of 3.1. The relation found between spalling resistance and abrasion resistance (fig. 3) is more pertinent than either of the individual relationships. It is apparent from the graph that spalling resistance is gained at the expense of abrasion resistance and vice versa. From this relationship, a heat treatment may be selected that will provide the correct balance between spalling resistance and abrasion resistance for the particular application. The net results of this investigation will be to increase the life of the high-Cr cast irons and thereby reduce Cr consumption.

The second approach to the research on white cast irons was to attempt to improve the toughness and abrasion resistance of the relatively low Cr NiHard 4 by alloy modification. NiHard 4, containing 8 to 10 pct Cr, is widely used in mineral processing equipment under limited impact conditions. The impact resistance, as well as the abrasion resistance, is generally less than that of the high-Cr white cast irons. In the research, the composition of NiHard 4 was modified by reducing the Si from the normal 1.6 to about 1.1 pct, increasing Mn from the normal 0.7 to 2 pct, and adding 0.8 pct Mo. As seen in table 1, not only was the toughness increased, the abrasion resistance was improved.

TABLE 1.—Effect of modified composition of NiHard 4

Alloy	Impacts on block to fracture[1]	Abrasion resistance,[2] m/g
NiHard 4	3,400	7,800
Modified[1]	>100,000	22,000

[1] 1.8-kg ball dropped 3.5 m onto block, 5 cm thick.
[2] Dry-sand, rubber-wheel test, 133-N load, 1,435 m.
Both alloys received the same heat treatment.

WELDED HARD FACINGS

The research approach was to seek an Fe-based, welded, hard facing that contained no Cr or Co and had reasonably good wear resistance. Present wear-resistant, commercial hard-facing alloys are based on either a work-hardenable Mn alloy or a high-Cr white cast iron, a Cr-Co alloy, or a Cr-Ni-Co alloy in which carbide particles provide the wear resistance. The Bureau investigated the potential of intermetallic precipitates for providing wear resistance. The Fe-Mo-Ni system was chosen because these elements are not strategic and the intermetallic phases exist over a wide range; namely, about 15 to 50 pct Ni and Mo.

Because this is a relatively new area of research, a considerable effort was required to obtain information on phase identification, solidus temperatures, and welding parameters. The effects of adding up to 1 pct C and up to 5.4 pct Si also were evaluated. Specimens were prepared by submerged-arc welding on 2-in-thick mild steel plate, using Mo-Ni powder additions and an Fe-Mo-Ni filler wire. Additional information was reported by Scholl (*10*).

Abrasive wear by pin wear tests of the welds showed that none was as wear resistant as commercial high-Cr hard

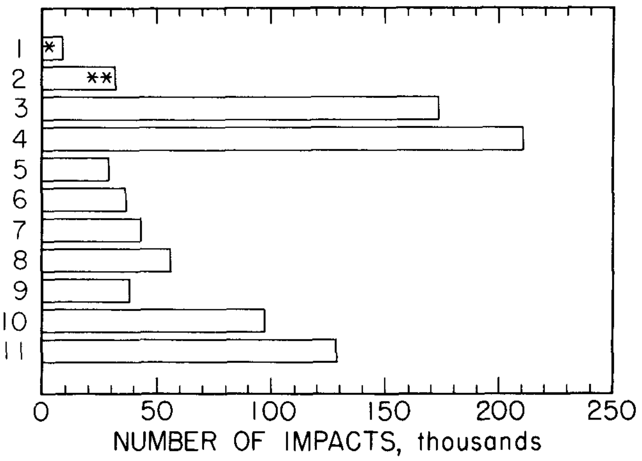

FIGURE 2.—Effect of heat treatment on spalling life of high-Cr white cast iron. Life is for 100-g loss; each * donotes breakage of a ball. In the following numerical code, S = subcritical and R = reaustentized.

1. As-cast
2. S at 1,000° F
3. S at 1,100° F
4. S at 1,200° F
5. R at 1,750° F
6. R at 1,850° F
7. R at 1,950° F
8. R at 1,850° plus S at 850° F
9. R at 1,850° plus S at 900° F
10. R at 1,850° plus S at 950° F
11. R at 1,850° plus S at 1,000° F

