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NATIONAL EMISSIONS INVENTORY OF SOURCES AND EMISSIONS OF CHROMIUM

U.S. ENVIRONMENTAL PROTECTION AGENCY
Office of Air and Water Programs
Office of Air Quality Planning and Standards
Research Triangle Park, North Carolina 27711

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NATIONAL EMISSIONS INVENTORY OF SOURCES AND EMISSIONS OF CHROMIUM

by

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ABSTRACT

A national inventory of the sources and emissions of the element chromium was conducted. The study included the preparation of an overall material flow chart depicting the quantities of chromium moving from sources of mining and importation through all processing and reprocessing steps to ultimate use and final disposition. All major sources of chromium-containing emissions were identified and their chromium emissions into the atmosphere estimated. A regional breakdown of these sources and their emissions was also provided. The physical and chemical nature of the chromium-containing emissions was delineated to the extent that information was available, and a methodology was recommended for updating the results of the study every 2 years.

ACKNOWLEDGEMENT

The continued cooperation and dedication of Mr. Carl Spangler of EPA, who served as Program Monitor until his death, is deeply appreciated.

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I. INTRODUCTION

A. PURPOSE AND SCOPE

The Monitoring and Data Analysis Division, Office of Air Quality Planning and Standards of the U.S. Environmental Protection Agency (EPA) has contracted with GCA Technology Division to conduct a national inventory of the sources and emissions of the element chromium. The purpose of the study was to define as accurately as possible, based on existing and available published and unpublished information, the levels, nature and sources of chromium-containing emissions for defined geographic regions throughout the United States.

The scope of this program is outlined below:

- Develop an overall material flow chart depicting the quantities of chromium moving from sources of mining and importation, through all processing and reprocessing steps, to ultimate use and final disposition as far as the movements can be traced.
- Identify all major potential chromium-containing emission sources and estimate the total quantity of chromium emitted to the atmosphere from each source. Emission factors and level and types of air pollution control will also be provided for each of these sources to the extent that available information permits.
- Define those sources which contribute at least 80 percent of the total emissions of chromium.
- Provide a regional breakdown of these major sources and their emissions.
- Present the nature of the chromium-containing emissions for each of these major sources including a delineation of their physical and chemical forms and particle size distribution to the extent that information is available.
- Provide recommendations as to a methodology for updating the results of this study every 2 years.

B. CONCLUSIONS

1. Material Flow

Based on all available data, 428,000 tons of chromium in ore form was consumed in the U.S. in 1970. As shown in Figure 1, this was nearly all new material with very little scrap being recycled. All new material was imported, there being no domestic mining of chromium ore.

Nearly all the chromium was used for metallurgical products, chiefly ferrochromium and subsequently for stainless and other grades of steel containing chromium.

Certain assumptions made in preparing the above estimates, due to a deficiency of data in certain areas, are explained in detail in Section II.

2. Principal Emission Sources

Just over one half of the total estimated U.S. atmospheric emissions of chromium are estimated to be from ferrochromium production. Another 20 percent results from the production of refractory materials and chromium steels. About 20 percent results from processes outside the chromium industry, including the combustion of coal and oil, and the production of cement.

3. Regional Estimates

The region of the U.S. in which most of the chromium is estimated to be emitted is Region 5* (Ohio and vicinity). Region 2 (New York and New Jersey) is estimated to contain the largest total emission of chromium per average square mile. These findings are partly weighted by the emissions from ferrochromium production, which are substantial in both of these regions.

4. Nature of Emissions

Based on the principal emitting processes, most of the chromium is estimated to be emitted in micrometer-sized particles

*See page 21 for a list of regions.

