Chromium Compounds

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1. Introduction

Historical. Chrome iron ore (chromite) was discovered in 1798. A few decades later this ore was being subjected to oxidative roasting in the presence of soda and lime in manually operated furnaces to produce water-soluble sodium dichromate. This was processed further to yield yellow, red, and green chromium pigments which were used, among other things, for dyeing wallpaper; they replaced the toxic arsenic dyes that had been used until then. Chromium salts soon found their way into the textile industry as mordants for the dyeing of wool.

The importance of dichromates increased considerably in the period following 1870 when the rising coal tar dye industry needed large quantities for the oxidation of chemical intermediates. With the advent of the 20th century, chrome tanning was introduced in leather factories and in many areas replaced vegetable tanning.

The manufacture of chromium compounds received a further boost after 1930, when metallic chromium was successfully precipitated from chromic acid solutions by special additives. Since then this possibility has been used extensively in electroplating for bright and hard chromium plating.

Chromium compounds are used in numerous fields. In addition to the applications mentioned, chromates have long been used in printing as an aid

Table 1. Uses of chromium compounds

Branch of industry	Product	Use
Building industry	chromium(III) oxide	pigment for coloring building materials
Chemical industry	dichromates, chromium(VI) oxide	oxidation of organic compounds, bleaching of montan waxes, manufacture of chromium complex dyes
	chromium(III) oxide	catalysts
Printing industry	dichromates	photomechanical reproduction processes
	chromium(VI) oxide	chromium plating of printing cylinders
Petroleum industry	chromates(VI)	corrosion protection
Paints and lacquers	chromates, chromium(III) oxide	pigments
Refractory industry	chromium(III) oxide	additive for increasing slag resistance
Electroplating	chromium(VI) oxide	bright and hard chromium plating
Wood industry	chromates, chromium(VI) oxide	in mixtures of salts for protecting wood against fungi and insects
Leather industry	basic chromium(III) sulfates	tanning of smoothed skins
Metal industry	chromium boride, chromium carbide	flame sprays
	chromium(III) oxide	polishing agents
Metallurgy	chromium(III) oxide	aluminothermic extraction of pure chromium metal
Textile industry	dichromates	dyeing with chrome dyes
	basic chromium(III) acetates and chromium(III) fluorides	mordanting of textiles
Recording industry	chromium(VI) oxide	magnetic information storage
Pyrotechnics industry	dichromates	additive to igniting mixtures

in photomechanical reproduction. For some time, chromium dioxide has been a component of magnetic tapes for information storage. Table 1 lists important applications of chromium chemicals.

2. Chromium Ores [4–16]

The distribution of chromium in terrestrial rocks is closely linked to magmatic intrusions and their crystallization. The average content in the ten-mile crust of the earth is 100 ppm of chromium [10]. Table 2 contains a worldwide estimate of chromium ore resources.

The most important applications of chromium ores are in the manufacture of stainless steel, grey cast iron, iron-free high-temperature alloys, and chromium plating for surface protection. In the nonmetallic mineral industry, chromite is processed in conjunction with magnesite (sintered

Table 2. Estimated reserves of chromium ore [70]

	Reserves, 10^6 t			
	Total	Metallurgical[a], $> 45\% \; Cr_2O_3$	Chemical[a], $> 40\% \; Cr_2O_3$	Refractory[a], $> 20\% \; Al_2O_3$
Republic of South Africa	2000[b]	100 (5 %)	1900 (95 %)	–
Zimbabwe	600	300 (50 %)	300 (50 %)	–
Turkey	10	9 (90 %)	–	1 (10 %)
Philippines	7.5	1.5 (20 %)	–	6 (80 %)
United States	8	0.4 (5 %)	7.4 (92.5 %)	0.2 (2.5 %)
Canada	5	–	0.5 (100 %)	–
Finland	7.5	–	7.5 (100 %)	–
Others	11.35	8.175 (72 %)	0.2 (2 %)	2.975 (26 %)
Total	2649.35	419.075 (16 %)	2220.1 (84 %)	10.175 (0.4 %)
Former USSR and other Eastern bloc countries	51.5	26.5 (51 %)	15 (29 %)	10 (20 %)
Total worldwide (rounded off)	2701	446 (17 %)	2235 (83 %)	20 (1 %)

[a] Graded according to Cr_2O_3 or Al_2O_3 contents.
[b] Ores containing 30 – 50 % Cr_2O_3.

Table 3. Quality requirements (mass fractions in %) for chromium ores (according to U.S. Bureau of Mines)

	Metallurgical[a] (high-chromium chromite)	Refractory[b] (high-aluminum chromite)	Chemical[c] (high-iron chromite)
Cr : Fe ratio	3 : 1 or higher	–	–
Cr_2O_3	>48	>31	>44
$Cr_2O_3 + Al_2O_3$	–	>58	–
Fe	–	<12	–
SiO_2	<8	<6	<5
S	<0.08	–	–
P	<0.04	–	–
CaO	–	<1	–

[a] Zimbabwe, South Africa, Turkey, former USSR.
[b] Turkey, Philippines.
[c] South Africa, former USSR.

magnesia, calcined magnesia) and binders (clay, lime, gypsum, bauxite, corundum). The products are intended to have good resistance to pressure, fire, and temperature change, as well as good insulating properties between basic and acidic masonry. The chemical industry uses chromium ores in the production of chromium compounds (Chaps. 3–7). Table 3 shows quality requirements of chromium ores for different areas of application.

Minerals. Of the many minerals that contain chromium only the chromium spinels are of economic importance. The formula for the series of isomorphous mixtures of chromium spinels that form geological deposits is

$$(Fe^{II}, Mg)O \cdot (Cr, Al, Fe^{III})_2O_3$$
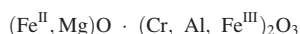
The proportion of Cr_2O_3 in the chromium spinels varies widely, causing the Cr : Fe ratio (also known as the Cr – Fe factor) to vary as well; this can have a profound effect on the evaluation of a deposit. In an ideal chromium spinel (FeO · Cr_2O_3; 67.8 % Cr_2O_3, 32.2 % FeO) the chromium : iron ratio is 2. As a result of the isomorphous inclusion of MgO, the Cr : Fe ratio may rise to between 2.5 and 5. Figure 1 shows the region of isomorphism with varying composition of the spinels. Natural chromium spinels usually contain 33 – 55 % Cr_2O_3, 0 – 30 % Fe_2O_3, 0 –30 % Al_2O_3, 6 – 18 % FeO, and 10 – 32 % MgO. Table 4 lists some physical properties of chromium spinels.

Chromium also occurs in all groups of silicates where chromium replaces Al^{3+}, Fe^{3+}, and Mg^{2+}. Sulfidic chromium ores do not occur
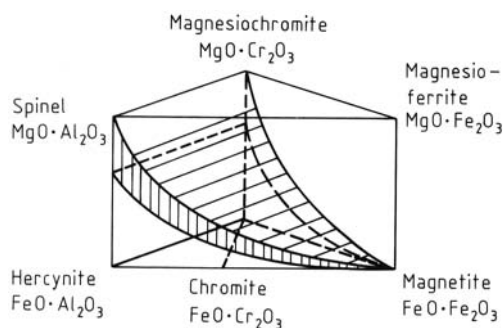
Figure 1. Ternary spinel system showing main isomorphous region

on earth. Chromates and chromium iodates are described, which originate from the weathering zone of sulfidic lead deposits (e.g., crocoite, $PbCrO_4$).

2.1. Ore Deposits

Chromium ore deposits can be divided into two genetically different types:

1. Seam-like deposits, also called stratiform or anorogenic deposits. Main representatives are Bushveld, Great Dyke, and Stillwater.
2. Deposits which are shaped like sacks or tubes; they are called podiform or orogenic deposits. Main representatives are Selukwe, Guleman, and Tiébaghi.

Various intermediate types such as adjacent "seam" pockets, striated chromite slabs, mottled ores, and vein-like deposits also occur. "Placer" deposits, i.e., enrichment due to chromite lumps and grains on or near primary deposits, are now achieving economic importance.

Table 4. Physical properties of chromium spinels

Properties	Notes
Specific density: 3.8 – 4.8	increases as Fe and Cr contents increase
Hardness (Mohs): 4.5 – 8	increases with increase in the ferrochromite component, very high for Al spinels
Melting point: 1545 – 1730 °C	inclusion of Mg raises melting point, inclusion of Fe^{2+} reduces it
Color: dark brown to black	reddish with high Cr_2O_3 content
Streak on porcelain plate; hammer striking mark: brown	important feature for differentiating from serpentine

The seam-like deposits reveal layers or strata of chromite enrichment, with thicknesses ranging from centimeters to decimeters; the layers are regularly interlaminated with banded series of olivine-rich or pyroxene-rich rocks. The Main Seam of the Western Bushveld is, for example, 1.10 – 1.30 m thick and can be traced for over 65 km without any significant change in the mineral composition or thickness.

The demarcation between the chromite enrichment and the underlying bed is usually razor-sharp; in the direction of the overlying layer, disintegration into layers or mottled ores as a result of increased silicate content is observed.

The chromite bodies that are sack-like to tube-like in appearance are usually aligned with the direction of the magmatic stratification, i.e., the lowest sections are massive chromite ores; in the direction of the overlying layer, these merge into striated slabs or mottled ores.

The internal texture of the chromite ore bodies varies widely. The closest chromite crystal packing results in the formation of massive ores containing 75 – 85 vol% of chromite. Sphere or leopard ores, which consist of round chromite crystal aggregates 0.5 – 2 cm in diameter in a silicate matrix (olivine, pyroxene, serpentine), are also characteristic. Banded ores are closely related to the massive ores, but they are frequently richer in silicate and then form a link with the mottled ores (chromite single crystals in silicate matrix).

During transformation (serpentinization), the silicate content within the chromite ore bodies has resulted in the formation of friable and pulverizable masses (friable ore) which are encountered not only near the surface but also at depths of several hundred meters below the present-day land surface.

Chromite transformation in the course of more recent tectonic superficial modification under pneumatolytic or hydrothermal conditions has resulted in the striking colors of recent uvarovite, smaragdite, and kammererite formations which act as pathfinders in prospecting and exploring for chromite deposits. Table 5 shows some analyses of selected chromium ores.

Table 5. Chemical analyses (mass fractions in %) of some chromium ores (crude ores, concentrates)

Country	Cr_2O_3	FeO	SiO_2	MgO	Al_2O_3	CaO	V_2O_5	Cr : Fe ratio
South Africa								
Rustenburg (c) [a]	44.5	26.4	3.5	10.6	14.4	n.d.[b]		1.7 : 1
Lydenburg (c)	44.3	24.6	2.3	11.2	16.1	0.4		1.8 : 1
Zimbabwe								
Great Dyke (m) [a]	48.5	18.3	5.6	13.4	11.5	0.8		2.6 : 1
Great Dyke (r) [a]	50.7	16.4	4.3	13.2	13.0	0.8		3.1 : 1
Selukwe (m)	47.0	12.0	5.7	15.5	12.6	1.8		3.9 : 1
Selukwe (r)	42.0	15.7	8.6	15.8	13.8	0.3		2.7 : 1
Turkey								
(m)	48.3	14.1	5.1	16.8	13.0	0.9		3.4 : 1
(r)	37.0	15.2	4.3	17.7	24.3	0.2		2.4 : 1
Philippines								
(Masinloc) (r)	33.3	13.2	4.6	19.6	28.2	0.4		2.5 : 1
Finland (Kemi)								
Crude ore	26.5	15.0	18.5	19.5	9.5	–	0.04 – 0.1	1.8 : 1
Concentrate	45.7	33.8	0.4	2.9	13.6	n.d.	0.1	1.4 : 1
Albania								
(m, r)	43.0	16.2	9.8	22.2	7.9	0.1		2.6 : 1
Former USSR								
(m)	53.9	12.6	5.8	13.3	9.6	1.1		4.3 : 1
(r)	39.1	14.0	9.4	16.1	17.4	0.7		2.8 : 1

[a] (m) = metallurgical, (r) = refractory, (c) = chemical.
[b] n.d. = not determined.

Former Soviet Union. The former Soviet Union is one of the most important producers of chromium ore in the world. All the deposits are distributed in ultrabasite massifs in the Central and Southern Urals. The deposits that are most important at present were found in the late 1930s in the Akhtiubinsk region (North Kazakhstan). The Donskoye deposit, which is associated with the mining settlement of Khrom Tau, contains high-grade chromium ores for ferrochromium production and low-grade ores for chemical purposes. Mining is carried on in numerous open-pit mines, which implies that the ore bodies are small. A new open-cast mine was put into production near Donskoye, as is a processing plant with a throughput of 10^6 t/a. Strong prospection effort for new occurrences is being made in the Northern Urals, but because of the rough climate no mine has been opened up to 1986.

Bushveld. In the Bushveld (Republic of South Africa) mining began in the 1920s in two districts: the Lydenburg district (Eastern Bushveld) and the Rustenburg district (Western Bushveld).

From a geological and petrological point of view this is a large intrusion of 500×250 km with a thickness of over 5 km. The chromite "seams" are located in the pyroxenite – norite zone of the basal section of the intrusion, always below the platinum-bearing Merensky Reef. In the case of Rustenburg there are up to 25 chromite seams on top of each other. The thickness of the individual seams varies from a few centimeters to 1.80 m. The seams are workable from 0.35 m upward, especially if they can be combined into mining units (Cr_2O_3 content in the crude ore 30 – 40 %; Cr : Fe ratio = 1.6 – 2.3). In the Lydenburg district, which is genetically very similar to the Rustenburg district, only two seams are being mined; the Cr_2O_3 content is 44 % and the chromium : iron ratio 1.6 – 1.7. The iron content is frequently high, which may cause difficulties in the case of metallurgical ores; however, these ores are highly valued as chemical ores.

Great Dyke. The Great Dyke (Zimbabwe) is an intrusion which is 610 km long and 6 – 9 km thick – a remarkable length : thickness ratio which is unique in the world. The internal structure is similar to that of the Bushveld. From north

Table 6. Analysis of chromium ores from Zimbabwe

	Cr_2O_3 content, wt %	Cr : Fe ratio	Proportion, wt %
Metallurgical	over 48	over 2.8	80
Chemical	45 – 48	2.2 – 2.5	17
Refractory	42 – 46	1.8 – 2.0	3

to south, the individual complexes are Musengezi, Hartley, Selukwe, and Wedza. Selukwe consists of sack-like deposits containing 48 % Cr_2O_3 and even more, with a chromium : iron ratio greater than 2.8 (a highly valued metallurgical ore). In the Hartley region, on the other hand, numerous bands and seams 2 – 75 cm thick are being mined; these are separated by serpentinized peridotite layers, some of which are very thick and make mining very difficult. However, the Cr_2O_3 content varies between 48 and 57 %, and the chromium : iron ratio is over 2.8 (Table 6).

According to conservative estimates, 1 km^2 of the Great Dyke contains around 1.4×10^6 t of crude ore, which corresponds to assured reserves of 600×10^6 t (geologically 4.6×10^9 t are possible).

Other Ore Deposits.
Madagascar. On the island of Madagascar, chromium ores are being mined since 1967 with an annual production of around 60 000 t of metallurgical grade ore. Total output is calculated to be almost 2×10^6 t since the beginning of the operation (50 – 52 % Cr_2O_3). The reserves are said to be around 5.5×10^6 t.