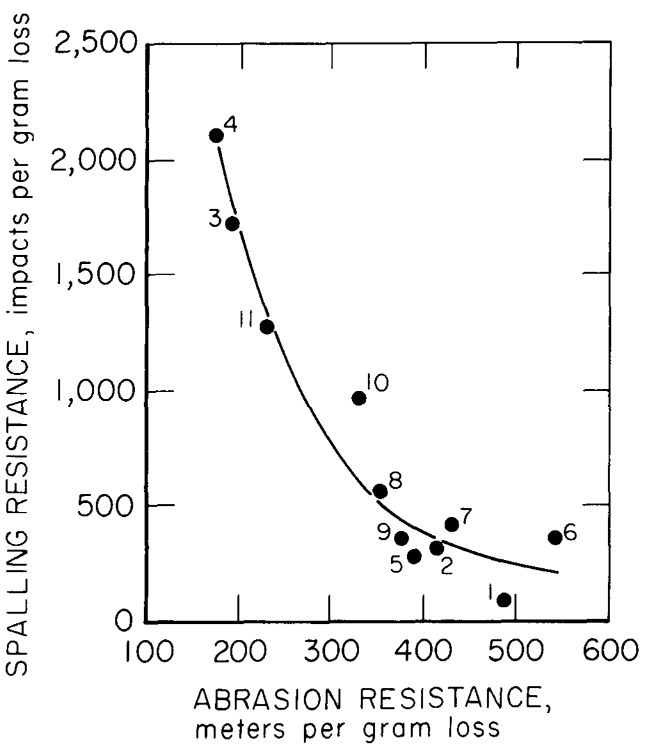

FIGURE 3.—Relationship between abrasion resistance and spalling resistance of a high-Cr white cast iron. Numbers refer to heat treatments in figure 2. Abrasion is by 105-mm garnet, 2-body, 66.7-N load.

facing. The amount of wear of the experimental weld alloys did not correlate with hardness, but the wear resistance did increase as the Mo and Ni contents were increased. The microstructural constituents and morphology affect wear in some ways not fully understood. The lamellar eutectic microstructure decreases wear resistance; whereas complex multiphase intermetallics in an austenitic matrix improve wear resistace. The weld hard facing with the best wear resistance to date was an Fe-20Mo-15Ni-5.4Si composition. It possessed a multiphase microstructure with at least two eutectics and two intermetallics in a matrix of Fe-Ni austenite. The pin wear resistance of 158 m/g was equivalent to that of a heat-treated, high-Cr white cast iron, even though the hardness was only HRC (Rockwell C) 40.

PLASMA-SPRAYED COATINGS

Plasma spraying, as a method of applying hard surfacings, has potential for forming alloys that cannot readily be achieved by welding. The research approach, carried out at the Bureau's Rolla Research Center by McIlwain and Neumeier (*11*), is to provide wear resistance by the addition of TiB_2 to an Fe-base, Cr-Ni alloy. The alloy is intended to replace Co-based hard-facing alloys and also may replace high-Cr white iron hard facings.

Powders are prepared by mechanical alloying of TiB_2 with elemental powders Fe, Cr, and Ni, plus lesser amounts of C, Mn, Mo, W, Si, and Cb. Blended powders are sprayed onto steel by a plasma arc gun using argon-hydrogen as the plasma gas and argon as the carrier gas. The resulting coatings contain a network of oxides, carbides, and fine precipitates and have low porosity. The optimum TiB_2 content is about 5 pct. The abrasive wear resistance and adhesive wear resistance appear to be superior to those of plasma-sprayed Stellite 6. Other properties, such as hot hardness, where Stellite 6 excels, are being compared. The bond strength to the steel base needs to be improved, and research is continuing on this problem.

ABRASION-CORROSION OF HIGH ALLOYS

The approach is to determine whether high alloys, such as Ni-based alloys and stainless steels, are justified for use where abrasion occurs simultaneously with corrosion. It is known that high-Ni alloys and stainless steels resist most acids. However, when abrasion occurs simultaneously with corrosion, the passivated protective film can be destroyed as fast as it forms, and the question arises whether the alloy additions are worthwhile for reducing the overall wear.

Tests were carried out by the Bureau in a laboratory ball mill by grinding phosphate rock in phosphoric acid waste liquid with alloy test balls. The results, reported by Singleton and Blickensderfer (*12*), are summarized in figure 4. The nickel alloys and stainless steels are resistant to corrosion but wear significantly when abrasion is combined with corrosion. The alloyed white cast irons, normally very abrasion resistant, suffered the highest wear rate under the combined action of abrasion and corrosion. The low-alloy, high-C steel, under the given conditions, is the most cost-effective material. This example shows that some alloys containing relatively little Cr may actually wear less under certain corrosive wear conditions than alloys containing significant amounts of Ni and Cr.

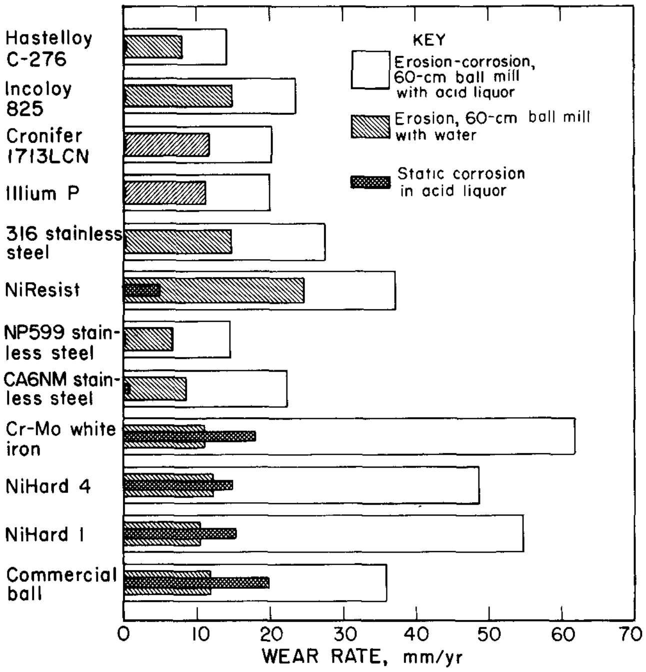

FIGURE 4.—Wear and corrosion of 12 alloys during laboratory milling of phosphate rock.

