

International Chromium Development Association



**Health Safety and Environment
Guidelines for Chromium**

2007 Edition

Health Safety and Environment Guidelines for Chromium

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This document is the fourth revision of the ICDA Chromium Industry Guidelines, first published in April 1992.

Based on relevant published data and discussions with international experts and regulatory authorities, it is intended to help companies implement appropriate practices and procedures for the protection of their workers, the local community and the general environment.

This document has been designed as a practical guide to provide an overview of the current legislation and of the health, safety and environmental effects of chromium and its compounds.

It also includes references to documents where more detailed information can be found on specific aspects of chromium properties or regulation.

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INTRODUCTION

Health, Safety and Environmental Considerations for the Chromium Industry

Widespread concern has been generated over substances or processes that may have adverse effects on the health of individuals or the well-being of the environment. This is fact and it is not just the prerogative of chromium.

However, enormous progress has been made in understanding the toxicological behaviour of chromium, which is highly dependent on the specific chromium species involved.

Chromium has characteristics that range from being an essential trace element, important in glucose metabolism, to a chemically inert and biologically inactive material (the metal itself) or to the extreme case of ultimately being a genotoxic carcinogen, depending on the state of oxidation of the chromium (a property of certain hexavalent chromium compounds).

The acute, chronic and environmental toxicity of hexavalent chromium has attracted special attention from several international organisations.

In spite of considerable reduction in exposure, the chromium industry is often judged on its past performance. Recognition should be given to the significant changes in manufacturing processes and industrial hygiene that have been introduced and that have considerably improved occupational health, safety and environmental conditions.

History and past practices have had a negative effect on the image of the chromium industry. The industry today should correct that perception by producing information and statistical data that will give an accurate assessment of the present risks for health and the environment. Industry should also provide a balanced and realistic contribution to the regulatory process.

1 Biological Effects of Chromium

1.1 Human Health

Chromium occurs widely in nature, almost exclusively in the trivalent oxidation state and most commonly in the mineral chromite.

Other common valency states occur as a result of manufacturing processes:

- Zero valency for metallic chromium and many chromium-containing alloys, including stainless steels. Note that in these cases the chromium on the surface is oxidised spontaneously to the trivalent state creating a passive film which prevents further oxidation and which is responsible for corrosion resistance. This layer is also responsible for determining the health effects-see FIOH, in press.
- Hexavalent chromium occurs predominantly in chemical manufacturing processes and to a much lesser extent in metallurgical processes such as ferrochromium and stainless steel production, stainless steel welding and in some high temperature furnace operations which use chromium-containing refractories
- Trivalent chromium is recognised as an essential trace element in human and animal diets and important in glucose metabolism. Most diets are considered to be deficient in chromium for which the recommended daily intake is 200 µg for adults. For more detailed information, refer to Anderson, 1999.

The most significant occupational health effects are related to hexavalent chromium compounds. Exposure to such compounds may result in acute effects such as skin irritation, ulceration and sensitisation, nasal irritation, ulceration and nasal septum perforation and respiratory sensitisation. The most serious health effect is respiratory cancer. Epidemiological studies have confirmed that long-term exposure to high levels of hexavalent chromium as encountered historically in chromate chemicals and chromate pigments manufacture and electrolytic plating processes using chromic acid has led to a measurable excess incidence of respiratory cancer with a latency period in excess of 15 years.

In addition to epidemiology, many studies have been reported in which laboratory animals, mainly rats or mice, have been exposed to various chromium species by a variety of techniques. These studies are reviewed comprehensively in the following publications: ATSDR,2000; DECOS, 1998; Health and Safety Executive, 1989; IARC, 1990, ICDA, 1997,

The IARC classification for carcinogenicity of chromium compounds as follows:

Final IARC Evaluations

Chromium/Chromium Compounds	Degree of evidence for carcinogenicity		Overall evaluation
	Human	Animal	
• Chromium (VI)			1
• Chromium (VI) compounds as encountered in the chromate, chromate pigment production and chromate plating industries:	Sufficient		
• Barium Chromate		Inadequate	
• Calcium Chromate		Sufficient	
• Chromium Trioxide		Limited	
• Lead Chromates		Sufficient	
• Sodium Dichromate		Limited	
• Strontium Chromate		Sufficient	
• Zinc Chromates		Sufficient	

• Chromium (III) compounds	Inadequate	Inadequate	3
• Metallic chromium	Inadequate	Inadequate	3
• Welding Fumes			2B
• Welding fumes and gases	Limited		
• Welding fumes		Inadequate	

Note:

Group 1:	Carcinogenic to humans
Group 2:	Group 2A = probably carcinogenic to humans Group 2B = possibly carcinogenic to humans
Group 3:	Not classifiable as to its carcinogenicity to humans
Group 4:	Probably not carcinogenic to humans

Despite many human, animal and mechanistic studies, knowledge of the precise range of compounds and exposure levels capable of causing cancer, the mechanism of the carcinogenic process and the relationship between exposure and cancer is somewhat limited. The carcinogenic effect of hexavalent chromium is thought to relate to the ability of chromate ions to cross cell membranes, where subsequent chemical valency reduction is accompanied by genetic damage. The relationship between exposure and effect is complicated by the fact that extra-cellular body fluids can detoxify hexavalent chromium by reducing it to the trivalent state.

Human data relating to effects on reproduction are limited to female workers from which no conclusion can be drawn because of the poorly reported studies, but in animal studies on mice and rats receiving potassium dichromate in drinking water, adverse effects were observed on fertility and development of the offspring.

Because of these health effects, all commercially available hexavalent chromium compounds are heavily regulated and in many areas are classified as occupational carcinogens. Atmospheric exposure control standards are strict - see below, Section 5.1.

In contrast, the toxicity of trivalent and metallic forms of chromium by conventional exposure routes is low. Trivalent chromium is poorly absorbed by the body and does not easily cross cell membranes. Metallic and alloyed forms need to be ionised in order to cross any cell membrane.

Some trivalent chromium compounds are irritants and may elicit an allergic response in people already sensitised by previous exposure to hexavalent chromium.

Trivalent chromium products are not regulated for manufacture, supply and use and Occupational Exposure Limits (OELs) are less stringent than for hexavalent chromium – see Section 5.1.

1.2 Environmental Risks

As with human health, the environmental toxicity of chromium is species dependent. In nature, chromium is bound to other elements forming different compounds, such as chromite. Generally, trivalent chromium compounds are neutral or essential to organisms, but hexavalent compounds are toxic. Chromium is typically a metal which does not accumulate in the terrestrial or marine food chain or animals

Natural processes such as erosion and leaching of minerals actuates chromium to be physically present in soil, water and air. In the trivalent state, chromium has low solubility, and also man made chromium metal, chromium-containing alloys and insoluble trivalent chromium products such as chromic oxide are essentially inert and not bio-available.

Some water-soluble trivalent chromium compounds of strong mineral acids exhibit aquatic toxicity but this may be associated with their highly acidic properties. Under normal ambient conditions in aquatic and terrestrial environments, trivalent chromium also forms relatively stable complexes with many

naturally occurring organic species thus limiting its bio-availability. In some cases complexation may enhance chromium bioavailability depending on the solubility of the ligand (Saleh et al, 1989). Unless complexed, trivalent chromium is readily removed from aqueous effluents by precipitation and filtration and rendered insoluble in solid waste.

Because of the above considerations, the majority of trivalent chromium species are insoluble (Bartlett & James 1988), very poorly absorbed and do not bio-accumulate through the food chain. This characteristic is very important, taking into account that chromium is an essential element in human nutrition..