Turkey. Turkey still is the traditional country for chromite deposits of metallurgical quality, but because of falling prices on the world market and exhaustion of reserves, many mines have been forced to close. The most important regions belong essentially to the alpidic era, e.g., Bursa, Mugla district, and Elazig, including the Guleman chrome ore field. Open-pit mining, and in some places underground mining at shallow depths, are employed.

Iran. Chromite deposits are described in two regions of Iran: northwest of Sabzawar near Mashad and 200 km northeast of the Gulf port of Bandar Abbas. These deposits are pocket-like, sometimes containing only 500 t of ore. Extraction is by open-pit mining and by primitive underground mining. Only hard lump ore

for metallurgical applications is sometimes exported.

Philippines. On the Philippine island of Luzon the most important chromite deposits are to be found in the Coto region (near Masinloc, province of Zambales). These are chromite seams and pockets within layered dunites and harzburgites. They are classical metallurgical and refractory ores. More recently a new type of chrome ore has been put into production: chromite from lateritic soils. The concentrates are suited for the chemical industry.

Finland. In 1959 a fairly large deposit of chromite was discovered near Kemi, which has been developed into a productive mine. Chromium ore occurs in a serpentinite – anorthosite massif 12 km long and 1 – 2 km wide; the ore zone, however, is only 15 – 100 m thick and dips at an angle of $60°$ toward the north. The Cr_2O_3 content of the crude ore of the various ore bodies varies between 17.5 and 21.9 % (locally even up to 30.5 % Cr_2O_3); the chromium : iron ratio is low (0.81 – 1.87).

Former Yugoslavia. The deposits of chromite in former Yugoslavia are restricted to the Raduša massif near Skopje, but the mining of metallurgical ores there has fallen considerably. Native ores are being processed in a new plant, whereas ores imported from Albania are being processed in the old one. The chromium ores are always associated with serpentinized ultrabasites. The striated slab type predominates, but massive chrome ores are encountered in some places.

Albania. Since 1960, Albania has become the third largest producer in the world. All actual data are based on estimates because the Albanian government withholds production and export figures. Albanian deposits belong to the podiform type and normal grades are reported to be 43 % Cr_2O_3 with a Cr : Fe ratio of 3 : 1. The largest chrome ore mines are Bulquize and Matanesh with concentration plants of 300 000 t/a each.

2.2. Ore Beneficiation

The simplest method of concentrating chromite is by hand picking; this is still employed today at many pits, including those in Turkey, Brazil, Iran, and the Philippines. Because the mining of richer ores continues to decline, concentrating

procedures, chiefly using the gravity method, have been developed to separate the serpentine from the chromite. For example, in South Africa or Brazil the chromite ores are enriched by crushing, milling, screening, and sophisticated gravity procedures. In South Africa, spirals and diamond pans are standard equipment. A combination of Reichert cones and Reichert spirals has also been employed. Although the costs are higher, the use of hydrocyclones for separating the fine chromite grains from waste is of great importance in the recycling of tailing dumps. Some chromium ores contain magnetite which can be removed by means of magnetic separation. However, if the magnetite is present as an individual phase within the chromite grains or as a fringe around the grains, this method is only suitable if Cr_2O_3 is further enriched. Flotation and electrostatic processes have so far enjoyed little success in the concentration of chromium ores. If the Cr_2O_3 content or the chromium : iron ratio is sufficient, fine-grained chromite concentrates can be briquetted or pelleted with the aid of binders.

The yield (65 – 85 % of the chromite actually contained in the crude ore) depends on many factors including the nature of the chromite – serpentine intergrowth, grain size, and Cr_2O_3 content of the ore or individual grain.
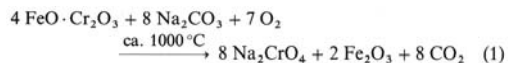
At the chromite concentration plant at Kemi in Finland a fraction of the crude ore (70 %) is crushed to below 10 mm in a primary crusher plant at the open-pit mine. After further grinding (rod and ball mill) and removal of sludge, the intermediate product is dried in a rotary kiln. The magnetic separation (a combination of weak and strong fields) produces two concentrates: concentrate 1 containing 45.9 % Cr_2O_3, which is sold or used as molding sand, and concentrate 2 containing 42.0 % Cr_2O_3 for the production of ferrochromium.

3. Production of Sodium Dichromate

Directly or via several intermediate stages, sodium dichromate [7789-12-0], $Na_2Cr_2O_7 \cdot 2\,H_2O$, is the starting material for the production of all chromium compounds and pure chromium metal.

Sodium dichromate is made in a three-step process: (1) alkaline roast of chromite under

oxidizing conditions (Eq. 1), (2) leaching, and (3) conversion of sodium monochromate to sodium dichromate by means of an acid (Eq. 2).

$$4\,FeO \cdot Cr_2O_3 + 8\,Na_2CO_3 + 7\,O_2$$
$$\xrightarrow[\text{ca. 1000 °C}]{} 8\,Na_2CrO_4 + 2\,Fe_2O_3 + 8\,CO_2 \quad (1)$$

$$2\,Na_2CrO_4 + 2\,H^+ \longrightarrow Na_2Cr_2O_7 + H_2O + 2\,Na^+ \quad (2)$$

3.1. Alkaline Roasting

Soda ash (sodium carbonate) is generally used as the alkali component but sodium hydroxide may also be employed [17–19]. The degree of solubilization of chromites by the roasting process depends on their composition. For optimum results, the process is controlled by adding so-called carrier materials. These ensure sufficient porosity of the material so that oxygen can diffuse into the roast. Porosity is maintained by means of such materials as iron oxide, bauxite, or dried leach residue; CO_2-emitting additives include lime and/or dolomite. The inert additives dilute the sodium carbonate and sodium chromate, which both melt at the reaction temperature. In the *low-lime process* the carbonates evolve CO_2, decrease the reaction temperature to below 1000 °C, and raise the melting point of the reaction products; the amount of lime added must be controlled so that the compound 5 $Na_2CrO_4 \cdot CaCrO_4$ [20] is produced in the roast. Temperatures above 1150 °C must be avoided because they result in the subsidiary components of the ore being attacked. At still higher temperatures the degree of conversion is markedly decreased. The optimum temperature range is very narrow and depends strongly on the type of ore used and the composition of the mixture.

Process Description. A typical roast mixture contains 100 parts of ore, 60 – 75 parts of sodium carbonate, 0 – 100 parts of lime or dolomite, and 50 – 200 parts of inert materials. The components are first finely ground, then mixed, and fed into the furnace. Annular hearth furnaces or rotary kilns are commonly used in large plants today.

The *annular hearth furnace* (Fig. 2) is made from steel with a refractory lining (inner diameter ca. 20 m; outer diameter ca. 30 m); it is driven by a gear wheel underneath and has rails running on rollers. The rotating hearth is sealed from the stationary parts of the furnace by sheets of metal dipping into annular water troughs. The furnace is heated by several burners from the side or from the top with gas, coal dust, or oil. The exhaust gas can be utilized to preheat the burner air or to generate steam. The mixture is fed to the outer edge of the annular hearth by a feed screw. A water-cooled ribbon screw transports the mixture inward, each time the annular hearth revolves, and finally removes it in the middle.

In the annular hearth furnace, the mixture is uniformly heated to the reaction temperature and made to travel toward the center of the hearth with a well-defined layer thickness. The furnace process is fairly independent of the sintering of the roast; it allows the production of melts that contain 40 wt % of water-soluble sodium chromate. The yield is 80 – 95 %, based on the chromite feed. The roast takes 2 – 6 h, depending on the composition of the mix.

Most of the kiln tube of the *rotary kiln* (Fig. 3) between the feed point and the reaction zone is used to heat the mixture. Shortly before the mix reaches the actual reaction zone, the soda melts and calcines. At this point the mixture bakes, and pellets or wreath-shaped cakes may be formed. If the furnace is operated inexpertly (temperature too high) or the composition of the mixture is wrong (too little carrier material) the kiln tube may get substantially clogged. In such cases, the constriction can be cleared by using an industrial gun.

The roast from the rotary kiln contains up to 30 wt % of water-soluble sodium chromate. The yield is 75 – 90 %, based on the chromite feed. The roast takes 3 – 8 h, depending on the composition of the mixture. The hot exhaust gas from the rotary kiln can be used to preheat the burner air.

Gas Purification. Exhaust gas purification systems able to achieve a high degree of separation are required for dust collection. They essentially consist of two components: (1) an exhaust gas cooling system, with optional energy recovery, for example, steam generation; and (2) the exhaust gas purification system, usually an electrostatic separator. The size and the design of the purification system depend on the type of furnace. In the rotary kiln, ca. 10 % of the feed mixture is carried off by the exhaust gas, whereas
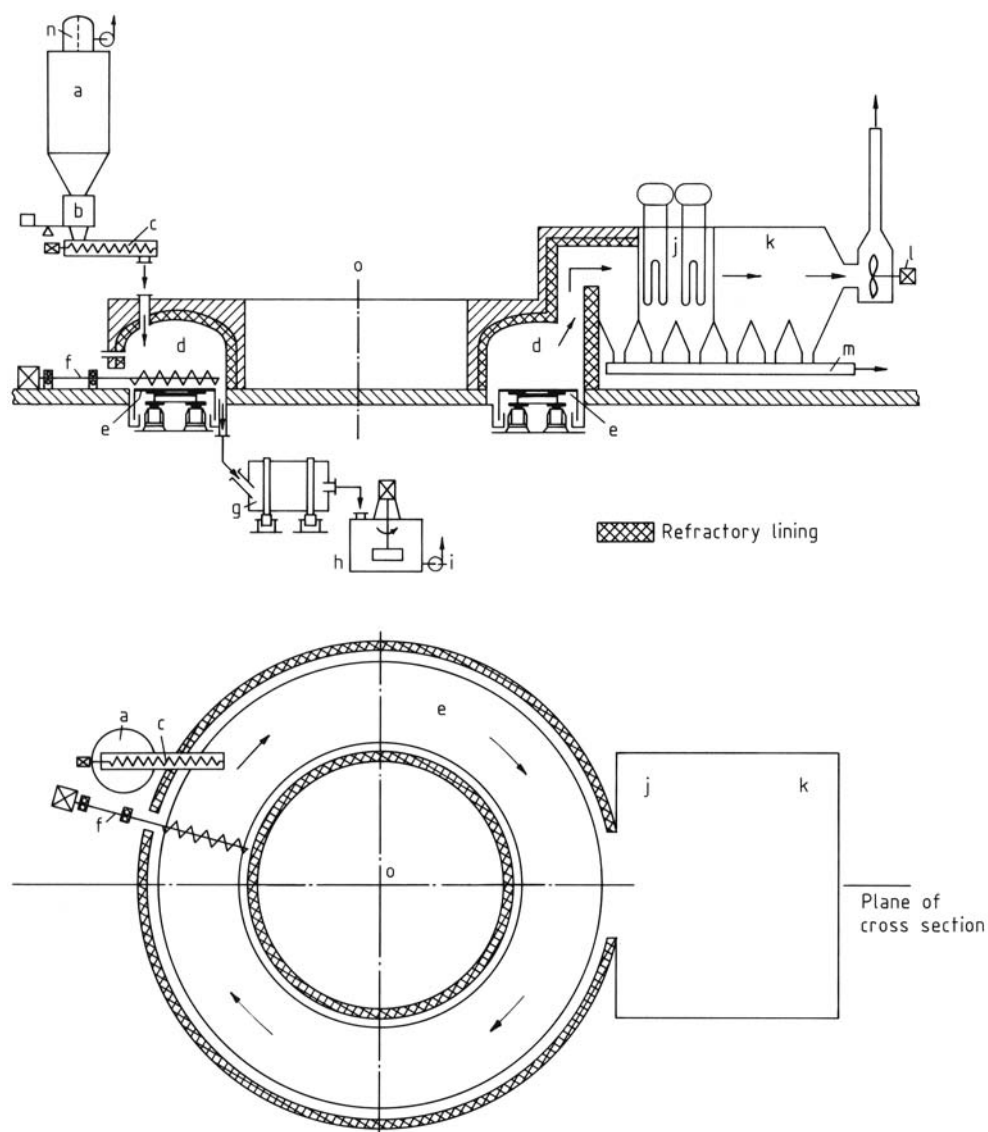
Figure 2. Annular hearth furnace a) Mixture silo; b) Scales; c) Feed screw; d) Furnace; e) Annular hearth; f) Water-cooled ribbon screw; g) Wet tube mill; h) Stirred vessel; i) Pump for filtering system; j) Waste heat boiler; k) Electrostatic gas purification; l) Exhaust gas fan; m) Dust drag chain; n) Bin filter; o) Rotation axis

in the annular hearth furnace, less than 1 % is carried off. However, operation of the annular hearth furnace necessitates a considerable expenditure on gas cooling.

Other Processes. In the literature, other processes are proposed but so far these have not achieved any industrial significance. Thus, attempts have been made to roast chromium ore in a shaft furnace [21] or in a fluidized-bed

reactor [22]. A fundamentally different process involves the reaction of the chromium ore and soda in a molten salt mixture with oxygen-containing gases being injected [23].

3.2. Leaching of the Roast

After the oxidative process, the roast is a mixture of soluble salts and insoluble components. It
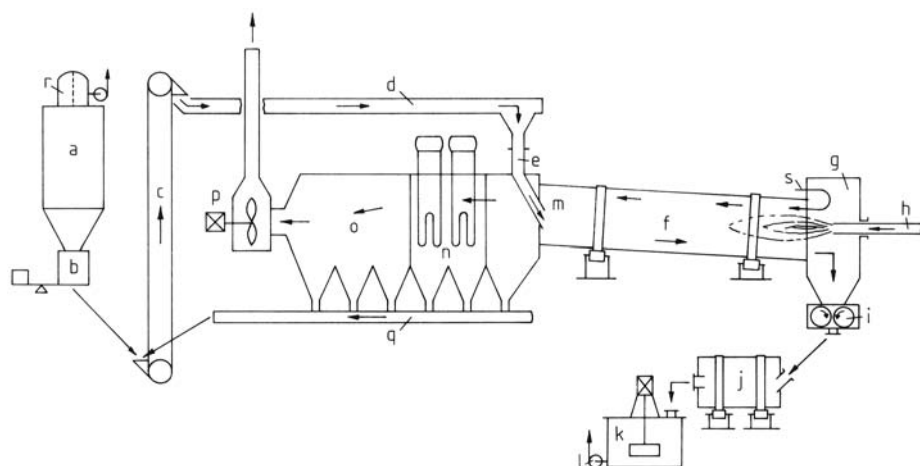
Figure 3. Rotary kiln for roasting chromium ores a) Mixture silo; b) Scales; c) Elevator; d) Drag chain; e) Inlet tube; f) Rotary kiln; g) Combustion chamber; h) Burner; i) Crusher; j) Wet tube mill; k) Stirred vessel; l) Pump for filtering system; m) Kiln inlet; n) Waste heat boiler; o) Electrostatic gas purification; p) Exhaust gas fan; q) Dust drag chain; r) Bin filter; s) Air inlet

contains sodium chromate, sodium aluminate, magnesium oxide, sodium vanadate(V), iron(III) oxide, unused alkali, unchanged chromite, and small amounts of sodium chloride originating from the soda.