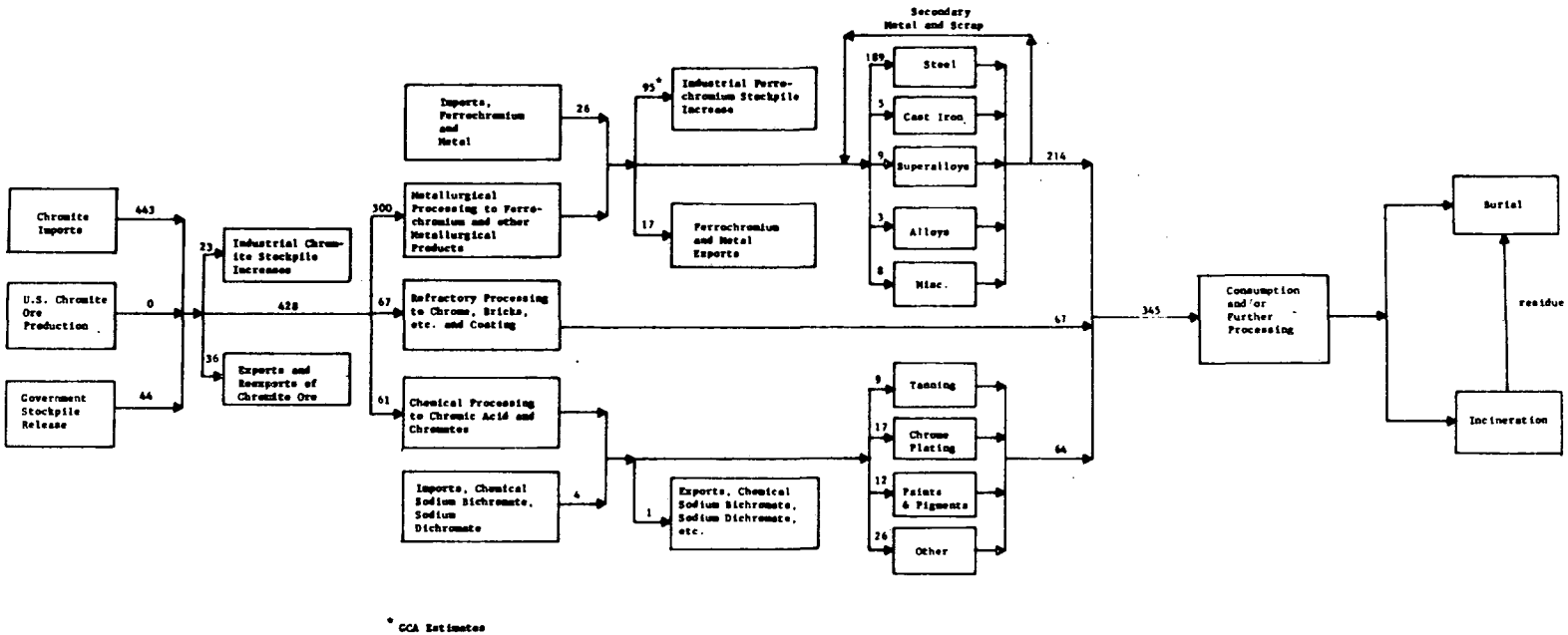

Figure 1. Chromium 1970 material flow
(Thousand Short Tons contained Cr)

and smaller. The chemical forms of the emissions from these processes are not established, although some forms are stated in the literature to be toxic.

5. Degree of Control

The overall level of control of chromium emission is estimated to have been about 54 percent in 1970. The estimated degree of control would have been greater, but for the relatively low control of ferrochromium processes estimated at 40 percent in 1970. More recent reports in 1973 indicate, however, that a 76 percent degree of control has been achieved in the ferrochromium industry, resulting in a current overall level of control of 72 percent.

II. OVERALL U.S. MATERIAL FLOW CHART FOR CHROMIUM

Figure 1* presents a flow diagram depicting the total quantities of chromium products moving from sources of mining and importation through the processing and reprocessing steps to ultimate use and final disposition. Each of these sources is discussed below.

A. U.S. PRODUCTION AND ORE PROCESSING

There has been no mining or ore processing of chromite in the U.S. since 1961 when the Government's Defense Production Act sponsorship was phased out.[1] There are known deposits of possible future commercial value in the northwest and Alaska, the largest being the Stillwater Complex in Montana.

B. IMPORTS OF CHROMIUM-CONTAINING ORE

Total imports of chromite in 1970 totaled 1,405,000 short tons.[2] The total Cr_2O_3 content of the ore varies, depending on consumption usage of the ore, from 30 to 50 percent. The total Cr_2O_3 content of the ore was 647,000 short tons[2] averaging 46 percent. Based on chromium content in Cr_2O_3 of 68 percent by weight, 443,000 tons of chromium in ore form was imported in 1970.

C. GOVERNMENT AND INDUSTRIAL STOCKPILE CHANGES

Due to the politically unstable nature of the supply of chromium ore, stockpiles tend to be larger than ordinarily expected; hence, shifts in stockpiles must also be considered to justify consumption figures. The National Stockpile re-evaluated its needs and reduced its inventories of chromium in 1970 by an estimated 44,000 tons of contained chromium.

Industrial stocks rose in the metallurgical industry, dropped in the chemical industry and remained relatively constant in the

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*Data in Figure 1 and in this section are left rounded, for purposes of information control. On average, the typical statistic is accurate to within 10 percent, in the opinion of the authors.

refractory industry resulting in a net increase of 69,000 short tons of chromite ore stocks[2] containing 23,000 tons of chromium.

D. EXPORTS AND RE-EXPORTS OF CHROMITE

Exports and re-exports of ore have been primarily for the production of chromite based in Canadian or South American plants owned by U.S. firms.[1] There is little processing of this ore except perhaps some finer crushing. In 1970, 114,000 tons were exported[2] with a chromium content of 36,000 tons.

E. CONSUMPTION

Chromite ore is classified into three major categories based on its composition. Table 1 contains the National Stockpile specifications for stockpile grade ore. Based on chromium content, 70 percent of the ore in 1970 was consumed by the metallurgical industry, 16 percent by the refractory industry, and 14 percent by the chemical industry.

TABLE 1

NATIONAL STOCKPILE ORE-PURCHASE SPECIFICATIONS
(Weight-percent, dry basis)

Grade	Cr: Fe Ratio Minimum	Cr_2O_3 Minimum	Fe Maximum	Cr_2O_3 Al_2O_3 Minimum	SiO_2 Maximum	S Maximum	P Maximum	CaO Maximum
Metallurgical	3.1	48.0			8.0	0.08	0.04	
Refractory		31.0	12.0	58.0	6.0			1.0
Chemical		44.0			5.0			

1. Metalurgical Industry

Chromite ore of metallurgical grade is converted entirely to various grades of ferrochromium and to chromium additives and metal. Metallurgical consumption of goods totaled 300,000 tons of contained chromium of which 290,000 tons, or 96 percent was in ferrochromium.[2]

2. Refractory Industry

The refractory industry is a major consumer of chromite ore using it in the production of chrome brick, chrome-magnesite brick and magnesite-chrome brick. Chrome ore is also used as patching material for refractories. Consumption totaled 278,000 short tons of chromite containing 67,000 tons of chromium.[2]

3. Chemical Industry

Chemical processing of chromite ore into various industrial chemicals proceeds from sodium dichromate or sodium chromate which are the primary products. The chromate chemical industry is extremely vertically integrated and four processing plants produce all the chromium containing chemicals in the country.