On the other hand, hexavalent chromium compounds are classified as dangerous for the environment and releases into all environmental compartments are regulated. It should be noted that there are also differences in solubility among hexavalent chromium species (James 1996). The presence of hexavalent chromium is rare in nature and it is mainly released as a result of anthropogenic activity. Environmental effects of hexavalent chromium are related to its nature as a relatively mobile anion and a strong oxidiser. The action can persist both in acid and alkaline soils (Yassi & Nieboer 1988) that are sandy or have low organic content (Cary 1982). So, the anion will remain mobile only if its concentration exceeds both the absorbing and reducing capacities of the soil (Cary 1982; Smith et al. 1989). Once in contact with organisms, the strong oxidiser reduces rapidly forming intermediates and reactive oxygen species that can cause adverse effects (Costa 1997; Goyer & Clarkson 2001)

Redox reactions can convert Cr(VI) to Cr(III) and vice versa (Rai et al. 1989; Kimbrough et al. 1999; Kotas & Staticka 2000). The Cr interconversion is controlled at the same time by several factors, including the presence and concentrations of Cr species and oxidising or reducing agents, ambient temperature, light, sorbents, acid-base reactions, pH, complexing agents and precipitation reactions (Saleh et al. 1989; Kotas & Staticka 2000). In the presence of iron (II) compounds, sulphides and organic matter, Cr (VI) is readily reduced to Cr (III) (Rai et al. 1989; Fendorf 1995). Only few oxidising agents exist in environmental situations at high enough concentrations to actually oxidise Cr (III) to Cr (VI) (Rai et al. 1989; Kimbrough et al. 1999). The presence of natural reducing agents in air, water and soil normally ensures that hexavalent chromium entering the environment is reduced to the trivalent state.

Hexavalent chromium is phytotoxic. Normally it is chemically reduced in the plant roots and is deposited as trivalent chromium there rather than in the above-ground foliage. The lowest chromium concentration in above ground plant tissues is observed in fruit with increases in the stem and the leaf (Smith et al. 1989; Zayed & Terry 2003). The concentrations of chromium in plants vary widely among different species, tissues and stages of growth (Kabata-Pendiasa & Pendias 2001). Generally, only a small fraction of the total chromium content of soils is available to plants. Plant to soil ratio has been shown to vary between 0.1 and 0.3 (Zayed & Terry 2003). The chromium concentration in plants is controlled mainly by the soluble chromium content of the soils (Kabata-Pendias & Pendias 2001)

Techniques are available to ensure that the hexavalent chromium content of releases to the environment is either eliminated or reduced to levels, which are consistent with no realistic risk. Such techniques relate i.a. to reduction of Cr⁶⁺ by e.g. Fe²⁺ followed by stabilisation/solidification for soluble chromates or in-situ remediation of e.g. contaminated soils, again with suitable reducing agents such as FeCl₂.

2 Risks by Industry Sector

The species-specific health and environmental effects of chromium have been discussed in sections 1.1 and 1.2 above.

It is essential that any industry using chromium carries out tests to confirm whether or not hexavalent chromium species are formed as a result of their activities. Such tests, which include monitoring of work place atmosphere and releases to the environment, are essential to assessing the risks associated with operations and to identify those controls which are necessary to protect workers and the environment.

Although control of hexavalent chromium is of particular importance, adequate means are also available to control human and environmental exposure to other chromium species to within acceptable limits.

Generation of waste is a reflection of inefficiency and best available techniques must be applied to minimisation on the one hand and effective treatment on the other.

2.1 Chromite Ore Mining

Chromite ore consists mainly of a spinel, which contains chromium (III), iron, aluminium and magnesium ions in an oxidic matrix. The approximate average chemical analysis as oxides, which can vary considerably from one geographical region to another, is:

- Chromic Oxide (Cr_2O_3) 46 %
- Iron Oxide (FeO) 25 %
- Aluminium Oxide (Al_2O_3) 15 %
- Magnesium Oxide (MgO) 12 %

The percentages of other minerals vary according to the source of the ore. Small amounts of silica, titanium oxide and vanadium oxide may also be present.

Non-specific skin rashes may occur in workers involved in chromite ore mining. Health hazards associated with chromite ore production are those found in any dusty mining operations and are due to the inhalation of dust. This may result in bronchitis. Chest x-rays have not shown evidence of fibrosis related to such exposure. Exposure to noise and heat stress must also be considered in underground mining.

Where possible, dust should be eliminated or reduced at source through engineering practices. Respiratory protective equipment (RPE) can be considered as a preventive measure of last resort in order to reduce the inhalation of dust. Hearing defenders are of importance in reducing exposure to noise during the course of work. Periodic medical assessments should form part of a general health surveillance programme.

2.2 Ferrochromium Industry

Ferrochromium is generally considered to have no hazardous properties. However, during the production of ferrochromium, workers may be exposed to dust and fumes containing trivalent and hexavalent chromium compounds. Hexavalent chromium compounds are found in small amounts in highly oxidised fumes from the melting/smelting processes, particularly during the tapping process.

Dust from bag filters contains hexavalent chromium. Dry milling of chromite and roasting of chromite pellets also produce small amounts of hexavalent chromium.

Epidemiological studies have shown no increased risk of lung cancer in workers in ferrochromium

plants. Nevertheless, on-going efficient industrial hygiene practices such as environmental monitoring, exhaust ventilation of fumes, dust and gases and noise suppression are essential. Certain work processes and work stations may require the use of approved personal protective equipment (respirators, masks, ear protection etc). Periodic health examinations should be undertaken. Fumes, dust and effluent should be handled so as to avoid any risk to the environment (see section 1.2).

Note: Polycyclic aromatic hydrocarbons (PAHs) resulting from the incomplete combustion of carbon and hydrogen in furnaces and coke ovens are potential carcinogens. The use of Soderberg electrodes in ferrochromium production is associated with the formation of these PAHs.

2.3 Chromium Metal Industry

Chromium is a stable, pure metal and is considered to have no hazardous properties. Pure chromium production processes may however involve hexavalent chromium compounds, either as raw materials (electrolytic process starting from chromic acid) or in fumes (alumino-thermic process).

Hence, fumes, dust and liquid effluent should be appropriately handled and disposed of so as to avoid any risk to the workers and the environment.

2.4 Stainless Steel and Chromium Alloy Industries (excluding Ferrochromium)

Hexavalent chromium compounds can be found in small amounts in highly oxidised fumes during the melting/smelting and pickling stages of the production process and during welding operations.

Stainless steel and chromium alloys in massive form do not present a health risk, but welding, cutting, brazing, grinding, etc may release potentially hazardous fumes or dust into the air. It is essential that all health and safety precautions be observed when welding and cutting operations are carried out.

Metallic chromium contained in scrap metal is considered harmless in this physical state.

For further information refer to Eurofer,1999 .

2.5 Chemical Industry

The manufacture of chromate and dichromates through the roasting of chromite ore produces hexavalent chromium compounds which are classified as carcinogens – see the IARC table under Section 1.1.

Discontinuing the use of the high lime roasting process together with improved industrial hygiene practices may have contributed to the decrease of lung cancer incidence in this industry.

All other industrial chromium chemicals are in turn made from sodium dichromate or, to a much lesser extent, from sodium chromate.

Sparingly soluble hexavalent chromium compounds such as zinc, strontium and calcium chromates have been associated with an increased risk of lung cancer.

Exposure to hexavalent compounds may cause skin ulcers, nasal septum perforations, allergic conditions (skin and respiratory) and kidney damage. Effective occupational health and environmental programmes are essential.

Because of the environmental hazards and classification of hexavalent chromium compounds, best available techniques must be applied to controlling releases to air, water and land. Since the industry produces significant quantities of solid waste, it is essential that this is treated to a degree, which renders

it non-hazardous prior to landfilling. Landfilling should be carried out to best practice standards and in compliance with local regulatory requirements.

Due to their carcinogenic classification, hexavalent chromium compounds must be used with great care and then only by professional industrial operators.

In a number of regions, users are required by law to use less hazardous substitutes where available to give the same or similar end products.

2.6 User Industries

2.6.1 Welding and Cutting

Welding of stainless steel is known to result in the formation of fumes containing hexavalent chromium due to the presence of alkali metals in fluxes. Because of this, all reasonable precautions must be taken to reduce exposure as far as is possible, even though the current weight of epidemiological evidence does not indicate an excess cancer risk amongst stainless steel welders in comparison to other welders.

The use of suitable personal protective equipment for all welders is stressed, together with regular medical examinations in order to detect any early symptoms of asthma, for example.