When the roast is extracted with hot water, a pH of 10.5 – 11.2 results. The pH is controlled by adding acids or carbonates so that all chromate dissolves, whereas the alkali-soluble impurities hydrolyze and form a readily filterable precipitate along with the iron hydroxide and the unchanged ore components.
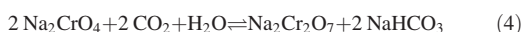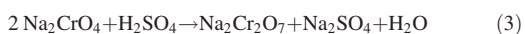
The roast is first cooled on a Fuller grate or in a cooling drum. Then it is either ground in a wet tube mill after addition of water or wash solution (see below) with carbonates or acids added, or it is dissolved in a stirred vessel. The insoluble residue is separated from the sodium chromate solution and thoroughly washed with a countercurrent of water. Continuous multistage Dorr plants or rotary filters are used; after separation, the insoluble residue is extracted two to three more times in counterflow. Dorr plants only exhibit satisfactory separation of residue and solution if the sodium chromate concentration is not too high. Rotary filter plants can be employed without difficulty for nearly saturated hot sodium chromate solutions; such filters are frequently preferred because the higher water consumption of the Dorr plant results in unnecessary steam costs in the subsequent evaporation process.

After removal of residual aluminum hydroxide and other undissolved components in a final purification process (e.g., thickener), the concentrated sodium chromate solution is acidified (Section 3.3).

Some of the filter residue is dried and added to the roasting mix (Section 3.1). The remainder is subjected to reducing treatment to convert the residual chromate content into an ecologically harmless form. To do this, the residue is suspended in water and treated with sulfuric acid and sodium hydrogen sulfite or iron(II) sulfate; chromate residues are converted into chromium(III) compounds in this way. Subsequent addition of alkali precipitates trivalent chromium (and iron(III), if present) as hydroxide. The suspension is then filtered and the cake (optionally after further removal of water) is dumped.

3.3. Acidification

The sodium chromate solution is converted into sodium dichromate solution by acidification with sulfuric acid (Eq. 3) or carbon dioxide (Eq. 4). The sequence of individual steps depends on the acid.

$$2\,Na_2CrO_4 + H_2SO_4 \rightarrow Na_2Cr_2O_7 + Na_2SO_4 + H_2O \qquad (3)$$

$$2\,Na_2CrO_4 + 2\,CO_2 + H_2O \rightleftharpoons Na_2Cr_2O_7 + 2\,NaHCO_3 \qquad (4)$$

Sulfuric Acid Acidification. Sulfuric acid is added to the concentrated sodium monochromate solution in an agitated vessel until the pH is about 4. The sodium dichromate solution is then concentrated in a continuous evaporation plant. Each liter of sodium dichromate solution yields 400 – 500 g of anhydrous crystalline sodium sulfate. The sulfate is removed by centrifugation. The clear, dark-red sodium dichromate solution contains 900 – 1200 g of $Na_2Cr_2O_7 \cdot 2\,H_2O$ per liter and additional small amounts of sodium sulfate; it is dispatched in tanks, e.g., of steel. The solution is either used directly as an oxidizing agent or processed to yield dichromate crystals.

Carbon Dioxide Acidification.   After filtration the sodium monochromate solution from the first filtration stage is concentrated to ca. 850 g of Na_2CrO_4 per liter. The saturated sodium chromate solution is then acidified with a countercurrent of carbon dioxide at 0.5 – 1.5 MPa (5 – 10 bar) to yield sodium dichromate and sodium hydrogen carbonate. A series of stirred autoclaves is preferred for this reaction. They must be cooled to remove the heat of neutralization; the slurry leaves the last reactor at room temperature. The degree of conversion is about 80 – 90 %.

The sodium hydrogen carbonate is removed by centrifugation or filtration, preferably under pressure to prevent reaction (4) from being reversed. After it has been washed, water can be removed in a pusher centrifuge. Still moist, the sodium hydrogen carbonate is then transferred to a calcining furnace. The carbon dioxide produced in the furnace may be fed back to the acidification autoclaves [2]; the sodium carbonate obtained is recycled for alkaline ore roasting [24].

To obtain commercial sodium dichromate solution, further evaporation to a concentration of 1000 g of sodium dichromate per liter is required. This is then followed by a second acidification with carbon dioxide or sulfuric acid.

Production of soda is the main advantage of carbon dioxide acidification. However, this is offset by a number of difficulties, particularly the formation of deposits on the evaporator during the concentration of the sodium monochromate solution. Other problems include mastering the pressure technology and cooling, separation of the sodium hydrogen carbonate, yield loss due to reverse reaction, and clogging of the calcination furnace.

3.4. Crystallization

For the purpose of crystallization the sodium dichromate solution (950 – 1200 g/L) is further concentrated and may, if necessary, be filtered while hot to remove additional sodium sulfate or sodium chromate. It is then slowly cooled to 30 – 35 °C with constant stirring to obtain orange-red crystals of $Na_2Cr_2O_7 \cdot 2\,H_2O$.

Today continuous vacuum crystallization is carried out to an increasing extent. The initial difficulties of this process, particularly in obtaining coarse, dust-free crystals, have largely been overcome. The crystalline slurry is continuously separated from the mother liquor and dried. Precise control of the drying temperature is important because hydrated sodium dichromate is converted into anhydrous sodium dichromate above 84.6 °C and, therefore, cakes if overheated.

For reasons of occupational health, care should be taken to ensure that workplaces and production plants are dust free when sodium dichromate, especially the dried product, is being handled. In such locations, extensive ventilation and dust removal systems (wet scrubbers, electrostatic separators) are necessary.

4. Chromium Oxides

4.1. Chromium(III) Oxide and Chromium Hydroxide

Chromium(III) oxide   [*1308-38-9*], Cr_2O_3, M_r 151.99, ρ 5.2 g/cm^3, is green in finely dispersed form, whereas fairly large crystals have a blackish green hue and a metallic luster. The crystals have a hexagonal rhombohedral structure of the corundum type. The compound melts at 2435 °C, but begins to evaporate at 2000 °C to form clouds of green smoke; the boiling point is estimated to be 3000 – 4000 °C. The enthalpy of formation is − 1141 kJ/mol. Macrocrystalline chromium(III) oxide has a hardness of 9 on the Mohs scale. An amorphous form of the oxide is also known; this crystallizes on heating.

Chromium(III) oxide does not dissolve in water, acid, alkali, or alcohols. It is converted by a molten bath of sodium peroxide into soluble sodium monochromate(VI). Chromium(III) oxide and chromates(III) are used in organic chemistry as catalysts, e.g., in the hydrogenation of esters or aldehydes to form alcohols and in the cyclization of hydrocarbons. They also catalyze the formation of ammonia from hydrogen and nitrogen.

Production. The industrial production of chromium(III) oxide involves the reduction of solid sodium dichromate, generally with sulfur. The finely divided components are thoroughly mixed, fed into a brick-lined furnace, and brought to dark-red heat. The reaction proceeds exothermically. After the reaction mass has cooled, it is broken up and the sodium sulfate produced is leached out with water. The remaining solid is separated, rinsed, dried, and ground. To obtain 100 kg of chromium(III) oxide, 200 kg of sodium dichromate must react with at least 22 kg of sulfur; usually an excess of sulfur is used. Additives such as ammonium chloride or starch in the crude mixture affect the pigment properties. When sodium dichromate is replaced by the corresponding potassium salt, the hue of the pigment becomes more bluish.

The compound can also be prepared by a wet route involving reduction of sodium chromate by sulfur [25], with sodium thiosulfate being produced as a coproduct. The hydrate initially obtained is washed by decanting, filtered, and calcined to form the oxide.

Chromium(III) oxide destined for aluminothermic production of pure chromium metal must be heated additionally at 1000 °C to increase its grain size. If products particularly low in sulfur are to be produced for this purpose, charcoal can be used for the reduction instead of sulfur. High-purity oxides can also be obtained by thermal decomposition of chromium(VI) oxide or ammonium dichromate(VI), the latter yielding a material of very low density.

Chromium (III) Oxide Pigments contain 99.1 – 99.5 % Cr_2O_3. The aluminum oxide and silicon dioxide impurities each amount to ca. 0.1 %; the annealing loss at 1000 °C is about 0.3 %. The individual particles are spherical, with a diameter of 0.3 µm predominating. Chromium(III) oxide finds widespread application as a green pigment resistant to atmospheric conditions and heat. In addition, it is used as a colorant in glass products and printing inks, as a vitrifiable pigment in the ceramics industry, and as a polishing agent because of its considerable hardness (→ Pigments, Inorganic, 1. General).

Chromium(III) Aquoxides [*12292-46-5*], [*12182-82-0*]. Pure chromium(III) hydroxide [*1308-14-1*], $Cr(OH)_3$, M_r 103.02, can only be prepared with difficulty because the hydrates initially obtained by precipitation are subject to aging.

After drying in air, specimens prepared by precipitation with alkali in the cold from violet chromium(III) salt solutions have a composition corresponding to $Cr_2O_3 \cdot 9\ H_2O$ [*12182-81-9*], and are usually formulated as $Cr(H_2O)_3(OH)_3$ [*41993-26-4*]. They are bright bluish green powders with limited life. All three hydroxyl groups react immediately with acids. Upon careful heating, dehydration occurs in steps and compounds containing 8, 5, 3, and 1 mol of water are formed. The density increases as the water content falls. Above 50 °C, conversion to a gelatinous green aging product occurs, and the solubility and chemical reactivity decrease; oxygen bridges are formed through the elimination of water, and polynuclear complexes are produced. The composition approaches that of chromium(III) oxide hydroxide, $CrO(OH)$ [*20770-05-2*]. Aging is accelerated by the presence of hydroxide ions.

In freshly precipitated hydroxides a crystalline phase isomorphic with bayerite [$Al(OH)_3$] is observed (→ Aluminum Oxide), whereas aged compounds are X-ray amorphous. The chromium(III) hydroxide hydrates are amphoteric compounds. With acids they form Cr^{3+} salts, whereas they dissolve in strong hydroxide solution to form chromates(III), e.g., the deep green sodium chromate(III), $Na_3Cr_4O_4$ (previously known as sodium chromite). When ammonium hydroxide is added, red solutions are formed. Oxidizing agents in the presence of alkali produce chromates(VI). With halogens this takes place immediately on gentle heating, but with oxygen several hours are required at a pressure of 4 MPa (40 bar) at 175 °C.

Chromium(III) hydroxide forms a stable colloid solution, whose isoelectric point is at pH 5. At higher pH the sol becomes negatively charged and adsorbs cations, whereas below pH 5 the charge is positive and anions are adsorbed. The adsorption capacity of chromium(III) hydroxide sols is higher than that of aluminum or iron(III) hydroxide sols. Sols containing 127 g of Cr_2O_3 per liter have been obtained from concentrated chromium(III) chloride solution by addition of ammonium carbonate and dialysis while the solution is hot [26].

Production. In industry chromium(III) hydroxide hydrates are usually produced from solutions of chromium(III) sulfate or chromium alum by precipitation with soda, sodium hydroxide solution, or ammonium hydroxide. Production by reduction of sodium chromate with sodium sulfide [27] has also been proposed.

For production from potassium chromium alum 54 kg of soda is dissolved in 300 L of water and a solution of 180 kg of alum in 900 L of water is added slowly. After the evolution of carbon dioxide has subsided, about 220 kg of moist chromium hydroxide containing 12 % Cr_2O_3 is obtained by filtration. Chromium(III) hydroxide hydrates are used for the production of chromium(III) salts by reaction with the corresponding acids.

Hydrated Chromium(III) Oxide, $Cr_2O_3 \cdot x$ H_2O, is a brilliant emerald-green pigment known as Guignet's green [*12001-99-9*] that consists of very finely divided chromium(III) oxide to which water is bonded by adsorption. It is produced by heating a ground mixture of one part by weight of potassium dichromate and three parts by weight of boric acid in a muffle furnace to a faint red heat, which results in the formation of chromium(III) and potassium tetraborates. The molten mass still contains 6 – 7 % water and, after cooling, already has a deep green color. When this mass is boiled with water, it decomposes into chromium(III) oxide hydrate and boric acid. The product is coarse-grained and difficult to grind. Use of sodium dichromate as raw material results in a more yellowish color, whereas addition of thiourea or polysulfide to the reaction mixture produces a pigment with a bluish hue. The composition of the commercial products varies; typical values are: Cr_2O_3 79.3 – 82.5 %, H_2O 16.0 – 18.0 %, B_2O_3 1.5 –2.7 %.

Hydrated Chromium Oxide Green is a pigment with properties similar to those of Guignet's green but with a somewhat less intensive coloration. This pigment is prepared by reducing sodium chromate or sodium dichromate in aqueous solution with sulfur or sodium formate in a stirred autoclave or pressure tube [28]. The temperature required is 250 – 270 °C. The solid is separated by filtration, washed, dried, and ground. The finished pigment consists of fine needles, with a particle size of 0.02×0.1 µm predominating. The product contains 79 – 80 % Cr_2O_3, the annealing loss is about 19 %, and the density 3.7 g/cm^3. The coloration changes at elevated temperature. Because of its high reflecting power at infrared wavelengths the product had at times been of special importance in camouflage paints.

4.2. Chromium(IV) Oxide (Chromium Dioxide)

WÖHLER discovered ferromagnetic chromium dioxide in 1859 when he decomposed chromyl chloride [29]. About 100 years later, Du Pont produced it in pure form by decomposition of chromic acid under hydrothermal conditions [30], [31]. Industrial exploitation began after the morphological and magnetic properties had been modified by doping chromium dioxide with heavy metals [32], [33] in order to meet the requirements for a magnetic pigment [34]. The marketing of chromium dioxide at the beginning of the seventies initiated the development of cobalt-doped iron oxides which are nowadays used as an alternative to chromium dioxide for information storage.

Physical and Chemical Properties [35]. Chromium dioxide [*12018-01-8*], CrO_2, M_r 84.00, crystallizes in black tetragonal needles. The lattice is of the rutile type and belongs to the space group 4/mmm. The dimensions of the unit cell are $a = b = 44.21$ nm and $c = 29.16$ nm. The X-ray density is 4.89 g/cm^3, and the phase width is between $CrO_{1.89}$ and $CrO_{2.02}$ [36]. The enthalpy of formation is $- 590$ kJ/mol [37]. The temperature coefficient for the *c*-axis is negative [38]. At 100 °C, agglomerated blocks

have a linear coefficient of expansion of -6×10^{-6} K^{-1} [39].

At room temperature chromium dioxide is ferromagnetic, the magnetic moment being 2 Bohr magnetons. The Curie temperature is 120 °C and increases to 155 °C as a result of doping with iron [40]. Finely crystalline needle-shaped chromium dioxide has a specific magnetic saturation M_s/ϱ of 77 – 92 A m^2/kg, whereas in single crystals M_s/ϱ rises to 100 A m^2/kg [32]. The magnetocrystalline anisotropy constant is 22×10^3 J/m^3 [41]. The coercivity H^c depends on the size of the crystals and on their shape and magnetocrystalline anisotropies. The coercivity is affected to differing extents by various heavy metals [42]. Iron, antimony, and tellurium increase H^c from 35 kA/m to 60 kA/m, whereas iridium increases it to 220 kA/m [43].