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BUREAU OF MINES RESEARCH RELATED TO REFRACTORIES CONTAINING CHROMIUM

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ABSTRACT

Past research at the Bureau of Mines directed toward reducing the quantity of imported refractory-grade chromite, included a study of the recycling of waste refractory furnace linings. Samples of used magnesia-chromite refractories removed from steel furnaces and copper smelters were beneficiated to remove metal and other contaminants. Refractories produced from recycled argon-oxygen decarburization (AOD) linings compared favorably with conventional commercial magnesia-chromite refractories of similar composition. Slag resistance was superior for the recycled brick.

The high-temperature modulus of rupture (MOR) and hot-load properties of domestic periclase grain, used in magnesite refractories, were improved by adjusting the calcium-to-silica ratio and/or by minor additions of ZrO_2 or MnO_2. Additions of minor amounts of soluble salts or oxides to both MgO and Al_2O_3 brick dramatically improved their high-temperature properties–particularly hot MOR and slag resistance. These improved refractories, produced from domestic resources, could substitute for magnesia-chromite refractories in many applications.

INTRODUCTION

Virtually all chromite used in the United States is imported, and approximately 20 pct of these imports are used in the production of refractories, primarily for the steel, copper, glass, and cement industries (*1*). Chromite ore, in combination with magnesia, is the primary constituent of these refractories. Approximately 300,000 st of chromite-containing refractories (chromite contents ranging from 10 to 90 pct) are consumed annually in the United States. This represents an average rate of consumption of 7.5 lb/st Cu produced (*2*) and 4.9 lb/st steel produced (*3*).

Bureau of Mines research during the past 6 yr related to reducing the quantities of imported refractory-grade chromite can be categorized into three general areas:

1. A study of the recycling of magnesia-chromite refractories used to line steel and copper furnaces.
2. Improvement of the high-temperature properties of domestic magnesite grain and refractories.
3. Introduction of Cr into alumina refractories using soluble Cr_2O_3.

Abbreviations Used in This Paper

°C	degree Celsius
cm^2	square centimeter
g/cm^3	gram per cubic centimeter
in	inch
in^2	square inch
in/(in·°C)	inch per inch · degree Celsius
lb/ft^3	pound per cubic foot
lb/st	pound per short ton
pct	weight percent
psi	pound per square inch
st	short ton
yr	year

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RECYCLING OF MAGNESIA-CHROME REFRACTORIES

STEEL FURNACE LININGS

Samples of waste magnesia-chromite refractories from argon-oxygen decarburization (AOD) and electric steelmaking operations were obtained from two steel producers in Ohio and Pennsylvania (*4-5*). The samples of waste refractories consisted of whole and parts of used refractory brick. Some of these brick were partly enclosed in metal casings, others had metal and slag readily visible in cracks, and some were contaminant-free.

The waste refractories were crushed, screened, and magnetically separated. The handpicked metal casings and the magnetic product from the magnetic pulley were combined and accounted for 1.3 and 4.5 pct of the total weight received for the AOD and electric furnace waste refractories, respectively.

Chemical analyses of the head samples from each waste refractory and of a commercial refractory brick are listed in table 1. These analyses indicate that the waste refractories had compositions similar to that of an unused commercial brick.

Energy-dispersive X-ray analysis showed only Mg, Cr, Al, Fe, Si, and Ca as the major elemental constituents of the samples. However, traces of Mo, S, V, and Ti were also observed in the AOD furnace sample, and Ti and Zn were observed in the electric furnace samples. Semiquantitative spectrographic analyses indicated that trace amounts of Ag, Co, and Ni were also present.

X-ray diffraction (XRD) analyses were made of each sample for mineralogical determinations. XRD patterns were also valuable in determining that no significant phase changes occurred in the refractory grain during furnace operations that might alter the refractory properties of the beneficiated refractory grain (chromite concentrate). Chromite [$(Fe^{2+}, Mg^{2+})O \cdot (Al^{3+}, Cr^{3+}, Fe^{3+})_2O_3$], periclase (MgO), and minor amounts of forsterite (Mg_2SiO_4) were identified in all the samples.

Table 2 lists the chemical analyses of chromite concentrates beneficiated at minus 6-, minus 28-, and minus 65-mesh for each of the three starting waste materials, and for samples prepared from two commercial bricks. Both SiO_2 and CaO were slightly higher in the beneficiated materials than in the commercial brick. No "free" lime, present as CaO, was detected by chemical analysis in any of the samples. In commercial magnesia-chromite refractories, the Cr_2O_3, Fe_2O_3, MgO, and Al_2O_3 contents vary over wide limits depending on the source of the chromite ore and the chromite-periclase ratio. The variation of these oxides in the materials tested falls well within these ranges.