2.6.2 Chromium Plating (excluding Passivation)

Conventional electrolytic processes for chromium plating use chromic acid to deposit chromium metal on surfaces of other metals. The process may release a fine mist containing chromic acid to which workers may be exposed if effective engineering controls are not in place to remove the mist or if mist suppressants are not used. Most suppressants cause pitting of the plated surfaces and therefore are not always used.

There is an association between electroplating using chromic acid solutions and an increased risk of lung cancer. Skin ulceration and nasal septum perforation may also occur in this industry and there is the potential for skin and respiratory sensitisation. Therefore, all health and safety precautions must be in place to minimise exposure to chromic acid.

One way of limiting exposure for some decorative chromium plating applications is to use trivalent chromium-based plating systems. These are available from a number of industry suppliers. Until similar technology is available for hard and engineering plating requirements, the above precautions must be taken.

2.6.3 Leather Tanning

Basic chromium sulphate, in which chromium is present in the trivalent state, has been used in leather tanning for nearly 150 years. Although historically hexavalent chromium salts were converted to chromium sulphate by tanners, this practice is now rare in most countries, where tanneries are supplied with chromium tanning agents which contain no detectable levels of hexavalent chromium.

Epidemiological studies have shown no excess of respiratory cancer among exposed workers (Nurminen, 2006)

Nevertheless, because of the highly acidic nature of chromium sulphate, care must be taken to follow and maintain modern standards of workplace hygiene.

The tanning industry generates significant quantities of liquid and other waste. Liquid waste can be readily treated to remove chromium to acceptable standards. Solid wastes, containing trivalent chromium are not necessarily classifiable as hazardous. Nevertheless, there is sufficient justification for the industry to identify realistic possibilities to eliminate these wastes and those arising from end of life articles.

Refer to Van den Bossche et al, 1997

2.6.4 Spray Painting

There is evidence of increased risk of lung cancer in workers engaged in the manufacture of zinc chromate and sparingly soluble chromate compounds which are classified as carcinogenic – see section 1.1.

These materials are used in anticorrosion primer paints applied to metal surfaces. Therefore, it is essential to minimise exposure by using local exhaust ventilation and personal protection equipment.

Refer to UK Health and Safety Executive, 1999.

2.6.5 Refractory Industries

Although chromium-based refractories are generally considered to be inert, some hexavalent chromium compounds may be present during the manufacturing stages.

Many chromium-containing refractories are used in processes where the conditions may lead to the formation of hexavalent chromium, particularly high temperature operations in atmospheres containing oxygen. It is therefore appropriate to assess the risks for each situation and apply the requisite standards of control and personnel protection.

Chromium containing refractories must be characterised prior to disposal. This enables appropriate classification of the waste and choice of treatment before being used as a landfill.

2.6.6 Wood Preservation Industry

Chromium based wood preservatives are commonly used in the treatment of timber to extend its useful life. The chromium acts to fix the other ingredients into the timber. Copper-chromium-arsenic (CCA) preservatives have historically dominated the world market. However, regulatory and voluntary restrictions, associated with arsenic, in the EU and USA have limited their use to specific applications. The EU Biocidal Products Directive has eliminated the use of CCA preservatives among Member States from September 2006. It is anticipated that chromium-based, arsenic-free preservatives will continue to be used in the EU beyond this date.

Modern treatment techniques are designed to achieve a high degree of penetration by the preservative solutions and to ensure the effective reduction of the initial hexavalent chromium in the preservatives is reduced to the trivalent state during fixation in the wood.

The long-term effectiveness (> 50 years) of the treatment regime is due to the extremely strong fixation of the active ingredients in the wood by the chromium. In use, very little chromium is leached from the treated wood.

Generally acceptable precautions for use of treated wood include avoidance of dusts from cutting, sanding and drilling.

Due to the possible release of arsenic or other toxic substances, treated wood should not be burnt for cooking purposes or in open fires.

Sound occupational health practices in production plants are required to minimise inhalation and skin contact with the preservatives.

Refer to Murphy, 1998.

2.6.7 Cement Industry

Chromate dermatitis is a recognised occupational health hazard in the construction industry.

This dermatitis is due to the presence of hexavalent chromium in the cement originating from the raw material and historically from the refractory lining in cement kilns. Levels of less than one part per million of hexavalent chromium can be achieved and maintained.

Hexavalent chromium-free cement can also be produced by the addition of ferrous sulphate during manufacture. In any event, it is necessary to ensure that inhalation of, and skin contact with, cement as a raw material are avoided and that all necessary health and safety precautions are in place.

In many areas, significant reductions have been achieved by, for example, moving to chromium-free refractories and processes have been developed to eliminate residual chromate levels.

2.6.8 Surface Treatment of Metals

Solutions containing hexavalent chromium have traditionally been, and continue to be used to treat the surfaces of some metals or alloys such as steel, zinc and aluminium to provide a high degree of resistance to corrosion in many applications.

Because of the classifications mentioned above such uses are coming under increasing pressure through regulations which seek to restrict the use and presence of hazardous substances and some give specific mention to hexavalent chromium. For example, the EU End of Life Vehicle Directive (2000/53/EC) and Waste Electrical and Electronic Equipment Directive (2002/96/EC) will effectively ban the presence of hexavalent chromium from being present in such new articles from 2007 and 2006 respectively. It should be noted that these regulations do not impact on either metallic or trivalent chromium

For many applications, satisfactory alternatives containing trivalent chromium are available and continue to be developed.

2.6.9 Manufacture of Pigments and Dyes

Sodium dichromate is used for pigments based on the chromate ion and on chromium (III) oxide.

Lead, strontium, barium and zinc chromates are mainly used as colorants or anticorrosives in paints, plastics and fireworks.

Chromium (III) oxide is by chemical reduction of sodium chromate or dichromate or thermal decomposition of chromic acid and is used as a green colorant in different applications.

Health and safety precautions are required to minimise skin contact and inhalation of both raw materials and products.

Waste water may contain hexavalent chromium and must be treated prior to disposal.

3 Health, Safety and Environment Programmes

Employers have a responsibility to provide a clean, safe and healthy workplace for their workers and to protect the environment

All reasonable care should be directed toward achieving these conditions in order to eliminate or reduce any undesirable conditions, which could affect the health of employees or the well-being of the environment, both in the short and long term.

Most countries have specific legislation dealing with these matters and employers should be familiar with the laws of their country and comply with them.

However, it is not only legislation that should determine these standards but also a commitment by management to achieve and maintain the highest degree of health care and safety in their plants and of protection of the surrounding environment. These responsibilities also include assisting customers in applying appropriate standards.

Employers are expected to be familiar with all materials and processes used in a plant, and to be aware of any real or potential health and/or environmental risks which may occur as a result of exposure to such conditions.

All workers have the right to know about the materials and processes with which they work and to obtain any information regarding the possible ill health effects arising from exposure to these substances or processes. Employers should have programmes in place to inform their employees accordingly.

The general public living in proximity to the plant also have a right to know if operations are likely to have an adverse effect on their health and on the local environment.

Effective and appropriate occupational health, safety and environmental management programmes, which at least meet national regulatory obligations for both workplace and environmental situations, are essential.