The chemical industry consumed 213,000 tons of chromite ore containing 61,000 tons of chromium to produce 148,000 tons of chemicals (sodium dichromate equivalent). These chemicals were consumed in a host of industries. Metal plating, paints and pigments, and leather tanning were the predominant uses, consuming about 60 percent of the total chromium used by the chemical industry.

III. SOURCES AND ESTIMATES OF CHROMIUM-CONTAINING EMISSIONS

A. DATA PRESENTATION AND ACCURACY

Table 2 presents a summary of the data from which emissions were estimated for all major potential sources. Each of the columns comprising this table will be discussed below.

1. Emission Factors

Except where indicated, this gives the pounds of total particulate emitted per ton of production. Such considerations as:

- variations in process conditions among individual plants comprising a source category
- inaccuracies in existing data
- a limited quantity of existing data,

may, however, result in an average emission factor for a source category varying by more than an order of magnitude from the value presented. In recognizing the need to indicate the level of accuracy of these emissions factors, a reliability code is presented along with each emission factor value appearing in the table. This reliability code system is described below and is based on the system utilized in EPA Document No. AP-42, "Compilation of Air Pollutant Emission Factors":[4]

A: Excellent

This value is based on field measurements of a large number of sources.

B: Above Average

This value is based on a limited number of field measurements.

C: Average

This value is based on limited data and/or published emission factors where the accuracy is not stated.

D: Below Average

This emission factor is based on engineering estimates made by knowledgeable personnel.

2. Level of Production Activity

This column depicts the quantity of material produced (unless otherwise stated) annually. When multiplied by the emission factor, an estimate of the total particulate emissions for that source in pounds per year is obtained.

The values in this column are based on the material flow calculations presented in Section II. Consequently, they have the same accuracy as those material flow values which is estimated at ± 10 percent.

3. Percent Metal in Emissions

The method of analyzing or assaying a dust sample for the amount of metal it contains determines to a large extent the reliability of the data. For example, analytical chemistry techniques for dust containing substantial fractions of metal can be accurate to within a small percentage. On the other hand, optical spectroscopy methods for determining concentrations on the order of parts per million can be inaccurate by a factor of 2. Because of this variability, the reliability codes discussed above for the emission factors are also utilized to estimate the relative accuracy of the percentage values listed in this column.

4. Level of Chromium Emissions Before Control

The values in this column are derived by multiplying the values in columns 1 through 3. The result is converted to tons/year of emissions before control.

5. Estimated Level of Emission Control

The overall effectiveness of control for a source category is based on two factors:

- the portion of the processes which are under control
- the typical degree of control

For example, if 60 percent of vertical roasters have some type of particulate emission control, and these include both scrubbers and precipitators such that the apparent weighted average efficiency of control is 85 percent, the overall control effectiveness is estimated to be 60x85 = 51 percent.

The accuracy of control efficiency data varies with the degree of control. For a wet scrubber operating at 80 percent efficiency; i.e., passing 20 percent material, the actual emission may safely be assumed to be between 15 and 25 percent because of the relative ease of making determinations at this level. Thus the emissions after control may be assumed to accurate within $\pm$ 5/20 or 25 percent. On the other hand, for a baghouse reported as being 99 percent efficient, or passing only 1 percent of the material, the actual emission may vary from 0.5 percent to perhaps 2 percent because it is frequently difficult to make low-level measurements with accuracy. In such case, the resulting emission data could be in error by a factor of 2.

Unless otherwise specified, it is assumed that the reported overall level of particulate control applies equally to all chromium-containing particles, independent of size, resistance, and other important collection parameters. This assumption results in a correct estimate of chromium emissions after control when the particulate is chemically homogeneous; i.e., the chromium is contained in the same concentration in all particles. If however, chromium is concentrated in certain particles and in addition, the efficiency of the control equipment is not uniform for all particles, then the utilization of an average control level is less valid for calculating chromium

emissions after control. Data on the preferential control of chromium-containing particles is seldom available, but is included in this report when possible.

The accuracy of estimating the level of control for a specific source category is dependent on the quality of available data. The investigators feel that, in general, the level of control data will contribute an accuracy to the resulting emissions estimates within ± 25 percent.

6. Level of Metal Emissions After Control

The values in this column are derived by multiplying the values in column 4 by the value (100 minus estimated Level of Control).

B. DEVELOPMENT OF EMISSIONS ESTIMATES - 1970

Estimates of particulate emissions containing chromium in the U.S. atmosphere are developed in the following paragraphs, and in Table 2. The table indicates that metallurgical and refractory processes produce most of the emissions, as will be shown.

1. Mining and Ore Processing

There are presently no operating mines for chromium in the United States. There are various low-grade ore deposits in the United States predominantly in the Northwest and in Alaska.