Preliminary refractory properties of small samples fired at 1,500° C are shown in table 3. These results indicate that samples produced from the beneficiated materials compare favorably to similar test specimens prepared from commercial refractory grain using the same procedure.

Beneficiated samples of the AOD and electric steel furnace refractories were shipped to a commercial refractory manufacturer for producing full-size brick. Portions of three size fractions were recombined, and suitable binders were added to allow pressing of approximately sixty 9- by 4½-by 3-in brick.

No difficulty was encountered in pressing and burning the brick produced from beneficiated AOD linings. However, because of the high calcium content of the beneficiated electric arc furnace lining, the brick produced from this material hydrated and cracked during drying. Because of the hydration cracks present in the bricks produced from electric steel furnace refractories, they were not subjected to further refractory evaluation. Samples of the recycled AOD refractory brick were prepared for additional testing of their refractory properties, including cold

TABLE 1.—Chemical analysis of waste refractories

Sample	Chemical analysis, pct						
	Cr_2O_3	MgO	Al_2O_3	CaO	Fe_2O_3	SiO_2	Fe[1]
Electric furnace:							
Lining A	15.0	56.7	10.8	5.6	8.8	3.0	4.5
Lining B	15.2	60.9	9.7	1.5	9.9	2.3	NAp
AOD furnace	16.3	59.8	6.5	3.0	10.8	3.1	1.3
Commercial brick No. 1	14.5	63.8	13.2	.7	6.3	1.5	NAp

NAp Not applicable.
[1] Removed from minus 1-in crushed materials before analysis.

TABLE 2.—Chemical analysis of beneficiated waste refractories reported as oxide equivalents

Sample	Particle size of beneficiated material, mesh	Chemical analysis, pct					
		Cr_2O_3	MgO	Al_2O_3	CaO	Fe_2O_3	SiO_2
AOD furnace lining	Minus 6[1]	16.1	59.0	6.5	2.6	11.0	3.5
	Minus 28	16.1	60.3	7.2	3.4	10.5	2.9
	Minus 65	16.1	58.7	6.5	2.6	10.4	3.5
Electric furnace:							
Lining A	Minus 6[1]	14.9	57.9	10.4	5.2	9.1	3.4
	Minus 28	15.2	56.8	12.4	4.5	8.2	3.0
	Minus 65	15.1	55.5	9.8	5.2	8.6	3.5
Lining B	Minus 6[2]	15.5	60.7	9.4	1.8	8.6	1.8
	Minus 28	15.4	61.5	10.7	2.0	9.3	2.0
	Minus 65	15.4	60.8	10.4	2.0	9.4	1.7
Commercial brick:							
No. 1	NAp	14.5	63.8	13.2	.7	6.3	1.5
No. 2	NAp	20.7	49.4	17.9	.6	9.4	2.0

NAp Not applicable.
[1] Magnetically separated using Davis tube magnetic separator.
[2] Magnetically separated using Carpco low-intensity magnetic separator.

TABLE 3.—Refractory properties of chromite concentrates and commercial refractory bricks

Sample	Particle size of beneficiated material mesh	MOR[1] at 1,350° C, psi (av of 6 bars)	Bulk density, g/cm³ (av of 3 bars)	Apparent porosity, pct (av of 3 bars)
AOD furnace lining	Minus 6	1,000	2.9	23.9
	Minus 28	750	2.8	25.1
	Minus 65	850	2.9	23.1
Electric furnace:				
Lining A	Minus 6	2,200	3.1	28.6
	Minus 28	1,750	3.0	28.0
	Minus 65	3,000	3.2	27.1
Lining B	Minus 6	1,450	2.7	25.3
	Minus 28	1,150	2.9	29.3
	Minus 65	1,400	2.9	29.0
Commercial brick:				
No. 1	Minus 65	700	2.7	27.2
No. 2	Minus 65	1,050	2.7	27.2

[1] Modulus of rupture.

crushing strength, modulus of rupture (MOR) at 1,500° C, hot load, thermal shock resistance, and thermal expansion. These data are summarized in table 4 along with manufacturers' data for two commercial refractories.

The relatively low MOR value obtained for the recycled brick at 1,500° C and the corresponding high percentage change measured by the hot-load test at 1,750° C are due to the relatively low initial firing temperature for these brick. When refractories of this type are fired, a glassy-bond phase is present between the more refractory periclase and Cr-spinel grains up to at least 1,500° C. When refractories are fired to higher temperatures (>1,700° C), a direct bond is formed between the periclase and Cr-spinel grains, accompanied by a substantial decrease in the amount of glassy phase present at the grain boundaries. This decrease results from a redistribution of the silica, which reacts with MgO to form forsterite and with CaO to form $2CaO \cdot SiO_2$, both of which have high melting points. Hot-load tests were repeated for brick after firing to 1,730° C, and deformation averaged only minus 1.55 pct, compared with the minus 6.20 pct reported for samples fired to 1,450° C.