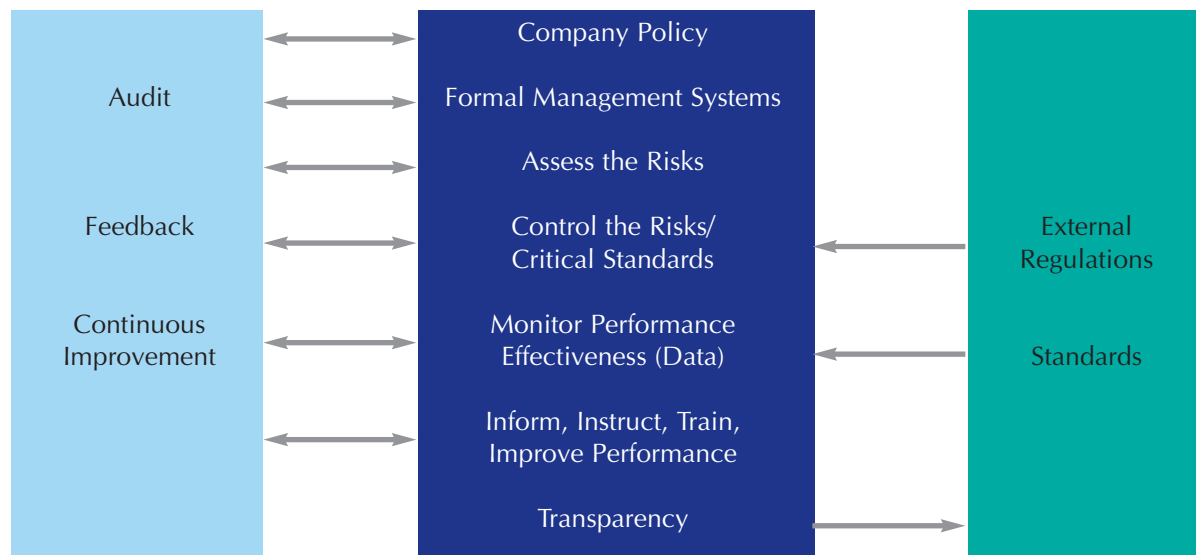
It is recommended that plants should have health and safety committees to identify and solve specific problems in the workplace. In order to monitor and measure the data necessary for effective health and safety programmes, properly constituted departments employing people with special expert knowledge should be part of the operation.

It is further recommended that companies set up and operate formal management systems based on written procedures and standards covering all important aspects of operations. These should be based on International Standards e.g. ISO 14001 and ISO 18001.

The flow chart as shown in the following Figure 1 illustrates the key elements of an effective system:

Figure 1

Common Features of Health, Safety and Environment Management Systems



3.1 Health Surveillance

All companies producing or using chromium compounds should have efficient medical surveillance programmes in place to monitor the ongoing health of their employees. Such programmes would include the following:

3.1.1 Pre-Employment Medical Examination

- | | |
|------------------------|---|
| Full History | <ul style="list-style-type: none"> • Previous employment and occupational exposure • Past and current medical conditions • Smoking history |
| Physical Examination | <ul style="list-style-type: none"> • Special reference to skin, nasal mucosa and lungs |
| Special Investigations | <ul style="list-style-type: none"> • Baseline chest X-ray • Spirometry • Other clinical/laboratory investigations where indicated |

3.1.2 Periodic Medical Examinations

Review of symptoms and state of health by an occupational health physician or nurse should be undertaken on a periodic basis. Workers should be made aware of the importance of recognising relevant symptoms and they should be encouraged to report such symptoms to their occupational health department for further evaluation and advice.

Access to the occupational health service for such advice should be available in addition to any scheduled periodic assessments. The frequency of periodic medical examinations should depend on exposure characteristics, legislation and codes of practice. Referral to a chest, skin or other clinical specialist for further x-ray and other investigations should be considered when indicated.

3.1.3 Specific Medical Examinations

Employees who report any untoward symptoms, especially if alleged to be work-related, should be assessed medically and symptoms investigated.

Specific medical examinations and laboratory tests should also determine the ability of the employee to return to their current work or to be redeployed. Indications for modifications to the system of work should be discussed fully with the individual worker and the managers and reduction of exposure should be considered.

Note: Plant physicians should be familiar with the plant, the processes and environmental conditions in the workplace, and the health risks, symptoms and signs of health effects associated with chromium and its compounds.

The examining physician should consider occupational factors in the differential diagnosis and involve the worker and management in dealing with any adverse health effects, which may be work-related. Health effects should then be investigated by designated plant personnel and appropriate preventive measures implemented.

3.1.4 Record Keeping

It is essential that up-to-date, accurate medical records be kept for all workers. Included in the record should be the job title, work area, duration of employment, relevant exposure data from workplace monitoring and/or biological monitoring and occupational, medical and smoking histories.

Such records are essential for investigating ill-health claims against the employer, determining entitlement to disability benefits, resolving disputes regarding exposure and ill-health in the workplace and for inclusion in future epidemiological investigations.

For research purposes, records must be kept systematically, be easily retrieved and summarised and should be complete, accurate and up-to-date. Records of ex-employees should be retained for at least 30 years. All records should be stored securely, with adequate provisions for maintenance of confidentiality.

3.1.5 Personal Hygiene in the Workplace

Employees should be advised on appropriate personal protective equipment and personal hygiene when working with chromium compounds. Where provided for use, workers must be instructed in the wearing and maintenance of personal protective equipment and comply with the instructions.

Where exposure is likely, workers should use and change into clean overalls regularly to reduce the likelihood of skin contact with soiled clothing. Facilities for the handling and cleaning of soiled clothing should be established to avoid contamination of the domestic or other off-site environment. Hands should be washed before meals and breaks, and the face washed to prevent dust particles from being inhaled or ingested. Meals should not be taken in areas where there is a risk of exposure to chromium in dust, fume, chemicals etc, and smoking in the workplace should not be allowed.

3.2 Workplace Monitoring

Monitoring of the workplace environment is carried out in order to determine the composition and concentration of any contaminants in the workplace and surrounding areas and to ensure that control systems and procedures are effective.

Environmental hygiene measurements in the workplace can be taken in the breathing zone of a worker (personal sampling), around specific processes or machinery (area sampling), or in the working environment (general area sampling).

The frequency and nature of sampling depends on many factors. It may be implemented as part of a planned programme involving collection of epidemiological data, as a hygiene investigation into an accident involving inadvertent exposure, to confirm reduced exposure following improvements in plant processes, or to comply with regulatory requirements.

It also depends on the extent of existing dusty conditions and current workplace practices. Once satisfactory hygiene conditions have been achieved and work procedures are stable, sampling is usually required once or twice a year on a regular basis or as required by regulations. The results of sampling will indicate processes where the concentration of airborne substances is either adequately controlled or if it exceeds Occupational Exposure Limits, in which case corrective measures should be taken.

Minimum monitoring requirements include total dust, total chromium and hexavalent chromium, and all expressed in mg/m³ or µg/m³.

Refer to section 5.1 for specific limits applicable in given regions or countries.

3.2.1 Personal Sampling

This is performed using a portable battery-operated pump. Air is sampled for a specific period of time through a filter, which is positioned near the worker's nose or mouth (breathing zone). The filter is weighed before use and again after the sampling has taken place and the total weight of the dust, fume or mist then carefully measured. The sample is analysed to identify chromium specifically as metallic chromium (0), chromium (III) or chromium (VI). Analysis of samples should be carried out in a suitable laboratory by appropriately qualified people.

The total weight of dust should also be determined.

Personal sampling is legally compulsory for scheduled processes in certain countries. It should be recognised that because of the differences in prescribed sampling methods, the results obtained with one method may not be directly comparable with the results obtained using a different method. The method used should be that prescribed or recommended by the relevant regulatory authority.

3.2.2 Area Sampling

This is usually performed using a stationary sampling device and is used to determine the general contamination in an area of the workplace, or in the vicinity of certain operations, to identify where corrective action is necessary and to assist with designing effective exhaust and ventilation systems.

3.2.3 Biological Monitoring

Reference values for biological monitoring, sometimes called Biological Exposure Indices (BEI) or Guidance Values have been developed by several organisations including ACGIH (USA), HSE (UK) and DFG (Germany) to assist occupational health professionals in evaluating and controlling exposure. A thorough discussion of these and how they should be used can be found in Cocker, 2005.

In some cases, urinary chromium can confirm worker exposure to chromium but does not necessarily equate with the occurrence of health effects. Such monitoring may be used as an adjunct to workplace monitoring to indicate systemic absorption of chromium by the worker. However, the absence of excess chromium in the urine does not effectively mean that there was no exposure to chromium as it may have been in an insoluble form. In addition, chromium in urine does not distinguish between trivalent or hexavalent chromium as the source of exposure.