Chromium dioxide behaves as a metallic conductor [35], [44], with a specific electrical resistivity between 2.5×10^{-4} and 4×10^{-2} Ω cm [38], [45].

At room temperature and normal pressure chromium dioxide is metastable; when heated to temperatures above 350 °C, it decomposes into chromium(III) oxide and oxygen. Chromium dioxide has an oxidizing action on reactive organic compounds [46]; the reactivity is considerably decreased by enveloping it with iron(III) and chromium(III) oxides [47–49]. Chromium dioxide is insoluble in water. Reaction with water occurs at the crystal surface, with disproportionation to chromate and Cr^{3+} ions. The aqueous suspension has a pH of 3. However, chromium dioxide is soluble in concentrated sulfuric acid or concentrated alkali solution.

Production [50]. Chromium dioxide is made by decomposition of chromyl chloride, chromic acid anhydride [50], and chromium(III) chromate [51], or by oxidation of chromium(III) compounds with oxygen, hydrogen peroxide, chromic acid anhydride [52], or ammonium perchlorate [43].

Industrial production employs a process originally carried out under licence from Du Pont [42], which involves hydrothermal oxidation of chromium(III) oxide with excess chromic acid:

$$Cr_2O_3 + 3\,CrO_3 \rightarrow 5\,CrO_2 + O_2$$
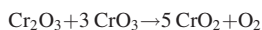
Iron(III) oxide and antimony(III) oxide are used as a dopant. Finely divided chromium(III) oxide is obtained either by thermal decomposition of ammonium dichromate or by dehydration of chromium(III) hydroxide [52].

A highly viscous paste (50 – 100 Pa · s) is produced by intensively homogenizing the starting materials. This paste is heated at 300 °C and 35 MPa (350 bar) to form a hard agglomerate of fine chromium dioxide needles which must be drilled out of the reactor trays, broken, and carefully ground. If the residual moisture exceeds 5 %, the product is reheated in a rotary kiln. The chromium dioxide is deagglomerated in an aqueous sodium sulfite suspension, and the crystal surface is simultaneously reduced; this forms a chromium(III) oxide hydroxide layer about 1 nm thick. To do this, the suspension is circulated through a mill which generates intense shear fields and the fine component is removed by using a hydrocyclone. After filtration and washing, drying is carried out in a spray tower. The chromium dioxide obtained has a bulk density of 0.8 g/cm^3.

Production is carried out to a large extent in closed equipment. Less than 2 mg of dust is emitted per 1 m^3 of exhaust air (STP). The chromium-containing wastewater from the production is worked up by reduction.

Use and Economic Importance. Chromium dioxide is used as a magnetic pigment. So far no other uses have achieved any significance [33].

In the audio field, chromium dioxide is used in mono- and multilayer tapes, the layers in the latter containing chromium dioxide of different coercivity. In video tapes, it is employed either on its own or mixed with cobalt-doped iron oxides. Because of its low Curie point, chromium dioxide allows high-speed thermomagnetic copying of prerecorded audio and video tapes [53]. Chromium dioxide has been used in digital data storage since 1985. Since the magnetostriction of chromium dioxide is low, repeated playing results in virtually no level losses [54]. Table 7 contains data on chromium dioxide powder intended for various applications.

In 1984 the demand for magnetic pigments was about 50 000 t, about 10 % of this being chromium dioxide. The most important manufacturers are Du Pont (United States) and BASF

Table 7. Powder data for typical chromium dioxide pigments

Application	Particle geometry				Magnetic data[d]		
	SSA^a, m^2/g	l^b, µm	l/d^c	V^c, 10^{-4} µm	H_c, kA/m	M_r/ϱ^e, A m^2/kg	M_s/ϱ^f, A m^2/kg
Audio	28	0.29	9	2.5	41	35	77
Video	35	0.29	11	1.5	49	34	74
Data storage	24	0.32	8	3.5	39	35.5	79

[a] Specific surface area (SSA) determined by N_2 adsorption using the BET method (1-point measurement).
[b] Mean length l determined by electron microscope photography with a magnification of 20 000 times.
[c] Diameter d and volume V calculated from SSA and l.
[d] Measured with a vibration magnetometer, $H_m = 800$ kA/m.
[e] M_r/ϱ = specific remanent magnetization.
[f] M_s/ϱ = specific saturation magnetization.

(Federal Republic of Germany). In addition, there is a chromium dioxide plant in the former Soviet Union.

4.3. Chromium(VI) Oxide

Chromium trioxide [1333-82-0], chromic acid anhydride, chromic acid, CrO_3, M_r 99.99, ϱ 2.7 g/cm^3, forms dark red crystals which deliquesce in air. The enthalpy of formation is − 594.5 kJ/mol. The oxide melts at 198 °C and starts to decompose, giving off oxygen and brownish red vapors with a pungent smell. The rate of decomposition reaches a maximum at 290 °C, chromium(III) oxide, Cr_2O_3, being produced as the final product via various intermediate stages. Chromium(VI) oxide dissolves in water to form chromic acids (see 6.1); the solubility depends only slightly on temperature. A saturated solution contains 166 g of CrO_3 at 20 °C and 199 g of CrO_3 at 90 °C per 100 mL of water. The compound also dissolves in sulfuric acid and nitric acid. Chromium(VI) oxide is a powerful oxidizing agent, particularly in the presence of acids. Reactions with alkali metals and numerous organic compounds, e.g., low-boiling hydrocarbons, acetone, or benzene and its derivatives, proceed explosively with considerable heat being produced. Esters of chromic acid are also known, e.g., with such cyclic tertiary alcohols as methylfenchol and methylborneol.

Chromium(VI) oxide is made by the reaction of sodium dichromate with sulfuric acid. The reaction can be carried out with solid sodium dichromate or with solutions or suspensions. Both methods are in use industrially. The reaction proceeds rapidly and completely after the components have been mixed, with heat being evolved. Isolation of chromium(VI) oxide from the reaction mixture or purification of the crude product obtained from the aqueous solution is difficult. Quantitative separation of sodium hydrogen sulfate is possible only if the chromium(VI) oxide is melted, but at this temperature the product begins to decompose. The melting process must therefore be controlled very precisely.

Dry Process. Even today the old *discontinuous* process is in use to some extent. The reaction vessels are made from carbon steel or stainless steel. The conical containers are equipped with stirrer, exhaust facilities, and external heating. Sulfuric acid and sodium dichromate are added simultaneously with stirring. The paste heats up to 80 °C during mixing and is heated further to evaporate water. At 170 °C sodium hydrogen sulfate melts, followed by chromium(VI) oxide at 198 °C. As soon as the reaction products are liquid, the heating and the stirrer are turned off. After a few minutes the heavier chromium(VI) oxide (ϱ 2.2 g/cm^3) settles at the bottom, and is covered by a layer of the lighter sodium hydrogen sulfate (ϱ 2.0 g/cm^3). Liquid chromium(VI) oxide is drawn off the bottom and conveyed to a cooling drum where it solidifies to form scales. Sodium hydrogen sulfate is subsequently drained. The yield of chromium(VI) oxide is about 85 %; 175 kg of sodium dichromate and 140 kg of 96 % sulfuric acid are required to obtain 100 kg of chromium(VI) oxide. About 150 kg of sodium hydrogen sulfate is obtained as byproduct.
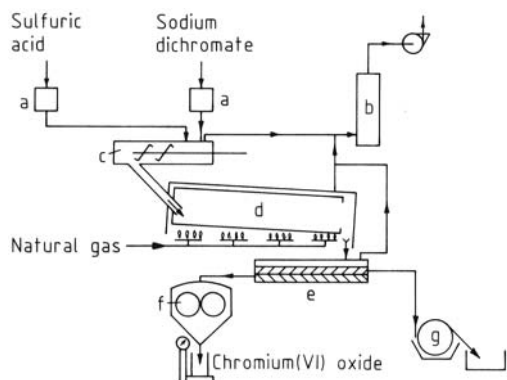
Figure 4. Continuous production of chromium(VI) oxide
a) Metering device; b) Wash tower; c) Mixer; d) Rotary kiln;
e) Separation cell; f) Cooling drum for chromium(VI) oxide;
g) Cooling drum for sodium hydrogen sulfate

Figure 4 shows a *continuous* dry process [55]. The raw materials are fed to a mixing screw for intimate mixing. A viscous paste of chromium (VI) oxide, sodium hydrogen sulfate, and water forms which is fed into a heated rotary kiln of stainless steel where it is melted. The heating must be controlled very carefully. The melt flows into a separator, where the heavier chromium (VI) oxide collects at the bottom of the trough, is removed by means of a rising pipe, and is converted into scales on cooling drums. The upper sodium hydrogen sulfate layer leaves the separating cell via an overflow and is also cooled on drums. Exhaust air from the various pieces of equipment is purified in a wash tower. The yield of this process is over 90 %.

If a highly concentrated solution is used instead of dichromate crystals, the kiln can be heated directly [56].

Wet Process. A hot saturated solution of sodium dichromate, which may still contain dichromate crystals, reacts with sulfuric acid [57]. In the course of 30 – 60 min the chromium(VI) oxide precipitates from the hot solution. On filtration a crude product is obtained, with a yield of about 80 %. Sodium hydrogen sulfate must be removed from the crude product by fusion. The filtrate can be recycled for converting sodium monochromate into dichromate; it can also be used in a fresh reaction mixture [58] if sodium hydrogen sulfate is first crystallized and removed at 20 – 25 °C. The crude chromium (VI) oxide is purified by continuous successive fusion and decanting [59].

As an alternative to production by reaction with sulfuric acid, Diamond – Shamrock developed an electrochemical process [60–62] in which chromic acid is produced from sodium dichromate in a two- or three-compartment cell.

Chromium trioxide is usually sold in the form of flakes, but the coarsely or finely ground product is also marketed. Good commercial products contain 99.5 – 99.7 % CrO_3 and a maximum of 0.1 % of sulfate. In the form of flakes, the product has a bulk density of 1.1 kg/L whereas that of the ground product is 1.4 kg/L. Steel drums must be used as containers and they must be tightly sealed because the product absorbs moisture from the air.

Chromium trioxide is classified as a dangerous substance in the EEC list and must be marked as fire-promoting and corrosive. In the IMDG code chromic acid has been put in class 5.1., UN No. 1463. The MAK of CrO_3 is 0.1 mg/m^3.

Electroplating is the most important field of application of chromium(VI) oxide. Numerous mixtures containing chromium trioxide are on the market; these "compounds" often contain hexafluorosilicates which improve the properties of the chromium coatings. Chromic acid solutions are also used for passivating zinc, aluminum, cadmium, and brass. Proprietary mixtures predominantly contain additions of fluoride, nitrate, and phosphate ions. Other uses for chromic acid are in the production of chromium dioxide and in wood preservation.

5. Chromium(III) Salts

5.1. General Properties

Water Content. In contrast to many other inorganic salts, chromium(III) salts occur in a variety of forms that depend on water content and on the particular conditions under which they are formed. Anhydrous compounds do not dissolve in pure water.

However, some of them, e.g., chromium(III) chloride or chromium(III) sulfate, dissolve in the presence of chromium(II) ions. In this process, one dissolved divalent ion transfers an electron via an anion bridge to a trivalent chromium ion in the solid crystal. Having become divalent, this ion detaches itself, acts in a similar manner on

another chromium(III) ion in the crystal array, and reverts again to the trivalent state.

Complex Formation. Dissolved chromium(III) ions are always coordinated by various ligands. In the simplest case of the hexaaquochromium(III) ion, $[Cr(H_2O)_6]^{3+}$, six water molecules surround the central chromium ion in an octahedral arrangement as ligands. In addition to the aquo complexes, numerous coordination compounds with other molecules are known, and research on them, particularly studies of the ammine complexes (NH_3 as ligand), has played an important part in the development of coordination compound chemistry [63].

When negatively charged ligands enter the chromium complex, the charge is decreased appropriately. If the sum of the negative charges is four or more, the complex becomes anionic, an example of this being the diaquodisulfatochromium(III) ion $[Cr(SO_4)_2(H_2O)_2]^-$. In this case, each sulfate radical with a double negative charge occupies the position of two ligands.

The tendency of negatively charged ligands to form complex compounds with chromium increases in the following order:

$$Cl^- < SO_4^{2-} < CH_3CO_2^- < HCO_2^- < OH^-$$

Nitrato complexes are unknown.

Hydrate Isomerism. Chromium(III) complexes exhibit hydrate isomerism due to the positioning of anions and water molecules.

Thus chromium(III) chloride hexahydrate [*10060-12-5*] is known in three different forms:

1. Hexaaquochromium(III) chloride, $[Cr(H_2O)_6]Cl_3$, bluish grey
2. Pentaaquochlorochromium(III) chloride hydrate $[Cr(H_2O)_5Cl]Cl_2 \cdot H_2O$, bright green
3. Tetraaquodichlorochromium(III) chloride dihydrate $[Cr(H_2O)_4Cl_2]Cl \cdot 2\,H_2O$, dark green

The anions that are directly bound to the central atom do not dissociate in water and consequently do not react with the common precipitating agents; therefore, in the two green chlorides, only one-half and one-third of the chloride ions, respectively, are precipitated by silver nitrate.

Basic Salts. Hydroxide ions form coordinate bonds, with central ion of the hexaaquo-

chromium complex being hydrolyzed. In this process, the pentaaquohydroxochromium(III) ion with a double positive charge is first formed:

$$[Cr(H_2O)_6]^{3+} \xrightarrow{OH^-} [Cr(H_2O)_5OH]^{2+} + H^+$$
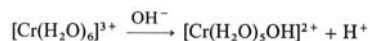
When more alkali is added, chromium hydroxides are precipitated immediately. Finally, with a strong hydroxide solution, a soluble deep green hydroxo salt is produced:

$$Cr(OH)_3 + 3NaOH \rightarrow Na_3[Cr(OH)_6]$$

Pentaaquohydroxochromium(III) complexes are very weak bases. Their salts hydrolyze and the pH of aqueous solutions usually is 2. The basicity of these salts is defined as the ratio of hydroxyl groups (in percent) bound to chromium to the number of hydroxyl groups in chromium(III) hydroxide, that could theoretically be bound to chromium. Pentaaquohydroxochromium(III) complexes therefore have a basicity of 33 %. When a second hydroxyl group enters the complex the basicity increases to 67 %. However, from a basicity of 60 % onward, chromium(III) hydroxide precipitates and these compounds are not used in practice.

5.2. Chromium(III) Sulfates and Chrome Tanning Agents

Chromium(III) Sulfate. *Anhydrous chromium sulfate* [*10101-53-8*], $Cr_2(SO_4)_3$, M_r 392.18, ϱ 3.0 g/cm^3, is a violet powder which is insoluble in water but dissolves to form complexes when reducing agents are added. For its preparation, chromium metal or chromite is heated over 250 °C with sulfuric acid.

The *octadecahydrate* [*13520-66-6*], $[Cr(H_2O)_6]_2(SO_4)_3 \cdot 6\,H_2O$, M_r 716.45, ϱ 1.86 g/cm^3, forms cubic crystals. The violet compound gives off water on heating and above 70 °C it is converted, with further loss of water, into a dark-green crystalline *pentadecahydrate* [*10031-37-5*]. As the water content diminishes, the solubility decreases.