The slag resistance of recycled AOD refractories was evaluated using a rotary slag-test apparatus developed at the Bureau's Tuscaloosa Research Center (*6-7*). Tests were conducted using a highly reactive basic oxygen furnace (BOF) slag having the composition shown in table 5. Commercial refractory brick No. 2 was included in the test for comparative purposes.

Average area change for the recycled AOD refractory was 3.00 cm², compared with 3.64 cm² for the commercial refractory. The smaller change for the recycled brick would indicate superior resistance to slag corrosion and/or erosion.

TABLE 4.—Refractory properties of recycled waste AOD refractory lining and commercial brick of similar composition

Properties[1]	Beneficiated AOD lining	Commercial brick
Apparent porosity ....pct..	15.4	16.0-19.0
Bulk density ....g/cm³..	3.2	3.1
Cold crushing strength ....psi..	12,000	4,000-6,000
Modulus of rupture ....psi..	[2]150	[3]600-1,200
Load test at 25 psi (deformation) ....pct..	[4]1.55	([5])
Spalling resistance index	7.4	NA
Thermal expansion ...in(in-°C)..	[6]0.11×10^{-6}	NA
Slag resistance (area loss) cm²..	3.0	3.64

NA Not available.

[1] All tests were according to ASTM specifications.

[2] At 1,500° C.

[3] At 1,480° C.

[4] For brick fired to 1,730° C.

[5] Negligible deformation under load to 1,800° C.

[6] For brick fired to 1,450° C.

TABLE 5.—Chemical analysis of slag used in rotary slag test, percent

SiO_2	33
CaO	33
Fe_2O_3	20
Al_2O_3	4
MgO	5
MnO	5
Total	100

COPPER SMELTER LININGS

Three copper smelters in Arizona supplied samples of used magnesite-chromite refractories from converter and reverberatory furnaces (*8*). The as-received samples consisted of whole and partial bricks. Metallic copper was visible in the refractories.

The waste refractories were crushed to pass a 1/4-in screen, and a product recovered by handsorting was essentially metallic copper that could be recycled directly to the copper smelting furnace. This product accounted for 0.5, 0.4, and 1.2 pct of the total weight received for samples A, B, and C of table 6, respectively.

Chemical analysis of commercial brick of the same type as those used by the copper smelters and those of each head sample are presented in table 6.

TABLE 6.—Chemical analyses of magnesia-chromite waste refractories and magnesia-chromite brick, percent

	Sample			Commercial brick No. 1
	A	B	C	
Cr_2O_3	17.9	18.1	18.7	21.7
MgO	35.4	46.2	38.7	46.3
Al_2O_3	14.7	15.9	16.3	15.9
CaO	.8	.8	.6	.7
Fe_2O_3	11.0	9.4	11.0	11.9
SiO_2	4.1	3.6	3.6	3.5
Total Cu[1]	6.4	3	5.2	0

[1] Includes copper recovered in screen oversize products.

X-ray diffraction analyses identified periclase (MgO), chromite $[(Fe^{2+}, Mg^{2+})O \cdot (Al^{3+}, Cr^{3+}, Fe^{3+})_2O_3]$, and minor amounts of forsterite (Mg_2SiO_4) in all the samples. Traces of cuprite (Cu_2O) were also detected in samples A and B.

From microscopic examinations of the size fractions, it was ascertained that most of the contaminants (copper oxide, copper sulfides, and metallic copper) were liberated from the refractory grain between 65 and 100 mesh.

Magnetic separation was used to remove copper matte. At high magnetic field intensities, the chromite also reported with the matte in the magnetic fraction. As a result, all magnetic separations were made with a low-intensity magnetic field to remove the matte without attracting the chromite. A Davis tube low-intensity wet magnetic separator[2] was selected for this purpose.

In flotation tests, sodium isopropyl xanthate (collector), sodium silicate (dispersant), and pine oil (frother) were added at rates of 0.1, 3.0, and 0.16 lb/st respectively. Flotation resulted in chromite concentrates having the chemical analyses shown in table 7.

The copper concentrates would be of sufficient grade to be recycled to copper smelting furnaces. This represents an 87-pct recovery.

Table 8 shows the 1,350° C MOR, bulk density, and apparent porosity values for a chromite concentrate from magnetic separation and froth flotation along with samples prepared from two commercial bricks. As shown, MOR values for samples fired to 1,500° C are low; however, when the samples were fired to 1,700° C (typical for direct-bonded mag-chrome refractories), their MOR values were higher than those of the standard samples produced from commercial bricks.

As previously stated, in order to liberate the majority of copper and allow removal by magnetic separation and froth flotation, it was necessary to grind the waste copper refractory linings to minus 65 mesh, which creates an additional problem in the recycling of the material. Preliminary sintering of the concentrate would be required to obtain particle-size distribution needed for refractory brick fabrication. Beneficiation by leaching offers the only feasible alternative for lowering the copper content to acceptable levels in a coarser material. This may increase the cost of benefication, and any advantages would have to be weighed against the cost of prefiring the minus 65-mesh material to form a refractory grain.

