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Miljøprojekt

Mass Flow Analysis of Chromium and Chromium Compounds

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Contents

Preface

This project was carried out for the Danish Danish Environmental Protection Agency in connection with the development scheme under the Programme for Cleaner Products, etc. The project was carried out during the period November 2000–October 2002 by staff from dk-TEKNIK ENERGY & ENVIRONMENT and DHI Water & Environment.

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Pia Bruun Poulsen from dk-TEKNIK collected statistics on import/export and production of products which contain chromium, and Allan Astrup Jensen from dk-TEKNIK was in charge of Quality Assurance. The project was supervised by a steering committee comprising the project group and the Danish EPA as represented by Henriette Seiler Hansen and Henri Heron. Henriette Seiler Hansen was president of the steering committee up to and including September 2001, and Henri Heron assumed the position as president from October 2001 onwards.

The report was submitted to the Confederation of Danish Industries (DI) for consultation.

Summary and conclusions

Introduction

A mass flow analysis of chromium and chromium compounds has been carried out. This survey updates the previous mass flow analysis of chromium and chromium compounds (Tørsløv & Hansen, 1985). The new analysis has been carried out on the basis of information from Statistics Denmark, the Danish Product Register, previously completed mass flow analyses, and information from importers and manufacturers. The work presented in this survey has been ranked in order of priority on the basis of general knowledge about the use and occurrence, hazardousness and potential exposure of chromium as well as on the basis of a preliminary analysis of statistical information about the chromium supply to the community via goods and products.

Thus, a detailed survey of the use of chromium for surface treatment and in wood preservatives, pigments, leather tanning, laboratory chemicals, accelerators/catalysts/hardeners, corrosion inhibitors and textiles has been carried out. In contrast, the survey of the use of chromium as an alloy metal in connection with iron, aluminium and copper as well as in electronic storage media has been carried out at a general level. Special emphasis has been placed on identifying consumption and diffusion of chromium(VI) compounds (hexavalent chromium).

The balance presented covers imports, production and exports for the year 1999, calculated as an average for the years 1998, 1999 and 2000. In cases where discrepancies between data from the three years were observed, the most probable data were included in the calculations.

Occurrence and production of chromium and chromium compounds

Chromium occurs naturally as red lead ore ($PbCrO_4$, crocoite) and as chromium ironstone (FeO, Cr_2O_3). Metallic chromium is produced by reducing chromium oxide (Cr_2O_3) with aluminium. Chromium deposits are found in countries such as South Africa, Kazakhstan, India, Brazil, Finland, Turkey and Zimbabwe. These countries account for more than 90% of the total production. Metallic chromium is used as an alloy metal in iron, aluminium and copper and for surface treatment. The Danish Product Register includes records of approximately 130 chromium compounds, and chromium(III) oxide, chromium(VI) oxide, metallic chromium and lead(II) chromates account for more than 95% of the total registered consumption. No production of chromium compounds takes place in Denmark.

Chromium balance for Denmark

Figure 1 shows a simplified chromium balance for Denmark. The balance is described and discussed in section 6.3, "Chromium balance for Denmark 1998–2000".

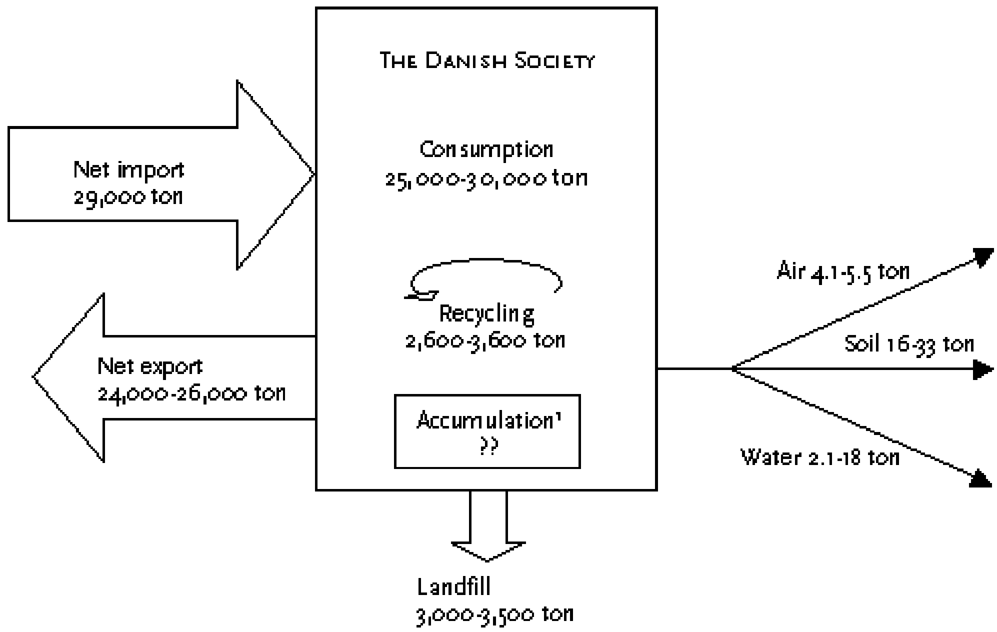

Figure 1
Chromium balance for Denmark 1999

1. On the basis of the calculated net import, net export and the quantities deposited at landfills, the accumulation is estimated to be about 0. Metals containing chromium (iron, aluminium and copper) represent a high value within the recycling system. This means that they will be taken out of the system for recycling when they are no longer serviceable. This does not, however, mean that accumulation is entirely out of the question.

Chromium is imported in metallic form with iron and iron alloys, aluminium and aluminium alloys as well as copper and copper alloys. Chromium also occurs as an impurity in these metals. Chromium is exported as metal scrap; such export is carried out with a view to recycling.

Chromium compounds are imported with a view to production of finished goods in Denmark, and as ingredients in finished goods. In most products, the chromium content is not sufficiently high to warrant labelling or any other special attention. As a result, we do not have a great deal of knowledge about which products contain chromium compounds, nor about the relevant contents of chromium compounds in those products.

Below is a summary of the consumption of finished goods containing chromium and of emissions into the environment.

Consumption

Consumption of chromium as an alloy metal, chemical compounds and as a trace constituent has been analysed for Denmark for 1999 (average for the years 1998, 1999 and 2000).

Table 1 shows an overview of the consumption of chromium and chromium compounds in Denmark, by field of application. The survey of different fields of application has been carried out at different levels of detail as described in section 1.4, "Prioritisation of the survey". The survey was carried out on the basis of information from Statistics Denmark, the Danish Product Register, previous mass flow analyses, and information provided by selected trade associations, importers and manufacturers.

Table 1
Consumption of chromium, chromium compounds and chromium as a trace constituent in Denmark in 1999 (average for the years 1998, 1999 and 2000), by field of application. Figures on the consumption of Cr(VI) are also provided for relevant applications.

Field of application	Consumption (tonnes/year)	%	Of which Cr(VI) (tonnes/year)
Chromium, metallic			
– Iron and steel	24,300–29,300	97	–
– Aluminium alloys	11–106	0.2	–
– Copper alloys	6–9	0.03	–
Chromium compounds			
– Surface treatment	37.7	0.14	37.7
– Pigments in paint and plastic	12.6–116.7	0.23	1–2
– Impregnation	8.8	0.03	8.8
– Tanning	164–302	0.8	0.016–0.035
– Hardeners	13–47	0.11	<<1
– Laboratory chemicals	<1	0	<1
– Other applications	208–522	0.77	–
Chromium as a trace constituent			
– Coal and oil	147	0.53	–
– Cement	67	0.24	2.1–4.2
In total	24,964–30,354	100	49.6–52.7

In the survey of the consumption of chromium compounds, emphasis has been placed on identifying consumption and emissions of chromium(VI) compounds, as they represent a significantly greater risk to the environment and health than other chromium compounds. The use of chromium(VI) compounds is subject to a number of restrictions, which explains the drop in consumption within some fields of application.

Chromium, metallic

Metallic chromium mainly occurs as an impurity and alloy metal in iron, aluminium and copper. This is also the reason why the survey of metallic chromium is primarily based on updates of previous mass flow analyses of these substances. This particular field of application accounts for more than 97% of the total consumption of chromium in Denmark. Metallic chromium is also used as a coating/surface treatment, for example, for metals and plastic in the form of chromium plating. The actual process is described under the section on chromium compounds below. Metallic chromium in iron, aluminium and copper is recycled. A substantial part of all recycled metallic chromium is exported in the form of alloy steel sent for recycling.

Chromium compounds

Chromium compounds are used in a wide variety of products, e.g. for surface treatment, colour pigments, leather tanning, wood impregnation, textiles, etc. Chromium compounds are no longer used in wood preservatives, but because of the long lifetime of such products, disposal of impregnated wood will be a source of chromium in waste flows for many years to come. Chromium compounds are not recycled as such.

Chromium as a trace constituent

Chromium occurs as a trace constituent in considerable amounts in cement and fossil fuels (primarily in coal). Recycling of residual products (fly ash) in cement contributes to chromium content in cement, as do other raw materials.

Emissions to the environment

Table 2 contains an overview of the information available about disposal and emissions of chromium into the environment in Denmark in 1999. Emissions to various recipients are discussed below.

Emissions to air

Chromium and chromium compounds are stable compounds with a high melting point/boiling point. This means that emissions to air are mainly associated with thermal processes. Thermal processes occur in connection with waste incineration, energy conversion, and production and reprocessing of iron, aluminium and copper, including alloying of these metals. Primary production of these metals or alloys does not take place in Denmark, but reprocessing might well do so, as might recycling of metals. Energy conversion is regarded as the most important general source of emissions of chromium to air.

Discharges to water

Discharges of chromium and chromium compounds into the aquatic environment occur, for example, through the discharge of process chemicals from surface treatment processes or wastewater from the paint/varnish industry. During the use phase, discharges to water will primarily take place through corrosion of iron, steel, aluminium and copper, through use of paints containing chromium pigments, through leaching from impregnated wood or through disposal of laboratory chemicals. The greatest secondary sources of chromium discharges into water are emissions via atmospheric deposition and/or discharges from municipal wastewater treatment plants.

Emissions to soil

During the use phase, emissions of chromium and chromium compounds will primarily take the form of corrosion of iron, steel, aluminium and copper, leaching from impregnated wood and painted surfaces as well as peelings from chromium-plated products. The largest secondary sources of chromium emissions to soil are via atmospheric deposition and/or sludge from municipal wastewater treatment plants.

Landfill

Chromium and chromium compounds end up in landfill as part of a range of products. It is estimated that the most significant sources are iron and stainless steel, and residual products from waste incineration. Furthermore, smaller amounts are added to landfill with construction waste, leather and textiles.

Table 2
Disposal and dispersal of chromium to the environment in Denmark, 1999

Process/source	Air	Water	Soil	Landfill	Total
Industrial processes					
– Processing, use and disposal of iron and steel					
– Reuse of iron and steel	?	?	15.5–31	–	15.5–31
– Processing, use and disposal of aluminium	0.1–0.2	0.017–0.034	–	2.3	2.4–2.5
– Processing, use and disposal of copper	0–0.1 ~0	0.2–2 –	0.1–1 0.1–0.2	3–37 1–2	3.3–40 1.1–2.2
– Conversion of energy (coal and oil)	3.5	–	–	?	3.5
– Other industrial processes	–	0.2	–	–	0.2
– Surface treatment	–	0.089	–	–	–
– Impregnation	–	?	–	–	?
– Tanning	–	0.27	–	–	0.27
– Transport	0.2	–	–	–	0.2
Use of products					
– Impregnated wood	–	0.3–0.6	0.3–0.6	–	0.6–1.2
– Chromium-plated products	–	–	??	–	??
– Paint	–	0.03–13	–	–	0.03–13
– Laboratory chemicals	–	<<1	–	–	<<1
Waste treatment					
– Waste incineration	0.3–1.5	–	–	36–96	36–98
– Biological waste treatment	–	–	0.086	–	0.086
– Deposit of solid waste	–	–	–	??	??
– Kommunekemi	?	–	–	104–107	104–107
– Municipal wastewater	–	1.2	–	–	1.2
– Residual sludge	–	–	2.1	1.4	3.5
In total	4.1–5.5	2.3–17	16–33	148–244	170–302

Summarizing evaluation

The total consumption of chromium is calculated at 25,000–30,000 tonnes/year, of which metallic chromium accounts for more than 97%. Chromium compounds and trace constituents account for the remainder. Chromium(VI) compounds are estimated to account for 50–53 tonnes per year. It is estimated that the consumption of chromium(VI) compounds will fall as a result of the restrictions on their use. Metallic chromium in waste is recycled extensively with iron, aluminium and copper, while there is no recycling of chromium compounds.

The most substantial emissions to air come from energy conversion processes, while the most substantial contributions to the water environment come from atmospheric deposition. The most substantial emissions to soil come from atmospheric deposition and reprocessing as well as use and disposal of iron and steel.

1 Introduction

1.1 Objective of the analysis

The objective of this project is to identify the main flows of chromium through Denmark. The survey has been prioritised in accordance with the following criteria:

- General knowledge about the use and occurrence of chromium
- Hazardousness and potential exposure
- Chromium supply via goods and products

This prioritisation is described in greater detail in section 1.4.

Due to the health risks associated with chromium(VI) compounds (hexavalent chromium), efforts have been made to identify all flows of this substance.

1.2 Method and scope

A mass flow analysis is based on the principle of substance balance over a given period of time. This principle states that:

Input + formation = accumulation + output + degradation

Chromium is an element, which means that it will neither form nor be degraded. As a result, the mass flow is simple: the quantities entering the community (input) equal the sum of the quantities leaving the community (output) and the accumulated mass. See Figure 1.1.

Figure 1.1
The principle of mass flow analysis

Danish raw materials
Import of raw materials
To soil and air

Export of
Processing of raw materials
Solid waste and wastewater

Export of products
Production in Denmark
To soil and air

Import of products
Consumption of products in Denmark
To soil, water and air

Export of waste products
Waste treatment
To soil, water and air

Landfilling, disposal, etc.

Soil and groundwater
Water
Air

The survey of the mass flow for chromium is based on statistics from Statistics Denmark about imports and exports (Statistics Denmark, 1999a; 2000a; 2001a) and sales of domestically produced goods in Denmark for 1998–2000 (Statistics Denmark, 1999b; 2000b; 2001b). This information has been supplemented with information from the Product Register about the supply and composition of products containing chromium and their use within various functions. Among other things, the information from the Product Register is used to identify CN[1] numbers for chromium and products containing chromium for which Statistics Denmark has compiled figures on import, export and production. Efforts have been made to confirm the statistic information by contacting relevant industry organisations, companies and the like.

The mass flow analysis looks at the flows of chromium and chromium compounds in Denmark during a single year. In order to take fluctuations in sales into account, average figures from Statistics Denmark have been used. These average figures are for import, export and sale of domestically-produced goods in Denmark in the years 1998, 1999 and 2000. More years have also been included in the analysis in order to determine development trends as regards the use of chromium.

When we look at the data basis from Statistics Denmark, we see examples of significant variations in the sales of goods between the years 1998–1999 and 2000. One of the reasons for this is that in 2000, Statistics Denmark made an extra effort to have companies report quantities which they had not previously felt able to report information on (Statistics Denmark, 2002).

This means that 2000 may be a more accurate reference year than the preceding ones, as reports on quantities of chromium and chromium compounds have been made for more items in 2000 than ever before. On the other hand, the reports on these hitherto unreported quantities may not be entirely accurate. This uncertainty has to do with the fact that they cannot be compared with previous reports, and the people supplying the new information may not be used to doing so, and may make mistakes as a result of their lack of experience.

If, for example, we look at item no. 74122000, "Pipe fittings made from copper alloys", the statistics tell us that a total of 54,325 tonnes of this product were sold in Denmark in 2000. This seems unlikely, as it would mean that every citizen in Denmark bought approximately 10 kg of pipe fittings. One explanation for this mistake might be that the report has been made using the wrong unit, e.g. "pieces" instead of "tonnes". In cases where the quantities stated for a year (primarily 2000) appear obviously unrealistic, the year in question has been disregarded in the calculations of the average quantities for 1998–2000[2].

[1] The Combined Nomenclature is the EU's product nomenclature which must be used by companies which are under an obligation to submit information in connection with intra-EU trade.
[2] Large building projects might, however, be an explanation.

1.3 Chromium and chromium compounds

1.3.1 Occurrence and use of chromium

Chrome is a shiny, very hard and brittle metal. It belongs to the group of heavy metals and is the 13th most common element on Earth. It occurs in nature as red lead ore ($PbCrO_4$, crocoite) and as chromium ironstone (FeO, Cr_2O_3). Metallic chromium can be produced by reducing chromium(III) oxide (Cr_2O_3) with aluminium.

Chromium is used in many contexts, either in metallic form or in chemical compounds. The Danish Product Register includes records of approximately 130 chromium compounds, and chromium(III) oxide, chromium (VI) oxide, metallic chromium and lead(II) chromates account for more than 95% of the total consumption if we take a worst case scenario view[3].

As metallic chromium is very chemically stable, it is often used to cover the surface of less durable metals. This is known as chromium plating. Chromium is also widely used as an ingredient in metallic alloys. Among other things, it is used in ferrous chromium, a carboniferous 60% chromium-iron alloy, in chromium steel with 12–13% chromium, in 18/8 steel (18% chromium and 8% nickel), and in particularly heat-resistant special steel (25–30% chromium and up to 15% nickel).

Among other things, chromium compounds are used as pigments in paints, printing colours, artists' colours, and similar products. Particularly popular are lead chromate and zinc chromate – both of them yellow – and the greenish chromium oxide. Tanning of leather involves chromium in the form of chrome alum, a double salt consisting of potassium sulphate and chromium sulphate. Within the chemical industry, the reactive chromium(VI) is used as an oxidising agent, particularly in the form of chromic sulphuric acid (potassium dichromate and concentrated sulphuric acid) and in catalysts.

1.3.2 Physical/chemical characteristics

The environmental and health-related characteristics of chromium and chromium compounds depend on the relevant oxidation level. As a result, a brief description of the electrochemical characteristics of chromium in the environment is given. The most significant physical-chemical characteristics of chromium and a number of inorganic chromium compounds are presented in tables 1.1 and 1.2.

Table 1.1
Physical-chemical characteristics for chromium and selected inorganic chromium compounds

Substance	Chromium	Chromium hydroxide	Chromium(III) oxide	Chromium(VI) oxide
CAS no.	7440–47-3	1308-14-1	1308-38-9	1333-82–0
Formula	Cr	$Cr(OH)_3$	Cr_2O_3	CrO_3
Oxidation level	0	3	3	6
Molar weight (g/mol)	51.996	103.0179	151.99	99.99
Density (g/cm^3)	7.2	-	5.22	2.70

[3] When products are registered with the Product Register, the consumption of chemical substances in products is often stated in the form of intervals. When calculating the quantities of chemical compounds, the highest value within these intervals has been used.

Melting point (°C)	1,857	-	2,435	195
Boiling point (°C)	2,672	-	4,000	decomposes
Solubility in water (g/l)	Insoluble	Insoluble	Insoluble	625 (20°C)

Table 1.2
Physical-chemical characteristics for chromium and selected inorganic chromium compounds

Substance	Chromium hydroxide sulphate	Lead(II) chromate 1)	Barium chromate	Sodium dichromate
CAS no.	12366-95-7	7758-97-6	10294-40–3	10588-01–9
Formula	$Cr(OH)(SO_4)$	$PbCrO_4$	BaCrO4	$Na_2Cr_2O_7$
Oxidation level	3	6	6	6
Molar weight (g/mol)	165.06	323.19	253.32	261.9673
Density (g/cm^3)	-	6.12	4.50	2.35
Melting point (°C)	-	844	decomposes	356.7
Boiling point (°C)	-	decomposes	-	400
Solubility in water (g/l)	-	0.000058 (25°C)	0.0044 (28°C)	1,800 (25°C)

1) Alkaline lead chromate (18454-12–1; 1344-38-3) also occurs.

1.3.3 Electro-chemicals characteristics

Chromium occurs within the oxidation levels 3, 6 and 2, listed in order of decreasing stability. Cr(VI) can be reduced to Cr(III) by Fe(II). In all likelihood, soluble Cr(III) complexes are formed with the organic ligands. Similarly, Cr(VI) is reduced in soil with high humus contents and in connection with microbial activity.

The conditions for reduction of Cr(VI) are not good in surface water, in sea water, in aerobic soil and in sediment. Cr(VI) will, however, often be mobile. As a result, it may reach anaerobic areas (such as lower layers of sediment) where reduction can occur.

It is not very likely that oxidation of Cr(III) to Cr (VI) will occur in nature. Oxidation is only to be expected under aerobic conditions and when MnO_2 is present.

At pH< 1, Cr(VI) will appear as H_2CrO_4; at 2< pH <6 it will appear as an equilibrium between $HCrO_4$ and $Cr_2O_7^{2-}$, and at pH>7 it will appear as CrO_4^{2-}. Similarly, in acid liquids Cr(III) will appear as Cr^{3+}, $Cr(OH)^{2+}$, $Cr(OH)_2^{+}$, $Cr(OH)_3$ and $Cr(OH)_4^{-}$ as pH values increase. At pH>5, however, Cr(III) is deposited as $Cr(OH)_3$, even though complex formation with organic ligands may compete with this process, thereby increasing solubility. Chromium compounds are not volatile. In the atmosphere, they will mainly occur in association with aerosols and particles.

1.3.4 Classification of chromium compounds

The classification of chromium compounds on the basis of their inherent characteristics is of great significance to the use – and limitations on use – of the substances in question. Table 1.3 shows the classifications of the most frequently used chromium compounds.

Table 1.3
Classification of the most frequently used types of chromium and chromium compounds

Substance	Classification/labelling
Chromium(III) oxide	Not included in the List of Dangerous Substances
Chromium(VI) oxide	O, T, N, C, Carc1; R49–8–25–35–43–50/53
Chromium	Not included in the List of Dangerous Substances (2002)
Chromium hydroxide sulphate	Not included in the List of Dangerous Substances (2002)
Lead(II) chromate	T, N, Carc3, Rep1; R61–33–40–50/53–62
Potassium dichromate	T, N, Carc3, Mut2; R46–49–21–25–26–37/38–41–43–50/53
Sodium dichromate	O, Tx, N, Carc2, Mut2; R46–49–8–21–25–26–37/38–41–43–50/53
Ammonia dichromate	E, Tx, N, Carc2, Mut2; R46–49–1–8–21–25–26–37/38–41–43–50/53

Due to their classification as carcinogenic and mutagenic, chromium(VI) oxide, lead(II) chromate and the other chromates are all subject to a number of limitations on sale and use (The Danish Ministry of the Environment, 2000). The substances are not available in retail shops and may only be sold to buyers who submit requisitions in accordance with specific rules. Limitations have been introduced for the use of products which contain hexavalent chromium compounds. These limitations include a requirement for notification of the Danish institute for occupational safety and health, the National Working Environment Authority (the Ministry of the Environment, 1997). The limit value for chromic acids and chromates in the working environment is 0.005 mg/m^3. (National Working Environment Authority, 2000).

1.4 Prioritisation of the survey

The survey began with a prioritisation of the work to be done. This prioritisation was carried out on the basis of:

- General knowledge about the use and occurrence of chromium
- Hazardousness and potential exposure
- Chromium supply via goods and products

The results of this prioritisation are briefly outlined below.

1.4.1 Hazardousness and potential exposure

Chromium primarily occurs as metallic chromium and as chromium compounds, where chromium has an oxidation level of 3 or 6. The toxicological and eco-toxicological properties of chromium depend on the chemical combinations in question. Due to their high bio-availability and highly oxidising properties, Cr(VI) compounds are far more toxic to biological systems than Cr(III) compounds. This means that Cr(VI) compounds are far more hazardous than Cr(III) compounds (EU, 2000a). Generally speaking, metallic chromium is not available for absorption in organisms in nature and is generally held to present little hazard and little potential for exposure.

The risk of being exposed to chromium is particularly high for people working in industries where chemicals containing chromium are used. Cigarette smokers are also at risk[4]. For most people, however, food will be the greatest source of chromium intake (ATSDR, 2000). Occurrences of chromium in products can, however, lead to direct human exposure which is not work-related. Examples include chromium in dust from brake linings and cement dust. People working with wastewater from chromium-plating industries, tanning, textile industries and waste containing chromium also risk exposure. Chromium might occur in drinking water as the result of pipes made from alloys containing chromium in the supply system; this does not, however, seem likely, as such chromium alloys are very stable. Contamination from landfills is another possible source of chromium in drinking water. Finally, exposure to chromium may occur due to incineration of products which contain chromium, e.g. impregnated wood and fossil fuels (ATSDR, 2000).

As was the case for human exposure, the main source of potential environmental problems is exposure to Cr(VI) due to the toxic effects and high bio-availability of this substance. Cr(VI) is relatively stable in water, a fact which increases the risk of critical exposure. It is estimated that the aquatic environment is mainly subjected to exposure through wastewater from companies using chemicals which contain chromium, but household wastewater and atmospheric deposition can also be sources of exposure. Alloys containing chromium are not expected to cause significant exposure as far as the aquatic environment is concerned, as the chromium is firmly bound in these alloys. Small amounts of chromium may be released into the aquatic environment in connection with oxidation of steel alloys in water (rust).

Significant chromium exposure must be expected for organisms in soil due to leaching of chromium from impregnated wood, waste deposits/landfills and spills of chemicals containing chromium. Atmospheric deposition and wastewater sludge will also give rise to more diffuse exposure. It is expected that Cr(VI) in soil is rapidly reduced to Cr(III), and this reduces the risk of impacts (EU, 2000a). As was the case for the aquatic environment, release of chromium from alloys is held to be of little significance in terms of soil exposure.

To sum up, chromium exposure from alloys which contain chromium is regarded as unproblematic for human beings and the environment. It is estimated that environmental exposure mainly comes from impregnated wood and wastewater from industries using chemicals which contain chromium, as well as from disposal in the form of incineration and landfilling.

1.4.2 Chromium supply via goods and products

1.4.2.1 Statistics Denmark

Based on the information about use of chromium and chromium compounds appearing in various materials and products, the list of CN numbers (the Combined Nomenclature, Statistics Denmark) has been studied with a view to identifying product groups which may contain chromium.

Information on import, export and production has been obtained for the selected CN numbers. This information covers the years 1998, 1999 and 2000.

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[4] This path of exposure is not examined in more detail.

As far as possible, "tonnes" have been used as the preferred unit when collecting information on product quantities. For some product groups, however, Danish production is measured in other units (pieces or m^2). In such cases, the figures for production in tonnes are estimated on the basis of the assumption that values per weight unit are the same for goods manufactured in Denmark as for exported/imported goods. This approach could not be used with a few product groups. In those cases, weight per unit or m^2 has been estimated on the basis of actual testing and weighing or studies of the available literature. Worst-case scenarios were applied in all cases to make sure that chromium contributions from the relevant product groups were not underestimated.