Urine analysis for chromium should not be undertaken unless the analytical laboratory is sufficiently experienced in such analysis and belongs to a quality control scheme. Also there must be measures at the collection and transport stages to prevent external contamination of the samples, which would render the exercise useless.

Blood samples may also be used for biological monitoring. The collection of such samples is more

difficult compared to urine samples and the experience at the worksite with this method is limited. The analysis of chromium in body fluids must be carried out with all the precautionary measures necessary to prevent contamination of samples..

Note: Hair and nail analyses are not recommended for monitoring occupational exposure to chromium.

3.2.4 Record Keeping

It is essential that companies should keep accurate records of all workplace measurements. This information is not only useful to the company but will assist the whole industry should epidemiological studies be conducted in the future. Individual health records must be kept confidential. Environmental monitoring records should be stored in a format such that group and individual exposure data may be readily retrieved.

3.2.5 Procedures

Companies requiring information regarding dust sampling procedures in the workplace may refer amongst others to the UK Health and Safety Executive 1993.

This document also contains the names of suppliers of equipment and a list of procedures dealing with the analyses of the industrial hygiene samples that are available from the Health and Safety Executive.

For information on the laboratory analysis of chromium and inorganic compounds of chromium in the air, the following references are useful:

- The UK Health and Safety Executive, 1981.
- The United States OSHA, 2000

Information regarding personal protection equipment and dust protection is available in UK Health and Safety Executive, 1991.

The above publications are invaluable for companies planning workplace monitoring and who currently do not have routine environmental hygiene monitoring in place.

They do not substitute for the services of professional industrial hygienists, nor should they be seen as substitutes for the legally binding monitoring requirements of certain countries.

3.3 Workplace Safety

Safety and Risk management go hand in hand. No business can implement a Safety, Health, Environmental and Quality (SHEQ) Management system if it does not understand where it stands in terms of risk. It is essential to understand that safety is not magic, but a management method based on the principle of "the more you practise the basics, the better you get at achieving a safe environment".

In many instances, businesses err by implementing "control measures" without really understanding:

- the hazards that have the potential for risk (loss/harm);
- the potential outcome should the risk be realised; and
- applying the hierarchy of controls to mitigate the chance of loss/harm.

Then, and only then, should control measures be implemented to manage "residual risk".

Many organizations have implemented formalised risk assessments that are conducted on a daily basis. During the course of work, individuals note changes in working practices, they recognise unsafe working conditions and practices and take the necessary corrective action. It is a legal requirement that a systematic, formalised approach be implemented to identify, control and manage risks in the workplace. It is essential that the results of a risk assessment are recorded and verified for completeness and accuracy. In assessments, employers should undertake a systematic examination of the work activities and work environment and then record the significant findings of the risk assessments conducted.

The risk assessment at an organisation should be continuous and should not be regarded as a once-off exercise. While it will be necessary to establish a baseline, most countries' legal requirements will not be satisfied by a once-off risk assessment report. It is thus essential to implement a system to ensure regular revisions, thereby ensuring continual improvement. Everything in the SHEQ world starts with a risk assessment. Otherwise one would not understand the terms of risk that one needs to deal with!

There are three essential forms of risk assessment. All are part of an SHEQ Management System and need to be carried out diligently as per legal requirements.

Having a systematic approach is very important:

- How bad are the hazard / risk?
- How much do we know about it and how do we control it?
- Are the ways to control the risk in place?
- Are they effective?
- What alternative measures are there?
- Will these measures have the desired effect and will they be beneficial?

The main purpose is to:

- Identify the risk;
- Assess the risk; and to
- Evaluate or develop controls.

Controls should be focused on:

- Eliminating risk / controlling at source;
- Remaining risks – provide personal protective equipment as last defence.

Understanding the terminology:

Hazard:

A condition that poses a risk.

Risk:

The chance of loss - calculated as the product of probability of occurrence and the potential severity and consequence of the loss should the event occur expressed qualitatively or quantitatively.

Risk Assessment:

It is the overall process of recording hazards and estimating the magnitude of the risk. Secondly, it involves deciding whether or not the risk is tolerable through the evaluation of existing control measures.

Baseline Risk Assessment:

A process by which the business or process can identify and understand where it stands in terms of risk. A process of identifying hazards that, purely through their existence, pose a potential for causing loss or harm.

Issue Based Risk Assessment:

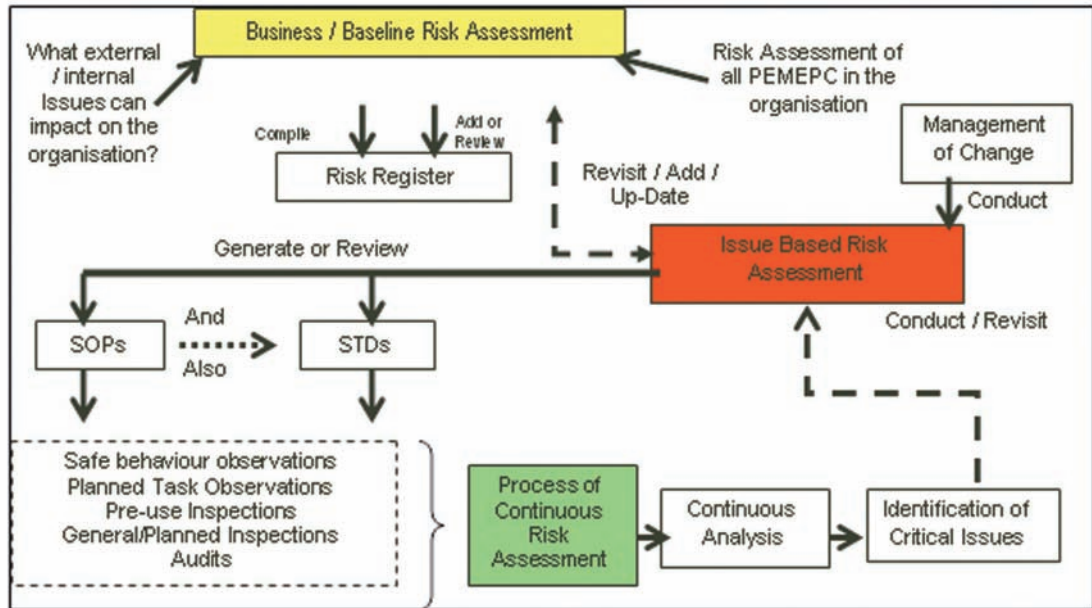
Could be derived from high ranking baseline risk assessments or as circumstances change and needs arise. Separate risk assessment studies must be conducted, for example when:

- Any change occurs as an integral component of change management;
- New machinery or equipment is implemented;
- A loss occurred, etc.

Continuous Risk Assessment:

This is the most important form of risk assessment and should be conducted continually, as an integral part of day-to-day risk management. It will be mainly conducted by front line personnel. The source of the system is normally control measures identified from baseline- and or issue-based risk assessments aimed at controlling residual risk. The simplest form of continuous risk assessment is the ongoing monitoring and adherence of employees in wearing personal protective equipment.

Diagram depicting the interactive risk driven approach to Workplace Safety



It is important to understand the difference between a business risk analysis and baseline risk analysis.

Business Risk Analysis:

Consists of strengths, weaknesses, opportunities and threats (SWOT) analysis with the focus on political, economical, social, technological, environmental and legal exposures.

Baseline Risk Analysis:

Exposure to people, equipment, material, environment, process and cost are the drivers.

Risk Ranking Categories:

No matter what quantitative method is used, the outcome would be based on one of the following three risk categories:

- Negligible Risk ranking: Management maintain and monitor risk at this level.
- Tolerable Risk ranking: Develop risk control measures that reduce risk to within reasonable practical limits.
- Intolerable Risk ranking: Develop remedial actions as required. If necessary, STOP the activity.

How does all of this bring us to safety? Understanding the RISK is understanding the safety exposure that employees face through their exposure to these RISKS.

To ensure a common understanding, the Hazard pyramid is essential to enhance safety in the workplace throughout industry.

Hazard Pyramid

Safety statistics could be seen as the tip of an iceberg. Understanding the safety triangle is of utmost importance as it provides industry with a baseline from which to measure and understand how to enhance safety performance.