2. Metallurgical Processing

The use of chromite ore is divided into three major categories, the largest of which, metallurgy, accounts for 70 percent of chromium consumption. The major primary products are various grades of ferrochromium, ferrochromium-silicon, and chromium metal.

a. Ferrochromium

The production of high carbon ferrochromium involves smelting of chromite ore with coke, and tapping of the ferrochromium from the bottom of the furnace. Low carbon ferrochromium can be produced by the use of quartz in place of coke to form ferrochromium-

TABLE 2

SOURCES AND ESTIMATES OF CHROMIUM-CONTAINING EMISSIONS IN 1970

Source	Uncontrolled Emission Factor lb/ton	Uncontrolled Emission Factor kg/10^3 kg	Reliability Code	Production Level (tons/yr)	Percent Cr in Emissions	Reliability Code	Emissions of Cr Before Controls (tons/yr)	Estimated Level of Emission Control	Emissions of Cr After Controls (tons/yr)
MINING									
None in U.S.A.							0		0
REFINING									
Ferrochromium:									
Electric Furnace	(200-830) 500[a]	(100-415) 250[a]	C	375,500	22	B	20,600	40%	12,360
Material Handling	10	5	B	375,500	65	C	1,220	32%	830
Electrolytic Chromium	0.048	0.024	C	9,000	51	A	(neg)	95%	(neg)
REFRACTORY									
Non-Cast	150	75	C	60,300	b		4,500	64%	1,630
Electric Cast	225	112	C	6,700	b		754	77%	173
CHEMICAL PROCESSING									
Dichromate	30	15	C	61,000	b		920	90%	92
Other Chemicals	---	---	-	---	--		---	--	24[c]
STEEL AND ALLOYS									
Chromium Steels	25	12	C	189,000	b		2,362	78%	520
Cast Iron	75	38	C	5,000	b		188	99%	2
Super Alloys and Alloys	25	12	C	12,000	b		150	78%	33
General Steel making	N.A.	N.A.		N.A.	N.A.		N.A.	N.A.	100[d]
INADVERTENT SOURCES									
Coal Combustion	N.A.	N.A.		33,800,000[f]	0.026	A	8,700	82%	1,564
Oil Combustion	N.A.	N.A.		287,000[e]	0.13	B	370	0	370
Cement Production	N.A.	N.A.		934,000[e]	0.03	C	N.A.	N.A.	280
Incineration	N.A.	N.A.		931,000[e]	0.017	C	N.A.	N.A.	158
Asbestos	N.A.	N.A.		6,579	0.15	C	10	99%	0
Total							39,774	54%	18,136

[a] Intermediate value (see text)

[b] Emission factor multiplier equal to tons of Cr processed or handled annually.

[c] See text for explanation.

[d] Needs further investigation

[e] Emissions, after control.

[f] Emissions, before control.

N.A. - Not applicable.

silicon, followed by further smelting with additional chromite. In every case, ferrochromes are produced in an electric arc furnace. Emissions have previously been estimated at 200 lb/ton of product,[3,4] based on electric furnace emissions for other than ferrochromium production, because no ferrochromium data was available at that time. More recently, emission factors of 330 lb/ton of high carbon ferrochromium and 830 lb/ton of low carbon ferrochromium or ferrochrome silicone have been reported based on tests of specific ferrochromium furnaces.[5] Other data indicate a wide range of emission factors, but lack adequate process descriptions to make the data useful.[6,7]

The overall level of control effectiveness has been estimated at 40 percent, based on about 50 percent application of approximately 80 percent control equipment. These estimates were based on a survey of the ferroalloy industry in 1969-70 (11 companies, 22 plants, 127 furnaces included in the survey).[3] More recently, reports of a typical 95 percent control efficiency have been reported.[5,8] It is estimated that the level of application is now at least 80 percent, giving an overall control effectiveness of about 76 percent at the present time (1973).

Using a mean emission factor value of 500 lb/ton, a 40 percent level of control in 1970, and a production level of 375,500 tons of ferrochromium in 1970 results in 56,325 tons of particulate emissions after control. The fume emitted during ferrochromium production is reported to contain 15 to 30 percent chromium, depending on the type of ferrochrome being produced.[7] An average content of 22 percent is assumed. The resulting estimated emission from ferrochromium production of all kinds, is 12,360 tons of chromium emitted to the atmosphere.

Further emissions occurred in ferroalloy production from material handling estimated at 10 lb/ton of product with a control of 32 percent.[3,4] Composition of these emissions was estimated to be equivalent to the amount of chromium in the ferroalloy, about 65 percent. Total emissions are estimated at 830 tons.

b. Chromium Metal

Production of chromium metal is done predominantly by electroplating of the chromium from a chrome-alum solution. Approximately 75 percent of the metal or 9,000 tons were produced in this manner.[1] Practically no emissions data were found for chrome plating or even for electroplating in general. One reference reported that chromic acid mist from chrome plating was reduced from 42.65 MG/CU M (presumed milligrams per cubic meter, rather than micrograms) to 0.077 MG/CU M by "washing with water."[9] Using an estimated gas release rate of 1000 CU M per ton of metal plated,[10] a pre-control emission of 0.094 pounds of acid or 0.048 pounds of chromium per ton of chromium plated, is obtained. This reference indicates an estimated degree of control of 95 percent. This results in a negligible level of emissions. The form of the chromium, $HCrO_2$, is toxic.[9]

The remaining chromium metal is produced by an aluminothermic reaction in which chromite is crushed and intimately mixed with powdered aluminum and ignited. The aluminum replaces the chromium forming Al_2O_3 and Cr metal. Due to the explosive nature of the reactions, the process is carefully regulated. No data was found that would allow estimation of an emission factor for this process. However, metal production by this process totaled only 3,000 tons in 1970, indicating a negligible quantity of emission, at most.