Solutions of chromium(III) sulfates can be made by treating chromite with sulfuric acid in the presence of chromium(VI) compounds [64]. Since other components of the ore are solubilized

at the same time, the solutions are strongly contaminated; separation of magnesium, aluminum, and iron presents such great difficulties that this process has not yet gone beyond the experimental scale. Chromium(III) sulfate solutions are also obtained by dissolving ferrochromium in sulfuric acid, a process in which iron(II) sulfate is obtained as a coproduct. So far, the economical preparation of a pure product has been only partially successful.

Large quantities of chromium(III) sulfate solution are produced in the oxidation of organic substances with chromic acid or sodium dichromate in sulfuric acid solution. Examples of this are the preparation of anthraquinone from anthracene, the preparation of benzoquinone from aniline, or the bleaching of montan wax. These solutions are used to produce other chromium products; an electrolytic regeneration to dichromate is also possible.

Tanning Agents. *Basic chromium(III) sulfates* are used on a large scale as tanning agents for leather. Industrially, two processes are available for the reduction of sodium dichromate: (1) reaction with organic compounds (molasses, sugar) in the presence of sulfuric acid and (2) reduction with sulfur dioxide.

Reduction with molasses is carried out in aqueous solution; about 30 kg of molasses or 15 kg of cane sugar is required for 100 kg of sodium dichromate dihydrate. The amount of sulfuric acid required depends on the desired basicity. To adjust the basicity to 33 %, about 103 kg of 96 % acid is needed. The reaction is strongly exothermic; water evaporates in abundance and must be continuously replenished. Lead-lined vats have proved successful as reaction vessels. The exhaust gases have an unpleasant smell, but this can be eliminated by scrubbing with water in a wash tower or by heating them after condensing the water vapor.

The properties of the final product are, to a certain extent, dependent on how the reaction is performed. If sulfuric acid is added first to the dichromate solution and the reducing agent is then added slowly, relatively few organic acids are produced as result of side reactions. The proportion of these acids becomes considerably larger if the dichromate solution is mixed first with the reducing agent and the sulfuric acid is added last. The organic acids form chromium complexes and mask the tanning agent. This masking delays the tanning process.

In the *reduction with sulfur dioxide* sulfuric acid is generated in such proportions that the tanning agent produced has a basicity of 33 %. For the reduction of 100 kg of sodium dichromate dihydrate, 65 kg of SO_2 is theoretically required.

The reaction is carried out in lead-lined or brick-lined absorption towers containing ceramic packing material. Sulfur dioxide is produced by combustion of liquid sulfur which yields a gas containing 8 – 18 % SO_2; SO_2-containing gases from other manufacturing processes are also suitable for the reaction.

For the production of chrome tanning agents, chromium(III) sulfate solutions which are generated in the manufacture of organic intermediates may also be used. Impurities must be removed from such solutions, and the solutions are then converted to the correct basicity by acidification or neutralization. They must also be concentrated by evaporation.

To manufacture *solid tanning agents,* the concentrated solutions are dried in spray driers made of stainless steel. With a basicity of 33 %, the amorphous green powder obtained generally contains 24 – 26 % Cr_2O_3, 25 – 27 % SO_3, 22 –25 % Na_2SO_4, and 22 – 25 % water. In air, the powder absorbs moisture and the particles stick together. Under the microscope, the individual particles, which are often hollow spheres or fragments of such spheres, have a glassy appearance.

The product obtained by spray drying is sold under numerous trade names, e.g., Chrometan (British Chrome and Chemicals, UK); Chromitan (BASF, Federal Republic of Germany); Chromosal (Bayer, Federal Republic of Germany); Salcromo (Stoppani, Italy); Tanolin (Hamblett & Hayes Co., Mass., USA).

Paper or jute sacks with watertight polyethylene liners or wrappings, or plastic sacks are used for packing.

Solutions of basic chromium(III) sulfate containing 12 – 18 % Cr_2O_3 are also available commercially. Solutions of higher concentration must be kept warm because sodium sulfate precipitates at room temperature. The solutions are transported in rubber-lined rail or road tankers; lead-lined tankers are also suitable.

Besides the standard 33 % basic type, a large number of products of higher basicity are

available. To improve their stability toward alkali, these contain various quantities of organic acids. The market importance of chrome tanning agents containing 30 % chromium oxide and having a basicity of 50 % has increased.

In addition to the standard products, mixtures of chrome tanning agents have established themselves on the market. These contain basifying agents which react slowly and eliminate the need for the tedious basifying process. Mixed products containing special organic masking agents and having a high total basicity have been developed. These are used in combination with conventional chrome tanning agents and afford a high degree of chromium exhaustion in the liquors.

Potassium chromium(III) sulfate [*10141-00-1*], [*10279-63-7*], [*7788-99-0*], potassium chrome alum, $KCr(SO_4)_2 \cdot 12\ H_2O$, M_r 499.11, ϱ 1.813 g/cm^3, crystallizes in the cubic system forming violet regular octahedra which decay in air and melt at 89 °C, the color changing to green; the enthalpy of formation is $-$ 5788 kJ/mol. The solubility in water at 25 °C is 11.1 wt %. The solution is violet when cold, but becomes green above 50 °C, this change being accompanied by a decrease in the molar conductance. For 0.125 M solution at 50 °C, the molar conductance is 221 Ω^{-1} cm^2 mol^{-1} for the violet form and 202 Ω^{-1} cm^2 mol^{-1} for the green form. This change is reversible and its rate is increased by acids. The green form always occurs as an amorphous solid and crystals are unknown.

In addition to the alum containing 12 molecules of water of crystallization, potassium chromium(III) sulfates containing one [*35177-45-8*], two [*35177-44-7*], and six [*35177-43-6*] molecules of water are known.

For the preparation of potassium chromium alum, a saturated potassium dichromate solution is reduced with sulfur dioxide in the presence of sulfuric acid.

During the reaction, the temperature must be kept below 40 °C by cooling to prevent the green modification being produced. Apart from sulfur dioxide, such organic compounds as formaldehyde, methanol, or starch are suitable as reducing agents. Crystallization starts after sulfuric acid has been added and the temperature is kept further below 40 °C. If the solution is allowed to settle in vats, large crystals are produced, whereas fine ones result if the solution is stirred. The industrial product contains 15 % Cr_2O_3 and 0.01 – 0.03 % Fe. The mother liquor may be reused in the production of the alum solution, but after several cycles it is so enriched in magnesium and sodium sulfate that crystallization of the alum is retarded. The trivalent chromium is then precipitated from the solution with alkali and may be recycled. Lead-lined equipment is used for the production.

The alum can also be prepared from ferrochromium. The reaction with sulfuric acid first results in a solution of chromium(III) and iron (II) sulfates. The majority of the iron(II) sulfate can be removed by crystallization. With potassium sulfate added, the filtrate yields the alum which is contaminated with 0.1 – 0.2 % Fe.

Potassium chrome alum was formerly used on a large scale as a tanning agent in the leather industry, but its importance in this field has receded with the introduction of the basic chromium sulfates. Other fields of application are the textile industry and the film and photographic industry.

Ammonium chromium(III) sulfate [*10141-00-1*], ammonium chrome alum, $NH_4Cr(SO_4)_2 \cdot 12\ H_2O$, M_r 478.47, ϱ 1.72 g/cm^3, crystallizes in the cubic system forming bluish violet octahedra which appear ruby red when held against the light and slowly decay in air. When heated to 70 °C they turn green, and at 94 °C the compound melts in its water of crystallization. Ammonium chrome alum is obtained from chromium(III) sulfate solutions by addition of a stoichiometric amount of ammonium sulfate. Ammonium chrome alum crystallizes much more easily than potassium chrome alum. The preparation of ammonium chrome alum from carbon-rich ferrochromium has assumed relatively great importance in the electrochemical production of pure chromium metal [65].

5.3. Other Chromium(III) Salts

Chromium(III) Fluoride [*7788-97-8*], CrF_3, M_r 108.99, ϱ 3.8 g/cm^3. The anhydrous compound forms highly refractive rhombohedral crystals. It melts above 1000 °C and is distinctly volatile between 1100 and 1200 °C. Chromium (III) fluoride is insoluble in water if no divalent chromium is present. Double compounds are

formed with other metal fluorides, e.g., green $CrF_3 \cdot 2 KF \cdot H_2O$.

Hydrates are known which contain three [*16671-27-5*] to nine [*68374-27-6*] molecules of water. The violet hexaaquochromium(III) fluoride, $[Cr(H_2O)_6]F_3$, and its trihydrate, $[Cr(H_2O)_6]F_3 \cdot 3 H_2O$, can be obtained from hexaaquochromium(III) salt solutions and alkali fluorides. Products containing less water are green. The composition of the industrial product corresponds approximately to $CrF_3 \cdot 3.5 H_2O$ and the product contains about 30 % chromium.

For the production of chromium(III) fluoride hydrate, chromium(III) oxide hydrate is dissolved in hot aqueous hydrofluoric acid and the green salt crystallizes. Chromium(III) fluoride is used in the textile industry for mordanting wool, for chromating dyestuffs, and in vigoureux printing. Chromium(III) fluorides have also found application in rust-prevention paints as corrosion inhibitors.

Chromium(III) Chloride.

Anhydrous Chromium(III) Chloride [*10025-73-7*], $CrCl_3$, M_r 158.36, forms hexagonal reddish violet flakes which sublime at 950 °C yielding a vapor that dissociates above 1300 °C. The enthalpy of formation is − 554.8 kJ/mol. Chromium(III) chloride is insoluble in water if no reducing agent is present. On roasting in air, chromium(III) oxide is produced.

Anhydrous chromium(III) chloride is obtained along with iron(II) chloride by chlorinating roasting of chromite in the presence of carbon at 900 – 1050 °C [66]. Oxygen is added to the chlorine to prevent nonvolatile residues, in particular minor constituents of the ore, from sintering together. Fractionating condensation between 400 and 640 °C has been suggested for separating the chloride vapors [67]. The compound can also be obtained by chlorinating chromium(III) oxide in the presence of reducing agents or by treating ferrochromium with chlorine [68].

Chromium(III) chloride can be prepared readily from chromyl chloride by reaction with carbon monoxide and chlorine. The reaction proceeds rapidly in the gas phase at 750 – 850 °C [69]. Since chromium(III) chloride evaporates only at a higher temperature, a considerable portion of the product, which varies as a function of the partial pressure, is produced in the form of fine crystals. As the smoke cools down, these act as crystallization nuclei for any gaseous chromium(III) chloride still present. This procedure prevents the deposition of solid on the cooling surfaces.

Anhydrous chromium(III) chloride has been suggested for chromizing steel parts by surface diffusion; it can be used for the production of high-purity ductile chromium metal by reduction with magnesium and for the synthesis of organic chromium compounds.

Chromium(III) Chloride Hexahydrate [*10060-12-5*] is obtained in pure form by introducing hydrogen chloride and methanol into an aqueous solution of chromic acid. The reaction proceeds exothermally, and adequate cooling must be provided. Of the three isomeric hydrates (see 5.1) the dihydrate of the tetraaquodichlorochromium(III) chloride crystallizes in the cold. This is used as an intermediate in the production of chromium complex dyes and other chromium salts, e.g., chromium stearates, which are of interest as impregnating agents for textiles or paper. The solution is also used as a mordant in the textile industry.

Chromium(III) Acetate [*1066-30-4*].

The bluish violet hexaaquo salt [*66851-10-3*], $[Cr(H_2O)_6](CH_3COO)_3$, M_r 337.22, forms needle-shaped crystals. Basic chromium(III) acetates are green. For their preparation chromium(III) hydroxide hydrate is dissolved in dilute acetic acid, and the solid is obtained by drying on drums or in a spray drier. Basic chromium acetates are used as mordants in calico printing and worsted top printing, and also for fixing vigoureux dyes. Combinations of basic chromium(III) acetate and basic chromium(III) formate also find application in the textile industry as mordants. In addition, chromium(III) acetate is used as a starting compound in the production of organic chromium dyes.

Chromium(III) Nitrate [*13548-38-4*].

Normally, chromium(III) nitrate crystallizes with nine molecules of water, $[Cr(H_2O)_6](NO_3)_3 \cdot 3 H_2O$ [*7789-02-8*], M_r 400.15, ϱ 1.8 g/cm^3. The dark violet rhombic prisms become green above 36 °C and melt at 66 °C. The nitrate group

is not bound to the trivalent chromium in a coordination compound. The salt is readily soluble in water, acid, alkali, and alcohol. To prepare chromium(III) nitrate, chromium(III) oxide hydrate is dissolved in nitric acid and the nitrate is allowed to crystallize. The compound is also produced by reduction of chromic acid with methanol in the presence of nitric acid. During the exothermal reaction, the temperature is kept between 55 and 65 °C by cooling. Chromium(III) nitrate is used to a limited extent as a mordant in cotton printing, usually together with basic chromium acetates. In addition, the salt is suitable for producing alkali-free catalysts.

Chromium(III)   Phosphate. *Anhydrous chromium(III) phosphate* [*7789-04-0*], $CrPO_4$, M_r 146.97, ϱ 2.99 g/cm^3, is a black powder which belongs to the orthorhombic crystal system. It is insoluble in water, hydrochloric acid, and aqua regia but is attacked by boiling sulfuric acid. It is obtained by calcining its hydrates. The violet *hexahydrate* [*13475-98-4*], $[Cr(H_2O)_6]PO_4$, M_r 255.06, ϱ 2.12 g/cm^3, precipitates from chromium(III) salt solutions upon addition of phosphoric acid and disodium hydrogen phosphate. The crystals are triclinic and only sparingly soluble in water. Green chromium(III) phosphates precipitated hot contain two to three molecules of water after drying. A salt containing four molecules of water is also known. The green products are virtually insoluble in water. They are used to a small extent as pigments and have corrosion-inhibiting properties.

Chromium Lignosulfonates [*9066-50-6*] are prepared by reaction of sulfite waste liquor from the pulp industry with sodium dichromate solution, the hexavalent chromium being reduced by the organic material to trivalent chromium. After filtration, the pH is adjusted by means of alkali and the product is dried in spray driers. It is a free-flowing, water-soluble powder and normally contains cations in the following quantities: ammonium 1.5 – 2.5 %, chromium 2.5 – 4.2 %, iron 0 – 5 %, and sodium 1.5 – 2.5 %. These saltlike compounds are used to a large extent in the petroleum industry as additives for lowering the viscosity of drilling muds and decreasing liquid loss [70].
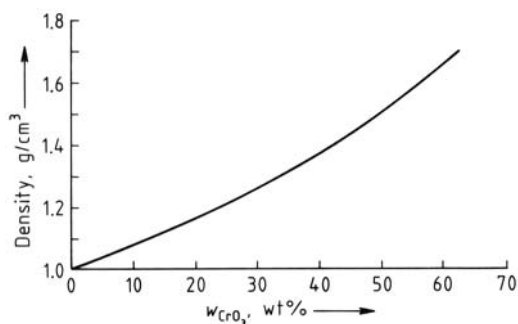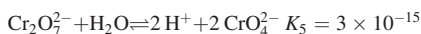

Figure 5. Density of aqueous chromic acid solutions at 15.6 °C (60 °F)

6. Chromic Acids and Chromates(VI)

6.1. Chromic Acids

Chromic acids are not known in the free state. Depending on the method of preparation, mono-, di-, tri-, or tetrachromic acids are formed in aqueous solution. In alkaline or dilute solution, formation of the yellow monochromate ion is favored, but in acid solution or at high concentrations, the orange-red dichromate ion is formed preferentially. Aqueous solutions of chromic acids are, therefore, yellow or red depending on their concentrations. Figure 5 shows the density as a function of concentration.