TABLE 7.—Chemical analyses of chromite concentrates from continuous flotation testing, percent

	Test 1	Test 2	Test 3
Cr_2O_3	21.4	23.7	21.9
MgO	43.4	42.4	43.7
Al_2O_3	17.0	18.0	17.2
CaO	.2	.2	.3
Fe_2O_3	10.6	10.6	10.5
SiO_2	ND	ND	ND
Cu	.2	.2	.2

ND Not determined.

TABLE 8.—MOR (1,350° C), bulk density, and apparent porosity values for a beneficiated copper refractory fired to 1,500° and 1,700° C and commercial brick (as-received)

Sample	MOR at 1,350° C, psi	Bulk density, g/cm³	Apparent porosity, pct
Beneficiated material:[1]			
Fired to 1,500° C	165	2.50	31.7
Fired to 1,700° C	1,500	2.77	28.5
Commercial brick (as-received)			
No. 1	700	2.70	27.2
No. 2	1,050	2.70	27.2

[1] Beneficiation by flotation, magnetic separation; beneficiation product minus 65-mesh.

IMPROVED MAGNESIA REFRACTORIES

Magnesia materials are used extensively in basic oxygen and electric arc steelmaking refractories. Greater use of high-magnesia materials in problem areas such as the slag-metal interface is limited owing to the superior properties of other materials, such as magnesia-chromite, which require imported chromite.

In the United States raw materials for magnesia refractories are generally mined as magnesite or processed chemically from brines or seawater as periclase grain. If techniques could be developed to improve magnesia brick properties, their increased usage could result in a decreased importation of critical raw materials.

IMPROVED PERICLASE GRAIN

The chemical analyses of periclase raw materials used for this study (*9*) are shown in table 9. Two of the periclase materials were produced from seawater, two from brines, and one from a natural magnesite. Reagent-grade oxide powders (minus 200 mesh in size) of MnO_2, ZrO_2, CaO, and SiO_2 were used as additives to produce calcined grain having optimized hot-MOR, hot-load resistance, and slag resistance properties.

Small additions of calcia or silica were made in order to adjust the C-S ratio (CaO-SiO_2), and small quantities of either MnO_2 or ZrO_2 were added as shown in table 9.

High-temperature properties of full-sized MgO bricks made from modified grain and fired to 1,730° C are compared in table 10 with those for commercial refractories fired to the same temperature. All of the 1,300° and 1,500° C MOR values for the five optimized periclase materials were signifcantly higher than the value obtained for a 98-pct-MgO commercial refractory. All five of the optimized periclase materials exhibited less hot-load deformation at 1,700° C than that obtained for the 98-pct-MgO commercial refractory. The 1,650° C BOF slag resistances of the optimized MgO bricks were similar to that obtained for the commercial 98-pct-MgO refractory, with one value (that for B-1) better than for the commercial bricks.

TABLE 9.—Partial chemical analyses of periclase raw materials, and additives to produce optimized periclase grains

	Sample No. and source				
	B-1, brine	B-2, brine	M-1, natural magnesite	S-1, seawater	S-2, seawater
Analysis, pct:					
MgO	95.3	95.9	93.5	97.4	93.9
Al_2O_3	0.20	0.13	0.44	0.12	0.41
CaO	0.61	2.30	3.30	0.89	0.96
Fe_2O_3	0.61	0.40	0.64	0.46	0.68
SiO_2	0.64	0.56	1.30	0.60	1.80
B_2O_3	0.11	0.02	0.02	0.05	0.13
Additives, pct:					
MnO_2	0	0	0	0.5	0
ZrO_2	2.0	1.0	1.0	0	0
C-S ratio:					
Raw materials	0.95	4.11	2.54	1.48	0.53
Optimized grains	2.5	3.0	3.0	2.5	3.0

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[2] Reference to specific products does not imply endorsement by the Bureau of Mines.

TABLE 10.—High-temperature properties of optimized and commercial MgO bricks

Sample	MOR, psi		Hot load (1,700° C, 25 psi) deformation, pct	Slag resistance, vol. loss, in^3	
	1,300° C	1,500° C		1,650° C BOF slag	1,600° C, glass slag
B-1	*360±134	*110± 15	0	1.80	1.45
B-2	*800±132	*690±106	−.03	2.11	.96
M-1	*930±133	*810±105	0	2.08	1.64
S-1	*700± 25	*790±132	+.92	2.20	1.55
S-2	*800±205	*490±179	+.89	2.00	1.78
98-pct-MgO commercial refractory	120± 20	40± 10	−.27	1.88	.94

*Indicates significant difference compared with 98-pct-MgO commercial refractory at 99-pct confidence level, using t-test. (Figures preceded by * are 95-pct standard deviation intervals.)