3. Refractory Processing

The production of refractory brick consumed 67,000 tons of chromium in 1970, or 16 percent of the total product. The three major types of brick produced were chrome, composed almost totally of chromite ore; chrome-magnesite, composed predominantly of chromite with some magnesite ore; and magnesite-chrome, comprised predominantly of magnesite with some chromite ore. The bricks produced are either fired, unfired, or electric cast. The emissions from firing alone are reported as negligible (one source reported 0.2 lb/ton uncontrolled),[4] and so fired and unfired brick emissions are treated together as "non-cast." The preliminary processing includes fine crushing and careful sizing and mixing to obtain appropriate porosity, and drying. Uncontrolled emissions

from these processes have been estimated at 150 lb/ton.[4,6] Production statistics are not sufficiently detailed, so it is estimated that 90 percent of the chromium used in refractory materials is used in non-cast materials. The concentration of chromium in the emitted particulate is assumed to be in the same proportion as the chromium in the product. Overall control effectiveness is reported as 64 percent,[4] giving an estimated emission of 1630 tons of chromium in 1970.

Electric casting includes, in addition to material preparation, melting in an electric arc furnace and pouring into molds. An emission factor of 225 lb/ton is estimated.[4] An estimated 10 percent of the chromium used in refractory materials is used in cast bricks. The concentration of chromium in the particulate is assumed to be the same as in the product. Overall control effectiveness is reported as 77 percent,[4] giving an estimated emission of 170 tons of chromium.

4. Chemical Processing

All chemical products containing chromium are made from either dichromate or chromate as the primary ingredient. Chromite ore is roasted with soda ash or lime to form a soluble chromate. This is leached, precipitated, and dried as a crystaline sodium dichromate.

Ore containing an estimated 61,000 tons of chromium was roasted in 1970. Typical emissions are reported to be 11 lb/ton before control[5] and in one other case, 62 lb/ton.[7] A weighted average of 15 lb/ton is utilized. The chromium content of the particulate is reported to be about 15 percent.[5] It is estimated that the level of control effectiveness was about 90 percent in 1970.[11] This results in an estimated emission of 46 tons of chromium.

Handling the roasted material preparatory to leaching generates enough particulate to be controllable by scrubbing.[12] The net emission is believed to be negligible in comparison with other sources. Drying of the precipitate in a kiln also generates some emissions. No data are available on these operations, but the net emission to the atmosphere is probably of the same magnitude as the roasting

process. In effect, therefore, the overall emission factor is estimated to be 30 lb/ton, giving a net emission estimate of 92 tons of chromium in the preparation of dichromate. This estimate for 1970 may be higher than appropriate for 1973. It is reported that one of the newer plants passes all its exhaust gases through one stack, after scrubbing plus electrostatic precipitation, with an effective control of 98 percent efficiency.

Subsequently, dichromate and chromate are made into other chemicals and used in a wide variety of applications, including tanning, chrome plating, paints and pigments, and other applications. In general, reliable emissions data are not available for these many processes. For chrome plating, an emissions factor of 0.048 lb/ton (Cr/Cr) is developed in a previous section of this report. It is estimated that among the approximately 1400 plating plants in the U.S., the level of control effectiveness is only half as good as in the production of chromium metal; that is, an effectiveness of 90 percent is assumed. This results in a net emission estimate of only 0.04 tons of chromium. As for paints and pigments, using an estimated 0.1 percent emission factor and assuming 50 percent control results in only 6 tons of chromium emission. At the same rate, tanning and other uses of dichromate would produce about 18 tons of emissions, for a total estimate of 24 tons.

5. Steel and Alloys

Emissions from the steel industry's use of ferrochromium and chromium metal are based on a weighted average of emissions from the production of steel. It is assumed that chromium is emitted to the same extent as the other constituents, based on the fact that the vaporization temperature of chromium (2665°C, Section V) is not extremely different from those of iron and nickel, all of which are well above the typical steel production temperature of about 1500°C. The level of control is also a weighted average of control in the iron and steel industry. Emissions from alloy and superalloy (high chrome) productions are judged to be comparable to steel production in that the types of processes employed are similar. Similar control methods are used and

consequently the control factor is estimated to be the same. The result of these assumptions is an estimated 555 tons of chromium emitted to the atmosphere. Most of this emission is contributed by the production of steel containing chromium as an ingredient (predominantly stainless steels; also tool steels).

Not included above is the production of ferrous products including iron and steel in which chromium or ferrochromium is not a deliberate ingredient. Chromium must be a trace metal in most steel products, particularly those containing scrap. Chromium is also a trace metal in coke, one of the ingredients utilized in steel manufacturing. Furthermore, a large tonnage of chromium-containing refractory materials is consumed by the steel industry for furnace lining and patching. In 1970, open hearth steel making consumed 60,000 tons of chrome-predominant basic brick, while electric furnace and basic oxygen furnace steel making consumed about 230,000 tons of unspecified basic brick.[13] Possibly one half of these materials are consumed in producing the steel, while the remaining brick is replaced periodically. The fate of the chromium in these furnace linings is not reported, but some may be emitted. Therefore, since scrap, coke, and refractory materials may possibly each contribute to chromium emissions, and since the tonnages are potentially large, a token 100 tons emission is included in Table 2 from this general source, subject to further investigation.

6. Inadvertent Sources

a. Coal Combustion

The concentration of chromium in coal ash has been reported as 0.026 percent (73 Appalachian coal ash samples, spectrographic analyses),[14] as 0.019 (four samples, emission spectrographic analyses),[7] and as 0.013 percent (survey of about 15 U.S. and European investigations).[15] The number 0.026 percent was utilized as the largest and therefore most conservative estimate. Coal consumption in 1970 amounted to about 517,000,000 tons.[2] The particulate generated has been estimated at 33,800,000 tons, of which 82 percent was controlled, leaving

6,100,000 tons of emission to the atmosphere.[3] This results in an estimated emission of chromium to the atmosphere of 1,564 tons in 1970.