Dissociation constants (at 25 °C) are as follows:

$$H_2CrO_4 \rightleftharpoons H^+ + HCrO_4^-\quad K_1 = 1.21$$

$$HCrO_4^- \rightleftharpoons H^+ + CrO_4^{2-}\quad K_2 = 3.7 \times 10^{-7}$$

$$H_2Cr_2O_7 \rightleftharpoons H^+ + HCr_2O_7^-\quad K_3 = 1$$

$$HCr_2O_7^- \rightleftharpoons H^+ + Cr_2O_7^{2-}\quad K_4 = 0.85$$

$$Cr_2O_7^{2-} + H_2O \rightleftharpoons 2\,H^+ + 2\,CrO_4^{2-}\quad K_5 = 3 \times 10^{-15}$$

$$Cr_2O_7^{2-} + H_2O \rightleftharpoons 2\,HCrO_4^-\quad K_6 = 0.023$$
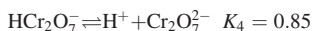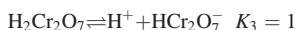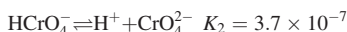
The standard redox potential for the reaction

$$Cr_2O_7^{2-} + 14\,H^+ + 6\,e \rightleftharpoons 2\,Cr^{3+} + 7\,H_2O$$
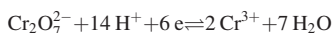
is 1.36 V.

Chromic acid solutions are strong oxidizing agents with a strongly acidic character; they form

Table 8. Solubility (in wt %) of various chromates in water

	Temperature, °C								
	0	20	25	40	50	60	75	80	100
Sodium chromate		44.3		48.8		53.5		55.8	56.1
Sodium dichromate dihydrate	70.6	73.18		77.09		82.04		88.39	91.43
Potassium chromate		39.96							45.0
Potassium dichromate	4.3	11.7		20.9		31.3		42.0	50.2
Ammonium chromate	19.78		27.02		34.4		41.2		
Ammonium dichromate	15.16	26.67		36.99		46.14		54.10	60.89
Silver chromate		0.0025			0.0053				0.0041

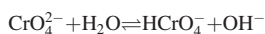salts with metals and bases. The monochromates (VI), M_2CrO_4, which are derived from chromic acid, hydrolyze in aqueous solution:

$$CrO_4^{2-} + H_2O \rightleftharpoons HCrO_4^- + OH^-$$

The easiest method of preparing chromic acid solutions is to dissolve chromium(VI) oxide in water. In industry, chromic acid is often produced from sodium dichromate(VI) and sulfuric acid.

Chromic acid solutions can also be prepared by anodic oxidation of chromium(III) sulfate solutions [71]; lead-lined cells with a diaphragm and lead electrodes are employed. To keep the concentration of sulfuric acid constant, the chromium(III) sulfate solution is introduced first into the cathode space, where it becomes depleted of sulfuric acid, and then into the anode space. Here, oxidation to chromic acid takes place and the concentration of sulfuric acid is restored to its original value.

In practice, several electrolytic cells are combined to form a unit. At a current density of 3 A/dm^2 the voltage is 3.5 V. Current efficiency is 80 %. Lost chromium is periodically replenished by adding chromium(III) oxide. The electrolytic preparation of chromic acid can also start from chromium hydroxide hydrate with chromic acid as electrolyte [72].

Aqueous chromic acid solutions are used as pickling and chromium-plating baths in the metal processing and plastics processing industries.

6.2. Alkali Chromates and Dichromates

Sodium Chromate [7775-11-3], Na$_2$CrO$_4$, M_r 161.97, *mp* 792 °C, ϱ 2.723 g/cm^3,

ΔH_{298}^0 −1329 kJ/mol, crystallizes in the orthorhombic system in small yellow needles or columns; transformation to the hexagonal form takes place at 413 °C. The bulk density of the powder is 0.7 g/cm^3; that of the crystals is 1.67 g/cm^3. For solubility, see Table 8. The compound is hygroscopic and forms several hydrates: below 19.5 °C the decahydrate [13517-17-4]; between 19.5 and 25.9 °C, the hexahydrate; and between 25.9 and 62.8 °C, the tetrahydrate [10034-82-9] which undergoes transformation into anhydrous sodium chromate above 62.8 °C.

To prepare the salt, sodium dichromate solution is usually mixed with a stoichiometric amount of sodium hydroxide, and the salt solution is then crystallized or spray dried. The 96.5 – 98.5 % product (0.4 % NaCl, 2 % Na$_2$SO$_4$) is stored and dispatched in watertight steel drums.

Sodium chromate is used as a corrosion inhibitor in the petroleum industry and as a dyeing auxiliary in the textile industry.

Sodium Dichromate. The *dihydrate* [7789-12-0], Na$_2$Cr$_2$O$_7$ · 2 H$_2$O, M_r 298.0, ϱ 2.348 g/cm^3, ΔH_{298}° −2194 kJ/mol, forms orange-red, monoclinic, translucent needles which are converted into the anhydrous salt above 84.6 °C. The bulk density is 1.2 g/cm^3. For solubility, see Table 8. The heat of solution is − 118 kJ/kg. The compound is very hygroscopic and deliquesces in air; in acid solution, it is a strong oxidizing agent.

The preparation of sodium dichromate is described in Chapter 3.

Sodium dichromate is the most important of the industrial chromium chemicals and is used as the starting compound for almost all chromium compounds. Large quantities are used in numerous industrial fields. In the textile industry (wool,

cotton, silk, and synthetics), sodium dichromate is used in mordanting and in aftertreatment baths. The leather industry virtually no longer uses sodium dichromate. Sodium dichromate has a variety of uses in the surface treatment of metals, e.g., in the pickling of steel, aluminum, magnesium, and other metals and their alloys. The ability of the chromates to convert gelatin or protein into an insoluble form on exposure to light is exploited on a large scale in printing technology (lithography). A further field of application for the dichromates is in corrosion protection; they are added to crude oil in pipelines and to water in closed cooling systems as direct corrosion inhibitors. Sodium dichromate is also used for the manufacture of wood preservatives.

In the chemical industry, sodium dichromate is used as a strong oxidizing agent in numerous cases; the most important include oxidation of anthracene to anthraquinone (dyes), of aniline to quinone (hydroquinone for the photographic industry), of camphene to camphor, and of contaminants in oils, fats, tallow, and waxes (soap industry, wax bleaching).

To these classical applications, the wide field of catalysts and catalyst carriers containing chromium(III) oxide or chromates has been added over the past thirty years. These are important in a variety of oxidation and carbonizing processes.

Anhydrous sodium dichromate [*10588-01-9*], $Na_2Cr_2O_7$, M_r 261.96, *mp* 356.7 °C, ϱ 2.52 g/cm^3, bulk density 1 g/cm^3, heat of solution ca. − 33.5 kJ/kg, forms light-brown to orange-red plates which are strongly hygroscopic. They decompose above 400 °C with the formation of sodium monochromate(VI), chromium(III) oxide, and oxygen.

Anhydrous sodium dichromate can be prepared by melting down sodium dichromate dihydrate, by crystallizing aqueous dichromate solutions above 86 °C, or by drying sodium dichromate solutions in spray driers.

Anhydrous sodium dichromate is required for cases in which the water content of the dihydrate has an interfering action. Thus, for example, the energy liberated in the oxidation with anhydrous sodium dichromate is greater than that liberated in the case of sodium dichromate dihydrate. Anhydrous sodium dichromate is, therefore, used in the prepara-

tion of chromium(III) oxide by the dry process (4.1), in pyrotechnics, and in anhydrous oxidation processes where it replaces the more expensive potassium dichromate. Compared with sodium dichromate dihydrate, anhydrous sodium dichromate has the advantage that it can first absorb two molecules of water (13 wt %) instead of deliquescing immediately when moisture is admitted.

Potassium Chromate   [*7789-00-6*], K_2CrO_4, M_r 194.2, *mp* 968.3 °C, ϱ 2.73 g/cm^3, $\Delta H_{298}^0 -$ 1383 kJ/mol, occurs as the stable β-modification. The lemon-yellow, nonhygroscopic prisms are isostructural with K_2SO_4. At 666 °C they are converted into hexagonal α-potassium chromate. For solubility, see Table 8. The heat of solution is −71.3 kJ/kg. The salt crystallizes from aqueous solution in anhydrous form and is thermally stable.

Potassium chromate is obtained by reacting potash with potassium dichromate. The potassium salt has been supplanted nearly completely by the cheaper sodium chromate and is used only for very specific purposes such as in the photographic industry.

Potassium   Dichromate   [*7778-50-9*], $K_2Cr_2O_7$, M_r 294.19, *mp* 397.5 °C, occurs in two modifications. α-$K_2Cr_2O_7$, tabular or prismatic, bright orange-red triclinic crystals, ϱ 2.676 g/cm^3, has a bulk density of about 1.3 – 1.6 g/cm^3; at 241.6 °C α-$K_2Cr_2O_7$ transforms to β-$K_2Cr_2O_7$. For solubility, see Table 8. The heat of solution is − 258.3 kJ/kg. The thermodynamic data are as follows: c_p 219.7 J mol^{-1} K^{-1}, ΔH_{298}° −2033 kJ/mol, S° 291.2 J mol^{-1} K^{-1}, heat of fusion 36.7 kJ/mol. The substance is not hygroscopic and, above the melting point, decomposes into potassium chromate, chromium oxides, and oxygen.

Today potassium dichromate is obtained primarily by conversion of sodium dichromate with potassium chloride. Potassium dichromate has largely been supplanted by the cheaper sodium dichromate but is still used whenever its advantage of being nonhygroscopic is important, for example, in the match, firework, film, and photographic industries. Potassium dichromate is of interest in the preparation of yellow and green zinc pigments (→ Pigments, Inorganic, 1. General).

Ammonium Chromate [*7788-98-9*], $(NH_4)_2CrO_4$, M_r 152.07, smells of ammonia and forms golden yellow needles, ϱ 1.886 g/cm^3, ΔH^0_{298} −1152 kJ/mol, S^0_{298} 656 J mol^{-1}K^{-1}. For solubility, see Table 8. In air, it decomposes into ammonia, water, and ammonium dichromate. On heating it ignites and decomposes into chromium(III) oxide, ammonia, and nitrogen. Ammonium chromate is prepared from ammonium dichromate with the addition of ammonia.

Ammonium Dichromate [*7789-09-5*], $(NH_4)_2Cr_2O_7$, M_r 252.06, forms large, bright orange-red crystals, ϱ 2.155 g/cm^3, bulk density ca. 1.0 – 1.3 g/cm^3. For solubility, see Table 8. The heat of solution is − 230.9 kJ/mol. Ammonium dichromate crystallizes in anhydrous form from aqueous solution and is not hygroscopic. Decomposition, which is not preceded by melting, sets in on heating to 180 °C; this becomes self-maintaining at 225 °C and above. Decomposition proceeds with displays of fire and heat, and large amounts of gas are developed. The products of decomposition are chromium(III) oxide, nitrogen, and water vapor. Ammonium dichromate reacts very violently with organic solvents.

Ammonium dichromate is prepared by reaction of sodium dichromate with ammonium chloride or, less frequently, ammonium sulfate. Ammonium dichromate is used as the starting material for preparing very finely divided chromium(III) oxide and, in addition, finds application primarily in pyrotechnics, wood preservation, and photography (lithography) for the preparation of light-sensitive solutions of gelatin or proteins. Ammonium dichromate is also used to prepare catalysts for organic syntheses. A further field of application is the production of magnetic chromium(IV) oxide. Because of its self-ignition properties and explosiveness, ammonium dichromate is subject to the German Explosives Law and the IMDG code, class 5.1, UN No. 1439. It is also distributed moist.

6.3. Other Chromates

Barium Chromate [*10294-40-3*], $BaCrO_4$, M_r 253.33, mp 1400 °C (decomp.), ϱ 4.498 g/cm^3, ΔH^0_{298}−1156 kJ/mol, crystallizes as light-yellow transparent rhombic crystals which are isomorphous with barium sulfate. Barium chromate is only sparingly soluble in water but dissolves readily in acids.

In the presence of excess alkali chromate or dichromate, barium chromate has a tendency to form double salts, among which special mention may be made of potassium barium chromate [*13819-19-7*], $K_2CrO_4 \cdot BaCrO_4$, and ammonium barium chromate [*13819-20-0*], $(NH_4)_2CrO_4 \cdot BaCrO_4$, both of which are light yellow.

These barium chromate double salts can be prepared by reaction of soluble barium salts or barium hydroxide with alkali chromate(VI) or dichromate(VI). In weakly acid solutions, as is the case, for example, if dichromates(VI) are used, the precipitation is incomplete. Quantitative precipitation is achieved by adding sodium acetate.

Yellow barium chromate and its double salts can be used for the production of chrome pigments for paints; the double salts, in particular, are excellent corrosion protection paints for all metals. They form sparingly soluble metal chromates, which prevent attack by moisture (condensation, seawater) even more readily than zinc chromate.

Calcium Chromate [*13765-19-0*], $CaCrO_4$, M_r 156.07, mp 1020 °C (decomp.), ϱ 3.12 g/cm^3, is a yellow powder which is sparingly soluble in water (4.3 wt % at 0 °C, 0.42 wt % at 100 °C). The compound has acquired no industrial importance, but its preparation directly from chromium ores is described in several patents [73], [74].

Calcium Dichromate [*14307-33-6*], $CaCr_2O_7$, M_r 256.06, ΔH^0_{298}−1821 kJ/mol, is thought not to constitute a uniform crystalline phase but to be a mixture of phases consisting of calcium monochromate and chromium(VI) oxide. The compound forms a series of readily soluble hydrates. Thus, below 10 °C, the hexahydrate $CaCr_2O_7 \cdot 6\ H_2O$ exists; between 20 and 40 °C, the pentahydrate [*61204-19-1*]; between 50 and 60 °C, the tetrahydrate; and above 70 °C, the monohydrate [*85752-77-8*]. A red deliquescent calcium dichromate trihydrate has also been prepared from the tetrahydrate.

Calcium dichromate can be made industrially by oxidative roasting of chromium-containing ores with calcium carbonate or calcium oxide

and subsequent leaching of the cake with an acid, e.g., chromic or sulfuric acid [74].

Copper Chromates. Neutral copper chromate [*13548-42-0*], $CuCrO_4$, M_r 179.53, is produced as a yellowish brown, water-containing compound by precipitation from a copper sulfate solution with sodium or potassium dichromate. The compound is used as the starting material for "chrome black" which is prepared by calcining the neutral salt under oxidizing conditions and subsequently leaching with hydrochloric acid.