Results of mineralogical analyses of the optimized periclase bricks indicated that periclase was the predominant phase in all five materials. The as-received materials contained minor amounts of monticellite ($CaO \cdot MgO \cdot SiO_2$) and merwinite ($3CaO \cdot MgO \cdot 2SiO_2$). Both samples with additions of ZrO_2 (M-1 and B-1) had minor amounts of calcium zirconate ($CaZrO_3$) present. This is a refractory phase with a melting point of 2,340° C; the original phases of monticellite and merwinite have melting points of 1,487° and 1,577° C, respectively. All of the optimized periclases, except B-1, indicated small amounts of dicalcium silicate ($2CaO \cdot SiO_2$), with a melting point of 2,130° C. One of the samples (B-1) with a 2.0-pct addition of ZrO_2 exhibited a minor amount of cubic zirconia.

IMPROVED MAGNESITE BRICK

To determine if property improvements might be possible in magnesia-based refractories, two commercial magnesia refractories (90 and 98 pct MgO) were impregnated with solutions of 14 different metallic salt and oxide solutions (*10*). After impregnation, samples were fired to 1,550° C to allow salt decomposition and reaction between the resulting oxide and the refractory phases present in the brick. Subsequently, hot MOR, deformation under load at elevated temperature (hot load), thermal spall resistance, and slag resistance tests were conducted. XRD was used to study the mineral phases that were formed, and energy-dispersive spectroscopy (EDS) to determine the distribution of the additives.

Additions of Al, Mg, or Sn to 90-pct-MgO brick resulted in statistically significant improvements in hot-MOR, slag resistance, and spalling resistance properties. The addition of only 1.14 pct SnO_2 resulted in dramatic improvements of hot MOR (200 psi to 450 psi at 1,500° C), slagging resistance (1.59 pct area removed to 0.82 pct), and spalling resistance (39 pct retained modulus of elasticity (MOE) to 52 pct). The high-temperature properties of 90-pct-MgO brick with additions of Al, Mg, or Sn salt and oxide solutions are equal to or approach those of untreated 98-pct-MgO brick.

CHROMIUM ADDITIONS TO ALUMINA BRICK

Relatively few mineral commodities have suitable characteristics, such as high melting point, mineral stability, and physical and chemical properties, for use in refractory materials above 1,000° C. Alumina easily satisfies all of these requirements and because of its excellent chemical inertness finds many applications in very diverse temperatures and environments. Impurities associated with alumina, including free iron, titania, and alkalies, can have a very detrimental effect on the high-temperature properties of alumina refractories owing to reactions that produce low-melting secondary crystalline phases or glasses, which soften at high temperatures, causing deformation and/or loss of strength. For this reason, these impurities are avoided as much as practical during beneficiation, batching, and forming. Small quantities of these impurities are found in all but the most expensive refractory products and often limit their upper use temperature. Based on the literature from several major refractory producers (*11-14*), impurity levels in commercial alumina refractories having Al_2O_3 contents from 42 to 70 pct range from 1 to 2 pct iron oxide, 1 to 3 pct titania, and 0.1 to 2.5 pct alkali. Analyses of refractories used in this study are shown in table 11. If small amounts of other refractory oxides could be added to react with these impurities to form high-temperature solid solutions or crystalline phases or to prevent the formation of amorphous, glassy phases at grain boundaries, then the high-temperature refractory properties, and thus the upper use temperature, could be increased.

TABLE 11.—Composition and refractory properties of commercial Al_2O_3 refractories

	Commercial refractory brick		
	A	B	C
Chemical analysis, pct:			
Alumina (Al_2O_3)	41.9	58.0	69.2
Silica (SiO_2)	53.2	38.0	26.2
Titania (TiO_2)	2.2	2.4	2.9
Iron oxide (Fe_2O_3)	1.0	1.3	1.3
Lime (CaO)	0.2	0.1	0.1
Magnesia (MgO)	0.3	0.1	0.1
Alkalies ($Na_2O + K_2O + Li_2O$)	1.2	0.1	0.2
Physical property:			
Bulk density, lb/ft^3	144-148	156-160	157-161
Apparent porosity, pct	11.0-14.0	12.0-16.0	15.0-19.0
Cold crushing strength, psi	1,800-3,000	7,000-10,000	6,000-9,000
Modulus of rupture (room temperature), psi	700-1,000	2,300-3,300	1,700-2,400
Hot load test (25 psi to 1,450° C), pct deformation	1.0-3.0	0.1-0.5	0.4-1.0

Thirteen different soluble additives were introduced to 42-, 58-, and 70-pct-Al_2O_3 brick (*15*); however, additions of Cr in the form of Cr_2O_3 solutions provided the largest improvement to the refractory properties of the brick tested. Test specimens consisting of 1- by 1- by 9-in bars and full size 9- by 4½- by 2½-in straights were soaked in solutions of Cr_2O_3, air-dried, and fired to 1,450° C. Mineralogical examination revealed that in each case $Cr_2O_3 \cdot Al_2O_3$ solid solutions formed, in addition to mullite and cristobalite present in the starting brick. Table 12 summarizes the effects of Cr_2O_3 additions on the hot MOR, hot-load resistance, and slag resistance.