The results of the preliminary data processing are presented as the supply of chromium within product groups (Table 1.4). The table also states the oxidation level for chromium within the various product groups and provides estimates of the potential exposure and hazardousness.

Table 1.4
Supply of chromium within product groups, oxidation levels (stated as 0, II or VI) and estimates of the potential exposure and hazardousness (ranked as L for Low, M for Medium or H for High).

Product group	Chromium supply[2] [tonnes Cr/year]	Oxidation level	Exposure	Hazardousness
Iron and steel and goods made from iron and steel[1]	22,567	0	L	L
Copper and goods made from copper	782	0	L	L
Aluminium and goods made from aluminium	479	0	L	L
Accelerators, etc.	354	II VI	H	H
Pigments	351	III VI	M	M
Chromium compounds	224	III VI	M–H	M–H
Firebricks	204	III	M	L
Chromium ore and concentrates thereof	201	III VI	M	M
Leather and leather goods	179	III	M–H	M
Textiles	17	III VI	M–H	M
Fossil fuels etc.	10	III VI	L	L
Total	25,368			

1) Chromium-plated iron and steel products are included in this product group
2) Preliminary calculation of the chromium supply in Denmark

The results of the preliminary data processing indicate that chromium in alloys is the most significant category: iron and steel, copper, aluminium and goods made from these metals. Next in line is chromium in the form of chemical compounds: accelerators etc., pigments and chromium compounds. The ranking of specific products indicates that special attention should be paid to stainless steel sheets (>600 mm>), pipes and hollow profiles, tanks, vats and similar containers, products made by means of hot rolling, wire mesh, and copper and copper products.

1.4.2.2 The Product Register

Three different searches of the Product Register were made:

1. A search for substances containing chromium

2. A search for import, export and production of substances containing chromium (inventory as at 1999, 2000 and 2001[5]); the supply was calculated and minimum and maximum values have been given
3. A search for the contents of specific chromium compounds in specific goods/functions

The first part of the search resulted in a list of approximately 900 names of substances which contain chromium. The second part of the search revealed that notification of use has been submitted for approximately 130 of these substances. Statistics on the supply of the 130 substances in question have been converted into a value for chromium supply, based on maximum chromium content in the relevant compounds. Thus, the figure for chromium supply through chromium compounds represents the maximum quantities possible according to the information in the Product Register. Table 1.5 illustrates the supply for the 15 chromium compounds accounting for the greatest supply, ranked in order of the quantities supplied. We see that chromium(III) oxide, chromium(VI) oxide, chromium, "not specified"[6] and lead(II) chromate account for more than 95% of the chromium supply registered in the Product Register.

[5] The information on quantities found in the Product Register is effectively updated regularly, as companies submit information on expected annual production, etc. This information is used in the following years until the company submits new information as a result of significant changes.
[6] The identity of this substance is confidential, as less than three instances of use of this substance were reported.

Table 1.5
Supply of the 15 chromium compounds accounting for the greatest supply in Denmark, calculated as an average of the supply during the period 1998–2000. The figures are based on statistics from the Product Register and reflect the maximum possible content.

Chromium compound	CAS no.	Oxidation level	Supply in Denmark (tonnes Cr/year)	Percentage of total supply
Chromium(III)oxide	1308–38–9	III	635.54	60%
Chromium(VI)oxide	1333–82–0	VI	338.63	32%
Chromium	7440–47–3	0	40.74	4%
				1%
Lead(II)chromate	7758–97–6	VI	9.24	1%
Chromate (1-), hydroxyl (2-hydroxy-3(((2-hydroxy-3-nitrophenyl)methylene)amino)-5-nitrobenzenesulfonato (3-))-, hydrogen, mixed with 3-((2-ethylhexyl)oxy)-1-propanamine (1:1)	85455-32–9	VI	8.85	1%
Xanthylium, 9-(2-carboxyphenyl)-3,6-bis(diethylamino)-, (2,4-dihydro-4-((2-hydroxy -5-nitrophenyl)azo)-5-methyl-2-phenyl-3 H-pyrazol-3-onato(2-))(2-((4,5-dihydro-3-methyl-5-oxo-1-phenyl-1h-pyrazol-4-yl)azo)benzoato(2-)) Chromate (1-)	84989-45–7	VI	4.87	<1%
Chromate (1-), *bis*(methyl (7-hydroxy -8-((2-hydroxy-5-(methylsulfonyl)phenyl)azo)-1-naphtalenyl)carbarnato(2-))-, sodium	71839-85-5	VI	4.39	<1%
Barium chromate ($BaCrO_4$)	10294-40–3	VI	3.3	<1%
Chromate (1-), *bis*(2-(3-chlorophenyl)-2,4-dihydro-4-((2-hydroxy-5- (methylsulfonyl)azo)-5-methyl-3 *H*-pyrazol-3-onato(2-))-, sodium	51147-75-2	VI	1.92	<1%
				<1%
				<1%
Chromium carbide (C_2Cr_3)	12012–35-0	III	0.73	<1%
Chromium hydroxide ($Cr(OH)_3$)	1308-14-1	III	0.69	<1%
Sodium dichromate ($Cr_2Na_2O_7$)	10588-01–9	VI	0.61	<1%

The grey areas have been blanked out due to confidentiality. This is to say that they have been reported within less than 3 functions.

These are followed by a number of less frequently seen hexavalent chromium compounds: potassium dichromate (0.51 tonnes of chromium), zinc chromate (0.35 tonnes of chromium), sodium dichromate dihydrate (0.17 tonnes of chromium) strontium chromate (0.13 tonnes of chromium), ammonia dichromate (0.12 tonnes chromium), and more.

The 15 most frequently seen chromium compounds are used in 85 different products/functions. These can be divided into a number of general groups:

- Accelerators, hardeners, catalysts, oxidation agents, chemical reagents
- Grouts and fillers
- Surface treatments
- Tanning agents
- Corrosion inhibitors
- Glue

- Paints, varnishes, etc.
- Wood preservation

The supply of chromium registered in the Product Register only covers part of the total supply, as it only includes those raw materials which are subject to a duty to submit notification. This is to say that the statistics include chromium pigments used to manufacture paint in Denmark, but they do not necessarily include imported paints made from pigments which contain chromium. This also applies to tanning agents and imported leather tanned by means of chromium. As a result, the figures from Statistics Denmark and the Product Register do not necessarily correspond in all cases. In addition to this, Statistics Denmark and the Product Register use different categories for goods. This means that it is rarely possible to match information about product supply from Statistics Denmark with information about chromium content from the Product Register. The information from the Product Register has mainly been used for guidance when identifying areas of use and specific uses within known areas of use (e.g. additives used to make paints glossy). The information from the Product Register has been carefully reviewed to make sure that significant uses are not overlooked.

1.4.3 Summary

The survey has been prioritised as illustrated in Table 1.6. This prioritisation is based on the discussion on hazardousness and exposure outlined above, as well as on information from Statistics Denmark and the Product Register.

Table 1.6
Survey priorities

Area of use	Level
Alloys – iron, stainless steel	General
Alloy/impurity – aluminium/copper	General
Chromating/galvanisation/surface treatment	Detailed
Wood preservation	Detailed
Pigments/corrosion inhibitors	Detailed
Leather tanning	Detailed
Laboratory chemicals/oxidation agents	Detailed
Accelerators/catalysts/hardeners	Detailed
Corrosion protectors	Detailed
Electronic storage industries	General
Textiles	Detailed

Electronics and glass are examples of product groups which were not accorded high priority on the basis of the initial survey. It may be relevant to include these product groups in connection with any subsequent studies.

1.5 International market and development trends

According to information from the international industry association for chromium (International Chromium Developing Association – ICDA), approximately twenty countries in the world extract chromium today. Of these, South Africa accounts for almost half of all the chromium extracted (47%), Kazakhstan accounts for 18%, and India accounts for 13%. The total extraction carried out in Brazil, Finland, Turkey and Zimbabwe amounts to 16%, and a total of 12 other countries account for the remaining 6%. In total, approximately 15 million tonnes of chrome iron ore were extracted in 2000 (ICDA, 2002).

According to the ICDA, chromium consumption worldwide is distributed as follows: 85% of all chromium is used within the metal industry, 8% is used within the chemical industry, and 7% is used for fireproof products and foundries.

2 Chromium use in Denmark

Chromium is not used in pure form as a metal. Instead, it occurs as a surface treatment for other metals and plastics (chromium plating), as an alloy metal, or as an impurity in a number of other metals. Here, attention is focused on:

- Iron and steel
- Aluminium
- Copper

Chromium also appears as an alloy metal or impurity in a number of other metals.

2.1 Iron and steel

Chromium is used as an alloy metal in ferrous chromium, a metal which contains very large amounts of chromium. It is also used in iron and various types of steel, primarily stainless steel. The use of metallic chromium in Denmark has been determined on the basis of information from Statistics Denmark on the registered foreign trade in Denmark and the registered sales in Denmark of products of Danish manufacture. The consumption of metallic chromium in industrial products has been determined on the basis of supply information from the Statistics Bank provided by Statistics Denmark. This information was divided into so-called Broad Economic Categories (BEC)[7]. The information from the Statistics Bank has been compared with information about stainless steel contents in various product types (The Danish EPA's Product Database). All figures are for the period 1998–2000. Table 2.1 shows the supply of metallic chromium on the basis of production, import and export of finished goods, raw materials and semi-finished goods made from iron, steel and ferrous chromium.

2.1.1 Products and semi-finished goods made from iron and steel

Ferrous chromium is a chromium-iron alloy with a chromium content of 60–65%. It is produced by reducing chrome iron ore with coke and/or silicon at high temperatures in furnaces. This alloy is primarily used in the manufacture of stainless steel, a process accounting for up to 90% of the total consumption of ferrous chromium.

The designation ***stainless steel*** covers a wide variety of alloys, including chromium steel (which contains 12–13% chromium), the widely used austenitic steel or 18/8 steel (18% chromium and 8% nickel), and particularly heat-resistant special steel containing 25–30% chromium and up to 15% nickel. Austenitic steel accounts for 70–90% of the stainless steel used in Denmark (Sandvik Steel Denmark, 2002; Avesta Polarit, 2002; Aco-drain, 2002).

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[7] Each Broad Economic Category comprises several product groups from the Combined Nomenclature.

As stainless steel contains relatively large quantities of chromium, certain significant product groups containing stainless steel have been included in the calculations of the metallic chromium supply in Denmark. Large portions of the finished goods which contain steel are included in calculations along with many other materials. As a result, the estimated flows in and out of Denmark are subject to considerable uncertainty.

The designation ***alloyed steel*** covers hundreds of steel types where steel is alloyed with other metals. The main reason for alloying steel is a desire for greater hardness and strength. Many types of alloyed steel contain chromium, but the relative quantities vary from 0.1% to 12.5%. A US study sets the chromium contents in the steel alloys used at 0.68±0.11% (US Bureau of Mines, 1994). It has not been possible to confirm this figure with people within the iron and steel industry in Denmark. The reason was that none of the people asked felt able to offer an estimate for the average chromium content in alloyed steel due to the many types of alloys found in the market. As the information from Statistics Denmark on import, export and production of alloyed steel does not provide any details about the types of alloyed steel found within the individual product groups, we have chosen to apply an average chromium content of 0.5–0.8% in alloyed steel.

The group of ***iron and unalloyed steel*** which is ***chromium-plated*** comprises products which are coated with a layer of chromium.

Iron and unalloyed steel contains chromium as an impurity. It is estimated that the chromium content due to such impurities is in the region of 0.05%. (Det Danske Stålvalseværk, 2002a/b).

Table 2.1
Import, export and Danish production of goods, raw materials and semi-finished goods

Raw material/semi-finished goods/finished goods:	Cr content 1) %	Production tonnes/year	Import tonnes/year	Export tonnes/year	Supply tonnes Cr/year
Ferrous chromium Alloys	60–65%	0	240	836	-358–-387
Stainless steel					
Rods and profiles	17–18%	4,653	19,895	6,885	3,003–3,179
Wire	17–18%	1,240	3,508	1,196	934–989
Plates, sheets, strip,	17–18%	0	81,924	16,768	11,077–11,728
foil	17–18%	17,360	26,618	25,597	2,753–2,915
Pipes and tubes	17–18%	203	361	109	77–82
Semi-finished goods	17–18%	2,001	8,505	4,720	998–1,057
Other goods					
Finished goods containing stainless steel					
Agricultural and dairy machinery	2.04–1.52%	23,329 3)	40,417	50,064	279–1,576
Ships	0.17–0.36%	223,998	189,094	289,436	210–445
Aeroplanes	0.85–0.9%	0 3)	445	718	-2.2–-2.4
Railway supplies and motor vehicles for commercial use 2)	0.17–0.36%	420,375	189,737	92,961	879–1,862
Passenger cars	0.17–0.36%	1,340 3)	219,796	23,372	336–712
Pleasure crafts, caravans and other vehicles for private use	0.17–1.26%	7,947 3)	16,089	2,464	37–272
Tools, knives, cutlery, etc. 4)	5)	8,537	16,397	7,663	733–837

Alloyed steel					
Rods and profiles	0.5–0.8%	3,291	19,161	201	109–174
Wire	0.5–0.8%	25,572	5,337	20,257	378–605
Plates, sheets, strip, foil	0.5–0.8%	0	36,806	3,012	169–270
Pipes and tubes	0.5–0.8%	124,852	479,211	420,301	711–1,138
Semi-finished goods	0.5–0.8%	4,354	2,609	672	31–50
Other goods	0.5–0.8%	53,563	50,475	49,559	272–435
Iron and unalloyed steel (chromium plated) Plate, sheets, strip, foil	0.05–1.5%	0	4,634	639	2–60
Iron and unalloyed steel					
Rods and profiles	0.05%	274,950	374,408	193,862	228
Wire	0.05%	15,526	39,608	1,391	27
Plate, sheets, strip, foil	0.05%	414,507	1,261,125	588,075	543
Pipes and tubes	0.05%	0	2,002	128	1
Semi-finished goods	0.05%	66,354	46,498	76,799	18
Other goods	0.05%	165,157	216,300	97,770	166
Total					23,237–28,532

1. The intervals given for chromium content have been determined on the basis of literature and information from people within the iron and steel industry (Det Danske Stålvalseværk, 2002a; Sandvik Steel Denmark, 2002; Avesta Polarit, 2002; Stålforeningen, 2002). As regards "finished goods made from stainless steel", the contents of stainless steel in the products have been determined on the basis of the Danish EPA's Product Database (Hansen, 1995). For passenger cars, the contents have also been determined on the basis of information about typical metal contents in passenger cars (American Metal Market, 2000). The contents of stainless steel have been set as follows: Agricultural and dairy machinery 12–64%, ships 1–2%, aeroplanes 5%, railway supplies etc. 1–2%, passenger cars 1–2%, pleasure crafts etc. 1–7%.
2. Including trucks and buses
3. The figures for production have been converted from pieces to tonnes on the basis of an assumption that the conditions applying to exports also apply to production. This assumption is based on the fact that a large part of the production is exported.
4. The group comprises information from Statistics Denmark about CN nos. 8201–8214 and 82152010 for 1998–2000 (see Appendix A). For several CN numbers, the quantities in tonnes are based on statistics provided in DKK or pieces. This means that the figures within this group are somewhat uncertain.
5. The content of stainless steel has been assessed for each individual CN number in the group (see Appendix A).

Stainless steel is not produced in Denmark. Scrap stainless steel is exported in order to be used as a raw material once again. According to Avesta Polarit (2002), the total production of new stainless steel is made up of 95% recycled steel and 5 % new raw iron.

Det Danske Stålvalseværk was the only manufacturer of steel in Denmark. Approximately 75% of the total quantities produced there were used for export (Det Danske Stålvalseværk, 2001). This steel was made from 90% scrap steel and 10% new raw iron (Det Danske Stålvalseværk, 2002a). The scrap steel primarily comes from Danish scrap merchants, whereas the raw iron comes from Russia and Poland. A total of 20% of the steel used in Denmark comes from the Stålvalseværk, while the rest is imported (Det Danske Stålvalseværk, 2002a; Stålforeningen, 2002).

Scrap metal and iron ore only contains small quantities of chromium – around 0.01% (Kjeldgaard, 1991). Naturally, this chromium will reappear in the steel materials made. Suppliers of scrap steel are good at sorting out scrap made from alloyed steel and cast steel, as these types of steel attract higher prices. This means that the chromium content in the steel produced remains low. As the steel is manufactured, it is monitored for levels of chromium and other substances. If the chromium levels are too high, the steel is diluted by means of additional raw iron (Det Danske Stålvalseværk, 2002a). During the production process, ferrous chromium is added to harden the steel. In 2001, for example, ferrous chromium was added in quantities corresponding to approximately 580 tonnes of pure chromium. Chromium sand is also used to transport the finished steel out of the furnaces. In 2001, a total of 170 tonnes of chromium sand was used, corresponding to approximately 16 tonnes of pure chromium (Det Danske Stålvalseværk, 2002b).

In 2001, Det Danske Stålvalseværk produced approximately 750,000 tones of raw steel. Approximately 665,000 tonnes were used for steel products (Det Danske Stålvalseværk, 2002b). Table 2.2 presents the mass balance for heavy metals in general and specifically for chromium per tonne of raw steel in connection with steel production.

Table 2.2
Mass balance for chromium and heavy metals in general in connection with production of 1 tonne of raw steel (calculated on the basis of Det Danske Stålvalseværk, 2001; 2002b)

	Heavy metals, total 1)	Chromium 2)	Unit
Input	11.0	1.13	Kg
Reuse	5.9	0.21	Kg
Steel	4.3	0.91	Kg
Landfill	0.8	0.003	Kg
Air	2.4		g

1. The designation "heavy metals" encompasses chromium, copper, nickel, cobalt, zinc, arsenic, molybdenum, cadmium, tin, mercury and lead. The Stålvalseværk has not specified the exact share accounted for by chromium. We do, however, know that copper and zinc account for 75% of the total quantities of heavy metals on the input side.
2. This information is for 2001.

This means that production of 750,000 tonnes of raw steel entails disposal / deposit of 2.25 tonnes of chromium. Table 2.3 shows the discharges of chromium into water associated with production of sheets and bars, respectively, at Det Danske Stålvalseværk.

Table 2.3
Discharges of heavy metals into water associated with production of steel at Det Danske Stålvalseværk (Det Danske Stålvalseværk, 2001)

Steel materials Unit	Steel sheets g/tonne	Bar steel g/tonne
Heavy metals (including chromium)	0.7	0.5

In 2000, a total of 326,000 tonnes of steel sheets and 223,000 tonnes of bar steel was produced. This corresponds to discharges of heavy metals into water in the region of 0.34 tonnes per year. We do not know the exact quantities of chromium involved, but on the basis of the information in Table 2.2 it is estimated that chromium accounts for between 5 and 10% of all the heavy metals. This corresponds to discharges of between 0.017 and 0.034 tonnes chromium each year. The chromium content of the landfill at Det Danske Stålvalseværk has not been assessed.

If the same assumption is applied to a calculation of chromium emissions to air, we arrive at the following figure: emissions of 0.12–0.24 g per tonne raw steel or 0.09–0.18 tonnes chromium per year from production at Det Danske Stålvalseværk.

2.2 Aluminium

Metallic aluminium may contain small amounts of chromium, mainly in the form of impurities. In the Combined Nomenclature (CN), metallic aluminium is divided into unalloyed and alloyed aluminium, and these categories are divided into five product groups: bars, profiles, wire, sheets/strip/foil and pipes. In the CN, one of the characteristics of unalloyed aluminium is that is has a limit value of 0.1 per cent (by weight) for ingredients other than aluminium. Naturally, this includes chromium. Alloys of aluminium are defined by having greater contents of other ingredients than unalloyed aluminium.

A life cycle analysis of chromium carried out on behalf of US authorities included calculations of the chromium contents in aluminium (US Bureau of Mines, 1994). The study used two methods to calculate the average chromium content of aluminium in general. One of these methods used an average of the chromium contents in aluminium alloys, categorised by alloy class, and this yielded a result of 0.02–0.06% chromium. The other method was based on the average chromium content in the aluminium alloys actually used. The result of this method was 0.13–0.21% chromium. It is, however, believed that the latter method results in too high a chromium content, as it only includes types of aluminium for which the chromium contents have been specified.

Based on the chromium contents in aluminium mentioned above, it is assumed that the chromium contents for unalloyed and alloyed aluminium as a whole are between 0.02% and 0.1%.

Table 2.4 shows information from Statistics Denmark about import, export, production and supply of aluminium for the years 1998–2000. This information is listed by CN nos. in Appendix B.

Table 2.4
Import, export and production of raw materials and semi-finished goods made from metallic aluminium (Statistics Denmark, 2001b)

Unit	1998 tonnes	1999 tonnes	2000 tonnes	Average Tonnes
Import [I]	196,704	200,658	217,993	205,118
Export [E]	132,654	137,368	140,649	136,890
Production [P]	90,935	92,373	113,280	98,863
Supply [I–E+P]	154,985	155,663	190,624	167,091
Corrected supply 1)	115,500	116,000	142,000	124,500

1. The supply has been corrected to avoid including the same amounts twice, as some of the quantities used in production also appear in the import figures. This correction has been carried out on the basis of (Hansen *et al.*, 1999)

In a mass flow analysis made for aluminium for 1994, the supply of raw materials and semi-finished goods made from metallic aluminium and aluminium alloys is calculated to be 140,095 tonnes (Hansen ***et al.***, 1999). Compared to the supply for 1994, the average supply for 1998–2000 is approximately 20% higher. This is consistent with the fact that there has been a general increase in the use of aluminium (the Secretariat for Aluminium and Environment, 2002).

Table 2.5 shows the mass balance for aluminium in Denmark as an average of 1998–2000. The figures have been rounded up. This mass balance was established on the basis of an assumption that the aluminium balance has remained unchanged in 1998–2000 compared to 1994. This assumption is subject to some uncertainty, but is deemed to be acceptable. This is because the contribution from aluminium to the mass flow of chromium in Denmark is of minor significance compared to other sources of chromium, partly due to the amounts involved, and partly because the chromium involved is metallic-bound chromium which will not appear as hexavalent chromium if it enters the environment. In order to counteract the uncertainty associated with extrapolating current values on the basis of 1994 figures, the interval quantities include the 1994 situation ***and*** a 20% increase in quantities.

Table 2.5
Mass balance for aluminium in Denmark 1998–2000 (Statistics Denmark, 2001b; Hansen *et al.*, 1999)

Mass balance Unit	Aluminium Tonnes	Of which chromium Tonnes
Consumption	73,000–128,400	14.6–1.28
Net import	54,400–106,100	11–1.06
Reuse	18,600–22,300	4–22
Accumulation	29,800–47,600	6–48
Net export as scrap	8,000–17,900	2–18
Landfilling	14,800–37,000	3–37
Emission to soil	590–1,100	0.1–1
Emission to air	10–60	0–0.1
Discharges to water	1,200–2,200	0.2–2

2.3 Copper

Like aluminium, metallic copper contains certain amounts of chromium. In the Combined Nomenclature (CN), copper is divided into the following eight product groups: refined copper; copper alloys; master alloys; bars and rods; profiles, wire; plates/sheets/strip/foil; and tubes and pipes. The contents of copper within the product groups vary from approximately 12% for copper foil to 99.9%, for example, for refined copper pipes.

In the Combined Nomenclature, refined copper is characterised by having a limit value for chromium of 1.4% by weight, whereas copper alloys and master alloys may have higher chromium contents. The chromium contents are not described in any more detail for the rest of the product groups.

The chromium content of copper has been calculated in the US authorities' life cycle analysis (US Bureau of Mines, 1994). These calculations are partly based on the average chromium contents of copper alloys based on alloy classes. They are also based on the average chromium content of the actual quantities consumed of copper alloys with specific chromium contents. In both cases, the result of the calculations was chromium contents of 0.024–0.026%.

As it has not been possible to distinguish between different types of copper, it has been assumed that refined copper and copper alloys in general have a chromium content of 0.024–0.026%.

The table below shows statistics on the import, export and production of raw materials and semi-finished goods made from metallic copper. This information is given by CN nos. in Appendix C.

Table 2.6
Import, export and production of raw materials and semi-finished goods made from metallic copper (Statistics Denmark, 2001b)

	1998 Tonnes	1999 Tonnes	2000 Tonnes	Average Tonnes	Average for 1998–1999 Tonnes
Import [I]	83,434	70,124	76,364	76,641	76,779
Export [E]	40,501	44,831	48,961	44,765	42,666
Production [P]	5,383	5,846	61,658	23,966	5,615
Supply [I–E+P]	48,316	31,139	89,061	56,172	39,728
Corrected supply 1)					35,000–40,000

1) As it has not been possible to ascertain whether certain quantities have been included twice, the supply is given as an interval in order to take this into account.

In a mass flow analysis for copper made for the year 1992, the supply of raw materials and semi-finished goods made from metallic copper is given as being in the region of 39,400–40,100 tonnes (Lassen ***et al.***, 1996). Compared to the figures for 1998–2000, this is consistent with the information for 1998 and 1999, whereas a very significant deviation can be seen for the year 2000. This deviation concerns the value of production. As a result, the values for 2000 will not be used. This means that the average value is based solely on the values for 1998 and 1999.

Table 2.7 below shows the mass balance for copper in Denmark. The figures are rounded up and constitute an average of 1998 and 1999 values. The mass balance has been established on the basis of an assumption that the copper balance has remained unchanged in 1998–1999 in relation to 1992. Such an assumption entails a certain level of uncertainty, but is deemed to be acceptable as the supply of copper in society in general has remained unchanged. In addition to this, the contribution made by copper to the mass flow of chromium in Denmark is of minor significance compared to other sources of chromium, partly due to the amounts involved, and partly because the chromium involved is metallic-bound chromium which will not appear as hexavalent chromium if it enters the environment.

Table 2.7
Mass balance for copper in Denmark 1998–1999 (Statistics Denmark, 2001b; Lassen *et al.*, 1996)

Mass balance Unit	Copper Tonnes	Of which chromium Tonnes
Consumption	28,000–42,000	7–10
Net import	26,000–33,000	6–9
Reuse	9,000–10,000	2–3
Accumulation	5,000–16,000	1–4
Net export as scrap	15,000–24,000	4–6
Landfilling	3,800–7,400	1–2
Emission to soil	500–700	0.1–0.2
Emission to air	2–7	0
Discharges to water	40–80	0

2.4 Summary

Chromium occurs as an alloy metal and as an impurity in iron, aluminium and copper. Table 2.8 shows the consumption and dissemination of chromium in connection with use of iron and steel, aluminium and copper in Denmark. This calculation is based on a general calculation of the consumption of iron and steel and an update of previous mass flow analyses made for aluminium (Hansen ***et al.***, 1999) and for chromium (Lassen ***et al.***, 1996).