Section V-D, presented later, indicates that chromium is more concentrated in particles smaller than 1.7 micrometers diameter than in larger particles. Control equipment is often less efficient on smaller particles, although this depends on the equipment and on other properties of the particles, as well as size. If flyash particles under 1.7 micrometers are less well controlled than average, then more chromium will be emitted than is indicated in Table 1.

b. Oil Combustion

An estimated 287,000 tons of flyash from the combustion of residual oil has been estimated[3] which escapes to the atmosphere almost completely uncontrolled. The amount of chromium in the ash varies considerably: 0.11 percent (two oils, method unspecified);[3] 0.27 percent (three oils, atomic absorption spectrophotometry);[7] 0.0064 percent (three oils, optical emission spectroscopy);[16] and 0.12 percent (one oil, method unknown).[17] Using 0.13 percent as the average percentage of chromium in residual oils, an estimated 370 tons of chromium were emitted to the atmosphere in 1970.

c. Cement Production

An estimated 934,000 tons of particulate emission after control has been found for cement production.[3] Again the concentration of chromium in the particulate varies. A preliminary survey reported 41 ppm, or 0.0041 percent content (method unspecified);[18] tests of dusts from three kilns and three clinker coolers indicated 0.17 percent; and tests from several cement mills, air separators, and bagging operations indicated an average of 0.039 percent (spectrographic analyses).[7] Using a median 0.03 percent results in an estimated 280 tons of chromium emitted to the atmosphere in 1970.

d. Incineration

An estimated 931,000 tons of particulate are released to the atmosphere from all types of incineration sources. Based on a single determination of chromium content in incinerator ash of 0.017 percent (spectrographic analyses),[7] a chromium emission of 158 tons is estimated.

e. Asbestos

Based on an estimated pre-control national emission of 6579 tons of asbestos[19] and a concentration of chromium in chrysolite, the chief constituent in asbestos, 0.15 percent, the net chromium emission is estimated at 10 tons. This however is before control, which is estimated to be sufficiently close to 100 percent that negligible chromium emissions result.

C. SUMMARY OF PRINCIPAL EMISSIONS

Table 3 summarizes the major sources and estimated emissions of chromium, as developed in Table 2 and accompanying discussion. The sources are grouped in two categories; those directly originating with the chromium industry and those having no relationship to the chromium industry, called inadvertent sources. The latter category represents about 12 percent of the total estimated emission.

These principal estimates are examined further in later sections of this report.

TABLE 3

SUMMARY OF PRINCIPAL SOURCES AND EMISSIONS OF CHROMIUM

Source	U.S. Tons/Year of Cr	% of U.S. Total
Chromium Industry Sources		
Ferrochromium production	12,360	68.3
Refractory production	1,800	9.9
Chromium steel production	520	2.9
Inadvertent Sources		
Coal combustion	1,564	8.6
Oil combustion	370	2.0
Cement	280	1.5

IV. REGIONAL DISTRIBUTION OF PRINCIPAL SOURCES AND EMISSIONS

For the purpose of showing geographical distribution, the U.S. was divided into ten regions identical to the Regional Branches of EPA.

Region	States
I	Connecticut, Maine, Massachusetts, New Hampshire, Rhode Island, Vermont
II	New Jersey, New York, Puerto Rico, Virgin Islands
III	Delaware, Maryland, Pennsylvania, Virginia, West Virginia, District of Columbia
IV	Alabama, Florida, Georgia, Kentucky, Mississippi, North Carolina, South Carolina, Tennessee
V	Illinois, Indiana, Michigan, Minnesota, Ohio, Wisconsin
VI	Arkansas, Louisiana, New Mexico, Oklahoma, Texas
VII	Iowa, Kansas, Missouri, Nebraska
VIII	Colorado, Montana, North Dakota, South Dakota, Utah, Wyoming
IX	Arizona, California, Nevada, Hawaii, and the South Pacific
X	Alaska, Idaho, Oregon, Washington

Emissions from the principal sources listed in Table 3 are distributed among these ten regions, as shown in Table 4. Also, the number of plants producing the emissions are shown in the table when such information is available.

The accuracy of the distribution by region varies with the category. The number of plants per category varied from one to several thousand in this study. When the number of plants was less than 100, an attempt was made to identify each plant and plant location, and include it in one of the ten regions. When production or capacity figures for these plants were available, total production or capacity for each retion was computed, and the U.S. emission estimate for that category was distributed by region accordingly. When production or capacity figures were not available, the emission was distributed by the number of plants

TABLE 4

REGIONAL DISTRIBUTION OF PRINCIPAL SOURCES AND EMISSIONS

Principal Sources	EPA Region 1	2	3	4	5	6	7	8	9	10	Total	Units	Reference
Chromium Industry Sources													
Ferrochrome Production	0	2852	1902	2852	3803	0	0	0	0	951	12360	(TPY)	
	0	3	2	3	4	0	0	0	0	1	13	(No. Plants)	2
Refractory Production	0	180	675	90	630	0	90	45	90	0	1800	(TPY)	
	0	4	15	2	14	0	2	1	2	0	40	(No. Plants)	20
Chrome Steel Production	33	204	120	10	120	4	7	0	18	4	520	(TPY)	
	9	56	33	3	33	1	2	0	5	1	143	(No. Plants	21
Inadvertent Sources													
Coal Combustion	11	89	339	328	643	22	64	52	11	5	1564	(TPY)	
	0.7	5.7	21.7	21.0	44.1	1.4	4.1	3.3	0.7	0.3	100	(% Coal)	2
Oil Combustion	67	108	55	35	28	14	3	7	43	10	370	(TPY)	
	18.0	29.1	15.0	9.6	7.6	3.7	0.9	1.8	11.6	2.7	100	(% Oil)	17
Cement Production	2	20	43	42	45	42	31	14	30	11	280	(TPY)	
	1	13	28	27	30	27	20	9	19	7	181	(No. Plants)	22
TOTALS	113	3453	3134	3357	5269	82	195	118	192	981	16894	(TPY)	
	0.6	19.0	17.3	18.5	29.0	0.5	1.1	0.7	1.1	5.4	93.2	(% of U.S.)	

in each region. If the number of plants was very small or there was reason to believe that certain plants were larger or produced more emission, distributions were weighted accordingly.