To understand the triangle it is important to define the concepts:

- **Fatality:** A death resulting from an occupational injury, illness or disease.
- **Lost Time Injury:** A work-related injury or disease that causes the injured person to be absent from any full, rostered shift, subsequent to that on which the injury occurred.
- **Restricted Work Injury:** An occupational injury, illness or disease which causes a person to be physically or mentally unable to perform all, or part of, their normal duties during any rostered shift subsequent to that on which the injury, illness or disease occurred.
- **Medical / First Aid:** Medical attention was needed – could be a plaster to more extensive medical treatment depending on the injury.
- **Near Miss:** An unsafe act or condition that could have led to a more severe injury had circumstances been slightly different.

Safety Triangle



Based on the Bird safety triangle there is a definite relationship between the different levels of the safety triangle. This has been statistically proven. The ratio can be seen below.

For every one fatal you will have:

- Ten lost time injuries.
- Thirty restricted / classified injuries.
- Three hundred medical / first aid cases.
- Thirty thousand potentials expressed as near misses, unsafe conditions / actions, etc.
- Summarised as 1:10:30:300:30000 ratio

Measurements used to express safety statistics:

- | | |
|-------|--|
| FFR | Fatal frequency rate. |
| LTIFR | Lost time injury frequency rate. |
| RWIFR | Restricted work injury frequency rate. |

What is important is that we have the same definition to calculate the frequency:

1. This includes employees and contractors.
2. Frequency is calculated as the number of injuries of that specific nature multiplied by a million divided by the hours actually worked.

i.e.; a plant had 11 lost time injuries involving employees and 5 lost time injuries involving contractors for the year. The total hours worked during the 12 month period accumulated to 3.8 million. What is the LTIFR ?

$$\text{LTIFR} = [(11+5) \times (1\,000\,000)] / 3.8 \text{ million} = 4.2$$

It is essential that we share and accumulate statistics to enable the Chromium industry to understand the impact the industry has on the lives of our employees. The first goal would be to see the industry not having any fatal injuries and from there to progress to minimise lost time injuries.

Through the sharing of information industry could share lessons learnt.

3.4 Environmental Management

The essential elements of an effective environmental management system are set out in Figure 1 above. Such a system should be designed to meet the requirements of ISO 14001. It is vital to recognise the importance of public opinion in this area, particularly that of interested and affected parties.

In many parts of the world, companies must acquire a permit to operate, issued by the regulatory authority. These permits require operators to prevent releases to all environmental compartments or, where a release cannot be prevented, it must be minimised using best available techniques or maximum achievable control technology.

Permits will normally also include numerical limits on individual process emissions to air, water and land as appropriate, together with an agreed improvement programme which may address waste minimisation, energy consumption, noise or any other aspects of the operation that may impact on the environment or the local community.

Further requirements may also include prior approval before modifying existing operations or building new plants, the routine reporting of monitoring data and the reporting of unusual events and breaches of permit conditions within a specified timescale.

3.4.1 Environmental Monitoring

Regular monitoring of all release points may be necessary to demonstrate compliance with permit or regulatory limits. Required monitoring levels are often specified in permits or regulations.

Monitoring should also extend to include the surrounding environment. This provides valuable data, which can be used in discussions with regulators and with neighbours.

It is proposed and recommended that internal limits be set lower than those required by regulations such that corrective action can be taken before the permit or regulatory limits are broken.

Substances, which are of particular concern, are solid particles, hexavalent chromium and total chromium. These can be measured or monitored at the outlet of the chimney stack, at the plant perimeter or at a specified distance from the boundary fence. For the second and third points, there are two existing methods of monitoring: by collecting the particles (expressed in mg/m²/week) or by continuous monitoring (expressed in mg/m³).

Refer to Section 5.5 for specific limits applicable in given regions or countries.

4 Regulatory Bodies by Region or Country

Note: The geographical regions or countries referenced below represent those with strict regulations, which should serve as appropriate guidelines.

In all matters relating to Health, Safety or Environmental Regulations, individual companies must consult with their national authorities for details of specific regulations, which may apply.

4.1 European Union

The following Directorates General (D.G.) deal with chromium-related hazards.

- D.G. Environment, Nuclear Safety and Civil Defence deals with Classification, Labelling and Packaging of Dangerous Substances.
- D.G. Employment, Industrial relations and Social Affairs deals with Occupational Health and Safety including setting Occupational Exposure Limits.
- D.G. Enterprise and Industry
- D.G. Health and Consumer Protection

These Directorates enact decisions through EU Directives or Regulations, which either lay down legally binding requirements or set out minimum standards for which Authorities within Member States may set more demanding limits.

National Authorities may also impose additional acts or regulations.

4.2 Japan

The Japanese Society for Occupational Exposure Limits (JSOH) recommends the Occupational Exposure Limits (OELs) as reference values for preventing adverse health effects on workers.

Chromium is strictly regulated through legal controls by the Industrial Safety and Health Law and Poisonous and Deleterious Substances Control Law for the workplace, by the Water Pollution Control Law and Wastes Disposal and Public Cleansing Law for water purity control and waste matter in the environment respectively. There are specific limits for air emissions.

The Industrial Safety and Health Law, the Poisonous and Deleterious Substances Control Law and the Wastes Disposal and Public Cleansing Law are under the control of the Ministry of Health, Labour and Welfare. The Water Pollution Control Law is administered by the Ministry of the Environment.

4.3 South Africa

The South African regulatory framework differentiates between mines and works.

The legislative structure is as follows:

Mines:

- Department of Minerals and Energy (DME)

Mines Health and Safety Act-occupational health and safety of mineworkers.

The Mine Health and Safety Inspectorate has responsibility for enforcing the Act via:

Regulations;

Codes of Practice-mines must prepare codes of practice as required by the Chief Inspector of Mines;

Safety in Mines Research Advisory Committee (SIMRAC)

- Department of Water Affairs and Forestry (DWAF)
National Water Act
Minimum requirements:
 - For the handling, classification and disposal of hazardous waste
 - For waste disposal by Landfill
 - For water monitoring at waste management facilities
- Department of Environmental Affairs and Tourism (DEAT)
National Environmental Management Act (promulgated 7th January 2005)
Environmental Impact Assessment (EIA) - new regulations promulgated during 2005.
Air Quality Act
Biodiversity Act

Works

- Department of Labour
Occupational Health and Safety Act
Hazardous Chemical Substance Regulations-drawn up in conjunction with the
Advisory Council for Occupational Health and Safety. Includes the following:
 - Air Monitoring
 - Medical Surveillance
 - Respirator Zone
 - Records
 - Personal Protective Equipment
 - Disposal of HCS
 - Biological Exposure Indices
- Department of Environmental Affairs and Tourism (DEAT)- as for Mines
- Department of Water Affairs and Forestry (DWAF)- as for Mines

4.4 USA

The American Conference of Governmental Industrial Hygienists (ACGIH) classifies, processes and recommends Threshold Limit Values (TLVs.) These are only guidelines.

The Occupational Safety and Health Administration (OSHA) has published the Hazard Communication Standard to ensure that all hazards of produced or imported substances are assessed and that the information is passed on to employers and employees. These rules deal with the labelling aspects, the preparation of Material Safety Data Sheets (MSDS) and the training of employees.

OSHA also publishes Permissible Exposure Limits (PEL) which are binding. On 28 February 2006, OSHA published a comprehensive Workplace Exposure Rule for exposure to hexavalent chromium. This rule contains a new, much lower Permissible Exposure Limit (PEL) of 5µg/m³ and a number of other requirements.

The National Institute for Occupational Safety and Health (NIOSH) is one of the Centers for Disease Control and Prevention and is part of the Department of Health and Human Services.

Acting under the authority of the Occupational Safety and Health Act of 1970 (Public Law 91-596), NIOSH develops and periodically revises recommendations or limits of exposure to potentially hazardous substances or conditions in the workplace.