From table 12 it is noted that Cr_2O_3 additions improved the hot MOR of each of the Al_2O_3 bricks. In the case of the 58- and 70-pct-Al_2O_3 refractories, this resulted in a twofold to threefold increase. Table 12 shows that Cr_2O_3 additions also improved the hot-load resistance, although less significantly than hot MOR. The most dramatic improvement was to the slag resistance. In the case of the 58-pct-Al_2O_3 brick, slag attack was reduced by a factor of 5. This results from reduced porosity, increased chemical inertness of the $Al_2O_3 \cdot Cr_2O_3$ solid solution, and decreased wetting by high-Fe slag. These improvements become even more significant since they result from additions of only 3 pct Cr_2O_3 as compared to 10-pct additions typically added in the form of chromite to commercial brick.

TABLE 12.—As-received and chromium-treated brick: average values for hot MOR, hot load, and area change following rotary slag test

	Al_2O_3, pct		
	42	58	70
Hot MOR:			
Test temperature °C..	1,350	1,400	1,400
As-received ....psi..	530± 70	590±110	370± 50
Cr_2O_3-treated ...psi..	650±100	*1,610± 40	*770± 30
Hot load:			
Test temperature °C..	1,680	1,725	1,760
As-received ....psi..	4.5±0.6	2.2±0.5	4.1±0.3
Cr_2O_3-treated ...psi..	3.6±1.0	2.0±0.5	2.2±0.3
Area change followed rotary slag test:			
Test temperature °C..	1,500	1,550	1,600
As-received ....pct..	11.4±5.0	10.2±1.6	11.0±0.8
Cr_2O_3-treated ...pct..	*4.1±0.9	*2.2±1.1	*3.0±0.4

*Indicates a statistically significant difference based on t-test with a 99-pct confidence interval.

SUMMARY AND CONCLUSIONS

Research results at the Tuscaloosa Research Center during the past 6 yr, related to reducing the quantities of imported refractory-grade chromite used in magnesia-chromite refractories, can be summarized as follows:

1. By using a combination of conventional beneficiation techniques such as crushing, screening, and dry magnetic separation, it was possible to beneficiate waste AOD and electric steel furnace magnesia-chromite refractories. Contaminants were liberated by crushing the waste refractory to minus 6 mesh, yielding a product having a particle-size distribution suitable for recycling into secondary refractory products.

Refractories produced from recycled AOD linings compared favorably with conventional commercial mag-chrome refractories of similar composition. Cold crushing strength, MOR up to at least 1,350° C, and slag resistance were actually superior for the recycled brick. Firing the brick produced from beneficiated AOD refractories to ≥1,700° C resulted in a direct-bonded brick having improved hot strength over brick fired to 1,450° C that had a glassy silicate bond phase.

Refractories produced from recycled electric arc furnace linings developed cracks during drying resulting from the hydration of calcium silicates.

Copper recovery from waste smelter refractories was readily achieved by standard physical beneficiation techniques. Since grinding to 65 mesh is required to liberate the metallic Cu, the beneficiated refractory material will require briquetting, calcining, and crushing to prepare a coarse refractory grain for reuse in magnesia-chromite refractories. Thus, the recycling of the chromite concentrate from waste copper smelter refractories is at an economic disadvantage with respect to chromite obtained directly from ore.

2. The high-temperature MOR and hot-load properties of brick produced from optimized periclase grain can be improved to exceed those for a commercial 98-pct-MgO refractory. Improvements in hot strength were attributed both to adjustment in the C-S ratio and/or to additions of ZrO_2 or MnO_2. The optimum additions were found to be different for each particular raw material. The hot strength improvements resulted from formation of the refractory phases of $2CaO \cdot SiO_2$ and $CaZrO_3$ in place of the lower melting silicates, monticellite and merwinite.

Adding minor amounts of soluble salts of Al, Mg, or Sn to an MgO brick results in significant improvements to its refractory properties. The high-temperature properties of 90-pct-MgO brick with these additions equal or approach those of 98-pct-MgO brick.

3. Additions of chrome solutions to 42-, 58-, and 70-pct-Al_2O_3 brick resulted in general improvement to hot-load resistance and very dramatic improvement to the hot MOR and slag resistance. Fivefold improvements to the slag resistance were noted, owing to decreased porosity, increased chemical inertness, and decreased wetting of the refractory by high-Fe slags. These improvements resulted from additions as small as 3 pct.

Hot-MOR, hot-load, and slag resistance measurements on 42- and 58-pct-Al_2O_3 brick indicated these properties were superior to those of untreated brick with significantly higher Al_2O_3 contents. Values for 58-pct-Al_2O_3 brick impregnated with Cr were two to five times better than values obtained for untreated 70-pct-Al_2O_3 brick. This could reduce the Nation's dependence on imported refractory-grade bauxite generally required for high-Al_2O_3 brick, as domestic alumina resources could be used to produce the improved refractories.

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