Table 2.8

Use	Consumption	Air	Water	Soil	Reuse	Dangerous waste	Waste treatment
Iron and steel							
– goods made from iron and steel	21,000–25,000	–	–	–	–	–	–
– goods made from other steel	2,700–3,700	–	–	–	–	–	–
– steel production	600	0.09–0.18	0.017–0.034	–	–	–	2.25
Aluminium	11–106	0–0.1	0.2–2	0.1–1	4–22	–	13–37
Copper	6–9	0	0	0.1–0.2	2–3	–	1–2
Total	24,300–29,400	0.09–0.28	0.22–2.03	0.2–1.2	6–25	–	16–41

3 Use of chromium compounds in Denmark

3.1 Introduction to chromium compounds

Chromium is used in many contexts within the chemical industry. For example, chromium compounds are used for surface treatment in order to prevent corrosion, to improve product durability, in tanning and to manufacture pigments. According to the information available in the Product Register, the chemical industry uses approximately 130 different chromium compounds to manufacture a wide range of products (the Product Register, 2001). As there is no central source of information on consumption of individual chromium compounds, it has not been possible to determine the exact quantities of chromium used within the chemical industry and other industries. For example, the Danish confederation of chemical industries, which numbers 47 members, has no central information about its members' products. Nor does it possess information on the use of chemicals containing chromium among its members.

Table 3.1 shows an overview of the information available from Statistics Denmark on the total import, export, production and supply of chemicals containing chromium during the period 1998–2000.

Table 3.1
Import, export, production and supply of chemicals containing chromium, 1998–2000 (Statistics Denmark, 2001b)

Substance name	Import Tonnes/year	Export Tonnes/year	Production Tonnes/year	Supply Tonnes/year	Chromium, percentage of total molar weight	Chromium quantities Tonnes/year
Chromium oxides (III and VI) and chromium hydroxide	438	5	0	433	51–68	26 1)
Chromium sulphate	2	1	0	1	17	0.17
Lead chromate and zinc chromate	0	0	0	0		0
Sodium dichromate	6	0	0	6	24	1.44
Potassium dichromate	0	0	0	0	35	0
Other dichromates	3	0	0.05	3	20–40	0.6–1.2
Carbides from chromium	0	0	0	0		0

1) Calculated in Table 3.3

When we compare the information available from Statistics Denmark about the supply of oxides and hydroxides of chromium with the information in the Product Register about the expected maximum import, export and production (i.e. supply), we arrive at an indication of the relative shares accounted for by individual substances. See Table 3.2 below.

Table 3.2
Expected relative shares accounted for by oxides and hydroxides of chromium (%)

Substance name	Expected supply 2001 Tonnes	Expected share %
Chromium(III) oxide	501–928	52.3
Chromium(III) hydroxide	0–1.4	0.05
Chromium(VI) oxide	650–651	47.6
Chromium(VI) hydroxide	0	0

Table 3.2 shows that the group consists almost entirely of chromium oxides. It has been assumed that the contributions to the mass balance made by the individual substances can be established by multiplying the supply by the expected percentage indicated above, and then multiplying this figure by the share of the molar weight accounted for by chromium in the relevant substance. See Table 3.3.

Table 3.3
Chromium quantities

Substance name	Supply 1) Tonnes/year	Chromium's share of the molar weight %	Chromium quantities Tonnes/year
Chromium(III) oxide	226	68	154
Chromium(III) hydroxide	0.21	51	0.11
Chromium(VI) oxide	206	52	107
Total			261

1) The supply is calculated on the basis of supplies of chromium oxide and chromium hydroxide – see Table 3.1 – and the expected shares accounted for by the various compounds – see Table 3.2.

The use of chromium compounds is described for the following areas:

- Surface treatment
- Pigments
- Impregnation agents
- Corrosion inhibitors
- Tanning agents for leather
- Accelerators, catalysts, hardeners
- Textiles
- Electronic storage
- Laboratory chemicals
- Other uses

3.2 Surface treatment

The information on surface treatment presented in this section is based on Dahl & Løkkegaard (2000) and Dahl (2002).

Chemical chromium compounds are widely used for metallic surface treatment. Most processes involve the use of Cr(VI) in the form of chromium acid (H_2CrO_4), but in a few cases, chromium may also be added in the form of sodium dichromate. The most common processes are:

1. Chromium plating (typically a 0.25 µm layer of chromium on top of nickel. Also known as decorative chromium plating)
2. Hard chromium plating (a 10–700 µm layer of chromium applied directly on top of steel)

3. Black chromium plating (a 0.1–2.0 µm layer of black chromium applied on top of a layer of nickel)
4. Chromating of zinc surfaces (also known as passivation)
5. Chromating of aluminium (usually as preparation for powder lacquering, possibly finishing)
6. Chromic acid pickling of aluminium
7. Chromic acid pickling of plastic
8. Anodising of aluminium (in strong chromium(VI) oxide)
9. Chromium passivation after phosphatising
10. Miscellaneous processes

A total inventory of chromium consumption, utilisation and waste is shown in Table 3.4.

Table 3.4
Chromium consumption and waste associated with surface treatment in Denmark

Process	Number	Production m^2/year	Chromium compound	Consumption Kg Cr/year	Waste Kg Cr/year	To sewer Kg Cr/year	On goods Kg Cr/year
Chromium plating	60–75	936,000	CrO_3	5,200	3,585	10.0	1,615
Hard chromium plating	Approx. 8	9,530	CrO_3	8,220	2,644	0.2	5,576
Black chromium plating	Approx. 5	164,000	CrO_3	2,756	2,403	0.2	353
Yellow chromating of zinc	70–75	5,119,000	CrO_3	11,873	9,825	13.0	2,048
Blue passivation of zinc	90–100	2,595,000	$Cr(NO_3)_3$	1,201	1,123	25.6	78
Olive/black chromating of zinc	15	701,000	CrO_3	2,844	2,178	3.5	666
Yellow chromating of aluminium	30	3,500,000	CrO_3	900	270	17.5	630
Green chromating of aluminium	20	3,500,000	CrO_3	1,145	515	17.5	630
Chromic acid pickling of aluminium	10	20,000	CrO_3	250	250	0.1	0
Chromic acid pickling of plastic	1	110,000	CrO_3	3,120	3,119	1.0	0
Chromic acid anodising of aluminium	Approx. 5		CrO_3	100	100	0.1	0
Chromium passivation after phosphatising	30		CrO_3	100	95	0.2	5
Total				37,709	26,107	89	11,601

3.2.1 Chromium plating

With decorative chromium plating, a thin layer of chromium (approximately 0.25 µm) is added onto a layer of nickel (10–15 µm) by means of electrolysis. The process takes place in a solution of CrO_3 (200 g/l) with H_2SO_4 (4 g/l) and small amounts of catalyst. The drag-out of bath chemicals is large compared to the consumption, but most companies have become good at collecting the drag-out in one or more still rinse tanks which can be used to replenish the bath, replacing what is lost due to evaporation from the 35–40°C bath. Without any recovery, the utilisation of CrO_3 would be as low as 2–5%, whereas recovery typically leads to recovery rates of 20–98% depending on the recovery system used.

It is estimated that a total of 75 companies in Denmark carry out decorative chromium plating (nickel plating + chromium plating), and approximately 80% of all nickel-plated surfaces will also be finished by means of chromium plating. If we assume that approximately 125 tonnes of nickel anode is used each year in Denmark, this means that a total surface of 1,170,000 m^2 is coated by a layer of 12 µm nickel. If we take 80% of this figure, we arrive at a total surface of 936,000 m^2 which is chromium plated after first being nickel plated. If we assume that the average layer of chromium applied is 0.25 µm, this corresponds to a theoretical consumption of CrO_3 of 3,105 kg. Two companies alone represent almost 45% of all the surface treatment carried out, consuming almost 6 tonnes of chromic acid. Both of these companies use disproportionate amounts of chromium(VI) oxide: theoretically, their consumption should be 1,124 kg, but in actual fact they consume 5,750 kg. The main reason for this is a very low recovery rate for chromium(VI) oxide, particularly at one of the two companies.

If we assume that the average recovery rate for the other manufacturers – which account for the remaining 55% of all production in Denmark – is 40%, the total consumption of chromium(VI)oxide can be estimated to be approximately 10,000 kg/year.

We can theoretically say that out of 10,000 kg chromium(VI) oxide, approximately 3,105 kg (= 1,615 kg Cr) end up on the actual goods. The rest ends up in wastewater or at Kommunekemi as discarded baths or semi-concentrates. We estimate that 25% ends up with Kommunekemi, whereas the rest ends up in the companies' treatment plants. Here, most of the chromium(VI) oxide is deposited to form filter cakes. These filter cakes are sent to Kommunekemi or for reprocessing abroad. A small part is discharged into the sewer system with wastewater. Today, such discharges of wastewater will typically feature chromium concentrations of 0.2 mg/l. The 936,000 m^2 treated surface mentioned above will probably correspond to wastewater quantities of 50,000 m^3 (at a water consumption rate of 50 l/m^2). We can then say that 50,000 m^3 wastewater containing 0.2 mg/l corresponds to 10 kg of chromium per year. This is to say that 10 kg of chromium is discharged into Danish sewers every year.

In principle, chromium baths can last forever. However, baths will be discarded from time to time because of contamination (typically due to excessive contents of alien metals). Even so, it is unlikely that more than 10 m^3 baths are discarded each year. With chromium(VI) oxide contents of 200 g/l, this corresponds to 2,000 kg/year.

3.2.2 Hard chromium plating

Hard chromium plating means that a thick layer of chromium (from 10 to 700 µm) is added directly onto steel by means of electrolysis. This process takes between ½ and 24 hours. The bath typically consists of CrO_3 (300 g/l) and H_2SO_4 (3 g/l), and the bath temperature is typically 55°C. Due to very considerable evaporation losses and low drag-out with the goods (due to long retention times), the goods will often be rinsed with a little deionised water directly above the bath. The goods and tools will then subsequently be rinsed in still rinse tanks. As a result, the drag-out of chromium(VI) oxide to rinsing water and treatment plants is very low, and the quantities of water used for rinsing are similarly low.

Approximately eight Danish companies carry out hard chromium plating, and three of these account for approximately 70% of the total production. Based on interviews with these three companies, the total chromium consumption, etc., associated with hard chromium plating can be estimated for all of Denmark. These estimates are shown in Table 3.5.

Table 3.5
Chromium consumption and chromium waste associated with hard chromium plating in Denmark

Subject	Comment
Chromium consumption	18,600 kg CrO_3 per year
Production	The thickness of the layers applied varies greatly (10–700 µm) depending on the intended use of the goods. If the average thickness is set at 125 µm, we arrive at a total hard chromium plated surface of 9,530 m^2.
Bath lifetime	4–10 years (some companies never change their baths). We assume that 15% of the total consumption of chromic acid is used for new baths to replace old ones. Discarded baths are sent to Kommunekemi.
To wastewater	On average, 2% of the chromium(VI) oxide purchased by companies ends up in their wastewater. This figure can, however, vary from 0.1 to 4% depending on the rinsing system used by the relevant companies.
To sewers	Most Danish companies discharge very small quantities of wastewater into sewers (the occasional 1 m^3), but one company carries out ongoing discharge and treatment of its rinsing water containing chromium. It is estimated that a maximum of 1,000 m^3 wastewater is discharged each year, and that the maximum chromium content is 0.2 mg/l. This corresponds to a total of 0.2 kg a year.

3.2.3 Black chromium plating

Black chromium plating means that a layer of black chromium (0.1–2.0 µm) is added onto a layer of nickel by means of electrolysis. Approximately five Danish companies carry out black chromium plating. Just one of these companies uses 85% of all the chromium(VI) oxide used for this process in Denmark, and accounts for 91% of the total surfaces treated in this manner. The chromium bath contains CrO_3 (340–375 g/l) and small amounts of catalyst.

At the main manufacturer described above, substantial amounts of the chromium baths (approximately 90% of the total consumption of chromic acid) are discarded due to contamination. The losses are less substantial among the other companies and are primarily caused by drag-out with the goods. As the bath temperature is low (18–20°C), not much chemical can be returned from the interim rinsing phase. This means that the rinsing water must be taken to Kommunekemi when the concentrations become too high. Table 3.6 provides an overview of chromium consumption and chromium waste associated with black chromium plating in Denmark.

Table 3.5
Chromium consumption and chromium waste associated with black chromium plating in Denmark

Subject	Comment
Chromium consumption	5,300 kg CrO_3 per year
Production	The thickness of the layers applied varies from 0.1 to 2.0 µm depending on the intended use of the goods. Based on interviews with two of the largest companies within this field, the total production is estimated to be 164,000 m^2. Of this quantity, the single largest manufacturer accounts for 150,000 m^2.
Bath lifetime	The largest manufacturer discards 11–12 m^3 of bath solution each year. The other companies do not usually change their baths.
To wastewater	On average, approximately 5% of the chromic acid purchased by companies ends up in their wastewater. This figure can, however, vary from 2–10% depending on the rinsing system used by the relevant companies. The largest manufacturer within this field captures dragged-out chromium in the rinsing water in an ion exchanger, where the eluate is concentrated and sent to Kommunekemi. This means that no chromium is discharged into sewers
To sewers	It is estimated that a maximum of 1,000 m^3 of wastewater is discharged each year, and that the maximum chromium content is 0.2 mg/l. This corresponds to a total of 0.2 kg a year.

3.2.4 Blue passivation of zinc

Chromating (also known as passivation) of zinc surfaces takes place in a weak solution of chromate. Here, a chemical reaction occurs between metallic zinc and chromate. The layer of chromate formed as a result of this reaction contains zinc and Cr(III) and Cr(VI). The chromated goods are considerably more resistant to corrosion than the untreated zinc surface. Today, blue chromating can be done exclusively on the basis of Cr(III) salts. As a result, the process ought to be known as blue passivation. During use, the bath will be contaminated by Cr(III), zinc and ions from the basic material. When this contamination becomes too great, the entire bath is discarded. Discarded baths are usually treated at the companies' own treatment plants.

A total of approximately 600 tonnes of zinc anode is used each year in Denmark. This figure is based on a study from 1996 (Dahl & Løkkegaard, 2000), supplemented by recent inquiries made to some of the largest manufacturers. All electrically zinced goods are chromated, as this final treatment provides better corrosion properties. The goods are treated as items plated in barrels (small items) with layers of 3–10 µm (7 µm on average) and as items plated on racks with layers of 10–20 µm (12 µm on average).

In 1996, most companies still used chromate for blue chromating. Today, more than 95% use a Cr(III) salt, most frequently chromium(III) nitrate, but chromium(III) sulphate or chloride may also be used. As a result, the phrase "blue chromating" is actually inaccurate today. Instead, the process should be known as blue passivation, as no chromates are involved in the process. The baths used for blue passivation contain slightly more chromium than the blue chromate baths used in the past, but the new baths last a lot longer (by a factor of 5). This is a significant improvement in environmental terms, as baths are now discarded much less frequently than before.

Olive and black chromating are treated as one in these calculations, but in actual fact, black chromating is much more widespread than olive chromating. The two processes share very similar process chemistry. Black chromating has become more common in Denmark during the period from 1996 up until today.

The rinsing water is treated directly by means of reduction and precipitation, or it may be concentrated first by means of an ion exchange process. The sludge from the treatment plant is either sent to Kommunekemi or for treatment abroad. The discarded process baths are usually also treated at the companies' own treatment plants, as their metal content is relatively low. Discarded chromating baths for black and olive chromating may also be sent to Kommunekemi for treatment.

Table 3.7 shows estimated, detailed process data for the four types of passivation of zinc.

Table 3.7
Chromium consumption and chromium waste associated with chromium surface treatment on zinc in Denmark.

Chromating on zinc	Total	Blue	Yellow	Black/olive
Part of total production, %	100	30.8	60.8	8.4
Zinc anode consumption, tonnes/year	600	185	365	50
Surface, 1,000 m^2/year	8,415	2,595	5,199	701
Discarded baths, m^3/year	650	175	445	30
Chemicals consumption, kg Cr/year	15,918	1,201	11,873	2,844
Chromium in discarded baths, g/l	–	2.25	10	20
Chromium in discarded baths, kg/year	5,444	394	4,450	600
Chromium in rinsing water, kg/year	7,683	730	5,375	1,578
Chromium to sewer, kg/year	42	13	26	4
Chromium layer contains xx g Cr per m^2	–	0.03	0.40	0.95
Chromium on goods, kg/year	–	78	2,048	666
Chromium on goods, % of consumption	–	6.5	17.2	23.4

3.2.5 Chromium treatment of aluminium

This process is very much like the corresponding process for zinc surfaces. It is a chemical process where the aluminium surface reacts with chromium(VI) oxide while forming a layer which contains both Cr(III) and Cr(VI) compounds with aluminium. The layer may also contain phosphate and fluoride depending on the type of chromating chemicals used.

Table 3.8 shows an overview of typical bath compositions.

Table 3.8
Bath compositions for chromating aluminium

Chemicals	Green chromate bath	Yellow chromate bath
Chromic acid, CrO_3	4–10 g/l	2–4 g/l
Phosphoric acid, H_3PO_4	10–20 g/l	–
Hydrofluoric acid, HF	3–5 g/l	1 g/l
Sodium dichromate, $Na_2Cr_2O_7$	(3–4 g/l)	(3–4 g/l)

The process is carried out at room temperature.

With suitable drag-out with the goods, it is often possible to avoid discarding the bath itself. This is because the drag-out, possibly supplemented by tapping in connection with the addition of new chemicals, removes enough of the bath to avoid accumulation of aluminium and chromium(III) in the bath.

Table 3.9 presents figures from the three largest companies within the industry, accounting for at least 80% of the profile production, as well as from the largest supplier of chemicals.

Table 3.9
Chromium consumption and other parameters for chromating aluminium in Denmark

Parameter	Green chromate bath	Yellow chromate bath
Treated surface, m^2/year	3,500,000	3,500,000
Treated profile surface, m^2/year	1,900,000	1,600,000
Chromate layer, g/m^2	0.6–0.8	0.6–0.8
Chromium in chromate layer	20–30%	20–30%
Chromate layer, g Cr per m^2	0.12–0.24	0.12–0.24
Chromium on goods, %	40–70%	60–80%
Chromium in rinsing water – discarded bath, %	30–60%	20–40%
Total chromium consumption, kg/year	1,145	900

3.2.6 Chromic acid pickling of aluminium

Acid pickling of aluminium is also known as deoxidation. These days, a nitric acid solution is usually used, but not long ago a chromic acid solution was widely used: CrO_3 (3–4 g/l), NH_4HSO_4 (15–25 g/l), and NH_4F (1 g/l). Ten years ago, 100–200 tonnes of these chemicals were used each year (of which CrO_3 accounted for 20–25%), but today this method has largely disappeared. It is estimated that approximately 10 small-scale companies still use this process, and that the chemical consumption for this purpose is as low as approximately 2 tonnes/year, corresponding to approximately 250 kg Cr/year.

The pickling liquid is dragged out into the rinsing water. When too much chromium(III) and aluminium has accumulated in the bath, the entire vat of pickling liquid is discarded. It will typically be treated at the companies' own treatment plants, but a few companies send the discarded baths to Kommunekemi. It is necessary to reduce, neutralise and precipitate the rinsing water on an ongoing basis.

3.2.7 Chromic acid pickling of plastic

Plastic which is to be chromium plated is normally first pickled in a strong chromic acid solution containing 400 g/l chromium(VI) oxide and 400 g/L sulphuric acid. The pickling liquid will gradually degrade, with chromium(VI) oxide transforming into chromium(III), and eventually the pickling bath has to be discarded. Only one Danish company carries out plastic metallising, and it uses approximately 6,000 kg chromium(VI) oxide for pickling. The total treated surface of the plastic goods is estimated to be approximately 110,000 m^2/year.

The discarded process baths are sent to Kommunekemi, but the continuous drag-out to the rinse water is treated at the company's own treatment plant, and the sludge is sent for reprocessing in Germany.

3.2.8 Anodising of aluminium

Anodising of aluminium is almost always carried out in sulphuric acid. Occasionally, however, anodising by means of chromium(VI) oxide is preferred in order to achieve particularly high resistance to corrosion, e.g. within the aviation industry. A chromic acid anodising bath typically contains 50–100 g/l. No more than five Danish companies carry out chromic acid anodising, and they do so on a very small scale. The total consumption of chromium(VI) oxide is estimated to be approximately 200 kg/year. The used baths are discarded when too much aluminium has been accumulated in them, and liquid from the bath is continuously being dragged out into the rinsing water. In principle, all the chromic acid added to the system becomes waste.

3.2.9 Chromium passivation after phosphatising

The corrosion resistance of phosphatised goods can be improved considerably by means of a final treatment in a weak chromic acid solution (100–500 mg/l of CrO_3) at a temperature of 20–45°C. Only a very small portion (< 5%) of the chromium is bound to the surface of the goods treated, whereas the rest ends up as waste when the solution is discarded. This process is carried out at approximately 30 Danish companies, but an increasing number of these companies (approximately 40%) now use a chromium-free method of passivation which yields the same results. It is very difficult to estimate the total surface area treated by means of chromium passivation.

Rinsing is not normally used after warm chromium passivation, but rinsing with deionised water may be employed after cold passivation. The discarded baths are usually treated at the companies' own treatment plants as the metal concentration is low.

3.2.10 Miscellaneous processes

Solutions which contain chromates can also be used for passivation of steel, brass and copper. These processes are, however, quite rare in Denmark, and it is difficult to establish the exact extent and scope of such production. It is estimated that the chromium consumption for these processes is negligible compared to the other processes described in this survey.

3.3 Pigments in paint and plastic

Some chromium compounds are used as pigments in paint and plastic. Chromium(III) oxides are the most widespread, but chromium(VI) oxides and various types of chromates are also used. According to the records in the Product Register, the industry expected to use a total of more than 80 different chromium compounds in pigments in 2001 (The Product Register, 2001). According to Den Danske Farve- og Lakindustri ("The Danish Paint and Varnish Industry"), consumption of hexavalent chromium compounds is falling or levelling out at low levels, while trivalent chromium is widely used within the industry (FDFL, 2002). In interviews, pigment manufacturers confirmed that consumption of hexavalent chromium compounds has fallen significantly in recent years (Liebeck Chem A/S, 2002; Scan-Rep ApS, 2002; Burcharth's Farve- og Lakfabrik A/S, 2002). For example, one manufacturer stopped using lead(II) chromate in the year 2000, marking a pronounced break with previous practice which involved annual consumption of 5–10 tonnes a year (Burcharth's Farve- og Lakfabrik A/S, 2002).

Previously, the hexavalent chromium compounds were mainly used in industrial paints and varnishes to be used on metal structures (Huse ***et al.***, 1992). The pigments used were chromium(III) oxide (for greens) and lead(III) chromate (for yellows, oranges and reds). Chromium(III) oxide is resistant to atmospheric conditions and heat, which makes it excellently suited as a pigment within the glass and ceramics industry and for ink cartridges in printers (Ullmann, 2002).

Lead chromates have excellent properties as pigments. The standard chromate, $PbCrO_4$, is made by means of precipitation where solutions of lead acetate or lead nitrate are added to potassium or sodium dichromate. Colour graduations are achieved by varying the type of lead chromate used (double salts and water of crystallisation) or by varying the production process (Encyclopædia Britannica, 2002). Lead(II) chromate is primarily used in maritime and industrial paint products. The use of lead(II) chromate in paint products is diminishing rapidly within the Danish market, but lead(II) chromate is still used in products intended for export to certain countries (Hempel, 2002).

Lead chromate has previously been used in the paint used to make red lines on cycle tracks. Such use has been banned in Denmark for several years, but up until 2001, lead chromate could be used in such products if they were intended for export. Up until this final ban entered into force, the annual consumption of lead chromate was slightly less than 1 tonne per year (LKF Vejmarkering, 2002).

In total, it is estimated that today, slightly more than 1 tonne of lead(II) chromate is sold every year to the paint and varnish industry in Denmark. If we go back just two or three years, the quantities sold were ten times higher (Andreas Jennow A/S, 2002). Today, chromates are only available on order, and customers can only order the products if they have permission to use them.

Chromium iron oxide can be used as a heat-resistant brown pigment, for example in oven varnish (Ullmann, 2002). It has not been possible to find any information on chromium iron oxide being used for this purpose in Denmark today. As a result, it is estimated that if such use occurs, the quantities involved must be quite small.

Previously, chromates of zinc and, to a lesser extent, sodium, potassium, strontium, ammonium and barium were used as rust preventives in paints. Today, there exist alternatives to chromates, and this means that chromates are rapidly being replaced (Hempel, 2002).

As was outlined in Chapter 1, one of the reasons behind the reduction in use of chromates in pigments is that chromates are regarded as being carcinogenic. This means that there are requirements on labelling of products which contain chromates, as well as requirements on how these products are handled.

Appendix D lists the information available in the Product Register about reported[8] substances which contain chromium in active products. Due to the rules on confidentiality applied by the Product Register, the list includes only those substances which are used by more than three manufacturers.

As illustrated in Appendix D, chromium is used in several types of pigments and in highly variable concentrations. Sometimes, chromium is not used as a pigment, but serves another purpose. It may, for example, be used as a rust

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[8] Reported substances in active products are those substances which manufacturers have told the Product Register that they expect to use. Some of these substances may no longer be in use even though they appear in the list. This is because reported substances are transferred from one year to the next unless the manufacturers provide instructions to the contrary.

preventive. It has not been possible to obtain detailed information on the reasons for the occurrence of various chromium compounds for each individual use.

Table 3.10 provides estimates of the chromium content of paints and pigments.

Table 3.10
Import, export, production and supply of paints and pigments which contain chromium, 1998–2000 (Statistics Denmark, 2001b)

Product type	Import Tonnes/year	Export Tonnes/year	Production Tonnes/year	Supply Tonnes/year	Chromium quantities 1) Tonnes/year
Paints and varnishes, dissolved in an aqueous media	15,803	49,224	74,905	41,484	0.5–31
Paints and varnishes, dissolved in non-aqueous media	12,747	15,763	53,672	50,656	0.5–38
Paints and pigments for leather dying	756	937	580	399	0–0.5
Pigments dispersed in non-aqueous media	1,985	466	517	2,037	5–15.5
Other pigments; inorganic products of the type used as luminophores, including chemically defined pigments and preparations based on chromium compounds	380	74	23	330	1–2.5
Dyes/colours used for porcelain, glass and enamel	2,101	506	0	1,596	4–12
Substratum pigments	20	1	0	18	0.1–0.2
Artist's colours	971	554	166	583	1.5–4.5
Inks and similar	9,528	6,499	13,428	16,456	0–12.5
Total					12.6–116.7

1) The chromium quantities have been estimated on the basis of information from Statistics Denmark and the Product Register, supplemented by interviews with people within the industry. It is estimated that somewhere between 0 and 5% of all paints and pigments contain chromium, and so an average value of 2.5% has been chosen. On the basis of Poulsen *et al.*, 2002, the content of pigment in the paints has been estimated at between 0.5 and 10%. The chromium content of the pigments themselves has been estimated at 10–30% on the basis of the chromium content of the chromium compounds listed in Appendix D.