On the other hand, when the estimated number of plants was greater than about 100, and the distribution of plants was not known, the regional breakdown was made on a different basis, such as population, geographical area, or shipments reported, as most appropriate for that category. Whether the distribution was by plant size, number of plants, or another statistic, the distribution is believed to be accurate to within 10 percent in most cases.

As indicated in Table 4, the distribution of ferrochromium emissions was according to number of plants, on the assumption that all plants are about the same size and produce similar emissions. Due to the large total estimated emission from ferrochromium production, this assumption is rather critical to the conclusions of the study, as a single ferrochromium plant is thereby assumed to emit about 4.4 percent of the total U.S. emissions of chromium.

The distribution of emissions from production of chromium-containing refractory materials is according to the number of plants. Somewhat more than the 40 plants identified in this study may produce these materials, according to the Bureau of Mines.[23] However, the principal plants should be included in the present distribution, and any small plants inadvertently omitted may be assumed to be distributed in about the same proportions as the large plants, to a first approximation.

Emissions from the production of chromium-containing steels are also distributed by number of plants. The reference used to identify these plants purports to survey all alloys made in the U.S. Most of the plants identified are located in the eastern U.S., however, which is where the survey is headquartered, indicating that possibly the survey does not truly cover the U.S. uniformly. In addition, parts of the survey date back to 1952. Thus the confidence in this particular distribution of emissions is relatively low.

The inadvertent emission sources are distributed as follows: Coal emissions are distributed according to tonnage of coal shipped, by state of destination. Oil emissions are distributed by total sales of residual oil, for all uses, by states. Cement emissions are distributed by number of producing plants, based on a fairly accurate survey which does, however, omit cement handling plants (loading, unloading, wet mixing stations, etc.), which are widely distributed across the U.S.

As a result of these distributions of the six principal emissions categories, Region V (Ohio-Minnesota) is estimated to have the largest emission of chromium (29 percent of U.S.), followed by Regions II, III, and IV (the eastern seaboard states). This distribution is largely the result of the estimated emissions from the production of ferrochromium, which makes up about half the total estimated U.S. emission of chromium.

Considering the geographical areas of the ten regions, Region II has the most concentrated emission of chromium with an average 0.057 tons of chromium emitted per square mile-year.

V. NATURE OF EMISSIONS

The physical and chemical properties of the emitted particles containing chromium are the direct results of the processes causing the emission, the types of feed materials, and the characteristics of chromium and its compounds. Some of the latter are summarized in Table 5. Of those listed, the boiling (vaporization) point for chromium of 2665°C may be the most important, in that temperatures below this point may be expected to produce relatively little chromium or chromate fume, while higher temperatures can produce substantial amounts of fume particulate. With this brief background, the emissions from the principal sources will be examined in turn.

TABLE 5

SOME PHYSICAL PROPERTIES OF CHROMIUM AND ITS COMPOUNDS*

Melting point:	1875°C
Boiling point:	2665°C (for Cr_2O_3:4000°C)
Density:	7.2 g/cm^3
Atomic weight:	52.0 a.w.u.
Heat of vaporization:	73.0 kg-cal/g-atom
Mineral hardness of chromite:	5.5 (Std. minerology scale)

*Reference 24, Table 3-169.

A. FERROCHROMIUM PRODUCTION EMISSIONS

Emissions from high-carbon ferrochrome furnaces are reported as follows:

- 1.07 grains/SCF,[8] before scrubber control at 98.2 percent efficiency
- Approximately 1.0 micrometer diameter particles[7] containing 29.3 percent Cr_2O_3
- Dust collected by an electrostatic precipitator contained 4 percent Cr, and 15 percent Mg[7]

- An unspecified type of ferrochrome furnace emitted particulate varying from 1 to 2 micrometers in diameter. Control by electrostatic precipitator did not alter the relative concentration of chromium and other metals in the dust, which included 14 percent chromium and 8.9 percent magnesium.[7]
- A maximum of 1.0 micrometer in diameter, with most particles from 0.1 to 0.4 micrometers; amorphous, spherical particles, including traces of spinel and quartz; 21 percent SiO_2; 11 percent FeO; 15 percent MgO; 29.3 percent Cr_2O_3; etc.[3]
- Fume resistivity: 9.4×10^{10} ohm-cm, 200-300°F; or with conditioning of gas to 20 percent moisture, 21×10^{10} ohm-cm.
- Emissions from ferrochrome silicon furnaces are reported as follows:

  1.43 grains/SCF[8] before scrubber control at 92.6 percent efficiency.

  0.245 grains/SCF[7] from a hooded furnace without control equipment. This particulate described as non-crystalline fused silica and impurities, the fume containing 1.3 percent chromium and 6.8 percent magnesium. 0.65 micrometer mass median diameter.