It also recommends appropriate preventive measures designed to reduce or eliminate adverse health effects of these hazards. To formulate these recommendations, NIOSH evaluates all known and available medical, biological, engineering, chemical, trade and other information relevant to the potential hazard.

These recommendations are then published, and transmitted to OSHA and the Mine Safety and Health Administration (MSHA) for use in promulgating legal standards.

The Environmental Protection Agency (EPA) generates and enforces all aspects of environmental regulation.

5 Regulatory Obligations

5.1 Occupational Exposure Limits (OELs)

Companies must always consult their national or regional regulatory authorities for advice on the current legal limits applicable to them. They should further check whether these limits are legally binding or only recommended guidelines.

Despite regional variations, there is a certain coherence in the current values for the Occupational Exposure Limits (OELs) given below and expressed as mg Cr/m³.

The values given are 8-hour time-weighted averages unless otherwise indicated. Short-Term Exposure Limits (STELs) are averaged over a period, which may vary from 5 to 60 minutes.

Chromium metal includes the pure metal and its alloys.

- **Denmark**

- Chromium as powder/soluble chromium (II) and (III) salts 0.5 mg/m³
- Chromic acid and chromates (VI) 0.005 mg/m³
- Strontium chromate 0.0005 mg/m³

- **European Union**

- Chromium metal, chromium (II) and inorganic chromium (III) compounds (insoluble) (Draft 2nd IOELV Directive) 2.0 mg/m³

Note: although there is currently no OEL for hexavalent chromium at EU level, the draft Human Health Workplace Risk Reduction Strategy for Chromates prepared for the EU by the UK HSE includes a proposal that an exposure level of 0.01mg.m³ should be considered to indicate adequate control. This is based on a recommendation by SCOEL, 2003.

- **Finland**

- Chromium, chromium (II) and (III) compounds
- Chromium (VI) compounds 0.05 mg/m³

- **France**

- Chromium metal 0.5 mg/m³
- Chromium (VI) compounds 0.05 mg/m³
- Chromic acid 0.05 mg/m³
- STEL value 0.10 mg/m³

- **Germany**

<i>Compound or Group</i>	<i>Classified according to MAK list</i>	<i>Limit value in mg/m³ expressed as Cr</i>	<i>Limit value in mg/m³ expressed as CrO₃</i>
- Zinc Chromate	Canc. Cat.1	0.05	0.10
- Chromium (VI)			
- Compounds (except insolubles)	Canc. Cat. 2	0.05	0.10
- In welding fumes from MMA arc welding with coated electrodes		0.05	0.10

- In manufacturing of soluble Cr (VI) compounds			
Cr (VI) compounds	Canc. Cat. 2	0.05	0.10
Any other Cr (VI) compound	Canc. Cat. 2	0.025	0.05

Note: Cancer Cat.1 = human carcinogen; Cancer Cat. 2 = animal carcinogen
(Source: MAK list)

• **Iceland**

- Chromic acid (VI)		0.02 mg/m ³
- Chromates (VI)		0.02 mg/m ³
- Chrome metal and chromium (III) compounds		0.5 mg/m ³

• **Italy**

Does not produce its own exposure standards – uses ACGIH values as per USA below

• **Japan**

Chromium (VI) compounds		0.05 mg/m ³
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• **Kazakhstan**

- Total Chromium		1.0 mg/m ³
- Chromium (VI)		0.01 mg/m ³

• **Norway**

	Cancer class	
- Chromium metal, Chromium (II) and (III) compounds		0.5 mg/m ³
- Chromic acid & chromates (VI)	K1	0.02 mg/m ³
- Lead chromate	K3	0.02 mg/m ³

• **South Africa**

- Chromium metal		0.5 mg/m ³
- Chromium (III) compounds		0.5 mg/m ³
- Chromium (VI) compounds		0.05 mg/m ³

• **Spain**

Does not produce its own exposure standards. Uses ACGIH values as per USA below

• **Sweden**

- Chrome metal/inorganic compounds excluding Chromic acid and chromates (Chromium and its inorg (II and III) compounds (as Cr), (total dust)		0.5 mg/m ³
- Chromates (VI) (Chromium (VI) compounds (as Cr), total dust		0.02 mg/m ³
Chromic acid (VI)		0.005 mg/m ³
- STEL value (STEL value)		0.02 mg/m ³
		0.05 mg/m ³
		0.015 mg/m ³

NOTE: the current categories and limits will change to those in brackets as a result of a set of proposals made in 2006 by the Swedish Work Environment Authority, Chemistry and Microbiology Division. The existing specific limit for chromic acid will disappear

• **United Kingdom**

- Chromium Metal		0.5 mg/m ³
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- Chromium (III) compounds	0.5 mg/m ³
- Chromium (III) compounds	0.5 mg/m ³
- Chromium (VI) compounds	0.05 mg/m ³

All of the above are defined as Workplace Exposure Limits (WELs) which have replaced OEL and MEL respectively.

• **USA**

- Threshold Limit Values (TLVs) as defined by the American Conference of Governmental Industrial Hygienists Inc. (ACGIH):

<i>Compound or group</i>	<i>Cancer class</i>	<i>Limit value in mg/m³ expressed as Cr (TWA)</i>
- Zinc chromate, as Cr	A1	0.01
- Water soluble chromium (VI) compounds	A1	0.05
- Insoluble Cr (VI) compounds	A1	0.01
- Chromite ore processing, as Cr	A1	0.05
- Lead chromate, as Cr	A2	0.012
- Strontium chromate, as Cr	A2	0.0005
- Calcium chromate, as Cr	A2	0.001
- Chromium metal and Cr (III) compounds	A4	0.5

TWA = 8 hour time weighted average

Cancer Class A1 = confirmed human carcinogen

Cancer Class A2 = suspected human carcinogen

Cancer Class A4 = not classified as human carcinogen (Source: ACGIH list)

- Permissible Exposure Limits (PELs) as defined by the Occupational Safety and Health Administration (OSHA). OSHA has established a comprehensive Workplace Exposure Rule for hexavalent chromium. This includes a PEL and an Action Level as well as requirements for industrial hygiene, air sampling, medical surveillance, training and record keeping..

- Hexavalent chromium compounds as Cr ⁶⁺	PEL 5µg/m ³ Action Level 1.5µg/m ³
- Chromium metal	1.0 mg/m ³
- Chromium (II) and chromium (III) compounds	0.5 mg/m ³

5.2 Biological Exposure Indices

<i>Country/Region</i>	<i>Chemical Determinant</i>	<i>Sampling time</i>	<i>BEI</i>
South Africa	Cr ⁶⁺ as water soluble fume	Increase during shift	10µg/g creatinine
	Total Cr in urine	End of shift at end of workweek	30µg/g creatinine
UK (Cr⁶⁺ exposure)	Total Cr in urine	End of shift	10µmol/mol creatinine

5.3 Emission Limit Values

This section gives specific emission limits for releases to different environmental compartments for countries for which information is available.

The following lists may not be exhaustive and numbers listed are subject to review/change, therefore it is essential to confirm with local, national or regional authorities.

5.3.1 Air

• European Union

The IPPC Directive 96/61/EC deals with atmospheric pollution by industrial plants and Directive 200/76EC deals with the incineration of waste.

Chromium and its compounds are on a list of several heavy metals. The total amount of these metals in the emission has to be less than 1 mg/m³.

• France

The following limits apply:

- Total Dust 100 mg/m³ (if total mass flow is <1kg/h)
40 mg/m³ (if total mass flow is > 1 kg/h)
- Metals 5 mg/m³ (if total mass flow is > 25 g/h)
(Metals = total content of the following metals: Sb+Cr+Co+Cu+Sn+Mn+Ni+Pb+V+Zn)

• Germany

Emissions are regulated through the "TA Luft" which is currently under revision. The limit values are as follows:

- Total Dust 50 mg/m³ (if total mass flow is > 0.5 kg/h)
- Chromium 5.0 mg/m³ as Cr for chromates of calcium, chromium (III), strontium and zinc (if total mass flow is > 5 kg/h)
- Chromium (VI) 1.0 mg/m³ as Cr for inhalable dust and for chromates of calcium, chromium (III), strontium and zinc (if total mass flow is >5g/h)

• Kazakhstan

- Total Chromium 4 - 4.8 mg/m³
- Chromium (VI) 0.0017 mg/m³

• South Africa

The National Environment Management Air Quality Act, 2004 legislates air quality in South Africa. The objective of the Act is to protect the environment thereby securing an environment that is not harmful to the health and well-being of people.