As is illustrated in the table above, the consumption of chromium is estimated to be between 12.6 and 116.7 tonnes. It is also estimated that chromium(VI) accounts for 1–2 tonnes of this total consumption. The content of chromium pigments in imported goods/products has not been assessed.

Studies have shown that considerable waste occurs in connection with painting projects. On the basis of Poulsen ***et al.,*** 2002, it is estimated that 5–30% ends up as waste (which is assumed to be sent for incineration), and that 0.2–11% ends up in the sewers. This means that discharges of chromium to wastewater can be estimated at 0.03–13 tonnes of chromium, of which 0.002–0.2 tonnes are believed to be chromium(VI). At the same time, 0.6–35 tonnes of chromium is incinerated, of which 0.05–0.6 tonnes is estimated to be chromium(VI).

3.3.1 Pigments containing chromium in plastic

Plastic products can also contain chromium-based pigments. A Swiss study, which included approximately 500 types of plastic, showed that 20% of all PVC, 11% of all PP and 4% of all PE contain 100–1,000 mg chromium per kg (Bundesamt für Umwelt, 1995).

Previously, lead chromates were used as pigments in plastic products to create bright reds, yellows and greens. During the 1990s, the use of lead chromates in plastic has been replaced by organic pigments which do not contain any chromium (the PVC Information Council Denmark, 1999). It appears that chromium is not being used in pigments in plastic today, but it has not been possible to confirm this (the PVC Information Council Denmark, 2002; The Danish Plastics Federation, 2002). Chromium may occur in fibreglass-reinforced plastics, but it is likely that this is because of the fibreglass (The Danish Plastics Federation, 2002a).

On this basis, it is estimated that today, chromium is probably not used in pigments in plastic products manufactured in Denmark. We cannot, however, rule out the possibility that imported plastic products may be coloured using pigments which contain chromium. The exact amounts are not known.

3.4 Impregnation agents/Wood preservation

Chromium in the form of chromates and chromium(VI) oxide has previously been used in large quantities within the wood industry to protect wood against fungi and insects. The purpose of chromium in this context is primarily to fix the other active substances (arsenate, borate, fluoride, copper, etc.). During the period 1993–1997, approximately 115,000–145,000 tonnes of wood containing chromium was produced (Hansen ***et al.***, 2000).

The use of impregnation agents containing chromium has been reduced very significantly in Denmark through voluntary agreements, and since January 1997, agents which contain chromium may only be used with the appropriate dispensations. Ever since 1997, only a few manufacturers have been allowed to use CCB (copper, chromium and boron) and CCP (copper, chromium and phosphate) agents. In 1998, a total of 17,300 tonnes of wood containing chromium was produced, and approximately 37 tonnes of chromium was used in the process. The quantities produced corresponded to approximately 12% of the total production of impregnated wood (Hansen ***et al.***, 2000). At the end of 1999, only a single manufacturer had a licence to use CCP agents (Dansk Imprægneringsstatistik, 2000). Some of the impregnated wood imported into Denmark may still, however, contain chromium. According to Hansen ***et al.***, 2000, almost 60 tonnes of chromium were imported as an ingredient in impregnated wood.

According to the Danish EPA's register of pesticides, the sales of wood preservation agents which contain chromium have fallen in Denmark during the period 1998–2000 (The Danish EPA, 2001a). This is consistent with the fact that the number of manufacturers with a licence to use chromium for impregnation has fallen during the same period. Table 3.11 shows statistics for the sales of wood preservation agents in the years 1998–2000.

Table 3.11
Sales of wood preservation agents containing chromium (the Danish EPA, 2001a)

Year Unit	1998 Kg	1999 Kg	2000 Kg	Average Kg
Dichromate	45,197	37,260	27,796	36,751
Of this, chromium accounts for 24.07%, corresponding to these quantities:				
Chromium	10,880	8,970	6,691	8,847

The figures given for sales of wood preservation agents in 1998 in (The Danish EPA, 2001a) are considerably lower than the quantities reported by Hansen, ***et al.***, 2000. This may be because not all quantities have been reported, or because the quantities used in production were bought the previous year and placed in storage. No figures have been established for imports of impregnated wood.

Table 3.12
Supply of chromium in impregnated wood in 1998, tonnes (Hansen *et al.*, 2000)

Production	Import	Export	Supply
36.7	59.4	27.3	68.7

On the basis of the sales illustrated in Table 3.11, it is estimated that production – and hence export – has fallen 20% since 1998, whereas import is deemed to be unchanged. Table 3.13 provides an estimate of the average supply of chromium in impregnated wood for the period 1998–2000.

Table 3.13
Estimated average supply of chromium in impregnated wood during 1998–2000, tonnes

Production	Import	Export	Supply
30	60	25	65

Due to its protection against degradation, impregnated wood often lasts for a long time. This means that impregnated wood made up to fifty years ago is only now being discarded.

A few years ago, a major study on the use of chromium-impregnated wood in Denmark throughout 40 years was prepared (Hansen ***et al.***, 2000). In this study, it has been estimated that impregnated wood for building, construction and outdoor applications has a functional lifetime of approximately 40 years. It is also estimated that an additional ten years should be added to this period because a lot of impregnated wood is reused. It should be noted that the functional lifetime of impregnated wood varies greatly. For example, building components may have functional lifetimes of 100 years, whereas fence poles, terrace boards, etc., may have functional lifetimes of 30–40 years (Hansen ***et al.***, 2000).

During the use phase, the impregnated wood emits chromium to the environment. The exact quantities emitted depend on many factors, including exposure to water and rain. It is estimated that only small emissions to air occur as the wood dries out, and so this type of emission has not been considered. Only a few studies exist about emission of chromium during the use phase. On the basis of Hansen ***et al.***, 2000, it is estimated that emissions of 1–2% of the chromium to soil and the aquatic environment take place every year. Leaching of chromium into the aquatic environment primarily takes place during the first few years. Emissions to water are estimated to be around

0.3–0.6 tonnes chromium(VI) per year, and the emissions to soil are believed to be similar in scope.

Table 3.14 shows statistics on the waste quantities associated with impregnated wood containing chromium for the period 1998–2000.

Table 3.14
Calculated waste quantities of impregnated wood containing chromium for the years 1998–2000 (Hansen *et al.*, 2000).

Year Unit	Reprocessed waste Tonnes	Landfilling Tonnes	Incineration Tonnes	Reuse Tonnes	Total waste Tonnes
1998	2,886	10,926	2,049	683	16,543
1999	2,984	9,105	1,707	569	14,365
2000	3,061	11,169	2,094	698	17,022
Average	2,977	10,400	1,950	650	15,977

The waste quantities have been calculated on the basis of the assumption that 70% of the impregnated wood has a functional lifetime of 40 years, while the rest of the wood has a functional lifetime of 25 years. It is also assumed that 2% is wasted during production, and that this waste ends up as reprocessed waste (Hansen ***et al.***, 2000).

According to the study's projections on the future waste quantities, the total transport of chromium associated with reprocessed waste, landfilling, incineration and reuse is around 26 tonnes. This corresponds to approximately 0.2% of the quantity of wood (Hansen ***et al.***, 2000). Table 3.15 presents the relative shares accounted for by the various types of waste treatment.

Table 3.15
Chromium from impregnated wood to landfills, incineration, reuse and reprocessed waste (Hansen *et al.*, 2000)

Year	Landfilling Kg	Incineration Kg	Reuse Kg	Reprocessed waste Kg	Total Kg
1998	21,568	4,044	1,348	734	27,694
1999	17,974	3,370	1,123	0	22,467
2000	22,048	4,134	1,378	0	27,560
Average	20,530	3,849	1,283	245	25,907

Even though only small quantities of wood are impregnated with chromium today, the chromium content in waste from impregnated wood will rise in the years to come. This is because of the long lifetime of impregnated wood. As illustrated in Figure 3.1, the chromium content in waste derived from impregnated wood will rise up until the late 2030s, at which time it will drop sharply to levels similar to those seen today. The drop in the curve around 2030 and the subsequent marked rise may be caused by the fact that the manufacturers have voluntarily phased out all use of impregnation substances which contain chromium, and had to use their stores before the substances became illegal in 1997.

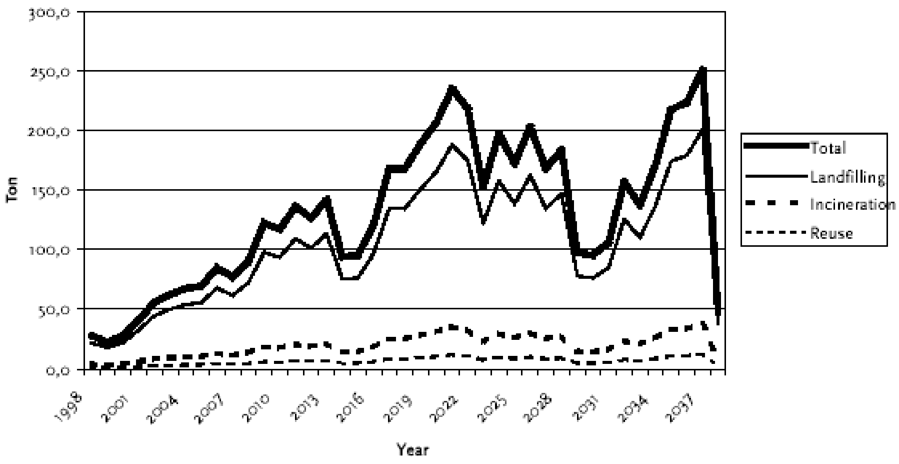

Figure 3.1
Projected chromium contents in waste derived from impregnated wood and distribution by landfilling, incineration and reuse (prepared on the basis of Hansen *et al.*, 2000).

Reprocessed waste has not been included in the figure above, but such waste will account for approximately half a tonne.

Figure 3.1 does not include impregnated wood which is disposed of in unauthorised ways. It should be expected that an unknown percentage of waste from private households is disposed of by means of uncontrolled landfilling, burning of garden waste and burning in household stoves.

Impregnated wood has attracted increasing attention in recent years. Since April 2001, a new requirement has been introduced on a trial basis in Denmark: all impregnated wood must be taken to recycling centres (R98, 2002). If this requirement becomes permanent, unauthorised disposal will decrease in the years to come. Kommunekemi A/S is currently planning a facility for the treatment of impregnated wood; construction is expected to commence within a year. This new plant will use a gasification process to separate out the heavy metals from the wood, allow the metals to be reprocessed and possibly recovered (Kommunekemi, 2002a; b). This means that we can expect a drop in the quantities of wood ending up in landfill if this new plant is established.

Projections on the chromium content in waste deriving from impregnated wood were also made in connection with a study of methods for treatment of various types of waste which contain heavy metals (Malmgren-Hansen ***et al.***, 1999). Figure 3.2 below illustrates the result of these projections. Compared to Figure 3.1, the development trend is approximately the same for the next twenty years. Nevertheless, the quantities are expected to be significantly lower (50–60% lower) than the quantities stated in Figure 3.1. As the projection extends further into the future, the figures become widely different. This illustrates the considerable uncertainties associated with such projections.

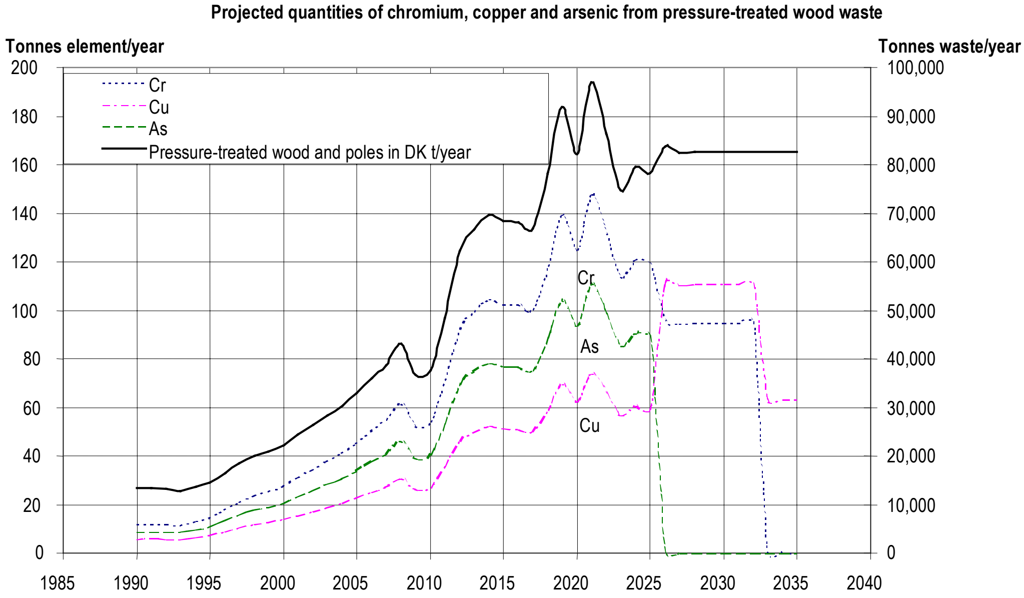

Figure 3.2
Projected contents of chromium, copper and arsenic in waste derived from impregnated wood, and total quantities of waste deriving from impregnated wood (Malmgren-Hansen *et al.*, 1999).

3.5 Chromium used as a corrosion inhibitor

According to the technical reference work ***Ullmann***, corrosion inhibitors made from sodium dichromate (Cr(VI)) are used in cooling towers and as additives in oil pipes in connection with transport of crude oil (Ullmann, 2002).

In actual fact, however, it turns out that corrosion inhibitor compounds containing chromium are no longer used for cooling towers in Denmark. Chromium compounds have previously been used in open cooling towers, but they have been phased out due to the aerosol formation associated with open cooling towers and the resultant emission of the dissolved Cr(VI) compounds (FORCE Technology, 2002).

Today, it is also rare to see any use of corrosion inhibitors containing chromium in connection with transport of crude oil in pipes. Transport of oil involves a range of auxiliary chemicals in addition to the chemicals used for oil extraction, but these days the products used hardly ever contain chromium (FORCE Technology, 2002).

In 1999, DHI Water & Environment carried out an environmental assessment of the auxiliary chemicals used by DONG in 1998 when transporting crude oil from the North Sea to the oil terminal in Fredericia, Jutland (Rasmussen ***et al.,*** 2000). In connection with this assessment, the suppliers of chemicals to DONG submitted confidential information to DHI Water & Environment about constituents in the chemical products used for the oil transport. According to the information submitted, none of the chemical products included in the assessment contained chromium. DONG informs us that the chemical products used today are no different from those assessed by DHI Water & Environment in 1998 (DONG, 2002a). On this basis, it is estimated that chromium is not used as a corrosion inhibitor in Danish installations for transport of crude oil.

3.6 Tanning/leather

Leather tanned using chromium will contain chromium throughout its entire lifetime. This means that all import, export and production of leather and leather goods affects the mass balance of chromium in Denmark. Chromium(III) compounds are particularly widely used for chrome tanning.

3.6.1 Leather tanning

In 1999, only a single tannery in Denmark carried out chrome tanning of leather: Elmo Leather in Svendborg on Funen. The company stopped tanning leather using chromium in August 1999 and has focused exclusively on organic tanning since then (Elmo Leather, 2002). According to several sources with ties to the industry, no other active tanneries exist in Denmark (Danish Technological Institute, 2002b; Thomsen, 2002), although a few research tanneries may exist. Such research facilities would not use chromium (Elmo Leather, 2002).

According to Statistics Denmark, the supply of synthetic inorganic tanning agents was 164 tonnes/year during the period 1998–2000. This average is derived from the following quantities for each year: 243, 145 and 105 tonnes/year. According to Elmo Leather, these quantities roughly correspond to their consumption during approximately eight months of 1999 (approximately 170 tonnes of basic chromium(III) sulphate). The higher consumption rate in 1998, covering a whole year, can also be explained with reference to the consumption at Elmo Leather, whereas the supply in 2000 – a total of 105 tonnes – is less easily explained. The quantities consumed by Elmo Leather in 1999 correspond to 40 tonnes Cr_2O_3/year or 27 tonnes Cr(III)/year. Of this quantity, 1% – corresponding to 0.272 tonnes Cr(III)/year – went to a treatment plant where most of it ended up in the sludge. The remaining 99% ended up in the leather (Elmo Leather, 2002). Small quantities of chromium also end up in wastewater, approximately 0.02 tonnes Cr(III)/year, due to the use of metal complex dyes (Elmo Leather, 2002).

Several sources have informed us that a new and very large tannery has been established on Funen (Danish Technological Institute, 2002b). This facility will include chrome tanning among its activities, which means that it may affect the future mass balance of chromium in Denmark.

3.6.2 Leather in finished goods

Leather is imported as part of finished goods (shoes, bags, etc.) or in a pre-processed form which is then used to manufacture products in Denmark.

Leather is typically used in the following products:

- Footwear: shoes, boots, sandals
- Gloves: fashion gloves and protective gloves
- Leather garments: jackets, trousers, skirts, waistcoats, tops, dresses
- Furniture: sofas and chairs
- Bags and luggage, purses, etc.

- Wallets
- Belts
- Horse saddles and bicycle saddles
- Other leather goods, leather-covered goods, leather upholstery for cars

Estimates of the mass balance for chromium associated with the leather objects which are deemed to have the greatest impact on the total mass balance are given below.

3.6.2.1 Footwear

Many different types of shoes typically contain leather: fashion footwear, working shoes, boots, and sports shoes. Usually, only the uppers are actually made from leather, but some shoes also have leather soles. Whereas uppers are almost always chromium-tanned (Danmarks Skohandlerforening, 2002), leather soles for men's shoes are frequently made from organically dressed leather. Leather soles for ladies' shoes are typically made from chromium-tanned leather (Shoes-international, 2002). Approximately 24–25 million pairs of shoes are sold every year in Denmark (Danmarks Skohandlerforening, 2002). This figure includes all forms of footwear, including sports shoes, Wellington boots, sandals, etc. This corresponds to 4.5–4.7 pairs of shoes per person per year. According to a rough estimate from the industry, approximately 15,000,000 pairs are leather shoes (the interval is set to be 13,000,000 – 18,000,000) (Danmarks Skohandlerforening, 2002).

The vast majority of all the shoes sold within the Danish market are imported (Danmarks Skohandlerforening, 2002). ECCO Shoes is by far the largest manufacturer of shoes in Denmark, producing 10.5 million pairs per year. Even though the company sells considerable quantities of shoes on the domestic market, it only manufactures a relatively small number of shoes in Denmark; approximately 260,000–520,000 pairs per year (ECCO Denmark, 2002). According to our information, Jacoform is the only other Danish shoe manufacturer of any real significance (Danmarks Skohandlerforening, 2002), and that company produces only around 150,000–170,000 pairs per year. This is to say that the total Danish production of leather shoes is estimated at 410,000–690,000 pairs per year.

The incoming supply of leather shoes to Denmark calculated on the basis of data from Statistics Denmark is considerably smaller than the estimated 15 million pairs quoted by the industry. This in spite of the fact that the method of calculation employed by Statistics Denmark entails a risk of overestimating the supply. According to the department for goods statistics at Statistics Denmark, production carried out for a Danish company outside of Denmark is registered as Danish production (sales of Danish products) if the raw materials come from Denmark. At the same time, the products in question are registered as imports if they are shipped to Denmark from production facilities abroad. This means that such goods are included twice in supply statistics.

Table 3.16
Supply of leather shoes (1998–2000) according to Statistics Denmark

Product	Import pairs/year	Export pairs/year	Production pairs/year	Supply pairs/year
Shoes and boots with uppers made from leather	13,662,230	8,295,437	2,728,557	8,093,623
Leather sandals	2,549,262	1,160,885	1,392,740	2,781,117
Shoes made entirely from leather	1,136,134	211,628	179,391	1,103,897
Total	17,347,626	9,667,950	4,300,689	11,978,637

On the basis of the statistics and information from the industry, it is assumed that the supply of leather shoes to the Danish market amounts to 10,000,000–15,000,000 pairs of leather shoes per year. Shoes and sandals account for the relative shares illustrated in the table below.

Table 3.17.
Maximum and minimum supplies, divided into shoes and sandals.

	Share of total	Supply pairs of shoes/year min	max
Shoes and boots with uppers made from leather	68%	6,756,714	10,135,072
Sandals made from leather	23%	2,321,730	3,482,596
Shoes made entirely from leather	9%	921,555	1,382,333
Total		10,000,000	15,000,000

On the basis of interviews with the industry (ECCO Denmark, 2002; Jacoform Sko, 2002), we have established that a pair of shoes usually contains approximately 261–378 g leather in the uppers, whereas sandals normally contain around 194–281 g. It is likely that many sandal “uppers” contain less leather than the quantities stated here. However, many ladies' sandals have leather soles, and these are likely to be chromium-tanned (Shoes International, 2002). It is assumed that men's shoes with leather outer soles have organically dressed outer soles, and that all other leather used in shoes is chromium-tanned.

Thus, the total supply in Denmark of chromium-tanned leather associated with shoes is estimated to be 2,455–5,338 tonnes chromium leather/year.

The chromium content in shoe leather is estimated to be 2.2%–5.0% weight/weight Cr_2O_3, but the average is likely to be around 3% weight/weight Cr_2O_3 or 2% Cr (Rydin, 2002). If we base our calculations on the average chromium content, the total supply of chromium into Denmark in the form of shoes can be estimated at 50–109 tonnes Cr/year.

The Danish EPA has measured Cr(VI) in concentrations greater than 3 mg/kg in two out of five pairs of shoes and a maximum concentration of Cr(VI) of 10.4 mg/kg leather. This corresponds to an average of approximately 4–5 mg Cr(VI)/kg. Based on this average, the supply of Cr(VI) associated with shoes can be established as 0.011–0.024 tonnes Cr(VI)/year. This is to say that virtually all the chromium found in shoes is Cr(III).

Shoes have relatively short lifetimes, as demonstrated by the large number of shoes bought by Danes each year. It is assumed that quantities corresponding to the annual supply are disposed of each year, and that discarded shoes are incinerated.

3.6.2.2 Gloves, garments, belts and straps
There is a certain supply of gloves, garments, belts and straps made from leather to Denmark. In terms of leather quantities, garments and protective gloves account for most of the supply. Only very small amounts of such goods are manufactured in Denmark, and the leather used to do so is usually imported.

According to Handskemagerlauget ("The Glove-makers' Guild"), 90% of all gloves are chromium-tanned, and leather used to make gloves needs a chromium content of 2–2.2% Cr_2O_3 (1.36–1.50% Cr(III)) (Handskemagerlauget/Randers Handsker, 2002). However, the Danish EPA has measured higher content levels (4.4% Cr_2O_3 or 3.0% Cr) in garments and gloves (Rydin, 2002). As almost all leather goods are imported, these figures are used as the average content of all leather goods.

Table 3.18.
Supply of leather goods (1998–2000) according to Statistics Denmark.

CN uh	Product	Import tonnes/year	Export tonnes/year	Production tonnes/year	Supply tonnes/year
42031000	Leather garments	1,011	591	3	423
42032100	Sports gloves, leather	20	5	1	15
42032910	Protective gloves, leather	1,592	848	0	744
42032991	Men's gloves	35	10	1	27
42032999	Ladies' gloves	48	15	1	35
42033000	Belts and straps	155	65	0	89
		2,861	1,533	5	1,333

It is assumed that 90% of the leather is chromium-tanned, and so the annual supply of chromium associated with gloves, belts, garments and straps is 32–39 Cr/year. Of this amount, Cr(VI) accounts for 0.005–0.007 tonnes, while the rest is Cr(III).

Some leather garments are sold on as second-hand clothes, a fact which can prolong the leather's lifecycle in Denmark, but ultimately they are incinerated like all other clothes. The second-hand organisations do not usually send clothes outside Denmark (Folkekirkens Nødhjælp, 2002), preferring instead to sell them in Denmark or to send them for incineration. It is estimated that the total disposal of leather in gloves, garments, belts and straps corresponds to the supply.

3.6.2.3 Furniture
Leather furniture is most frequently upholstered in chromium-tanned leather, which feels softer and more supple than leather tanned using vegetable agents. Organically dressed leather is not widely used, and is mainly used for hard upholstery (Design Møbler, 2002).

At Statistics Denmark, furniture is not classified according to the materials used for upholstery. This means that our estimates are based on interviews with people from the industry. There is no centrally compiled information about sales of leather furniture from the main associations within the industry: Dansk Møbelindistri and Møbelhandlernes Centralforening. The latter organisation represents 300 furniture retailers, accounting for 80% of all furniture sold to private individuals. They informed us that most leather in leather furniture is chromium-tanned, but that the chromium contents are typically not known. (Møbelhandlernes Centralforening, 2002).

A major Danish furniture retailer with a market share of approximately 24% sells around 24,000 leather suites (sets containing one three-seater and one two-seater sofa) each year and estimates the total sales in Denmark to be 100,000 sets a year (Inbodan, Idé Møbler, 2002). Sofa suites account for approximately 90% of all the leather furniture items sold in Denmark (Actona, 2002), and in terms of the quantities of leather sold, they also account for most of the leather sold as part of furniture in Denmark. In this document, the remaining 10% (of items) are assumed to be easy chairs; another popular type of leather furniture.

Each suite (one three-seater and one two-seater sofa) contains 250 square feet of leather (Inbodan, Idé Møbler, 2002; Actona, 2002), while an easy chair contains 50–60 square feet of leather. This is to say that approximately 30 million square feet of leather is sold in Denmark each year in the form of leather furniture. Assuming a thickness of 1–1.5 mm (Elmo AB, 2002) and a density of 0.86–1.02 tonnes/m^3 (Perry ***et al.***, 1997), this makes for a total of 2,361–4,359 tonnes of leather/year. If we base our calculations on the industry's estimate that most of this leather is chromium-tanned (80%–100%) and that it contains 3.0%–5.0% Cr_2O_3, the supply of chromium from leather in leather furniture in Denmark is around 51–119 tonnes Cr/year.

It is assumed that leather furniture is disposed of by means of incineration. Leather furniture is replaced with greater frequency in Denmark than in other countries, and it is estimated that the quantities disposed of correspond to the supply.