B. REFRACTORY PRODUCTION EMISSIONS

No useful description of these emissions was found, and consequently the following estimates are made. Most of the emissions from refractory production operations are from grinding, screening, mixing, and drying. All except grinding are relatively low-intensity operations which are therefore expected to generate particles and agglomerates roughly 5 micrometers in diameter and larger, having relatively short distances of travel before disposition. Grinding material having the moderate hardness of chromite is expected to generate moderately small rough-shaped particles, perhaps 1 micrometer in diameter and larger, of which the smallest may travel distances up to a few miles before disposition. Most of the chromium emitted is expected to be in the chromite form; i.e., $FeO \cdot Cr_2O_3$.

C. CHROME STEEL PRODUCTION EMISSIONS

Emission characteristics are known to be highly dependent on the material charged to the furnace.[3] Probably some particles consisting almost entirely of Cr_2O_3 will be emitted, while other particles will contain Fe_2O_3 and FeO up to 50 percent, plus numerous other metallic oxides. Most particles will be spherical, and submicrometer in size, although some will exceed 1 micrometer in diameter.

D. COAL COMBUSTION EMISSIONS

Analyses of flyash give average particle diameters from 2 to 30 micrometers (mass median diameter) depending on the type of feed to the furnace. From 1 to 10 percent of the particle mass may be submicrometer. The concentration of chromium in flyash as a function of particle size is reported:[25]

Particles less than 1.7 micrometers:	0.4 percent chromium
Particles 1.7 to 4.1 micrometers:	0.05 percent chromium
Particles 4.1 to 30 micrometers in 6 increments and over 30 micrometers:	0.02 percent chromium

This indication that chromium is concentrated in the smaller particles is not explained by the vaporization temperature of chromium, which is well above the combustion temperature of coal (about 1500°C).

E. OIL COMBUSTION EMISSIONS

Most particles are between 0.01 and 1 micrometers in diameter, depending on the atomization and combustion processes. Thus, these particles tend to travel long distances (tens to hundreds of miles) before being removed from the atmosphere by natural processes (settling, washout, agglomeration). The chemical form of the chromium contained in these emissions is not stated, although one report gives "chromium as CrO_2" data of 0.06 and 0.3 percent of ash, indicating that this may be the chemical form.[3]

F. CEMENT PRODUCTION EMISSIONS

Most emissions from cement plants come from the kilns from which 5 percent of the material may be submicrometer.[3] Up to 50 percent of the particulate can be CaO; and silicon, iron, and aluminum oxides represent a large portion of the remaining particle contents.

G. AMBIENT CHROMIUM AND TOXICITY

Analyses of the air in and near Cincinnati is reported to contain 0.28 and 0.31 micrograms of chromium per cubic meter, in particles of average size 1.5 and 1.9 micrometers (mass median diameter). Of the particles containing chromium, 45 and 74 percent were greater than 1 micrometer, somewhat larger than would be predicted from the preceding discussions.[26]

Although not a principal source of emissions, chromium plating releases chromic acid particles in the form of chromium trioxide which is said to be poisonous and injurious to the kidneys.[9] Dust from cement plants is said to cause skin problems with some workers, due to the chromium contained in the dust. Chromium-containing chemicals are used as preservatives of wood, slimicides, and herbicides, indicated a potential toxicity to organisms in at least some chemical forms.[18]

VI. UPDATING OF EMISSIONS ESTIMATES

The following recommendations are made for periodically updating the estimates made in this study:

A. VERIFICATION OF CURRENT ESTIMATES

1. Verify the estimates of chromium emission from the production of ferrochromium and ferrochrome silicon. Following the publication of Reference 5, comment should be obtained from the manufacturers of these products regarding the data and estimates contained in these two reports.

2. The refractory industry has not published much information establishing either particulate emission nor the form and content of chromium contained in the particulate. In view of the size of the emissions estimated here, a brief study should be made of this industry.

3. In view of the apparent toxicity of certain forms of chromium, and perhaps the non-toxicity of other forms, representative particulate samples from the six principal sources identified in this study should be analyzed to determine the form of chromium contained therein.

B. PERIODIC REVIEW OF ESTIMATES

1. The Bureau of Mines estimates for material flow, industry practices, and trends provide the best estimates of the size of the industry.

2. EPA activities are currently generating the best emissions data and should be reviewed using:

   a. Overall industry studies; e.g., Reference 5.

   b. The Source Test Program, in which specific individual plant emissions are measured. This information provides emission factors for specific examples of typical industrial operations; and also provides some analyses of the particulate usually including trace metal content and particle size.

c. NEDS (National Emissions Data System) is steadily being enlarged and improved. This system can provide emission factors for specific plants and plant operations, the type of particulate control equipment in use, and the actual, or estimated, control efficiency. The system may eventually be expanded to include description of the emissions.

3. The chromium industry should be consulted for its opinion and suggestions on the most recently published estimates. This may be best accomplished by interviewing the Chromium Commodity Specialist, Division of Non-ferrous Metals, Bureau of Mines in Washington; or, by interviewing one or more of the principal companies in the industry.

4. The literature should be reviewed using (a) industrial views as published from time to time in Chemical Engineering, for example; and (b) environmental views as summarized in Pollution Abstracts, for example.

5. Individual companies or plants may be approached for opinions, data, or cooperative tests of their own operations. This is a difficult approach to the problem of obtaining of fresh information due to the natural reluctance of the plants to discuss environmental problems. However, data thus obtained have a relatively high degree of reliability.

6. State agencies in which specific plants are located may be able to provide useful information, and should be contacted.

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16. ABSTRACT

A national inventory of the sources and emissions of the element chromium was conducted. All major sources of chromium-containing emissions were identified and their chromium emissions into the atmosphere estimated. Also, a method for updating the results of the study every two years was recommended.

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