The double salt *copper ammonium chromate* (cupric ammonium chromate) is required in dyeworks along with logwood and fustic extracts to obtain olive green wool or cotton dyes. Copper chromate is used as such or in reduced form as a catalyst in a number of petrochemical reactions.

Iron Chromates. No anhydrous iron(II) chromate is known. On the other hand, the water-soluble double salts, $KFe^{III}(CrO_4)_2 \cdot 2\,H_2O$ [*20161-12-0*] and $NH_4Fe^{III}(CrO_4)_2 \cdot 2\,H_2O$ [*20161-14-2*] do exist, and potassium iron(III) chromate is a corrosion inhibitor. A similar corrosion-inhibiting compound is also thought to be formed on steel surfaces that are treated with chromate solutions. Industrially, the compound is produced by the reaction of iron(III) chloride solution with potassium dichromate in an autoclave at 130 – 160 °C. The precipitate is filtered and dried.

Lead Chromate [*7758-97-6*], $PbCrO_4$, M_r 323.18, *mp* 844 °C (with evolution of oxygen), ϱ 6.123 g/cm^3, ΔH_{298}^0 −910 kJ/mol, is a yellowish orange powder which occurs in three modifications:

The solubility product in water is 1.5×10^{-14} at 18 °C. Lead chromate forms mixed crystals with lead(II) oxide, lead sulfate, and lead molybdate. All these salts are virtually insoluble in water; the molybdenum-containing compound is particularly well-known as molybdenum red. Lead chromate is prepared in a manner similar to that used for barium chromate. The composition, color, and quality of lead chromates depend on

the conditions of precipitation; they are used widely as yellow to red pigments in the lacquer and paint industry (→ Pigments, Inorganic, 1. General).

Silver Chromate and Silver Dichromate. Ag_2CrO_4 [*7784-01-2*], M_r 331.73, ϱ 5.625 g/cm^3, ΔH_{298}° −711.7 kJ/mol, S_{298}° 216 J mol^{-1}K^{-1}, c_p 142.3 J mol^{-1} K^{-1} (for solubility, see Table 8), and $Ag_2Cr_2O_7$ [*7784-02-3*], M_r 431.73, ϱ 4.770 g/cm^3, ΔH_{298}° −1218 kJ/mol, form dark red crystals and are soluble in acids, ammonia, and potassium cyanide solutions but not in water. The salts can be precipitated from a silver salt solution with chromate or dichromate solution and are used in the photographic industry.

Zinc Chromate [*13530-65-9*], $ZnCrO_4$, M_r 181.36, is sparingly soluble in water but dissolves readily in acids. A series of zinc chromate hydrates exists having the composition n ZnO · m CrO$_3$ · x H$_2$O. In industry zinc chromate is known as zinc yellow. Its color may be controlled by the mode of preparation. It is made by the reaction of either a suspension of finely ground zinc white (ZnO) in concentrated sulfuric acid or water-soluble zinc salts (ZnCl$_2$, ZnSO$_4$) with potassium or ammonium dichromate. The zinc chromates prepared in this manner always incorporate potassium or ammonium ions into their lattice. Zinc chromate is used in lacquer primers as a corrosion inhibitor instead of minium (red lead) because of its ability to form insoluble iron (III) chromates with iron or to passivate metal surfaces by oxidation.

7. Other Chromium Compounds

Chromyl Chloride [*14977-61-8*], CrO_2Cl_2, M_r 154.90, *mp* − 96.5 °C, *bp* 116.7 °C, ϱ 1.912 g/cm^3, is a blood red oily liquid with a pungent smell, c_p 545 J kg^{-1} K^{-1}, ΔH_{298}° −567.8 kJ/mol, S_{298}^0 510 J kg^{-1}K^{-1}, heat of fusion 268 kJ/kg. In the temperature range 178 – 390 K the vapor pressure obeys the equation

$$\log p = -3340 T^{-1} - 9.08 \log T + 35.06$$

where p is in hPa (mbar) and T in K. The liquid is electrically conducting.

Chromyl chloride is easily hydrolyzed; it is an extremely powerful oxidizing and chlorinating

agent and, therefore, reacts with organic solvents, often violently. It decomposes in daylight within a week via CrO_2 and Cl_2 to form a series of chromium oxides and chlorides with a low degree of oxidation.

Industrially chromyl chloride is produced from chromium(VI) oxide and hydrogen chloride gas, with concentrated sulfuric acid ($> 68\%$) being used primarily to bind the water of reaction. The higher density chromyl chloride is drained, distilled, and collected in cooled receptacles.

Chromyl chloride can also be prepared by using mixtures or molten baths of sodium chloride and alkali chromates or dichromates with fuming sulfuric acid. An elegant route involves the reaction of chromium(VI) oxide with liquid thionyl chloride; these reactants are converted quantitatively into chromyl chloride by elimination of SO_2.

Hexacarbonylchromium [*13007-92-6*], chromium hexacarbonyl, $Cr(CO)_6$, M_r 220.06, ϱ 1.77 g/cm^3, forms colorless, highly refractive crystals which belong to the orthorhombic system. The compound sublimes slowly even at room temperature; when heated in a sealed tube it melts at 149 – 150 °C. The boiling point has been calculated to be 147 °C. At 210 °C, explosive decomposition occurs. The enthalpy of formation is $-$ 1077 kJ/mol. Hexacarbonylchromium is somewhat soluble in chloroform and carbon tetrachloride but insoluble in benzene, ether, alcohol, and acetic acid. It is resistant to water and dilute acids at room temperature; there is no sign of attack even by concentrated hydrochloric acid or sulfuric acid in the cold, but concentrated nitric acid causes decomposition. No reaction with alkali occurs, but derivatives are produced with ammonia, pyridine, cyclopentadiene, and other organic ligands.

Attempts to synthesize hexacarbonylchromium directly from chromium and carbon monoxide have been unsuccessful. The action of carbon monoxide and a solution of phenylmagnesium bromide in ether on anhydrous chromium(III) chloride suspended in a mixture of benzene and ether produces intermediates that lead to hexacarbonylchromium upon addition of acid and distilling the ether in vacuo. Finely divided sodium can also be used for reduction instead of phenylmagnesium bromide. Yields of up to 80 % are reported when very finely divided

sodium reacts with anhydrous chromium(III) chloride below 0 °C with carbon monoxide at a pressure of about 6 MPa (60 bar); the reaction proceeds in the presence of diethylene glycol dimethyl ether; the mixture is subsequently hydrolyzed while the carbon monoxide pressure is maintained [75].

Applications quoted for hexacarbonylchromium include the tempering and hardening of metal surfaces by chromizing, use as a fuel additive, an intermediate in the preparation of organic chromium compounds, and a catalyst for oxo syntheses.

Chromium(II) Compounds. In general, compounds of divalent chromium are extremely unstable in air and, therefore, are of only minor importance in industry. Gaseous chromium(II) halides (for preparation, see [76]) are used to produce chromium diffusion layers on iron and nickel parts. Air stable sodium fluorochromate (II) is said to be suitable for the precipitation of metals in electroplating operations and for corrosion-protection coatings [77].

8. Analysis

Compounds that are insoluble in water and acids, for example, chromium ore, are solubilized by roasting with sodium peroxide [78] in the presence of soda. Chrome-tanned leathers are incinerated before being treated with sodium peroxide. Under these conditions, chromium is completely converted into water-soluble chromate(VI). The roasted mass is leached with hot water and after cooling sulfuric acid is added. Compounds of lower oxidation state that are soluble in water or acids are oxidized with ammonium persulfate to chromate(VI) in dilute boiling sulfuric acid in the presence of silver ions as catalysts [79]. Chloride ions must be removed beforehand. Traces of chloride ions are precipitated by adding a few drops of silver nitrate solution. The chromate(VI) solutions obtained in this way or solutions of chromium (VI) compounds that are soluble in water or sulfuric acid, are then titrated with iron(II) sulfate solution after phosphoric acid is added [80]. The end point of this titration can be determined potentiometrically or by means of a redox indicator, e.g., sodium diphenylamine-4-sulfonate [*6152-67-6*],

[80]. Iodometric titration of chromate(VI) is also possible [81]. For very low concentrations, e.g., in the analysis of water, atomic absorption spectrometry (AAS) and inductively coupled plasma atomic emission spectrometry (ICP-AES) have proved successful [83]. Trace amounts of chromium are also detected photometrically at 540 nm after oxidation to chromate(VI) and addition of diphenylcarbazide [*140-22-7*] (formation of a reddish violet complex) [82].

9. Transportation, Storage, and Handling

Both hexavalent and trivalent chromium compounds are of commercial significance. Whereas the trivalent compounds and chromium(IV) oxide are not subject to regulations governing transport, the hexavalent compounds are classified internationally as dangerous goods. According to the IMDG code [85], the following classifications are applicable for hexavalent chromium compounds:

Compound	Hazard class	UN No.
$Na_2Cr_2O_7 \cdot 2\ H_2O$, crystals	6.1	3288
$Na_2Cr_2O_7$ solution	6.1	3287
$Na_2Cr_2O_7$ anhydr., crystals	5.1	3087
$K_2Cr_2O_7 \cdot 2\ H_2O$, crystals	6.1	3288
$(NH_4)_2Cr_2O_7$	5.1	1439
CrO_3, solid chromic acid	5.1	1463
Chromic acid solution	8	1755

During handling and storage, chromates, dichromates, and chromic acid must not be brought into contact with readily oxidizable substances.

A limit of 50 µg/L of chromium recommended by the WHO has been adopted in drinking water regulations. This figure was estimated by the U.S. Public Health Services from toxicity data. The value considers the No Observable Adverse Effect Level (NOAEL) from animal tests and the calculated Average Daily Intake (ADI) of drinking water consumers [86].

10. Environmental Protection

Wastewater. In Germany limits for the chromium content of wastewaters have been set up. The permitted concentrations depend on the type of industry. For the leather tanning industry, for instance, the concentration of Cr(IV) must not exceed 0.5 mg/L, and that of total chromium, 1 mg/L [87].

To avoid the pollution of water supply facilities, the risk of a release to surface and ground water has to be minimized during transportation, storage, and handling. In Germany, soluble hexavalent chromium compounds are classified in the highest water pollution class [88].

Exhaust Gas. In Germany, the emission of such carcinogenic chromates as calcium chromate, strontium chromate, chromium(III) chromate, and zinc chromate is limited to 1 mg/m^3 max. (as Cr) [89]; the emission of the other chromium compounds is limited to 5 mg/m^3 (as Cr).

Waste. Within the European Community, waste containing Cr(VI) compounds is considered hazardous [90]. It can only be deposited in dumps with particular safety measures and drainage-water treatment.

In Germany, sewage sludge containing not more than 900 mg per kilogram of chromium may be used as fertilizers in soils for agricultural purposes provided the chromium content of the soil does not exceed 100 mg chromium per kilogram soil before the application [91]. According to the U.S. Environmental Protection Agency, the chromium content of the soil should not be regarded as a limiting factor for the application of sewage sludge [92]. Studies carried out in Germany on the use of sewage sludge containing a few percent of chromium(III) hydroxide as fertilizer did not reveal any adverse effects on soil and plants [93].

11. Ecotoxicology

Insoluble inert chromium(III) oxide, Cr_2O_3, is the stable mineral end product into which chromium compounds are converted in the environment as a result of natural processes.

Inland Waters. The natural concentration of dissolved trivalent chromium in surface waters is < 1 – 10 µg/L [94–96]. Hexavalent chromium does not occur in natural fresh

waters. If dissolved trivalent chromium from anthropogenic sources enters an inland body of water, it precipitates under neutral conditions as chromium hydroxide. This ages and becomes increasingly insoluble, and only a small proportion remains in solution. Chromium(VI) compounds entering inland waters are reduced to chromium(III) compounds by the natural content of organic substances in water and sediments [97], [98].

Table 9 summarizes toxicity data for chromium(III) and chromium(VI) compounds in relation to fish, bacteria, algae, daphnia, and plants.

Table 9. Ecotoxicology of chromium compounds

Species or medium	Chromium(III) compounds	Chromium(VI) compounds
Freshwater fish	**$CrCl_3$:** LC_{50} (48 h) minnows, static, 400 mg/L LC_{50} (48 h) trout, static, >1000 mg/L [99] LC_{50} (48 h) ides, static, 300 mg/L **$Cr_2(OH)_2(SO_4) \cdot Na_2SO_4$** LC_0 (30 days) *Brachydanio rerio*, static >1000 mg/L [100], [101]	**$K_2Cr_2O_7$:** 14 day no observable effect level (NOEL) for zebra fish (*Brachydanio rerio*) at 50 mg/L [107] or 80 mg/L [108]
Bacteria	**$KCr(SO_4)_2 \cdot 12 H_2O$:** 100 mg/L proved not to be poisonous for bacteria of the genus *Escherichia* [100], [101]	**$Na_2Cr_2O_7 \cdot 2 H_2O$:** toxic limiting concentration for *Pseudomonas putida* 0.78 mg/L [109]
Algae	**$KCr(SO_4)_2 \cdot 12 H_2O$:** incipient injurious effect at 4 – 6 mg/L (*Scenedesmus*) [100]	**$K_2Cr_2O_7$** (*Scenedesmus subspicatus*): EC_{10} (96 h) 0.5 mg/L [107]; 0.3 – 1.3 mg/L [110]; 1.8 mg/L [108] EC_{50} (96 h) 1.4 mg/L [107]; 1.6 – 4.7 mg/L [110]
Daphnia	**$KCr(SO_4)_2 \cdot 12 H_2O$** marked injurious effect at 42 mg/L [100]	**$K_2Cr_2O_7$** (21-day test): concentrations of > 0.1 mg/L markedly b decreased the production of offspring [108]; swimming ability of *Daphnia magna*: $EC_0 = 0.3$ mg/L; $EC_{50} = 0.9$ mg/L; $EC_{100} = 2.2$ mg/L [111]
Mammals (oral, rat)	**$Cr(NO_3)_3$:** LD_{50} 3250 mg/kg [102]	**$Na_2Cr_2O_7 \cdot 2 H_2O$:** LD_{50} 160 mg/kg [112]
Soil mobility	**$Cr(NO_3)_3$:** low, only certain complex compounds are biologically available [103]	**$K_2Cr_2O_7$:** low since chromate is strongly adsorbed on the podsol type of soil and is also reduced by organic soil constituents [108]
Bioaccumulation	**$Cr(NO)_3$:** plants, particularly the parts above ground, do not absorb much chromium; accumulation of Cr is prevented at the very beginning of the food chain [104], [105]	**$K_2Cr_2O_7$:** carp (*Cyprinus carpio*): no bioaccumulation detected [108]
Higher plants EC_{50}[*] (14 d)	**$CrCl_3 \cdot 6 H_2O$:** *Avena sativa* (oat) 560 mg of Cr/kg of soil [106] *Brassica rapa* (turnip) 230 mg of Cr/kg of soil [106]	**$K_2Cr_2O_7$:** oat: 27 mg/kg [107]; 32 mg/kg [108]; 96 mg/kg [110] turnip: 23 mg/kg [107]; 22 mg/kg [108]; 24 mg/kg [110]
Earthworm LC_{50} (28 d)	**$CrCl_3 \cdot 6 H_2O$:** not known	**$K_2Cr_2O_7$:** > 2000 mg/kg of soil [107] no lethal effects at 1000 mg/kg [110]

[*] EC = effective concentration; at EC_{50} growth is retarded by 50 % compared with control.