3.6.2.4 Bags, purses etc.

The information on the supply of luggage, bags, purses, etc., with leather surfaces comes from Statistics Denmark.

Table 3.19.
The supply of luggage, briefcases, bags, and purses (1998–2000) according to Statistics Denmark

CN uh	Product	Import tonnes/year	Export tonnes/year	Production tonnes/year	Supply tonnes/year
4202 11	Luggage and briefcases made from leather	388	146	0	242
4202 21 00	Handbags made from leather	249	28	3	224
4202 31 00	Purses, wallets and cases	235	39	0	197

It has not been possible to obtain exact information about the relative share accounted for by chromium-tanned leather. We do, however, know that Adax, a major Danish manufacturer of leather accessories, only uses organically dressed leather in their products (Adax, 2002). As leather used for leather accessories does not normally need to be particularly soft, it is assumed that much of the leather used for luggage and handbags is organically dressed (70%–80%). It is also assumed that chromium-tanned leather accounts for a greater percentage of the total quantities of leather used for purses, wallets and small cases (50%–80%). We estimate that leather accounts for 70%–90% of the total material contents of the goods, and that the average chromium content of this leather corresponds to the average chromium content of leather garments, belts and straps. This makes for a total supply into Denmark of 4.0–8.0 tonnes Cr/year in the form of luggage, bags, wallets, cases and similar leather accessories. A very small portion of this chromium may be Cr(VI), while the rest will be Cr(III).

3.6.2.5 Saddles and other leather products

A brief calculation based on the size of the Danish population and the number of bicycles in Denmark shows that the annual supply of leather in the form of bicycle saddles is in the region of two tonnes. This is to say that the potential chromium contents involved are very small. If all leather saddles were chromium-tanned, this would correspond to 0.030–0.090 tonnes Cr/year. It is estimated that the supply of chromium associated with other leather goods such as horse saddles and leather upholstery for cars is quite limited.

3.6.2.6 Leather as a raw material

The leather produced in Denmark or imported as a raw material for production of leather products is included in the statistics on the various uses outlined in the above. As a result, these leather quantities are not addressed in any detail here. On the basis of data from Statistics Denmark, we can, however, see that some leather is imported into Denmark as a raw material. According to the statistics, this is mainly due to sales of domestically produced goods (wet blue chromium-tanned leather). The statistics also indicate major sales of domestically produced goods in 2000, even though the industry states that no production took place in this year. These sales may, however, stem from stored goods produced in previous years.

Table 3.20.
Supply of raw leather (1998–2000) according to Statistics Denmark.

CN uh	Production	Import tonnes/year	Export tonnes/year	Production tonnes/year	Supply tonnes/year
4104 10 30	Chromium-tanned leather, horse or horned cattle	5	1	0	4
4104 22 10	Chromium-tanned leather, wet blue	3	239	1,695	1,459

In total, the supply of chromium with leather can be calculated to be 137–275 tonnes chromium/year for 1999. In addition to this, 27 tonnes of chromium are used each year for leather tanning in Denmark. The total consumption of chromium comprises:

- Leather tanned in Denmark: 27 tonnes chromium/year
- Shoes: 27 tonnes chromium/year
- Furniture: 51–199 tonnes chromium/year
- Bags, etc.: 4–8 tonnes chromium/year
- Saddles, etc.: 0.03–0.09 tonnes chromium/year

The chromium involved is mainly Cr(III). If we base our calculations on the figures from the Danish EPA, Cr(VI) accounts for 0.015% of the total chromium content in a number of products, corresponding to a total of 0.016–0.035 tonnes Cr(VI). All of this chromium is imported, and the vast majority of it is imported as part of the leather. It is estimated that the same quantities will be disposed of by means of incineration. The figures include chromium used to carry out tanning in Denmark, as they include all leather goods sold in Denmark. In 1999, the emission of chromium to treatment plants due to chrome tanning was 0.272 tonnes Cr(III).

3.7 Accelerators, catalysts, hardeners

According to technical literature on the subject (Ullmann, 2002), compounds containing chromium are used as accelerators and catalysts in the production of a wide range of products. According to the Product Register, such compounds are also used as hardeners in the products themselves. The following is a look at a number of products and processes which involve chromium in the form of accelerators, catalysts or hardeners.

3.7.1 Catalysts for chemical processes

Chromium can catalyse a range of different chemical processes used within the chemical industry. For example, chromium-aluminium catalysts are used for dehydrogenising butane and butadiene, for polymerisation of ethylene, and for aromatising n-alkanes (propane transformed into benzene). Binary oxide catalysts containing chromium can be used for hydrogenising, dehydrogenising, methanol synthesis and shift reaction with water (steam). Chromium can also be used as a catalyst in heterogeneous synthesis of methanol. In the processes mentioned here, the active component is the Cr(III) ion from Cr_2O_3 (Ullmann, 2002). Chromium can also be used in Ziegler-Natta catalysts, which are used for production of polymers (University of Aalborg, 2002). It has not been possible to identify enterprises using chromium as catalysts for these or other processes in Denmark (University of Aalborg, 2002). The association of Danish plastics manufacturers does not know which companies – if any – use chromium catalysts (The Danish Plastics Federation, 2002), and crude plastic is not manufactured in Denmark at all (Statoil, 2002b). Chromium may also be used to crack alkanes, but the only refinery in Denmark (owned by Statoil and located in Kalundborg) does not use chromium as a catalyst (Statoil, 2002).

Data from Statistics Denmark show that there is a relatively large supply of catalyst materials other than nickel and precious metals in Denmark, but at the same time the Product Register lists only few catalysts which contain chromium. Consequently, it is assumed that most of the catalysts occurring in the total supply do not contain chromium.

Haldor Topsøe is the only manufacturer of catalysts in Denmark. This company produces catalysts containing chromium for the water gas shift reaction $CO + H_2O = H_2 + CO_2$, which is widely used within the chemical industry. A total of 98% of their catalysts are exported, and there are no other major facilities of this type in Denmark, although it is likely that some small ones exist (University of Aalborg, 2002). Unfortunately, time constraints prevented Haldor Topsøe from contributing an estimate of their consumption of chromium and production of catalysts containing chromium. However, as the chromium raw materials are imported and the vast majority of the catalysts containing chromium are exported, the production carried out in Denmark does not have much impact on the supply. A competitor, ICI-Synetix, also makes catalysts for this reaction. Their catalyst, known as Katalco 71–5, is intended for high-temperature shift reactions and typically contains 9% Fe_2O_3 and < 10 ppm w/w Cr(VI) (Synetix-ICI, 2002a). It is expected that these contents also apply to the catalysts produced in Denmark (University of Aalborg, 2002). Catalysts for low-temperature shift reactions do not contain chromium (Synetix-ICI, 2002b; University of Aalborg, 2002). Small facilities for shift reactions are estimated to contain around 25–50 kg catalyst, which is replaced every two or three years (University of Aalborg, 2002). If we assume that there are 100 small facilities in Denmark, this adds up to 61.2–122.4 kg Cr(III)/year.

The Product Register contains a large number of accelerators and catalysts containing chromium. The products contain 15.6–52% Cr(VI) in the form of chromium(VI) oxide or 0.13–0.26% Cr(VI) in the form of strontium chromate.

Statistics Denmark has information on the supply of catalysts without nickel and precious metals, but their chromium content is not specified.

Table 3.21.
The supply of catalysts and reaction starters (1998–2000) according to Statistics Denmark

CN uh	Product	Import tonnes/year	Export tonnes/year	Production tonnes/year	Supply tonnes/year
3815	Reaction starters, reaction accelerators and catalytic preparations	1,873	10,928	13,903	4,848
38151910	Catalysts on carriers in the form of grains, not nickel and precious metals	20	113	0	–92
38151990	Catalysts on carriers, not grains, not nickel or precious metals	575	3,656	4,948	1,867
38159090	Catalysts, not on carriers	1,020	5,307	7,320	3,033

If we assume that 1–2% of the total supply consists of catalysts which contain chromium and that these catalysts have chromium contents of the type and quantity indicated in the Product Register, the supply of chromium in catalysts adds up to 0.1–100 tonnes Cr(VI)/year. However, one expert estimates the consumption of catalysts containing chromium in Denmark at just a few kg per year (University of Aalborg, 2002), so the actual consumption is estimated to be 0.1–1 tonne.

The emissions to the environment associated with use of catalysts containing chromium are believed to be very small, much less that 1 kg/year. This partly because the use of such catalysts is quite limited, and partly because the catalysts are most likely disposed of in ways which entail very small losses into the environment, e.g. at Kommunekemi.

3.7.2 Accelerators in plastic

It would appear that chromium is not added as an accelerator to any kind of plastic (Kemikalieinspektionen Sverige, 1995; Statens Forurensningstilsyn, 1991; Umweltsbundesamt, 2000; PVC Information Council Denmark, 2002), but it may occur due to impurities entering the plastic during production. This is the case for polypropylene and polyethylene (Statens Forurensningstilsyn, 1991; Ullmann, 2002). The quantities occurring in the form of impurities are believed to be very small. Some chromium contents have been measured in various types of plastic packaging: 670 ppm in plastic trays, 390 ppm in plastic lids, 2,500 ppm in plastic boxes, 2,900 ppm in a plastic beer crate. These occurrences are mainly associated with pigments

(Andreasen ***et al.***, 1997). As is mentioned in section 3.3.1 above, chromium is not used as a pigment in Denmark. It would appear that no plastic synthesis takes place in Denmark (Statoil, 2002; the PVC Information Council Denmark, 2002), but there is considerable import of plastic raw materials for a wide range of companies which process plastic.

Table 3.22
Supply of polyethylene and polypropylene (1998–2000) according to Statistics Denmark

KN uh	Product	Import tonnes/year	Export tonnes/year	Production tonnes/year	Supply tonnes/year
39012010	Polymers of ethylene in unprocessed form: Polyethylene with a density of 0.94 or more: With chromium contents of 2 mg/kg or less etc.	7,337	1,273	0	6,064
39011010	Polyethylene, unprocessed, linear, with a density of less than 0.94	7,243	1,056	9,157	15,345
39011090	Polyethylene, unprocessed, non-linear, with a density of less than 0.94	126,224	11,036	14,369	129,557
39012090	Polyethylene, unprocessed, with a density of 0.94 or more	62,093	6,583	2,902	58,412
	Polyethylene, total	202,897	19,947	26,428	209,378
39021000	Polypropylene, unprocessed, unspecified	150,431	16,141	1,767	136,058

If we assume that the residual contents of chromium from catalysts do not exceed 2 mg/kg (a value stated in the CN), the maximum supply of chromium associated with unprocessed polyethylene and polypropylene is 0.69 tonnes Cr/year.

3.7.3 Accelerators in paint

Chromium is not used in paints manufactured in Denmark, nor in imported paints registered in the Product Register, except insofar as chromium occurs in pigments. The most common chromium pigments are chromium yellow ($PbSO_4$, $PbCrO_3$), chromium oxide green (Cr2O3) and chromium green ($PbCrO_4$, $PbSO_4$, $FeNH_4Fe(CN)_6$) (Poulsen ***et al.***, 2002). A 1996 study of chemical substances in paint on the Swedish market shows the same result (Ahlborn ***et al.***, 1996). The available literature also fails to present any examples of chromium in paint except in the form of pigments (Bielman, 1993). Nevertheless, the Product Register includes records of 13 "paint and varnish hardeners" which contain some chromium. For some hardeners, chromium contents are said to be as high as 46%. Such chromium takes the form of chromium(III) oxide. The remaining products have small quantities (0–0.46%) of organic compounds containing chromium (possibly pigments) or inorganic Cr(III) compounds. The chromium content of such products is very low, and it is estimated that the use of chromium in pigments is by far the main reason behind chromium contents in paint. Statistics Denmark's survey of foreign trade (by products and country) does not include an inventory of hardeners for paint (Statistics Denmark, 1999; 2000; 2001).

3.7.4 Concrete hardener

The Product Register has a product listed under the group heading H1510 (Concrete hardeners) which contains 0.01% chromium in the form of chromium(III) oxide, Cr_2O_3. When asked, sources within the industry (Cementfabrikkernes tekniske Oplysningskontor, 2002b; Dansk Bykemi, 2002) did not believe that chromium is used for products where concrete is added. Concrete hardeners are not included in Statistics Denmark's survey of foreign trade by product and country (Statistics Denmark, 2001), so the exact supply is not known. It is, however, estimated that the quantities involved are very small.

3.7.5 Fillers, sealants, etc.

The Product Register has a number of products which contain chromium listed under the heading U510 (Fillers, sealants, etc.). Most of these have a chromium content of 0–21% Cr in the form of chromium(III) oxide. Other substances containing chromium can occur, but the information on these substances is confidential according to the rules governing the Product Register. The information has, however, been taken into account when estimating the total supply.

Table 3.23
Fillers, sealants, etc. which contain chromium and are featured in the Product Register. Notification of other substances has been submitted, but the rules governing the Product Register does not allow a detailed account.

	Product	Chemical			Concentration			
					%		% Cr	
					Min	Max	Min	Max
U0510	Filler (Fillers)	1308–38–9	Chromium(III) oxide	III	0	30.00	0	20.53

Nowhere in the literature is it stated that chromium is used as an agent in fillers and sealants (Evans, 1993; Flick, 1978). Persons within the industry have stated that they do not believe that chromium is used in fillers in Denmark (FOSROC, 2002). A study of a large number of data sheets for fillers and sealants from the companies 3M, Bostik and Alfix A/S (available on the Internet) did not reveal any chromium contents in these products (3M, 2002; Bostik A/S, 2002; Alfix A/S, 2002).

In theory, chromium could occur in fillers in the form of pigments. In actual fact, however, it is rare that customers want the colours which chromium pigments could provide in fillers, and there are no records of use of chromium pigments for this purpose within the industry (FOSROC, 2002; Dansk Bykemi, 2002). The most frequently used pigment in fillers is TiO_2 (Evans, 1993). It has not been possible to identify any filler which contains chromium(III) oxide or zinc chromate. Fillers may, however, contain cement, and so may also contain small quantities of chromium (see section 4.2). If we assume that CN no. 32141 – Sealants – are fillers, and that the cement content of this product group is 25% at most with chromium contents corresponding to those of standard, chromium-reduced cement (less than 2 mg Cr(VI)/kg), the total supply of Cr(VI) associated with fillers will not exceed 0.008 tonnes Cr/year.

Table 3.24
Supply of fillers, sealants and putties (1998–2000) according to Statistics Denmark

KN uh	Product	Import tonnes/year	Export tonnes/year	Production tonnes/year	Supply tonnes/year
32141010	Fillers and sealants	13,834	3,486	4,932	15,281
32141090	Putties for surface preparation	14,308	9,679	6,674	11,303

3.7.6 Putties

Like fillers, putties also contain cement – and therefore chromium. This category includes floor surfacers (self-levelling or not) (Casco, 2002). In addition to this, data from the Product Register shows that chromium(III) oxide is a common constituent of putties, which may contain up to 21% Cr. This makes for a maximum supply of 2,321 tonnes Cr(III)/year. In view of the fact that interviewees within the industry do not believe that Cr is used in putties at all, this theoretical supply is not realistic. Based on the fact that people within the industry deny any use, 1–2% of the figure stated above seems more likely. This corresponds to 23–46 tonnes Cr(III)/year. The supply of Cr from the cement included in the putties and compounds will not exceed 0.011 tonnes Cr(VI)/year and 0.18 tonnes Cr(III)/year. This means that all in all, the total supply of Cr associated with putties is 23–47 tonnes Cr(III)/year and 0–0.011 Cr(VI)/year.

Table 3.25
Putties which contain chromium and are featured in the Product Register. Notification of other substances has been submitted, but the rules governing the Product Register does not allow a detailed account.

	Product	Number	Chemical substance			Concentration			
						%		% Cr	
						Min	Max	Min	Max
U0520	Putty	27	1308–38–9	Chromium(III) oxide	III	0	30.00	0	20.53

3.7.7 Glue

The Product Register includes records of a number of hardeners which are used for glues and contain chromium. These hardeners contain 0–9% Cr in the form of inorganic Cr(III) or Cr(VI) salts. A study of a large number of data sheets for glues from the companies 3M, Bostik and Alfix A/S (available on the Internet) did not reveal any chromium contents in these companies' products (3M, 2002; Bostik A/S, 2002; Alfix A/S, 2002).

Chromium is, however, used to a limited extent in separate hardeners for white, waterproof PVA glues to be used with wood (Casco, 2002). This type of glue is produced by companies such as Casco and Dana. Normally, hardeners for PVA glue are made by means of an aluminium salt, but the ability to withstand water is increased by means of Cr hardeners. This type of hardener is not produced in Denmark (Casco, 2002). A Danish company with a significant market share (estimated at between 30 and 70%) has calculated that it imports and sells PVA glue hardeners in quantities corresponding to 0.077 tonnes Cr a year, and as a result the total supply is estimated to be around 0.11–0.26 tonnes Cr/year. Confidential information from the Product Register indicates that most of this chromium is Cr(III).

3.8 Textiles

When chromium appears in textiles, it usually does so as part of a dye or pigment added to the textile fibres, as an impurity in a dye/pigment or, for man-made fibres, as impurities in the relevant man-made material.

3.8.1 Chromium in dyes and pigments

Chromium occurs in several kinds of dyes and pigments as complex formers and impurities.

3.8.1.1 Chromium dyes

Chromium dyes are mainly used for wool, but also for silk and polyamide. What happens is that potassium dichromate ($K_2Cr_2O_7$) is added in addition to the dye itself, often an azo dye. Cr(VI) from the potassium dichromate is absorbed into the textile fibre (bound to amino acids) and is reduced to Cr(III). The Cr(III) moves slowly within the fibre, forming complexes with the dye which is then fixed in the fibre. This makes the textile highly washable. Dyes of this kind are not sold in Denmark (Larsen ***et al.***, 2000; Ullmann, 2002).

3.8.1.2 Metal complex or "pre-metallised" dyes

Metal complex dyes are used for wool, silk and polyamide. Within dyes of this type, a metal ion – such as Cr – is complex bound to one or two dye molecules containing –OH, $–NH_2$ or –COOH groups. When the metal dye complex is added to a textile, it is bound in the same manner as the chromium dyes (Larsen ***et al.***, 2000).

3.8.1.3 Chromium as an impurity in dyes

Because chromium can act as a catalyst, it is often found as an impurity in dyes and pigments. The content of Cr as an impurity in azo dyes has been measured as being approximately 6 mg Cr/kg dye on average (Burg ***et al.***, 1980). Potassium dichromate may be used as an oxidation agent for oxidation of, for example, sulphur dyes, but such use is less common (Ullmann, 2002; Larsen ***et al.***, 2000).

3.8.2 Chromium as an impurity in textile fibres

Chromium is used as an accelerator in the production of a number of plastic types. As a result, one might well expect to find small amounts of chromium in textile fibres. However, chromium is mainly used for production of polyethylene and polypropylene, and these materials are not very widely used as textile fibres. While it is true that polypropylene is used for special sports underwear, the quantities involved are small (Larsen ***et al.***, 2000).

3.8.3 Supply of chromium with textiles

Chromium pigments are not used to dye textiles in Denmark and most of Western Europe (Danish Technological Institute, 2002a), and the use of metal complex dyes is also very limited (Remmen & Rasmussen, 1999). This means that it is unlikely that textiles made with dyes containing chromium are produced in large quantities in Denmark. Thus, there will be very little export of chromium with textiles produced in Denmark. All this means that chromium associated with textiles will primarily reach Denmark in connection with import of textiles.

3.8.3.1 Chromium contents in textiles

Dyes containing chromium are mainly used for wool textiles. Generally speaking, high chromium concentrations can be found in wool. However, very high concentrations have also been found in printed textiles made from other fibres, so the averages for textiles made from wool and other fibres are more or less identical (Larsen ***et al.***, 2000). According to a Swiss study, protective clothes may contain high concentrations of chromium (Bundesamt für Umwelt, 1995). The use of chromium pigments in safety colours may be one reason for this. However, the protective clothing made by Kansas – one of Europe's largest producers of protective clothing and a prominent player within the Danish market – does not contain chromium in concentrations which can be detected (Kansas, 2002). As a result, protective clothing is treated like any other clothing in calculations.

On the basis of Larsen ***et al.*** (2000), we can make a rough estimate to the effect that the chromium content of wool products is 100–300 mg Cr/kg wool on average. In a number of other textiles – including polyester, silk, and cotton with PVC prints – average values of around 100–300 mg Cr/kg textile were measured for those textiles where the chromium concentrations were above the detection limit (approximately 40%). As regards impurities in azo dyes, the contents can be calculated as being around 0.14–0.22 mg Cr/kg textile (Larsen ***et al.***, 2000).

3.8.3.2 Supply in textiles in Denmark

Statistics Denmark divides textiles into categories such as wool and man-made fibres, but does not distinguish between various kinds of man-made fibres. Danish experts cannot provide any data on consumption by fibre type (Dansk Textil og Beklædning, 2002; Danish Technological Institute, 2002a). Consequently, this survey is based on information on consumption by fibre type at EU level (1998); see table 3.26.

Table 3.26
Consumption of fibres for clothing in the EU, by type (EU, 1998).

Consumption in the EU, by type	
Cotton	30%
Wool	16%
Polyester	20%
Poly-acrylic	13%
Polyamide	9%
Regenerate cellulose	10%
Other	1%

According to Larsen ***et al.*** (2000), the annual consumption of textiles in Denmark is approximately 22 kg/person. Of this amount, textiles for clothing account for 13 kg/person. This corresponds to a total consumption of 116,600 tonnes textiles/year, of which 68,900 tonnes/year are used for clothing.

The relative consumption of fibres by type is not known for fibres other than those used in textiles for clothes. We do, however, know that wool, cotton and various man-made fabrics are used, for example, for furnishing fabrics. It is estimated that synthetic fibres are more widely used within areas other than the clothing industry than within the clothing industry itself. For example, polyester is the most widely used textile fibre in tyres for cars and small lorries (Williams, 2002). As a result, we have applied a slightly different estimated consumption of fibres for purposes other than clothes. This estimated consumption is shown in table 3.27.

Table 3.27
Consumption of fibres for purposes other than clothing, by type (estimated)

Consumption by type	
Cotton	15%
Wool	8%
Polyester	40%
Poly-acrylic	18%
Polyamide	13%
Regenerate cellulose	5%
Other	1%

By using these figures, we can calculate the supply of textiles in Denmark by fibre type. The results are shown in Table 3.28.

Table 3.28
Supply of fibre types in Denmark

	Tonnes/year
Cotton	28,032
Wool	14,909
Polyester	32,929
Poly-acrylic	17,267
Polyamide	12,678
Regenerate cellulose	9,344
Other	1,442

Effort has also been made to calculate the total import and supply of wool by summing up data from Statistics Denmark for all CN entries for garment textiles and carpets made from wool. In 1999, for example, the import was calculated at 3,210 tonnes wool/year and the supply at 3,210 tonnes wool/year. These figures are less than those shown in Table 3.28, which is partly because they do not include all goods made from wool, furnishing textiles, etc. As a result, the calculations are based on the figures in Table 3.28.

3.8.3.3 Supply of chromium with textiles

We can calculate the supply of chromium associated with textiles by basing our calculations on the estimated contents from section 1.3.1. For these calculations, it is assumed that 40% of the non-wool textiles have chromium contents as measured, and that 50% of all textiles are dyed with azo dyes.

The calculations show that the supply of chromium with textiles to Denmark is around 5.6–16.7 tonnes Cr/year.

3.8.4 Disposal

Danish production of textiles leads to considerable amounts of textile waste, but it is estimated that the chromium content of this waste is very low and hence without significance in this context. It is assumed that the disposal corresponds to the supply less the net export of second-hand clothes. It is also assumed that no accumulation of textiles occurs in Denmark. According to Statistics Denmark, the year 1999 saw net exports of 9,381 tonnes of second-hand clothes (Statistics Denmark, 2000). Thus, we conclude that a total of 107,219 tonnes of textiles are disposed of every year. Textiles are mainly disposed of by means of incineration along with domestic waste, which is to say that around 5.1–15.3 tonnes of chromium from textiles is incinerated each year.

3.9 Electronic storage

3.9.1 Use of chromium in magnetic media

Chromium is used in magnetic media to store sound, images or data. Even though optical media such as CD-ROMs are becoming increasingly popular, the year 1999 still saw considerable use of magnetic tapes of various kinds, some of which contain chromium. The chromium compounds used in magnetic media are CrO_2 (Cr(IV)) and Cr_2O_3 (Cr(III)), which have excellent magnetic properties (Ullmann, 2002; TDK-Scandinavia, 2002; EMTEC, 2002a). There are no manufacturers of magnetic media in Denmark, so all goods of this kind are imported.

The companies Emtec, TDK, Sony and Fuji have been contacted with a view to collecting information about the chromium compounds used in their products – and the quantities used. Chromium is mainly used in VHS video tapes and audio tapes. There are a few other niche products which contain chromium. Chromium can also appear as unwanted impurities in magnetic materials in very low concentrations. One manufacturer tells us that their Mini Discs contain 0,000009 g Cr_2O_3 per Disc, which corresponds to approximately 1 g chromium per 150,000 Mini Discs. The level of chromium in such products can only be described as very low.

Magnetic storage media comprise a wide range of product types. Table 3.29 shows some of the products which fall within this heading. The table has been prepared on the basis of information from manufacturers of storage media (TDK-Scandinavia, 2002; EMTEC 2002a; Sony Denmark, 2002) and the industry associations for electronic products (Brancheforeningen Forbruger Elektronik (BFE)) and Brancheforeningen for Elektronik, 2002). The so-called professional tapes constitute a very varied product group. According to Emtec, chromium is not used in significant quantities in these products (EMTEC, 2002a), but it has not been possible to obtain information about the chromium content in all product types.

According to producers of magnetic storage media, by far the most significant source of chromium in such products is chromium which is added as a component in audio tapes and – particularly – video tapes. Both audio and video tapes are available in versions with and without chromium.

Table 3.29
Various magnetic storage media. Any presence of chromium is indicated.

Storage media	Chromium Yes/no	Source
Audio tapes	Yes/no	TDK, Emtec, Sony
Video tapes, VHS	Yes/no	TDK, Emtec, Sony
Mini Discs	(No), <100 mg/kg magnetic metal	TDK, Emtec
Disks for PCs	(No),<100 mg/kg magnetic metal	TDK, Emtec
Micro tapes	No	TDK, Emtec
Camera tapes	No	TDK, Emtec
Data tapes (Backup tapes)	No	TDK, Emtec

Statistics Denmark has information about the supply of blank and recorded media, calculated in tonnes. The quantities indicated also include cassettes/cases and covers; see Table 3.30.

Table 3.30
The supply of magnetic media (1998–2000) according to Statistics Denmark

CN uh	Product	Import tonnes/year	Export tonnes/year	Production tonnes/year	Supply tonnes/year
8523 11	Magnetic tapes <= 4mm	233	384	0	–151
8523 12	Magnetic tapes 4mm< <6.5 mm	43	114	0	–71
8523 13	Magnetic tapes > 6.5 mm	2,274	3,200	470	–455
8524 40 00	Vinyl albums, tapes, other media for recording/storage; magnetic tapes used to record phenomena other than sound and images	87	99	0	–12
85244010	Magnetic tapes with data	102	89	6	19
85244099	Magnetic tapes with data <= 4mm	65	18	547	594
85245100	Magnetic tapes <= 4mm, pre-recorded	16	127	0	–111
85245200	Magnetic tapes 4mm< <6.5 mm, pre-recorded	39	165	37	–89
85245300	Magnetic tapes > 6.5 mm, pre-recorded	629	3,053	3,820	1,396

3.9.2 Chromium in VHS video tapes

By weighing randomly selected VHS tapes, we have established intervals for the weight of pre-recorded tapes (purchased with pre-recorded films or similar) and blank tapes. The result is shown in Table 3.31.

Table 3.31
Weight of randomly selected VHS tapes

Type	Cover g/tape	Tape incl. cover g/tape
Blank VHS	10–50	220–240
Pre-recorded VHS	100–110	140–160

According to calculations made by Statistic Denmark, the supply of pre-recorded VHS tapes in Denmark is 1,396 tonnes per year, corresponding to approximately 5.7 million tapes per year with an average weight of 245 g including covers.

Sales of pre-recorded tapes are on the rise and now exceed the sales of blank tapes. Sales of blank VHS tapes amount to approximately 5 million a year, and the sales of pre-recorded tapes are estimated to be around 6–7 million per year (Brancheforeningen for Elektronik, 2002).

On this basis, it is estimated that the supply of VHS tapes in Denmark is 10.7–12 million VHS tapes each year.

According to information from producers, each tape contains 0.16–0.21 g chromium. It is estimated that 95%–100% of all tapes contain chromium. The total quantities of chromium correspond to 1.6–2.5 tonnes of chromium per year, mainly in the form of Cr(III). Cr(IV) occurs less frequently in tapes.

On the basis of sales statistics for VHS and DVD equipment, it is estimated that the sales of both pre-recorded and blank VHS tapes will fall in the long term. The sales of VHS equipment remain stable, whereas DVD equipment is sold in ever greater numbers (Brancheforeningen for Forbrugerelektronik, 2002). This leads to the natural assumption that the supply of VHS tapes will fall.

After use, and as the technology becomes obsolete, video tapes will end up in the waste system.

3.9.3 Chromium in audio tapes

Audio tapes are sold in much smaller quantities than video tapes in Denmark. No reliable surveys of the sales in Denmark are available. The producers estimate the sales to be around 1.0 million tapes per year, of which approximately 10% contain chromium (EMTEC, 2002b; Sony Denmark, 2002). If they contain any chromium at all, audio tapes contain approximately 2 g chromium compounds per tape (confidential information from manufacturers). In audio tapes, CrO_2 is typically used, whereas video tapes typically contain Cr_2O_3. On this basis, the supply of chromium associated with audio tapes has been calculated to be approximately 0.12 tonnes chromium per year, mainly Cr(IV).

The market for audio tapes is dwindling rapidly as audio tapes are replaced by digital technologies such as Mini Disc and CDs.

After use, and as the technology becomes obsolete, audio tapes will end up in the waste system.

3.9.4 Supply of chromium with magnetic media

The total supply of chromium associated with magnetic media is estimated to be around 1.8–2.6 tonnes Cr/year.

3.10 Laboratory chemicals

Chromium is part of a large number of laboratory chemicals. Among other things, it is used as a catalyst, an oxidation agent, and a pH regulator. These chemicals are often sold and used in very small quantities (Bie & Berntsen, 2002; VWR, 2002). As a result, it has not been possible to get a total overview of the quantities consumed in Denmark.

Table 3.32 shows information from the Product Register about the expected uses of chromium compounds as laboratory chemicals and the concentrations in which they are used.

Table 3.32
Laboratory chemicals containing chromium (The Product Register, 2001).

Chemical:	Oxidation level	Concentration
Chromium(VI) oxide	VI	100%
Lead(II) chromate	VI	100%
Sodium chromate	VI	98–100%
Potassium chromate	VI	98–100%
Potassium dichromate	VI	100%

Generally speaking, suppliers of chemicals for laboratories in Denmark supply the chemicals which their customers demand, and this is also true of the chemicals listed in Table 3.32. (Bie & Berntsen, 2002; BASF, 2002; VWR, 2002). It has not been possible to obtain information about the chromium compounds that are actually sold by suppliers today. This is because the quantities involved are small, which means that the sales are not registered centrally. Based on information from suppliers, it is assumed that efforts are made to avoid use of hexavalent chromium compounds due to their harmful impact on health.

Potassium dichromate and chromium oxide are used in laboratories as oxidation agents. In the widely used COD (Chemical Oxidation Demand) measurements, potassium dichromate is used as an oxidation agent to degrade organic matter in water. COD measurements are used to measure oxygen consumption in water, thereby indirectly measuring its content of organic matter. As a result, COD measuring is carried out every day at most Danish sewage treatment plants. On the basis of VWR (2002), it is estimated that 150,000–250,000 COD analyses are carried out every year in Denmark. According to Dansk Standard, 217.5 ml of reagent is used per test, containing 59 mg potassium dichromate. This means that 9–15 kg potassium dichromate is used every year, corresponding to 3–5 kg hexavalent chromium. In a 1998 study of analyses of chemical oxygen demand (COD) and non-volatile carbon (nonVOC) in wastewater, the annual consumption of chromium for COD was estimated to be 2–10 kg (DHI, 2002). It seems unlikely that the COD tests will be replaced by an alternative method anytime soon, so we must expect that the consumption of potassium dichromate for COD measuring will remain unchanged in future.

Chromic sulphuric acid, which is a mixture of 5% potassium dichromate and 95% sulphuric acid, is used to clean laboratory glassware. Today, chromic sulphuric acid is only used to a limited extent because of its dangerous properties. It is estimated that less than 100 litres of chromic sulphuric acid are used each year in Denmark (VWR, 2002), and that this use will cease in the long term.

Chromic sulphuric acid is also used in connection with oxidation of alcohols for carboxyl acids, the so-called Jones reagent ($CrO3/H2SO4/H2O$) (The Royal Veterinary and Agricultural University, 2001). The use of the Jones reagent is deemed to be limited.

When the chromium content of a metal compound is determined on the basis of atomic absorption, chromium is used as a standard to calibrate the measuring equipment (VWR, 2002), (DHI, 2002; Bie & Berntsen, 2002). It is estimated that very small quantities of chromium are used for this purpose.

In total, it is estimated that laboratory chemicals account for less than 0.1 tonne chromium each year, primarily chromium(VI).

Danish legislation states that after use in laboratories, chemicals which contain chromium must be submitted for special treatment as dangerous waste. Almost 95% of all chemical waste is disposed of at Kommunikemi A/S, while a smaller portion of the laboratory waste is disposed of at Special Waste System in Nørre Alslev (Waste 21; the Danish EPA, 1999).

The dangerous chemical waste from laboratories is mainly disposed of by means of incineration. Table 3.33 below shows the relative shares accounted for by the various treatment methods.

Table 3.33
Special treatment of chemicals from laboratories 1999–2000 (Prepared on the basis of Affaldsstatistik 2000, 2001).

Incineration	Landfilling	Special treatment	Recycling
89%	3%	7%	1%

At Kommunekemi, waste incineration takes place at 1,200°C, whereas standard incineration plants only reach temperatures of 900–1,000°C. The flue gas from all incineration carried out at Kommunekemi is cleaned by means of sophisticated technology. Slag and fly ash ends up at a controlled landfill where test samples of the percolate are taken regularly. If the limit values are exceeded, the percolate is returned for incineration (Kommunekemi, 2002a).

3.11 Other uses of chromium compounds

3.11.1 Fireproof products and foundries

Due to its high melting point (2,435°C), chromium(III) oxide is also used in fireproof products such as firebricks, fireproof sand, stone and clay. Such products are used, for example, in melting furnaces and foundry furnaces.

Most mixtures are based on magnesium-chromium ironstone. They are mainly used within the steel, copper and cement industries to line furnaces and similar installations against heat and flame in connection with production.

Table 3.34
Import, export, production and supply of firebricks 1998–2000 (Statistics Denmark, 2001b).

Unit	Import tonnes	Export tonnes	Production tonnes	Supply tonnes
Firebricks	1,008	15	0	993
Chromium content[1]	206	3	0	203

1. Firebricks contain approximately 30% chromium(III) oxide, corresponding to 20.4% pure chromium (Huse *et al.*, 1992).

As illustrated in Table 3.34, the use of firebricks is relatively limited in Denmark. Only a few companies in Denmark have the facilities to melt and cast materials and goods. For example, Aalborg Portland and Det Danske Stålvalseværk are the only companies in Denmark which produce cement and steel, respectively. In 2001, Det Danske Stålvalseværk placed 5,000 tonnes of firebricks in their furnaces, and some of these bricks contain chromium. According to the company's own estimates, this corresponds to about two tonnes of chromium (Det Danske Stålvalseværk, 2000b). It has not been possible to obtain further information about the consumption of firebricks, which in turn means that it has not been possible to arrive at figures for the relevant chromium contribution except for those stated in Table 3.34. It is estimated that some firebricks burn away, thereby ending up in the steel products or emissions. The rest are eventually replaced and end up in landfills. From there, no further emissions of chromium take place.

3.11.2 Chromium used in drilling mud when drilling for oil

Chromium lignosulfonates have previously been used in drilling mud as a conditioning and dispersing agent when drilling for oil (Ullmann, 2002; Offshore-environment, 2002) and are still available on the international market. Back when chromium lignosulfonates were used, discarded drilling mud from offshore drilling rigs was usually dumped in the ocean, while drilling mud from land-based drilling rigs was sent to landfills. Use of chromium lignosulfonate in drilling mud is not expected to contribute to chromium contents in the extracted oil, as the drilling mud is removed from the borings before oil extraction commences (Sea Consult, 2002).

In the Danish part of the North Sea, oil extraction is carried out by Maersk Oil, Statoil and Amarada Hess, but Dansk Olie og Naturgas (DONG) carried out the actual drilling work for some of these companies. DONG has built a database of all the drilling chemicals used and their constituents. According to this database, no chromium compounds – and hence no chromium lignosulfonates – occur in the chemicals used (DONG, 2002b). Statoil confirms that they do not use drilling chemicals containing chromium or chromium compounds in connection with their oil activities in the North Sea (Statoil, 2002a). Similarly, Maersk phased out their use of chromium lignosulfonate in the North Sea in the mid-1980s (Sea Consult, 2002).

In 1999, DHI Water & Environment carried out an environmental assessment of the offshore chemicals used in 1993 in quantities greater than 1 tonne (DHI ***et al.***, 1999). In this connection, suppliers of chemicals to the Danish part of the North Sea submitted confidential information about the contents of the chemical products used to search for and extract oil. The study comprised 273 chemical products, containing 306 different chemicals. None of these chemicals contained chromium or chromium compounds.

On this basis, the assessment is that chrome lignosulfonate is no longer used in the North Sea in connection with drilling activities. If chrome lignosulfonate is used elsewhere in the world, it will not contribute to chromium levels in crude oil, and so it will not affect the quantities of chromium entering Denmark. It is also estimated that chromium and chromium compounds are not widely used in connection with oil activities in the North Sea, except to produce the stainless steel used at the facilities.

3.12 Summary

Chromium compounds are used for a wide range of functions. Table 3.35 shows estimated figures for consumption and distribution of chromium in connection with compound use in Denmark.

Table 3.35
Estimated supply and distribution of chromium associated with use of chromium compounds in Denmark (tonnes Cr/year).

Use	Consumption	Air	Water	Soil	Reuse	Dangerous waste	Waste treatment
Surface treatment	37.7	–	0.089	–	8.7[1]	26.1	2.9[1]
Pigments in paint	12.6–116.7	–	0.03–13	–	0	0.3–17.5[2]	0.3–17.5[2]
Pigments in plastic	~ 0	–	–	–	–	–	–
Impregnation	8.8	–	0.3–0.6	0.3–0.6	1.3	?	24.4[3]
Corrosion -inhibitors	~ 0	–	–	–	–	–	–
Tanning in Denmark	27	–	0.27	–	–	–	27
Imported leather[4]	137–275	–	–	–	–	–	137–275
Catalysts	0.1–1	–	–	–	–	0.1–1	–
Hardeners	<1	–	–	–	–	–	–
Fillers	<<1	–	–	–	–	–	–
Putties	13–47	–	–	–	–	–	–
Glue	<1	–	–	–	–	–	–
Textiles	5.6–16.7	–	–	–	–	–	5.1–15.3
Electronic storage	1.8–2.6	–	–	–	–	–	–
Laboratory chemicals	<1	–	<<1	–	<<1	<1	–
Firebricks	200	–	–	–	–	–	–
Total	450–740		0.7–14	0.3–0.6	10	27–45	198–362

1. It is assumed that 75% of all chromium plated products are recycled, whereas 25% is disposed of through the standard waste treatment system.
2. It is assumed that 50% of all surplus paint is disposed of as dangerous waste, while the remaining 50% is disposed of as household waste for incineration.
3. The waste quantities of impregnated wood containing chromium will increase in future, as the accumulated quantities of such wood will be disposed of in the years to come, cf. Figure 3.1 and Figure 3.2.
4. "Imported leather" includes shoes, garments, gloves, furniture, luggage, bags, etc.

4 Chromium as a trace constituent

Chromium occurs as a trace constituent in a wide range of raw materials and products. The most significant of these are;

- Fossil fuels – coal and oil
- Aluminium – see section 2.2
- Copper – see section 2.3
- Cement

Here, we focus on chromium as a trace constituent in fossil fuels and cement.

4.1 Coal and oil

Fossil fuels like oil and coal contain a number of heavy metals, including chromium. The average contents are shown in Table 4.1. If we base our calculations on an annual consumption of oil and coal of 182 PJ/year and 386 PJ/year, respectively, in 1999 plus residual product quantities from Danish CHP plants, we can establish a balance for chromium as a trace constituent in fuels; see Table 4.1. The figures on fuel quantities describe the gross energy consumption and cover all kinds of coal and oil products. Coal is, however, primarily used at CHP plants, which means that the residual product quantities come mainly from coal.

Table 4.1
Balance for chromium as a trace constituent in fuels

	Quantity[5] (tonnes)	Quantities used (GJ)	Chromium con-centration (mg Cr/tonne)	Emissions factor[6] (mg Cr/GJ)	Chromium quantities (tonnes chromium)
Coal[1]	–	182 x 10^6	32	802	146
Oil[2]	–	386 x 10^6	0.055	2.21	0.85
Flue gas[3]	–	–	–	4.33/4.01[7] 0.72/0.66[8] 0.80[9]	3.5[10]
Fly ash[11]	795 x 10^3	–	78,000–230,000	–	62–183
TASP[4]	50 x 10^3	–	–	–	–
Plaster	366 x 10^3	–	–	–	–
Slag, etc.[11]	72 x 10^3	–	15,000–21,000	–	1.1–1.5

1. The total quantity of coal used in Denmark.
2. The total quantity of oil used in Denmark.
3. The consumption of coal and oil for energy conversion (heat and electricity generation) has been calculated to be 185 x 10^6 GJ coal and 48 x 10^6 GJ oil products (The Danish Energy Authority, 2000). In addition to this, 12 x 10^6 GJ coal are used directly by production industries, i.e. without any special flue-gas treatment facilities, and 318 x 10^6 GJ oil products are used directly by households and businesses or for transport.
4. Dry desulphurisation product.
5. The residual product quantities constitute 99% of the quantities produced (The Danish EPA, 2000)
6. Illerup *et al.* (1999).
7. Emission factors after electro filter and desulphurisation plant for coal (semi-dry/wet flue gas cleaning).
8. Emission factors after electro filter and desulphurisation plant for oil (semi-dry/wet flue gas cleaning).
9. Emission factor after SNOX facility for coal.
10. For other combustion of oil, it is assumed that 50% of the chromium contents are emitted to air. For other combustion of coal, it is assumed that 25% of the chromium contents are emitted to air.
11. Chromium contents in fly ash and slag (ELSAM, 2002).

A total 0f 99% of the residual products are reused in a wide range of products, e.g. cement, concrete, lightweight concrete, asphalt, etc. The remaining 1% is sent to landfills.

4.2 Cement

It is a well-known fact that cement can contain quite a lot of chromium. To ensure a safe working environment, there are rules for the content of Cr(VI). In all likelihood, chromium in cement probably comes from raw materials from specific areas, from coal used during firing, and from fly ash used as part of the cement. During the period 1998–2000, Aalborg Portland used 225,171 tonnes coal each year and 187,350 tonnes of petroleum coke/year on average (Aalborg Portland, 2001a). The chromium content of coal varies, but is often 32 mg Cr/tonne (ELSAM, 2002). If we assume that coal and petroleum coke have the same chromium content, we arrive at a Cr input of 0.013 tonnes Cr/year.

During the period, an average of 204,819 tonnes fly ash/year were used. Fly ash from CHP plants contains 78–230 mg chromium/kg (ELSAM, 2002). This corresponds to chromium contributions to cement of 16–47 tonnes/year.

The other raw materials used to make cement, chalk and sand, are not expected to contain large amounts of Cr. Analyses carried out at Aalborg Portland show that their "Basis" cement contains 32 ppm Cr-total, of which 5–6 ppm is chromate Cr(VI). Other types of cement – white cement and low-alkali cement – often have lower contents of Cr(VI) << 2 ppm. It is, however, assumed that the same relationship between total Cr and Cr(VI) applies (Cementfabrikkernes tekniske Oplysningskontor, 2002a).

Approximately 1.5 million tonnes of cement are used in Denmark each year. Aalborg Portland sells 1.3 million tonnes of cement on the Danish market each year and exports 5–600,000 tonnes, particularly to the USA (Cementfabrikkernes tekniske Oplysningskontor, 2002a).

During the period 1998–2000, the average production at the Aalborg factory was as follows; 2,487,123 tonnes cement/year, 145,963 tonnes clinker/year, and 3,450 tonnes filler/year (Aalborg Portland, 2001a). According to Statistics Denmark, the total quantity of cement produced in Denmark during this period was 2,622,168 tonnes/year on average. This is to say that almost all of this cement was produced at Aalborg Portland. As a result, their figures on chromium contents are used for general purposes.

The total quantities of cement produced are divided into grey cement and other cement. In 2001, Aalborg Portland produced 2.1 million tonnes grey cement (Aalborg Portland, 2001b). As the total production figures were more or less identical for 1999 and 2001, it is estimated that 2.1 million tonnes of the cement produced in 1999 are also grey cement. The rest (2,622,168 – 2,100,000 = 522,168 tonnes) is assumed to be of a kind with lower contents of chromium (white cement, low-alkali cement). The actual chromium content is not known, but the content of Cr(VI) is much less than 2 mg/kg. If the content is set at 0.2–1 mg Cr(VI)/kg, this leads to chromium quantities of 0.10–0.52 tonnes Cr(VI)/year and 0.6–3.0 tonnes Cr(III)/year.

Production of 2,100,000 tonnes grey cement/year containing 32 mg Cr/kg yields 67.2 tonnes Cr/year. Of this amount, 10.5–12.6 tonnes are Cr(VI). As far as possible, Cr(VI) is reduced to Cr(III) by adding Fe(II); this reduces the concentration of Cr(VI) to less than 2 ppm. Thus, production of 2,100,000 tonnes grey cement/year containing 1–2 mg Cr(VI)/kg yields 2.1–4.2 tonnes Cr(VI)/year and 63,0–65,1 tonnes Cr(III)/year.

Table 4.2
Supply of cement (1998–2000) according to Statistics Denmark

CN uh	Product	Import tonnes/year	Export tonnes/year	Production tonnes/year	Supply tonnes/year
25232900	Portland cement	221,581	530,696	1,951,783	1,642,668
25231000	Portland cement, clinker (cement clinker)	127	106,326	111,367	5,168
25232100	Portland cement, White cement	8,150	527,244	550,178	31,084
25233000	Portland cement, Aluminate cement	3,010	15	0	2,994
25239010	Clinker cement	1	11	0	–10
25239090	Hydraulic cement	17,799	47,837	27	–30,012
	Total cement	250,667	1,212,130	2,613,345	1,651,883

4.3 Summary

Chromium occurs as a trace constituent in, for example, fossil fuels – coal and oil – and in cement as a result of the use of coal and residual products from energy production in connection with cement production. Table 4.3 shows the estimated consumption and dispersal of chromium.

Table 4.3
Estimated consumption and dispersal of chromium associated with chromium as a trace constituent in Denmark

Use	Consumption tonnes Cr/year	Air	Water	Soil	Reuse	Dangerous waste	Waste treatment
Coal and oil	147	3.5	–	–	62–185[2]	–	–
Cement	67[1]	??	–	–	–	–	–
Total	214	3.5	–	–	62–185	–	–

1. Of which 2–4 tonnes Cr(VI).
2. Approximately 20% of the fly ash and slag used are for filler in accordance with Statutory Order 568 and filler in accordance with Chapter 5 approvals (The Danish EPA, 2000).

5 Circulation with waste

Disposal of chromium and chromium compounds mainly takes place in connection with disposal of products and waste products which contain chromium. Chromium is an element and so will not disappear. This means that we cannot dispose of chromium by disposing of products which contain chromium – we merely move it.

Once an object, a product, has been used for the last time, it can either be disposed of actively or simply "perish" where it was last used. In both cases, the contents of such products may enter the environment. This includes chromium. Active disposal allows some control over emissions into nature.

When we dispose of chromium, we often do so in the form of relatively small concentrations in other products: tapes, chromium plated objects, impregnated wood, painted objects, glass, etc.

The only known way to release chromium from the product it occurs in is to burn or melt it.

Active disposal includes the following forms of waste treatment:

- Landfilling (in principle, this is restricted to non-flammable objects)
- Incineration (flammable objects)
- Treatment plants (municipal), application of sludge to agricultural areas
- Treatment plants (at industries)
- Special waste (Kommunekemi)
- - Incineration
- - Landfilling

Passive disposal occurs when products which contain chromium are left to perish where they were last used. It is estimated that this type of disposal is quite infrequent in Denmark. There will, however, probably be some minor losses of chromium to the environment from products which contain chromium and which perish without being sent for incineration or landfilling, e.g. impregnated wood, painted objects (due to peeling) and chromium plated objects (due to oxidation). The quantities released in this manner have not been assessed.

A number of products containing chromium can be ***recycled*** or ***reused***. This means that the products remain usable for longer, which in turn means that the production of new goods of this kind can be reduced. Metal and glass are prime examples of products which can be recycled or reused and which contain significant amounts of chromium. Plastic and paper are also recycled, however, and may contain chromium from pigments, etc. The most significant recyclable material flows which contain chromium are:

- Iron and steel
- Aluminium
- Copper

5.1 Recycling of metallic chromium

As metallic chromium occurs as part of other metals, it is also recycled along with those metals – primarily stainless steel, steel, iron, aluminium and copper. When products made from these metals are worn out, they are collected for recycling, and of course the chromium in such metals will be included in this recycling.

5.1.1 Circulation of chromium with iron and steel

The quantities of metal collected in Denmark can be described as being equal to the net export of scrap metal plus metal recycled in Denmark plus losses from reprocessing.

In a life cycle analysis of steel, it is estimated that the scrap industry collects 97% of all steel scrap in Denmark (Kjeldahl, 1991, p. 103). In a new study prepared by DEMEX and others, it is estimated that 90% of all stainless steel in the building sector is reused, while the remaining 10% is disposed of by means of landfilling (5%) and incineration (5%). The study also estimates that 95% of all painted surfaces are disposed of by means of incineration, while the remaining 5% are sent to landfills (Lauritzen ***et al.***, 2002). Stainless steel is sent for re-melting in Sweden (Kjeldahl, 1991, p. 106).

Table 5.1
Recycling of iron and scrap metal in 1999 (The Danish EPA, 2000).

	Quantity, 1000 tonnes
Iron and scrap metal from Denmark sent to foundries and Stålvalseværket	417
Iron and scrap metal exported by scrap dealers	570
Iron and scrap metal imported by scrap dealers	22
Total recycled Danish iron and scrap metal	965
Iron and scrap metal imported by Stålvalseværket and foundries	230

According to Statistics Denmark, a total of 965,000 tonnes scrap metal is recycled in Denmark each year. In 1999, a total of 987,000 tonnes scrap metal was collected in Denmark. If we assumed that this corresponds to 97% of the total amount of scrap metal, this means that 3% – or 31,000 tonnes scrap metal – ends up in the environment. It is estimated that much of this scrap metal is iron with an average chromium content of approximately 0.05–0.1%. This means that 15.5–31 tonnes metallic chromium ends up in the environment, primarily in the soil.

Stålvalseværket and other Danish foundries do not accept stainless steel. As a result, we can safely assume that the 570,000 tonnes sent for export contain large amounts of stainless steel. As the exact figures are not known, it is estimated that stainless steel accounts for approximately 25%. This corresponds to 142,500 tonnes stainless steel or 24,000–26,000 tonnes chromium. It is assumed that the percentages stated for recycling of stainless steel within the building industry also apply to Denmark as a whole.

This means that approximately 2,700–2,900 tonnes chromium end up at landfills. Half of this chromium has passed through an incineration plant first.

5.1.2 Circulation with aluminium

By consulting the updated mass flow analysis for aluminium (see section 2.2), we can see that 18,600–22,300 tonnes of aluminium are recycled in Denmark each year. This corresponds to 4–22 tonnes chromium. Aluminium will be reprocessed by means of re-melting. The chromium content of the reprocessed material will not be any different from that of the source material. The total net export of scrap aluminium is 8,000–17,000 tonnes, corresponding to 2–18 tonnes of chromium.

5.1.3 Circulation with copper

By consulting the updated mass flow analysis for copper (see section 2.3), we can see that 9,000–10,000 tonnes of copper are recycled in Denmark each year. This corresponds to 2–3 tonnes chromium. Copper is reprocessed by means of re-melting. The chromium content of the reprocessed material will not be any different from that of the source material. The total net export of scrap copper is 15,000–24,000 tonnes, corresponding to 4–6 tonnes of chromium. The exported scrap is often reprocessed by means of electrolytic refining, which reduces or removes the chromium in the copper.

5.2 Waste disposal

5.2.1 Total annual quantities of solid waste

Various types of waste are actively disposed of. This concerns waste from households, industry, the building sector, etc. The waste statistics include figures on disposal of solid waste.