Limits for Chromium in Fresh Water. Various countries have set guidelines for the content of chromium in fresh water which can be considered tolerable [113–115]. Whereas the U.S. recommendations distinguish between trivalent and hexavalent chromium, both the Canadian and English guidelines consider total chromium.

Soil. The chromium content of the earth's crust varies from a few mg/kg to ca. 50 % in chromite deposits. The average chromium content of rock is 83 mg/kg. The chromium content of soil varies very widely, depending on the geological conditions. The range is from 5 to 1500 mg/kg, and the average concentration about 50 mg/kg [116]. The highest chromium contents are found in soils over basaltic rock. Chromium in soils is linked to the relicts of primary minerals such as chromite or olivine or bound by adsorption to clay minerals. Chromium is found everywhere in the soil of Germany [117], and levels of over 1100 mg/kg may be reached. Such levels are caused solely by geological conditions. All natural chromium is trivalent. Minerals of hexavalent chromium (eg. Crokoite) are extremely rare and can be found only in very few places worldwide.

Plants. As chromium occurs in soil only in the form of sparingly soluble chromium(III) compounds, which are available to plants only to a small extent, chromium is not enriched in the food chain [104], [105], [118–120].

Animals. Grazing animals are not subjected unduly to chromium since only small amounts enter the parts of plants above the ground [105]. Less than 1 % of the chromium contained in plants is available to animal and human organisms. To cover essential needs, the chromium must be in a special, biologically suitable form [121].

12. Nutrition

Chromium is an essential trace element both for the animal and human organism. A number of physiological functions in animal and humans can no longer proceed normally in a state of chromium deficiency [122], [123]. Examples include the role of chromium in glucose-tolerance factor, a cofactor for the action of insulin [124], in cytochrome C reductase [125], and in other metabolic processes [126].

The chromium content in food is in the range of 0.01 – 10 mg Cr/kg dry substance. Consumers in the western world ingest an average of 60 µg Cr per day in their food. The U.S. Food and Nutrition Board (1980) recommends [120] as the safe, but also adequate amount (average dietary intake): 50 to 200 µg per day.

The amount of chromium necessary to humans is not always guaranteed in the dietary intake and even with additional uptake from the environment. Therefore, nutrition science literature contains more references to deficiencies in chromium supply than any toxic effects due to chronic excess supply of chromium [127], [128].

For chromium the gap between essential and toxic concentrations is particularly large. Mammals can tolerate 100 to 200 times the normal chromium content of their bodies without adverse effects [129].

13. Toxicology and Occupational Health

The properties of chromium and its compounds which determine the toxicity and the impact on the environment differ greatly depending on the valency state. Only hexavalent chromium compounds are biologically active. Metallic chromium and the trivalent compounds, including those in chromium ores, are neither irritating, mutagenic, nor carcinogenic [129].

Reviews of the toxicity of chromium and its compounds are given in [130–132].

Chromium Dioxide. In a single administration, chromium dioxide is resorptively nontoxic; the lethal dose is greater than 17000 mg/kg (rats, oral). In rabbits, chromium dioxide causes slight primary irritation of skin and mucous membranes.

Since any chromium dioxide in the normal atmosphere may contain traces of hexavalent chromium, care is to be taken during production and further processing to ensure that the concentration of chromium(VI) compounds at the workplace does not exceed the TLV for chromium (VI).

Employees of chromium dioxide plants are examined annually for chromium exposure. So far no indications have been found of any disease caused by chromium in chromium dioxide production plants.

Hexavalent Chromium Compounds. Particularly chromic acid and the alkali chromates corrode and irritate the skin and mucous membranes.

Acute Effects. Sodium monochromate and dichromate, potassium dichromate, and ammonium dichromate are soluble chromium(VI) compounds. These substances are toxic when swallowed, very toxic when inhaled, and dangerous to health when they come into contact with the skin. In humans, inhalation of these compounds, even at low doses, leads to coughing, chest pain, difficult breathing and fever.

Sodium monochromate and dichromate, potassium dichromate, and ammonium dichromate irritate the skin, eyes and respiratory tract. The risk of serious eye damage cannot be ruled out. In humans, repeated contact of hexavalent chromium compounds with the skin may lead to so-called chromium ulcers, but only on previously damaged parts of the skin.

Potassium dichromate and sodium monochromate show a skin-sensitizing effect in animal studies. There is evidence that soluble chromium(VI) compounds have a skin-sensitizing effect in humans. Skin allergy in humans is generally tested with potassium dichromate.

Hexavalent chromium compounds are capable of sensitizing the skin strongly, which may lead to chronic eczemas, particularly when the source is cement dust containing chromium(VI). In contrast, no sensitization of the respiratory tract occurs.

Uptake by the digestive system (mostly suicidal cases) causes serious intestinal inflammation, sometimes with loss of blood. Damage to the renal tubules occurs mainly after dermal absorption. This can lead to kidney failure if the spontaneous reduction capacity of plasma of about 2 ppm (20 min) is not sufficient to reduce chromium(VI) to nontoxic chromium(III). The administration of high doses of ascorbic acid facilitates this reduction, and chromium(III) is then excreted in the urine without causing kidney damage [140].

Chronic Effects. Repeated inhalation of ammonium dichromate and sodium dichromate primarily affects the respiratory tract, while no corresponding studies are available with sodium monochromate and potassium dichromate. There are no significant data on repeated oral intake of ammonium dichromate or sodium dichromate, while liver and kidney damage have been described for sodium monochromate and potassium dichromate. In humans, prolonged inhalation of the dust damages the nasal mucosa or even the nasal septum (septal perforation) [139].

Chronic irritation of the nasal mucous membrane can lead to its atrophy. Chronic bronchitis has been reported following long-term exposure to hexavalent chromium compounds, but this does not occur normally under today's manufacturing conditions [129]. Impairment of breathing has not been observed.

Mutagenicity. Sodium monochromate and dichromate and potassium dichromate show mutagenic activity in tests with bacteria, microorganisms, cell cultures, and in animal studies. Ammonium dichromate shows mutagenic activity in tests with bacteria.

All hexavalent chromium compounds are mutagenic, but trivalent chromium compounds do not have any mutagenic potential. In some cases, the hexavalent compounds must first be solubilized to show a mutagenic effect. This effect is counteracted by the reduction of chromium(VI) to chromium(III), for example, by adding body fluids or organ homogenates [141], [142].

Carcinogenicity. Many animal experiments have been carried out to test the carcinogenicity of chromium compounds. These include subcutaneous injection, inhalation, intratracheal instillation, and introduction of pellets into the bronchial tree [143–147].

Depending on solubility, chromium(VI) compounds show carcinogenic activity after long-term inhalation. For this reason, the MAK Commission classed them under Group III A2 (substances with carcinogenic potential in animal studies).

Chromium(VI) compounds have been classed by IARC under Group I (carcinogenic in humans) based on early epidemiological studies, although clear classification of the

findings to the category of carcinogenic substances was not possible.

The EU has classified chromic acid and zinc chromates as category 1 carcinogens (human carcinogens), other chromates/dichromates ($SrCrO_4$, $CaCrO_4$, $Na_2Cr_2O_7$, $K_2Cr_2O_7$, K_2CrO_4) as category 2 carcinogens (animal carcinogens), and $PbCrO4$ as category 3 carcinogen (suspected carcinogens) [148].

In the United States [149], water-soluble Cr (VI) compounds and insoluble Cr(VI) compound – both "not otherwise classified" – are considered A1, i.e., "confirmed humans carcinogens"

Reproductive Toxicity. In animal studies, sodium dichromate and potassium dichromate do not induce deformities at nonmaternotoxic doses. An embryotoxic effect has been described for potassium dichromate. There are no data on an embryotoxic effect of ammonium dichromate or sodium monochromate.

In animal studies, inhalation of sodium dichromate does not impair fertility. Animal studies with potassium dichromate and sodium monochromate at doses that are nontoxic to the animals yield no evidence of a fertility-impairing effect. There are no data on a fertility-impairing effect of ammonium dichromate.

Epidemiology. Epidemiological studies among workers in chrome-tanning plants and chrome(III) pigment manufacturing plants have proved trivalent chromium compounds to be noncarcinogenic [150].

Earliest indications of increased incidences of lung cancer among workers in the chromate manufacturing industry were observed in the 1930s. More evidence in support of this observation came from a large number of epidemiological studies carried out after 1948 [151], [152]. Studies carried out between 1948 and 1956 showed a 25- to 29-fold increase in the incidence of lung cancer. In contrast, investigations performed since 1979 reflect the effects of improved hygienic working conditions and production processes, for example, by avoiding the use of lime in the oxidative roasting of chromium ores (low-lime process). These measures have led to a convergence between the incidences of lung cancer observed in the workers and that expected in unexposed persons [139], [153–156].

An increased incidence of lung cancer was observed among persons employed in the chromate pigment industry only after exposure to zinc chromate. Lead chromate showed no carcinogenic effect [157–159]. Results of epidemiological studies carried out during the handling of chromic acid, particularly during chromium plating, are blurred by confounding factors; a statistically significant increase in the rate of lung cancer was not observed [143], [160]. An increased risk of lung cancer has also not been clearly established in the manufacture of ferrochromium [161], [162]. Occupational health care has been provided in the chromate-producing industry for several decades.

Classification. According to the EU List of Dangerous Substances [148] the following labelling has to be applied for

$K_2Cr_2O_7$, $Na_2Cr_2O_7 \cdot$ 2 H_2O	
T+	very toxic
N	dangerous for the environment
R49	may cause cancer by inhalation
R46	may cause heritable genetic damage
R21	harmful in contact with skin
R25	toxic if swallowed
R26	very toxic by inhalation
R37/38	irritating to respiratory sytem and skin
R41	risk of serious damage to eyes
R43	may cause sensitization by skin contact
R50/53	very toxic to aquatic organisms; may cause long-term adverse effects in the aquatic environment
S53	avoid exposure; obtain special instructions before use
S45	in case of accident or if you feel unwell, seek medical advice immediately (show label where possible)
S60	this material and its container must be disposed of as hazardous waste
S61	avoid release to the environment; refer to special instructions / safety data sheet
$(NH_4)_2Cr_2O_7$	
E	explosive
T	very toxic
N	dangerous for the environment
R49 – 46	(see above)
R1	explosive when dry
R8	contact with combustible material may cause fire
R21 – 25 – 26 – 37/38 – 41 – 43 – 50/53	(see above)
S53 – 45 – 60 – 61	(see above)

Chromic acid (anhydride), CrO_3, carries the following labelling:

O	oxidizing
T	toxic
C	corrosive

N	dangerous for the environment
R49	may cause cancer by inhalation
R8	contact with combustible material may cause fire
R25	toxic if swallowed
R35	causes severe burns
R43	may cause sensitization by skin contact
R50/53	very toxic to aquatic organisms; may cause long-term adverse effects in the aquatic environment
S53 – 45 – 60 – 61	(see above)

Occupational Exposure Limits. *Germany* [163]. The TRK values for Cr(IV) compounds, except those which are practically insoluble in water, are (as CrO_3 in total dust) for

Arc welding	0.1 mg/m^3 (corresponding to 0.05 mg/m^3 as Cr)
Manufacturing of soluble Cr(IV) compounds	0.1 mg/m^3 (0.05 as Cr)
Others	0.05 mg/m^3 (0.025 as Cr)

United States [149]. The TLV values (as Cr) are as follows;

Cr metal and Cr(III) compounds	0.5 mg/m^3
Water-soluble Cr(IV) compounds	0.05 mg/m^3
Insoluble Cr(IV) compounds	0.01 mg/m^3

Biological Monitoring. In addition to the classical assay for chromium in blood or urine, the degree of previous exposure to chromium can be estimated by determining the extent of bound chromium in erythrocytes [164].

14. Economic Aspects

The output of chromium ore is subject to considerable variations. Rich ores which are obtained easily by handpicking have declined. This shrinkage in output has to be counterbalanced by exploiting low-grade ores and upgrading them to saleable concentrates. The statistical documents are incomplete and contradictory. Table 10 shows the output of chromium ores according to various sources of information.

Even the most pessimistic estimates of the worldwide reserves and the extraction possibilities in individual countries do not predict a chromium shortage before the end of this

Table 10. Output of chromium ore and concentrates (in 1000 t) [133–136]

	1901 – 1982	1982	1983	1984
Former USSR[*]	55 000	3 400	3 400	3 400
South Africa	50 000	2 200	2 250	2 450
Zimbabwe	22 000	430	450	450
Turkey	21 000	370	360	400
Philippines	18 000	350	360	400
Albania[*]	15 000	1 200	1 350	1 350
India	7 900	340	360	410
Brazil	4 100	400	370	400
Finland	3 700	400	360	400
Cuba[*]	3 700	30	40	30
Iran	3 400	40	40	30
Greece	2 000	40	50	50
Madagascar	2 000	60	40	40
Remainder	800	40	70	90
Total worldwide	208 600	9 300	9 500	9 900

[*] Estimated.

century. In addition, the huge lean-ore deposits in South Africa, Southeast Asia, and the United States, which are still completely untouched, afford a replacement for the rich ores being mined at present.

In Table 11 the consumption of chromium ore is broken down according to products. The refractory brick share is declining because Siemens – Martin steel is being increasingly supplanted by oxygen-blown steel produced in converters with a basic lining.

Table 12 shows chromium ore imports into the Federal Republic of Germany and Table 13 the

Table 11. Estimated consumption of chromium ore in terms of products in 1984 [134], [137]

Product	World	United States
Ferrochromium, FeSi chromium, chromium metal, and foundry sands	72 %	60 %
Refractory bricks	12 %	20 %
Chemicals	17 %	20 %

Table 12. Imports of chromium ore[*] into the Federal Republic of Germany [138]

	1981	1982	1983
1000 t	268	244	247
Millions of €	25.0	22.4	21.6
Price, €/t	93.00	91.57	87.58

[*] Includes all types of chromium ore.

Table 13. Estimated share (in %) of individual applications in the consumption of chromium chemicals, 1985[*]

	United States	Worldwide
Pigments	22	19
Metal processing	15	24
Tanning	12	32
Wood preservation	26	11
Corrosion protection	5	3
Petroleum industry	5	2
Textile dyes	2	1
Catalysts	2	1
Video tapes	2	2
Remainder	9	5

[*] Excluding countries with state trading organizations.

Table 14. Estimated 1985 sodium dichromate capacities in 1000 t of $Na_2Cr_2O_7 \cdot 2\,H_2O$ per year

Western Europe (EEC)	260
State trading countries	250
United States	220
Asia, Africa	110
Worldwide	840

Table 15. Estimated 1985 chromic acid capacities in 1000 t/a

Western Europe (EEC)	42
United States	40
State trading countries	32
Japan	15
Others	8
Worldwide	137

share of individual applications in the consumption of chromium chemicals.

The starting material for virtually all chromium chemicals is sodium dichromate prepared from chromium ore. Table 14 summarizes the production capacities for $Na_2Cr_2O_7 \cdot 2\,H_2O$.

In Table 15 the chromic acid production capacities are broken down according to countries.

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