Table 5.2
Waste Statistics 1999 (The Danish EPA, 2000).

	Quantities in 1999, 1000 tonnes
Households	2,963
Refuse	1,665
Bulky waste	672
Garden waste	464
Other	163
Institutions / retail, offices	955
Production companies, etc.	2,653
Building and construction	2,968
Treatment plants	1,379
Clinker, fly ash, etc. (coal)	1,299
Other	15
Total	12,233

In 1999, Denmark exported significant amounts of waste.

Table 5.3
Export of waste from Denmark in 1999 (The Danish EPA, 2000).

	Quantities in tonnes
Glass	12,400
Plastics	19,700
Iron and metal	403,700
Other flammable goods	8,100
Fly ash and clinker from coal-fired CHP plants	146,200
Slag and flue remediation products from iron production	11,000
Flue gas remediation products from waste incineration plants	56,400
Scrap iron from waste incineration plants	10,700
Other registered waste	58,800

In 1999, Denmark imported waste corresponding to 4% of the domestic waste production. This imported waste was, however, mainly "green" waste or metal and was exclusively intended for recycling or incineration. Except for the chromium content in the 252,000 tonnes scrap iron and metal imported for recycling, it is estimated that no significant quantities of chromium are imported with waste.

5.2.2 Thermal waste treatment

In Denmark, all the waste that can be burnt is burnt. The quantities of chromium sent for incineration are calculated to be;

- Impregnated wood: 3.8 tonnes Cr/year
- Discarded leather: 106–236 tonnes Cr/year
- Discarded textiles: 5.1–15.3 tonnes Cr/year
- Discarded chromium plated products: 2.9 tonnes Cr/year
- Discarded electronic storage media: 1.8–2.6 tonnes Cr/year

Waste incineration gives rise to some residual products. These are slag, bottom ash, boiler slag, economizer ash, fly ash and flue gas cleaning products. Table 5.4 shows estimates of the quantities involved.

Table 5.4
Quantities of residual products caused by waste incineration (Hjelmar & Hansen, 2002).

Residual product	Kg/tonne incinerated waste
Slag	250–400
Bottom ash	5
Boiler slag	2–10
Fly ash	10–30
Flue gas cleaning, dry process	20–50
Flue gas cleaning, semi-dry process	20–40
Flue gas cleaning, wet process	1–3

Table 5.5 shows the chromium content of the most important residual products. Assuming that a total of 2,929,000 tonnes waste is incinerated each year (The Danish EPA, 2000), we can estimate the total amount of chromium in residual products from waste incineration.

Table 5.4
Chromium content in residual products from waste incineration (Hjelmar & Thomassen, 1992; Hjelmar & Hansen, 2002).

Residual product	Chromium concentration (mg/kg)	Chromium quantity (tonnes/year)
Fly ash	650	19–57
Flue gas cleaning products from dry and semi-dry processes, with fly ash	180	18–47
Sludge from wet flue gas cleaning	240	0.7–2.1
Slag	230–600 (415)	119–312
		158–418

For 1995–1996, the emission factors for waste incineration plants equipped with various clean-up technologies have been set at 0.1–1.7 g Cr/tonne waste (Illerup ***et al.***, 1999). This makes for an emission of chromium to air of 0.3–5.0 tonnes. Only small amounts of waste (approximately 2%) were treated at the plant with the high emission factor in 1996/1996, so a more realistic estimate would be emissions to air of 0.3–1.5 tonnes chromium.

5.2.3 Landfilling activities

Some waste cannot be incinerated and is deposited along with non-recyclable residual products from incineration of waste and combustion of fossil fuels (coal). Table 5.6 shows the quantities deposited at landfills in 1999. Some dangerous waste is also deposited at landfills. For example, sludge from the chromium plating industry – which contains a great deal of chromium – is deposited with Kommunekemi. In 1999, approximately 106 tonnes of chromium were deposited with Kommunekemi. It should be noted that a very significant amount (99%) of all fly ash from coal incineration was recycled in 1999. Larger quantities than this have been deposited at landfills in other years.

Table 5.6
Waste deposited at landfills (The Danish EPA, 2000).

Deposited fraction	Quantity tonnes/year
Waste, excluding slag and fly ash	1,460,000
Slag, waste	92,302
Fly ash, waste	43,102
Sludge, dry matter, long-term depots	47,441
Clinker and fly ash, coal	12,990

If we use the Cr concentrations for slag and fly ash given in Table 5.5 and combine them with estimated contents in residual products from coal combustion (Hjelmar & Thomasen, 1992), we can calculate the quantities of chromium deposited at landfills. This figure does not, however, include the quantities deposited with standard non-flammable waste. No information on the chromium contents of standard non-flammable waste deposited at landfills is available from either Waste Centre Denmark or the Household Waste department within the Danish EPA.

Table 5.7
Chromium deposited at landfills

Deposited with fraction	Quantity Tonnes Cr/year
Waste, excl. slag and fly ash	unknown
Slag, waste	38
Fly ash, waste	28
Sludge, dry matter	2
Clinker and fly ash, coal	1
Total	69

Some chromium may enter the environment from landfills and in connection with leaching percolate. This issue is not addressed here.

All in all, it is estimated that approximately 175 tonnes chromium is deposited at landfills each year. This figure does not include all the deposits made in the form of standard non-flammable waste.

5.2.4 Biological waste treatment

Parts of the organic fraction of refuse and green waste from gardens, parks, etc. undergo biological treatment. Such waste ends up as compost or as residual products from biogas generation. Due to their nutrient content, these residual products are applied to agricultural soil. In addition to nutrients, however, they also contain various heavy metals, including chromium. The table below shows the chromium content in the residual products and the annual chromium input from residual products to agricultural soil.

Table 5.8
Average chromium contents and annual total chromium quantities in compost and residual products from biogas generation (The Danish Forest and Nature Agency, 1998).

Residual product type	Chromium content mg/kg dry matter	Annual quantity Tonnes dry matter	Chromium quantity kg/year
Compost from refuse	16	6,000	1.9
Compost from garden and park waste	9.1	130,000	47
Liquid residual product from biogas generation	5.6	56,500	37
Total quantities		192,500	86

5.3 Circulation with chemical waste

Chemical waste/dangerous waste is disposed of through approved specialists, including Kommunekemi. Table 5.9 illustrates the disposal of fractions of dangerous waste which may contain chromium. No chromium analyses of the individual waste fractions are available.

Table 5.9
Disposal of dangerous waste in 1999; fractions which may contain chromium (The Danish EPA, 2000).

Fraction	Recycling tonnes	Incineration tonnes	Landfilling tonnes	Special treatment tonnes	Total tonnes
Dyes/Varnishes/Paint containing organic solvents	14	10,640	2	815	11,471
Dyes/Varnishes/Paint without organic solvents		6,572	7	824	7,403
Organic metal compounds, except Hg		112		1	113
Acid aqueous solutions containing chromium compounds	855	95	4	419	1,373
Photographic development baths	3,051	1,116	10	60	4,237
Photo-process baths containing chromium		7			7
Fixative baths	1,293	20		963	2,276
Metal hydroxide and oxide sludge	1,266	1,306	3,683	145	6,400
Smoke scrubber sludge and smoke filter dust from iron and metal foundries		369	743	203	1,315
Dye works waste		2			2
Watery sludge from pressure-treatment of wood		14		7	21
Salts for hardening		15		52	67
Pharmaceutical waste		728		557	1,285
Chemicals from laboratories, etc.	1	1,056	54	67	1,178
Filter dust from flue gas cleaning	11,002				11,002
Fly ash	376		5771	22,413 (stored)	28,560
Flue gas cleaning products	5,170		37,434	7,183	49,787

Kommunekemi collects samples of their output every six months. In 1999, they had the following output (Kommunekemi, 2002b):

- 11,529 tonnes of slag with a chromium content of 120–210 mg/kg, corresponding to 1.4–2.4 tonnes chromium
- 5,472 tonnes residual products (fly ash, etc.) with chromium contents of 250–680 mg/kg, corresponding to 1.4–3.7 tonnes chromium
- 3,437 tonnes filter cake (from in-house treatment at Kommunekemi) with a chromium content of 7.500 mg/kg, corresponding to 26 tonnes chromium

- 3,579 tonnes filter cake from others (typically galvanic industries with in-house treatment plants) with a chromium content of 21,000 mg/kg, corresponding to 75 tonnes of chromium.

The 100–110 tonnes of residual products, etc., are deposited at landfills (Kommunekemi, 2002b).

In 1999, a total of 3.782 kg chromium(VI) was leached with percolate. This figure is above average due to the unusually high rainfalls in 1999. The corresponding figures for 2000 and 2001 are 0.492 kg and 1.478 kg. The landfill is located close to the coastline, which ensures that the leached chromium(VI) cannot reach the groundwater (Kommunekemi, 2002b).

5.4 Circulation with wastewater and wastewater sludge

During a period in 1996, studies were made in the towns Bagsværd and Skovlunde of xenobiotic substances in the run-off from built-up areas. Here, concentrations of 10.6–18.5 µg Cr/L were measured (Kjølholt ***et al.***, 1997). These levels correspond to those found in the input to a number of treatment plants.

Table 5.10
Inflow to specific treatment plants 1997 (Jepsen & Grüttner, 1997)

	Average concentration, µg Cr/L
IS Avedøre Kloakværk	28
Renseanlæg Damhusåen	19
Herning Centralrenseanlæg	47

In 1999, the average concentration of chromium in inflow to the “Lynetten” treatment plant was 7.8 µg/L, while the corresponding figure for "Damhusåen" was 8.9 µg/L. On average, the total input was 1.4 kg Cr/day to "Lynetten" and 0.7 kg/day to "Damhusåen" (Lynettefællesskabet I/S, 2000). The total amount of water treated in 1999 was in the region of 825 million m^3. If we take this information as the basis for assuming an average content of 5–10 µg Cr/L, the average inflow to treatment plants is 4.1–8.3 tonnes Cr/year. As we can see, these figures correspond well to the quantities found in sludge. In previous studies, it has been estimated that 80% of the chromium is transferred to the sludge at treatment plants (Grüttner & Jacobsen, 1994). If we assume that 80% is held back at the plants, we arrive at a discharge from treatment plants into the aquatic environment of 1.2 tonnes Cr/year. The Danish EPA states that discharges into the aquatic environment from specific industrial contributors is 0.219 tonnes Cr/year, possibly more (The Danish EPA, 1999b).

In 1999, a total of 1,409 treatment plants were registered in Denmark. These plants treat wastewater corresponding to 8.09 million person equivalents (PE). In 1999, the plants produced 155, 621 tonnes sludge (dry matter). That year, the limit value for chromium in sludge was 200 mg/kg total phosphorus (P) or 100 mg/kg sludge (dry matter). In 1999, the weighted average concentrations of chromium in sludge were 33.2 g Cr/tonnes sludge (dry matter) for all sludge, and 24.6 g Cr/tonne sludge (dry matter) for sludge applied to agricultural soil (The Danish EPA, 2001). This corresponds to a total content of 4.9 tonnes Cr in the sludge, of which 2.1 tonnes were applied to agricultural soil. The chromium which was ***not*** applied to agricultural soil was sent for incineration (approximately 45%) or to landfills (approximately

51%) (The Danish EPA, 2001b). This means that 1.3 tonnes chromium from sludge is sent for incineration each year, and that 1.4 tonnes chromium from sludge is deposited at landfills each year.

5.5 Emissions to air

As has been demonstrated elsewhere, large amounts of chromium are emitted to air in connection with combustion of fossil fuels and incineration of waste.

Table 5.11
Emissions of heavy metals to air in 1999
(National Environmental Research Institute, Denmark, 2002).

	kg Cr/year
Combustion – CHP plants and refineries	1,410
Combustion – dwellings and institutions	191
Combustion – industry	805
Production processes	0
Road transport	179
Other mobile sources	65
Total	2,650

Some of these emissions are caused by chromium contents in fuel.

5.6 Area deposition

Based on statistics from 7 stations, it has been ascertained that the bulk deposition of chromium onto Danish soil is 125 µg Cr/m^2 each year. This does not include aerosol deposition, which may correspond to 5–20% of the bulk deposition.

The total annual contribution to Danish soil (43,000 km^2) from atmospheric deposition is estimated to be 10 tonnes Cr (average for the last 10 years).

As regards Danish waters, approximately 167 µg Cr/m^2 falls on the Danish inland waterways (40,000 km^2) each year. This corresponds to a total of 7 tonnes per year (Hovmand ***et al.***, 2000).

5.7 Summary

Chromium emissions associated with waste treatment can be summarised as shown in Table 5.12.

Table 5.12
Chromium emissions associated with waste treatment in Denmark, 1999.

Process/source	Air tonnes	Water tonnes	Soil tonnes	Landfills tonnes	Total tonnes
Recycling		0.2–2	16–32	2,700–2,900	2,716–2,932
Waste incineration	0.3–1.5	–	–	36–96	36–98
Biological waste treatment	–	–	0.1	–	0.1
Waste deposit	–	?	–	–	–
Chemical waste / Dangerous waste		0.5–3.5	–	100–110	101–114
Wastewater	–	1.2	–	–	1.2
Wastewater sludge	–	–	2.1	1.4	3.5

5.7.1 Recycling

Chromium is not recycled in pure form in Denmark. Instead, it is recycled as part of iron, steel, aluminium and copper. The quantities of recycled chromium can be calculated as follows: 2,600–3,600 tonnes chromium with iron and steel, 7–22 tonnes chromium with aluminium, and 2–3 tonnes chromium with copper. Recycling of chromium as part of residual products (fly ash and clinker) from coal-fired CHP plants accounts for 62–185 tonnes Cr/year. Chromium compounds are not recycled as part of products. They can, however, be extracted from wastewater from relevant processes, e.g. chromating.

5.7.2 Waste treatment

Chromium enters the waste treatment system with household waste as well as commercial waste. No statistics on chromium in inflows to the various plant types are available, but more information ***is*** available on the outputs. For example, residual products from waste incineration plants (fly ash, residual products containing fly ash from flue gas cleaning, sludge, and slags) represent chromium quantities of 158–418 tonnes per year, while the emission to air can be estimated at 0.3–1.5 tonnes chromium. In 1999, a total of 77% of the residual products (corresponding to 122–322 tonnes chromium) was recycled, while the remaining quantities (corresponding to 36–96 tonnes chromium) were deposited at landfills.

5.7.3 Chemical waste/dangerous waste

Several waste fractions containing chromium are classified as dangerous waste. This means that they must be disposed of through approved specialists such as Kommunekemi. No analyses of inputs to Kommunekemi are available, but chromium contents have been determined for a number of residual products (e.g. clinker, filter cakes, etc.) deposited. A total of 100–110 tonnes residual products containing chromium is deposited.

5.7.4 Wastewater and wastewater sludge

Chromium contents have been identified in samples of inflow to three treatment plants. On the basis of concentrations of 19–47 μg Cr/L, the total input of chromium to wastewater treatment plants can be estimated to be 4.1–8.3 tonnes Cr/year. Of this amount, approximately 80% is held back. The emissions/discharges into the aquatic environment are estimated to be 1.2 tonnes Cr/year. The remaining quantities are caught in sludge. With a chromium concentration in sludge of 33.2/tonne dry matter (average for all sludge) and 24.6 g/tonne dry matter in sludge for application to agricultural soil, we arrive at an output of 4.9 tonnes chromium. Of this amount, 2.1 tonnes were applied to agricultural soil, 1.3 tonnes were sent for incineration, and 1.4 tonnes were deposited at landfills.

6 Overall assessment

6.1 Chromium consumption in Denmark, 1999

6.1.1 Net import of chromium and chromium compounds

Chromium and chromium compounds are imported with goods, raw materials and semi-finished goods (metals) as a chemical substance and as a trace constituent. The net import of chromium as a trace constituent/alloy metal in stainless steel, ferrous chromium, steel and iron has been calculated to be 23,200–28,500 tonnes. The net import of chromium as a trace constituent/alloy metal in aluminium and copper is 11–106 tonnes and 6–9 tonnes, respectively.

Chromium compounds are primarily imported in the form of chromium oxides, but also in the form of chromium hydroxides, chromium(III) sulphate, sodium dichromate and other dichromates. The total quantity of imported chromium compounds has been calculated to be 260 tonnes, of which chromium(VI) accounts for approximately 110 tonnes.

In addition to this, chromium is also imported as a trace constituent/impurity in a number of products. The most significant of these are fossil fuels (coal and oil, accounting for 147 tonnes) and chromium leather (accounting for 79–209 tonnes chromium).

6.1.2 Consumption of chromium and chromium compounds

The consumption of chromium as an alloy metal, chemical compound and trace constituent has been identified for Denmark for the year 1999 (average for the years 1998, 1999 and 2000). Table 6.1 provides an overview of this consumption.

Table 6.1
Consumption of chromium, chromium compounds and chromium as a trace constituent in Denmark in 1999 (average for the years 1998, 1999 and 2000).

	Supply (tonnes/year)	Share of total (%)
Chromium, metallic	24,300–29,400	97
Chromium compounds	450–740	2.2
Chromium as a trace constituent	214	0.8
Total	24,964–30,354	100

Table 6.2 provides an overview of the consumption of chromium and chromium compounds in Denmark by area of application.

In the effort to establish an overview of the consumption of chromium compounds, emphasis has been placed on identifying consumption and emission of chromium(VI) compounds. These compounds constitutes a significantly greater risk to health and the environment, as described in section 1.34, "Classification of chromium compounds". Use of chromium(VI) compounds is subject to a wide range of restrictions. As a result, consumption of such compounds is falling within many areas.

Table 6.2
Consumption of chromium, chromium compounds and chromium as a trace constituent in Denmark in 1999 (average for the years 1998, 1999 and 2000), by area of application. Consumption of Cr(VI) is also stated for the relevant applications.

Area of application	Consumption (tonnes/year)	Share of total[1] (%)	Of which Cr(VI) (tonnes/year)	Development trend
Chromium, metallic				
– Iron and steel				
– goods, iron and steel	21,000–	83	–	rising
– goods, other steel	25,000	12	–	rising
– steel production	2,700–3,700	2.2	–	rising
– Aluminium alloys[2]	600	0.2	–	rising
– Copper alloys[2]	11–106	0.03	–	rising
	6–9			
Chromium compounds				
– Surface treatment	37.7	0.14	37.7	rising
– Pigments in paint and	12.6–116.7	0.23	1–2	falling
plastic	8.8	0.03	8.8	falling
– Impregnation	~0	0	–	–
– Corrosion inhibitor	164–302	0.8	0.016–0.035	rising
– Tanning	0.1–1	0.002	–	?
– Catalysts	13–47	0.11	<<1	?
– Hardeners	5.6–16.7	0.04	–	no change
– Textiles	1.8–2.6	0.008	–	no change
– Electronic storage	<1	0	<1	–
– Laboratory chemicals	200	0.72	–	no change
– Firebricks				
Chromium as a trace				
constituent	147	0.53	–	no change
– Coal and oil	67	0.24	2.1–4.2	falling
– Cement				
Total	24,964–30,354	100.28	49.6–52.7	

1. The sum deviates from 100% due to rounded-off figures.
2. Including impurities in aluminium and copper.

6.2 Chromium input to the environment and landfills

Table 6.3 provides a summary of the information available about disposal and dispersion of chromium to the environment in Denmark in 1999. Emissions to various recipients are discussed below.

6.2.1 Emissions to air

Chromium and chromium compounds are stable compounds with high melting points/boiling points. This means that emissions to air are primarily associated with thermal processes. Thermal processes mainly occur in connection with production and processing of iron, aluminium and copper, including alloys of the various metals. No primary production of such metals or alloys takes place in Denmark, but processing may occur. Similarly, recycling of metals also takes place in Denmark. The most significant sources are incineration (energy conversion and waste incineration) and processing, use, recycling and disposal of iron, steel, aluminium and copper. The total emissions to air have been calculated to be 4.1–5.5 tonnes Cr/year.

6.2.2 Emissions to water

Chromium and chromium(III) compounds are relatively insoluble in water. Some chromium(VI) compounds, however, are more soluble, which means that emissions to water may occur, e.g. in the form of discharges of process chemicals from surface treatment or wastewater from the paint/varnish industry. During the use phase, emissions to water will primarily occur in connection with the following: corrosion of iron, steel, aluminium and copper; use of paint that contains chromium pigments; leaching from impregnated wood, or disposal of laboratory chemicals. The total emissions to water can be calculated to be 1.9–4.0 tonnes Cr/year.

6.2.3 Emissions to soil

The conditions for solubility of chromium compounds described above also apply in connection with emissions to soil. This is to say that emissions during the use phase will primarily occur in connection with corrosion of iron, steel, aluminium and copper, leaching from impregnated wood and painted surfaces, and peeling from chromium plated products. The total emissions to soil are in the range of 16–33 tonnes Cr/year.

6.2.4 Landfills

Chromium and chromium compounds enter landfills as part of various products and in residual products from incineration processes. In addition to this, small quantities will enter landfills as part of building waste, leather and textiles. The total chromium input to landfills is in the range of 148–244 tonnes/year.

Table 6.3
Chromium disposal and dispersion to the environment in Denmark,1999.

Process/source	Air tonnes/year	Water tonnes/year	Soil tonnes/year	Landfill tonnes/year	Total tonnes/year
Industrial processes					
– Processing, use and disposal of iron and steel	?	?	15.5–31	–	15.5–31
– Recycling of iron and steel	0.1–0.2	0.017–0.034	–	2.3	2.4–2.5
– Processing, use and disposal of aluminium	0–0.1	0.2–2	0.1–1	3–37	3.3–40
– Processing, use and disposal of copper	~0	–	0.1–0.2	1–2	1.1–2.2
– Energy conversion (coal and oil)	3.5	–	–	?	3.5
– Other industrial processes	–	0.2	–	–	0.2
– Surface treatment	–	0.089	–	–	–
– Tanning	–	?	–	–	?
– Transport	–	0.27	–	–	0.27
	0.2	–	–	–	0.2
Use of products					
– Impregnated wood	–	0.3–0.6	0.3–0.6	–	0.6–1.2
– Chromium-plated products	–	–	??	–	??
– Paint	–	0.03–13	–	–	0.03–13
– Laboratory chemicals	–	<<1	–	–	<<1
Waste treatment					
– Waste incineration	0.3–1.5	–	–	36–96	36–98
– Biological waste treatment	–	–	0.086	–	0.086
– Landfilling of solid waste	–	–	–	??	??
– Kommunekemi	?	–	–	104–107	104–107
– Municipal wastewater	–	1.2	–	–	1.2
– Wastewater sludge	–	–	2.1	1.4	3.5
Total	4.1–5.5	2.3–17	16–33	148–244	170–302

6.3 Chromium balance for Denmark, 1998–2000

The chromium balance for Denmark for the period 1998–2000 has been established on the basis of the information and data presented in sections 2–5 of this document. See Figure 6.1. This figure illustrates the quantities imported into and exported from Denmark, as well as the emissions to landfills, air, soil and water. Denmark is represented by the central box in the figure. This box lists the various uses of chromium. Collectively, these uses constitute the total consumption in Denmark. A certain percentage is re-circulated internally in Denmark. The accumulation within Danish society constitutes an expression of the balance between the chromium input to society and the chromium leaving the country through export and emissions.

The balance comprises:

- Net import with metals and chemical compounds and as a trace constituent
- Net export with scrap metal
- Emissions to air, soil and water

Metallic chromium includes chromium found in alloys or as a trace constituent in aluminium and copper.

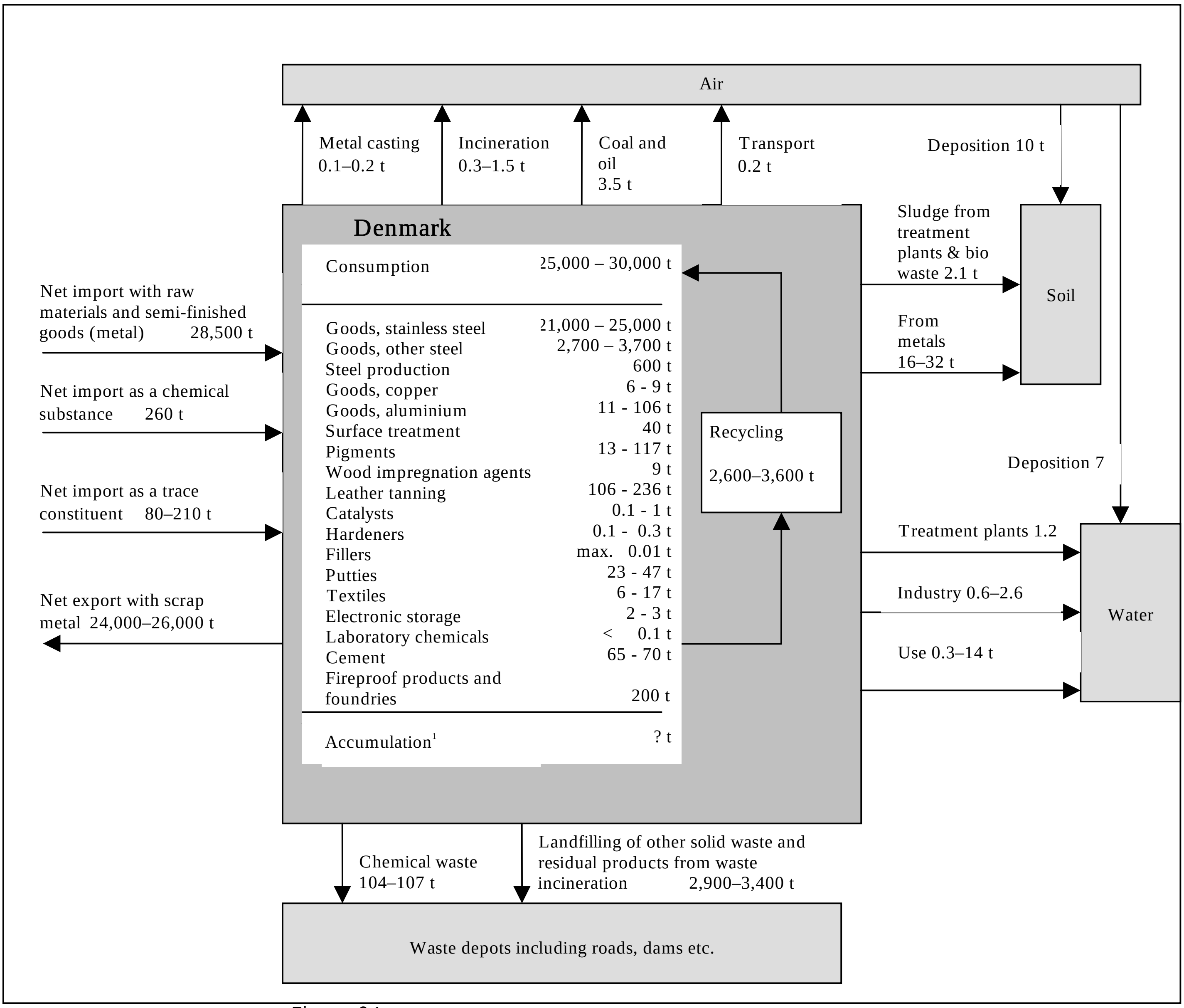

Figure 6.1
Chromium balance for Denmark 1999 (tonnes Cr/year, average of the years 1998, 1999 and 2000).

1. On the basis of the calculated net import, net export and landfilling, the accumulation is estimated to be around 0. Metals containing chromium (iron, aluminium and copper) are valuable within the recycling system. As a result, such metals will be sent for recycling. This does not, however, entirely rule out the possibility of accumulation.

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ANNEX A: Supply of tools, knives, and cutlery made from stainless steel in Denmark 1998–2000, tonnes

						Product composition			Estimated chromium content			
CN code	Product description	Import tonnes	Export tonnes	Production tonnes	Supply tonnes	Steel	Stainless steel	Other	Steel	Stainless steel	Other	Chromium content, tonnes
8201	Spades, shovels, mattocks, picks, hoes, ridgers, etc.	2,669	754	2,841	4,756	65%	5%	30%	0.5% – 0.8%	17% – 18%	0%	56 –68
8202	Hand saws, saw blades	1,003	1,831	1,928	1,099	90%	10%		0.5% – 0.8%	17% – 18%		24 – 28
8203	Files, rasps, pincers, nippers, etc.	772	188	90	674	90%		10%	0.5% – 0.8%	17% – 18%	0%	3 – 5
8204	Wrenches for hand use	837	259	10	588	15%	85%		0.5% – 0.8%	17% – 18%		85 – 91
8205	Hand tools	4,437	1,077	510	3,871	80%	10%	10%	0.5% – 0.8%	17% – 18%	0%	81 – 94
8206	Tools in retail sets	566	268	13	311	94.50%	0.50%	5%	0.5% – 0.8%	17% – 18%	0%	2 – 3
8207	Replacement tools for hand tools	2,199	1,718	1,864	2,345	70%	25%	5%	4%	17% – 18%	0%	165 – 171
8208	Knives and blades for machines and mechanical devices	563	242	80	401	30%	70%		0.5% – 0.8%	17% – 18%		48 – 52
8209	Sheets, rods, points and similar unassembled tool parts	124	394	336	65	90%	10%		0.5% – 0.8%	17% – 18%		1 – 2
8210	Mechanical tools, hand–operated, weighing no more than 10 kg	128	48	0	80	90%	10%		0.5% – 0.8%	17% – 18%		1.7 – 2
8211	Knives with cutting or jagged edges	765	117	104	752	10%	90%		0.5% – 0.8%	17% – 18%		115 – 122
8212	Razors (incl. electrical)	877	592	0	285	10%	90%		0.5% – 0.8%	17% – 18%		44 – 46
8213	Scissors and blades for scissors	223	33	0	190	10%	90%		0.5% – 0.8%	17% – 18%		29 – 31
8214	Other implements for cutting	127	19	4	112	10%	90%		0.5% – 0.8%	17% – 18%		17 – 18
82152010	Cutlery, stainless steel	397	60	99	436		100%			17% – 18%		74 – 78
Total		15,689	7,601	7,879	15,966							746 – 811

ANNEX B: Supply of metals and aluminium alloys in Denmark, tonnes, 1998–2000

Aluminium	Product description	Import				Export				Production				Supply			
CN code		1998	1999	2000	average	1998	1999	2000	average	1998	1999	2000	average	1998	1999	2000	average
76011000		41	243	460	248	7	11	8	9	0	0	0	0	34	232	452	239
76012010	Aluminium – aluminium alloys, primary	38,891	39,584	40,761	39,745	139	43	43	75	0	191	0	64	38,752	39,732	40,718	39,734
76012090		0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
76012091	Aluminium – aluminium alloys, secondary	6,091	3,288	3,266	4215	28,610	25,486	23,288	25,795	34,329	33,581	32,147	33,352	11,810	11,383	12,125	11,773
76012099	Aluminium – aluminium alloys, secondary	527	877	931	778	30	12	2	15	0	0	0	0	497	865	929	764
76020011	Aluminium waste and scrap – turnings	70	62	106	79	755	1,040	825	873	0	0	0	0	-686	-977	-719	-794
76020019	Aluminium waste and scrap – other goods	264	230	283	259	1,914	1,952	3,512	2,459	7,200	7,123	10,358	8,227	5,550	5,402	7,129	6,027
76020090	Aluminium waste and scrap – scrap	21,954	20,246	19,982	20,727	27,548	31,475	29,955	29,659	5,653	5,739	6,814	6,069	59	-5,489	-3,159	-2,863
76031000		11	44	21	25	0	0	0	0	0	0	0	0	11	44	21	25
76032000		10	10	7	9	5	2	0	2	0	0	0	0	4	8	7	7
76041010		46	33	10	29	34	43	6	28	0	0	0	0	12	-10	3	2

Aluminium	Product description	Import				Export				Production				Supply			
CN code		1998	1999	2000	average	1998	1999	2000	average	1998	1999	2000	average	1998	1999	2000	average
76041090	Bars and profiles made from aluminium – profiles made from unalloyed aluminium	2,951	2,615	2,523	2,696	658	763	520	647	0	0	0	0	2,294	1,852	2,003	2,049
76042100	Bars and profiles made from aluminium – hollow profiles	5,577	6,562	10,477	7,539	9,326	11,013	13,020	11,119	18,963	18,306	20,962	19,410	15,214	13,855	18,419	15,830
76042910	Bars and profiles made from aluminium – other goods	2321	3221	2877	2806	1001	979	748	909	0	0	0	0	1320	2241	2129	1897
76042990	Bars and profiles made from aluminium – other goods	18266	24574	29072	23971	3304	4525	6028	4619	0	0	7427	2476	14962	20048	30472	21827
76051100	Wire made from aluminium	5262	4177	1153	3531	2	2	0	1	0	0	0	0	5261	4175	1153	3530
76051900		22	25	17	21	2	4	2	3	0	0	0	0	19	21	15	19
76052100		3	1	1	2	7	0	0	2	0	0	0	0	-4	1	1	-1
76052900		249	272	236	252	7	17	20	15	0	0	0	0	242	254	216	237
76061110	Sheets and strips made from aluminium – made from unalloyed aluminium	1594	1146	1031	1257	621	435	302	453	0	0	0	0	973	711	729	804
76061191	Sheets and strips made from aluminium – made from unalloyed aluminium	6492	6845	6066	6468	833	933	714	827	0	0	0	0	5659	5912	5352	5641
76061193	Sheets and strips made from aluminium – made from unalloyed aluminium	1397	1582	951	1310	162	124	194	160	0	0	0	0	1234	1458	756	1149
76061199		116	371	69	186	70	54	39	54	0	0	0	0	47	317	30	131
76061210		1195	792	1290	1092	1290	1136	1278	1235	0	0	0	0	-95	-344	12	-142
76061250	Sheets and strips made from aluminium – other goods	10834	9752	12608	11064	962	1120	1504	1195	0	0	0	0	9872	8632	11104	9869
76061291	Sheets and strips made from aluminium – other goods	17560	16769	18085	17471	1318	3488	3798	2868	0	0	0	0	16242	13281	14287	14603

Aluminium	Product description	Import				Export				Production				Supply			
CN code		1998	1999	2000	average	1998	1999	2000	average	1998	1999	2000	average	1998	1999	2000	average
76061293	Sheets and strips made from aluminium – other goods	4131	4352	5360	4614	426	419	588	478	0	0	0	0	3704	3933	4773	4137
76061299	Sheets and strips made from aluminium – other goods	3669	3709	4236	3871	640	364	705	570	0	0	0	0	3029	3345	3531	3302
76069100	Sheets and strips made from aluminium – other goods, unalloyed	441	374	242	352	534	1245	894	891	0	0	0	0	-93	-871	-652	-539
76069200		377	681	961	673	247	210	215	224	0	0	0	0	130	471	746	449
76071110	Foil made from aluminium - rolled	4219	4136	5136	4497	616	304	630	517	2279	2108	2910	2432	5882	5940	7416	6413
76071190	Foil made from aluminium - rolled	8705	9227	8595	8843	1108	1512	700	1107	0	0	0	0	7597	7715	7895	7736
76071910	Foil made from aluminium – other	1221	1066	1164	1150	9	28	20	19	0	0	54	18	1212	1037	1198	1149
76071991		10	346	48	134	2	4	15	7	0	0	33	11	7	342	66	138
76071999		653	512	542	569	45	171	142	119	0	0	5	2	608	342	405	452
76072010	Foil made from aluminium – with underlay	2,843	1,759	1,856	2,153	5,704	5,071	7,113	5,963	0	0	7,050	2,350	-2,861	-3,311	1,793	-1,460
76072091		85	104	144	111	1	2	20	8	0	0	0	0	84	101	125	103
76072099	Foil made from aluminium – with underlay	606	1,152	1,365	1,041	206	166	182	185	0	0	0	0	400	986	1,184	857
76081010		0	3	0	1	1	3	51	18	0	0	0	0	-1	0	-51	-17
76081090		63	41	25	43	23	58	141	74	0	0	0	0	39	-18	-116	-31
76082010		0	0	0	0	0	2	0	1	0	0	0	0	0	-2	0	-1
76082030		753	330	310	464	1	1	3	2	0	0	0	0	752	329	307	463
76082091	Pipes made from aluminium - made from aluminium alloys	581	706	1,236	841	90	123	156	123	0	0	0	0	491	583	1,079	718
76082099	Pipes made from aluminium – made from aluminium alloys	771	736	1,004	837	11,104	10,258	10,243	10,535	16,466	16,912	18,563	17,314	6,134	7,390	9,324	7,616
76090000		317	209	233	253	344	98	38	160	0	0	0	0	-27	110	195	93

Aluminium	Product description	Import				Export				Production				Supply			
CN code		1998	1999	2000	average	1998	1999	2000	average	1998	1999	2000	average	1998	1999	2000	average
76101000	Structures – Doors, windows, surrounds and thresholds	1,387	1,437	1,824	1,549	8,263	7,988	7,790	8,014	0	2,685	1,089	1,258	-6,876	-3,866	-4,877	-5,206
76109010		3	3	42	16	0	19	8	9	0	0	0	0	3	-16	35	7
76109090	Structures – other goods	6,199	8,017	11,418	8,544	10,219	9,583	11,547	10,450	0	0	0	0	-4,020	-1,567	-130	-1,906
76110000		85	176	17	93	87	56	65	69	0	0	0	0	-3	120	-48	23
76121000	Tubes	10	12	7	10	4	3	15	7	311	273	298	294	318	282	290	297
76129010		41	166	225	144	0	0	0	0	0	0	0	0	41	166	225	144
76129020		14	15	6	12	0	0	0	0	0	0	0	0	14	15	6	11
76129091		121	137	125	128	8	523	53	195	0	0	0	0	113	-385	72	-67
76129098	Containers made from aluminium – less than 50 litres	9,956	9,694	9,324	9,658	6,441	7,125	5,992	6,520	241	369	328	313	3,756	2,938	3,660	3,451
76130000		308	539	597	482	24	2	19	15	0	0	0	0	285	537	578	467
76141000		33	65	29	42	10	1	67	26	0	0	0	0	24	63	-38	16
76149000		52	122	593	256	100	84	28	71	0	0	0	0	-48	38	565	185
76151010		0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
76151090		0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
76151100		79	48	39	55	4	2	1	2	0	0	0	0	75	46	38	53
76151910	Tableware and kitchen utensils made from aluminium	519	536	597	551	1,343	1,441	1,275	1,353	1,456	1,568	1,270	1,431	632	663	592	629
76151990	Tableware and kitchen utensils made from aluminium	986	1,080	1,401	1,156	61	79	246	129	15	9	9	11	940	1,010	1,164	1,038
76152000		115	153	167	145	38	196	199	144	0	0	56	19	76	-43	24	19
76161000	Pins, nails, bolts etc.	267	276	189	244	145	165	249	186	0	0	0	0	122	111	-61	57
76169010		0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
76169030		0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
76169091		0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0

Aluminium	Product description	Import				Export				Production				Supply			
CN code		1998	1999	2000	average	1998	1999	2000	average	1998	1999	2000	average	1998	1999	2000	average
76169099		0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
76169100	Wire mesh, wire net and wire fencing made from aluminium wire	42	17	26	29	35	23	51	36	0	0	0	0	7	-6	-25	-8
76169910	Cast	774	395	669	613	2,394	1,160	1,552	1,702	4,021	3,508	3,908	3,812	2,401	2,743	3,026	2,723
76169990	Other	4,525	5,007	5,957	5,163	3,772	4,220	3,830	3,941	0	0	0	0	753	787	2,126	1,222
Total		196,704	200,658	217,993	205,118	132,654	137,368	140,649	136,890	90,935	92,373	113,280	98,863	154,985	155,663	190,624	167,091

Please note: All figures in grey boxes are listed by units in the statistics. For this overview, the number of units has been converted into a total weight in tonnes on the basis of the weight of a single unit.

ANNEX C: Supply of copper metals and alloys in Denmark 1998–2000, tonnes

Aluminium	Product description	Import				Export				Production				Supply			
CN code		1998	1999	2000	average	1998	1999	2000	average	1998	1999	2000	average	1998	1999	2000	average
74011000		0	0	0	0	24	49	0	24	0	0	0	0	-24	-48	0	-24
74012000		0	0	0	0	24	24	0	16	0	0	0	0	-24	-24	0	-16
74020000		81	206	22	103	0	23	0	8	0	0	0	0	81	182	22	95
74031100		14	7	24	15	2	0	0	1	0	0	0	0	12	7	24	14
74031200		0	0	70	23	1	3	3	2	0	0	0	0	-1	-3	67	21
74031300		0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
74031900		19	13	31	21	99	1,154	780	678	0	0	0	0	-80	-1,141	-748	-656
74032100		14	17	10	13	0	0	26	9	0	0	0	0	14	16	-15	5
74032200		1,826	1,631	2,248	1,902	38	68	71	59	165	225	0	130	1,952	1,788	2,177	1,972
74032300		0	0	24	8	0	155	82	79	0	0	0	0	0	-154	-58	-71
74032900		339	266	364	323	7	10	8	8	0	0	0	0	332	256	356	315
74040010		15,020	2,293	3,797	7,037	6,812	6,251	5,714	6,259	19	8	10	12	8,228	-3,950	-1,907	790
74040091		1,768	1,695	2,110	1,858	17,390	18,098	20,445	18,644	1,682	2,404	2,541	2,209	-13,940	-13,998	-15,794	-14,578
74040099		2,884	4,398	4,766	4,016	7,988	10,612	12,819	10,473	0	0	0	0	-5,104	-6,214	-8,052	-6,457
74050000		125	34	31	63	1	92	0	31	0	0	0	0	124	-58	31	32
74061000		276	328	213	273	1	2	1	1	36	62	58	52	311	388	270	323
74062000		22	9	9	13	0	0	0	0	0	0	0	0	22	8	8	13
74071000		2,365	1,891	1,986	2,081	162	601	751	504	0	0	0	0	2,203	1,290	1,235	1,576
74072110		25,920	25,757	27,842	26,506	716	998	881	865	0	0	0	0	25,204	24,759	26,961	25,641

Aluminium	Product description	Import				Export				Production				Supply			
74072190		1,927	2,212	984	1,708	103	65	62	77	56	62	57	58	1,880	2,209	979	1,689
74072210		20	10	10	13	0	0	0	0	0	0	0	0	20	10	10	13
74072290		22	21	23	22	0	0	0	0	0	0	0	0	22	21	23	22
74072900		431	342	494	423	81	9	16	35	0	0	0	0	350	333	478	387
74081100		7,334	4,323	3,503	5,053	2	60	1	21	0	0	0	0	7,333	4,263	3,502	5,033
74081910		1,221	1,403	1,756	1,460	11	18	58	29	0	0	0	0	1,210	1,385	1,699	1,431
74081990		287	249	255	263	2	3	3	3	0	0	0	0	284	246	251	261
74082100		222	163	173	186	2	3	4	3	0	0	0	0	220	159	169	183
74082200		98	170	221	163	1	1	0	1	0	0	0	0	98	168	221	162
74082900		621	679	696	665	289	270	273	277	0	0	0	0	332	408	423	388
74091100		1,666	1,593	2,863	2,041	299	271	584	385	0	0	0	0	1,367	1,322	2,279	1,656
74091900		2,175	1,817	2,479	2,157	41	37	207	95	0	0	0	0	2,134	1,780	2,272	2,062
74092100		970	888	964	941	89	47	317	151	0	0	0	0	881	840	647	789
74092900		1,232	1,007	843	1,027	161	115	122	133	0	0	0	0	1,071	891	721	894
74093100		442	313	330	362	5	135	64	68	0	0	0	0	437	178	266	294
74093900		17	7	12	12	1	0	5	2	0	0	0	0	16	7	7	10
74094010		2	1	1	1	0	0	0	0	0	0	0	0	2	1	1	1
74094090		202	232	184	206	1	11	48	20	0	0	0	0	201	221	136	186
74099000		0	0	13	4	0	0	10	3	0	0	0	0	0	0	3	1
74099010		3	7	0	4	8	2	0	3	0	0	0	0	-5	6	0	0
74099090		9	15	0	8	15	14	0	10	0	0	0	0	-7	0	0	-2
74101100		485	443	783	570	0	0	1	1	0	0	0	0	485	443	781	570
74101200		4	1	106	37	0	0	0	0	0	0	0	0	4	1	106	37
74102100		1,419	1,382	1,705	1,502	63	127	89	93	0	0	0	0	1,356	1,255	1,616	1,409
74102200		3	7	1	4	8	2	9	7	0	0	0	0	-5	5	-8	-3
74111011		1,757	2,398	1,881	2,012	690	668	529	629	435	486	521	481	1,503	2,217	1,873	1,864
74111019		146	113	117	125	63	68	92	74	0	0	0	0	84	45	25	51
74111090		2,431	3,200	2,357	2,663	373	321	448	381	0	0	37	12	2,058	2,879	1,946	2,294
74112110		541	1,017	840	799	27	52	140	73	0	0	0	0	514	965	699	726

Aluminium	Product description	Import				Export				Production				Supply			
74112190		162	117	140	140	1	1	2	1	0	0	0	0	161	116	139	139
74112200		36	20	15	24	5	0	1	2	0	0	0	0	30	20	15	22
74112900		0	0	235	78	0	0	36	12	0	0	0	0	0	0	199	66
74112910		237	221	0	153	31	39	0	23	0	0	0	0	207	183	0	130
74112990		80	44	0	41	24	17	0	14	0	0	0	0	55	27	0	27
74121000		312	224	172	236	426	169	54	217	34	43	40	39	-80	98	158	58
74122000		2,463	1,908	1,613	1,994	868	846	1,016	910	0	0	54,325	18,108	1,594	1,061	54,922	19,193
74130010		2	2	0	1	0	0	0	0	0	0	0	0	2	2	0	1
74130091		816	1,185	3,530	1,844	29	20	0	16	0	0	0	0	787	1,165	3,529	1,827
74130099		117	249	299	221	2	12	8	7	0	0	576	0	115	237	867	406
74141000		0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
74142000		187	8	10	68	0	53	0	18	0	0	0	0	187	-45	9	50
74149000		17	109	18	48	3	62	6	24	0	0	0	0	14	48	12	25
74149010		0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
74149090		0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
74151000		41	32	34	36	0	2	0	1	0	0	0	0	41	30	33	35
74152100		18	26	64	36	0	0	0	0	0	0	0	0	18	26	63	36
74152900		198	127	94	140	36	59	72	55	0	0	0	0	163	68	22	84
74153100		10	11	9	10	1	1	15	6	0	0	0	0	9	10	-6	4
74153200		124	271	326	240	9	5	15	10	0	0	0	0	115	266	311	231
74153900		135	50	56	80	9	11	12	11	0	0	0	0	126	38	44	69
74160000		6	30	10	15	25	3	10	13	0	0	0	0	-19	27	0	3
74170000		8	50	35	31	0	0	2	1	0	0	0	0	8	50	33	30
74181000		0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
74181100		0	1	0	1	0	0	0	0	0	0	0	0	0	1	0	0
74181900		14	38	22	25	33	14	13	20	212	169	32	0	194	194	41	143
74182000		1,459	1,878	1,686	1,674	1,142	885	438	822	0	0	0	0	316	993	1,249	853
74191000		8	12	7	9	0	0	1	0	0	0	0	0	8	12	6	9
74199100		208	262	427	299	1,059	959	1,223	1,080	2,744	2,387	3,441	2,857	1,893	1,690	2,642	2,076

Aluminium	Product description	Import				Export				Production				Supply			
74199900		413	692	417	507	1,197	1,230	1,372	1,266	0	0	20	7	-784	-538	-935	-752
Total		83,434	70,124	76,364	76,641	40,501	44,831	48,961	44,765	5,383	5,846	61,658	23,966	48,316	31,139	89,061	56,172

ANNEX D: Substances containing chromium used as pigments

Chromium compound	Cas no.	Use	Chromium content	Concen-tration
Barium chromate	10294-40-3	Masking varnish	21%	0-4%
		Paint (varnish)		0-3%
		Protective varnish		0-28%
		Pigments		0-100%
Lead(II) chromate	7758-97-6	Masking varnish	16%	0-37%
		Paint (varnish)		0-10%
		Protective varnish		0-9%
		Pigments		0-100%
Chromium(III) oxide	1308-38-9	Paint (varnish)	68%	0-40%
		Other paints and varnishes		0-35%
		Binders for paint, glue, etc.		0-15%
		Primer		0.3-12.8%
		Masking varnish		0-40%
		Protective varnish		0-15%
		Floor paint		0-14%
		Ink		0.23-0.29%
		Paint and varnish hardeners		0-67%
		Gravure printing ink		0-20%
		Flexo printing ink		0-20%
Strontium chromate	7789-06-2	Primer	26%	2-30%
Silver chromate	7784-01-2	Protective varnish	16%	0-28%
Zinc chromate	13530-65-9	Primer	29%	0-15.8%
Zinc chromate hydroxide (ZN5(CRO4)(OH)8)	49663-84-5	Primer	9%	7.8-8.6%
Chromium hydroxide (CR(OH)3)	1308-14-1	Paint (varnish)	50%	0-0.64%
Chromate(1-), (1-((2-hydroxy-4-nitrophenyl)azo)-2-naphtalenolato(2-))(1-((2-hydroxy-5-nitrophenul)azo)-2-naphtalenolato(2-))-,sodium	59307-49-2	Paint (varnish)	8%	0-0.53%
		Ink		0-4%
		Other colourants		5.3-7%
Chromate(1-), (1-((5-(1,1-dimethylpropyl)-2-hydroxy-3-nitrophenyl)azo)-2- naphtalenolato (2-))(1-((2- hydroxy -4-nitrophenyl)azo)-2- naphtalenolato (2-))-, sodium	81361-06-0	Paint (varnish)	7%	0-0.4%
		Ink		0-3%
Chromate(1-), (1-((5-(1,1- dimethylpropyl)-2-hydroxy-3-nitrophenyl)azo)-2- naphtalenolato (2-))(1-((2- hydroxy -5-nitrophenyl)azo)-2- naphtalenolato (2-))-, sodium	81372-34-1	Paint (varnish)	7%	0-0.4%
		Ink		0-3%
Chromate (1-), (3-((4,5-dihydro-3-methyl-5-oxo-1-phenyl-1H-pyrazol-4-yl)azo)-2- hydroxy –5-nitrobenzenesulfonato(3-)) hydroxy -, hydrogen, mixed with 3-((2-ethylhexyl)oxy)-1-propanamine (1:1)	85443-67-0	Paint (varnish)	8%	0-2.65%
Chromate (1-), bis(1-((2- hydroxy -4- nitrophenyl)azo)-2-naphtalenolato (2-))-, sodium	64611-73-0	Paint (varnish)	8%	0-0.8%
		Ink		0-6%
		Other colourants		0-50%
Chromate (1-), bis(1-((2- hydroxy -5- nitrophenyl)azo)-2-naphtalenolato (2-))-, sodium	57206-81-2	Paint (varnish)	8%	0-1.06%
		Ink		0-8%
Chromate(1-), bis(1-((5-(1,1-dimethylpropyl)-2- hydroxy -3-nitrophenyl)azo)-2- naphtalenolato (2-))-, sodium	57206-83-4	Paint (varnish)	6%	0-0.8%
		Ink		0-6%
Chromate (1-), bis(2-((4,5-dihydro-3-methyl-5-oxo-1-phenyl-1h-pyrazol-4-yl)azo)benzoato(2-))-, sodium	41741-86-0	Other colourants	7%	2.6-5%
Chromate (1-), bis(2-(3-chlorophenyl)-2,4-dihydro-4-((2-hydroxy -5-(methylsulfonyl)azo)-5-methyl-3h-pyrazol-3-onato(2-))-, sodium	51147-75-2	Gravure printing ink	6%	0-4.5%
		Flexo printing ink		0-4.5%

Chromium compound	Cas no.	Use	Chromium content	Concen-tration
Chromate (1-), bis(methyl (7- hydroxy -8-((2- hydroxy -5-(methylsulfonyl)phenyl)azo)-1-naphtalenyl)carbamato(2-))-, sodium	71839-85-5	Gravure printing ink	6%	0-10.5%
		Flexo printing ink		0-10.5%
Chromate (1-), hydroxy (2- hydroxy -3-(((2- hydroxy -3-nitrophenyl) methylene)amino)-5- nitrobenzenesulfonato (3-))-, hydrogen, mixed with 3-((2- ethylhexyl)oxy)-1- propanamine (1:1)	85455-32-9	Gravure printing ink	8%	0-15%
		Flexo printing ink		0-15%
Chromium, tetrachloro-.mu.- hydroxy (.mu.-(2-methyl-2-propenoato-o:o'))di-	15096-41-0	Paint (varnish)	30%	0-0.2%
Xanthylium, 9-(2-carboxyphenyl)-3,6-bis(diethylamino)-, (2,4-dihydro-4-((2- hydroxy -5-nitrophenyl)azo)-5-methyl-2-phenyl-3h-pyrazol-3-onato(2-))(2-((4,5-dihydro-3-methyl-5-oxo-1-phenyl-1h-pyrazol-4-yl)azo)benzoato(2-)) Chromate (1-)	84989-45-7	Gravure printing ink	5%	0-15%
		Flexo printing ink		0-15%

The information in this Appendix is from the Product Register, 2001. Due to the rules on confidentiality applying to the Product Register, this overview includes only substances which are used by more than three manufacturers.