National air quality standards are being developed. Until such time, the WHO Air Quality Guidelines for Europe will be used.

• UK

The IPC Guidance Note S2 4.04 provides the following benchmark emission guidance for Inspectors:

- Total dust 20 mg/m³
- Chromium (III) as Cr 5 mg/m³
- Chromium (VI) as Cr 1 mg/m³
- Calcium, strontium, zinc and 0.5 mg/m³
zinc potassium, chromium (III)
chromates as Cr

Best Available Technique (BAT) must be employed to minimise releases to the environment.

Emissions are also assessed from an external environmental perspective.

Reference or Environmental Assessment Levels (EAL) are used to determine the need for further control measures at point of release.

For hexavalent chromium, the long term EAL is 0.1µg/m³ annual mean and the short term EAL is 3µg/m³ hourly mean.

For trivalent chromium, the long-and short term EALs are $5\mu\text{g}/\text{m}^3$ annual mean and $150\mu\text{g}/\text{m}^3$ hourly mean respectively.

Releases from a given process are considered insignificant if the Predicted Environmental Concentration (PEC) is less than 1% of the long term and 10% of the short term EAL.

A significant process emission may require further control and reduction.

5.3.2 Water

The substances, which are of particular concern, are:

- Matter in suspension (mg/l)
- Total chromium (mg/l)
- Chromium (VI) (mg/l)
- COD (Chemical Oxygen Demand)

These can be measured or monitored at several points, namely:

- Points of discharge
- Points of seepage

Generally the regulation considers both the instantaneous concentration (mg/l) and the flux (kg/hour).

• European Union

The Water Framework Directive (2000/60/EC) establishes a framework for Community action in the field of water policy. It aims to prevent further deterioration and to protect and enhance the status of aquatic ecosystems by ensuring that all surface and ground waters achieve and maintain good water quality status. The Directive requires the cessation or phasing out of discharges of priority hazardous substances and the progressive reduction of emissions/releases of priority substances. Chromium is not currently listed in either of these categories. Chromium and its compounds are covered by the Directive under Annex VIII " Indicative List of Main Pollutants 7, metals and their compounds."

• France

The limits are as follows:

Chromium (VI)	0.1 mg/l if total mass flow is $>1\text{g}/\text{per day}$
Total Chromium	0.5 mg/l if total mass flow is $5\text{ g}/\text{day}$

• Germany

Effluent water may not exceed:

- Leather Industry	
- Total Chromium	Max 1 mg/l
- Chromium (VI)	Max 0.05 mg/l
- Metal/Chemical Industry	
- Total Chromium	Max 0.5 mg/l
- Chromium (VI)	Max 0.1 mg/l

• Japan

Effluent standard:

- Public water systems	
- Chromium (VI)	0.5 mg/l
- Total chromium	2 mg/l

• Kazakhstan

Liquid Effluent Emissions

- Chromium (VI)	0.005-0.03 mg/l
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• South Africa

Effluent discharge total chromium	0.5 mg/l
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Target water quality range (TWQR)	
Agricultural use (Cr ⁶⁺)	0.1mg/l
TWQR-Aquatic ecosystems-(Cr ⁶⁺)	7µg/l
TWQR-Aquatic ecosystems-(Cr ³⁺)	12µg/l

- **UK**

The UK Environment Quality Standards for dissolved chromium are:

<i>Water Hardness (mg/l CaCO₃)</i>	<i>EAL (mg/l)</i>		<i>Estuary and Coastal Waters</i>
	<i>Salmonid</i>	<i>Cyprinid</i>	
0-50	5	150	15
50-100	10	175	
100-200	20	200	
> 200	50	250	

- **USA**

National ambient water quality criteria:

	<i>Continuous</i>	<i>Maximum</i>
- Chromium (VI)		
Fresh water	0.010 mg/l	0.015 mg/l
Salt water	0.050 mg/l	1.1 mg/l
	<i>4 day average</i>	<i>1 hour average</i>
- Chromium (III)	0.18 mg/l	0.55 mg/l

5.3.3 Drinking Water

• Germany	Chromium(VI)	0.05mg/l
• Japan	Total Chromium	0.05mg/l
• Kazakhstan	Total Chromium	0.05mg/l
• South Africa	TWQR (Cr ⁶⁺)	0-0.05mg/l
• UK	Total Chromium	0.05mg/l
• USA	Total Chromium	0.1 mg/l

5.3.4 Soil

- **Germany**

According to the Bundes-Bodenschutz und Altlasten Verordnung (Federal Directive for Soil Protection and Contaminated Sites) the threshold value for chromium is 30 to 100 ppm (dry soil basis) depending on type of soil.

- **Kazakhstan**

- Total Chromium	400 mg/kg
- Chromium (VI)	0.558 mg/kg

- **UK**

The Contaminated Land Environmental (March 2002) guideline values for chromium are:

- For residential land with plant uptake: 130mg/kg;
- For allotments: 130mg/kg
- For industrial land use: 5000mg/kg (9UKQAA.2003)

Note: these values are for total chromium taking into consideration that all could be present as hexavalent.

5.4 Worker Information

Full information regarding health hazards related to chemical agents including metallurgical products or processes should be passed on to the employees concerned together with the precautions which need to be taken to effectively control the risks associated with their use of these substances. The following are the three main routes of workplace information.

5.4.1 Labelling of Packages and Containers

• European Union

Substances and preparations may be classified as hazardous for supply or transport purposes.

While there are many similarities between the two systems, they are separate from each other and must be dealt with separately.

The first step in all cases is to classify the material. Where it is not hazardous for supply or transport, there are no special requirements for packaging, labelling or documentation. Where it is classified as hazardous, certain national and international regulations will apply. The decision on classification rests with the supplier, and must be based on good scientific data.

- Supply

In the European Union, Directives have created national regulations which include lists which specify the hazard classification for a large number of substances.

Where a substance is classified, the listed Risk (R) and Safety (S) phrases must be used on all labels and safety data sheets WITHOUT ALTERATION.

The label must also meet stringent requirements regarding content, hazard pictograms/symbols, size, position, method of attachment and language(s).

Where a substance is not listed, the manufacturer must use available data within strict rules to self classify the product correctly i.e. to assign the appropriate Risk and Safety phrases if it is hazardous or alternatively to classify it as not hazardous for supply purposes.

- Transport

If the above classification process has concluded that the product is hazardous for transport purposes, then a series of international regulations will apply depending on the method(s) of transport to be used.

These regulations were created initially as a series of model regulations by the UN (known as the Orange Book, or the UN Recommendations on the Transport of Dangerous Goods). They are updated every two years and are then translated into a series of modal regulations for the different modes of transport. These are:

- IMDG Code (International Maritime Dangerous Goods Code). A set of legally enforceable international regulations for the transport of dangerous goods by sea.

- ICAO Technical Instructions. These are legally enforceable regulations covering the transport of dangerous goods by air. These result in the publication of the IATA Dangerous Goods Regulations which in themselves are not legally enforceable as it is an industry publication. However it is based on ICAO and is preferred by most users as it is more user friendly.

- ADR/RID/ADN These are regulations set up by agreement within Europe for the transport of dangerous goods by road, rail and inland waterways respectively. They are derived from the UN recommendations. Similar regulations exist outside Europe, with corresponding national regulations for each mode of transport e.g. CFR in the USA.

In each case they specify packaging, labelling, documentation requirements and signed declarations to ensure:

- Use of the correct type of approved, tested and UN marked packaging;
- Use of the correct type, and proper fitting of, approved diamond descriptor hazard labels to the packages and, if travelling by sea, also the container;
- Allocation and display of the correct Proper Shipping Name and UN number for the labelled material;
- Proper marking of the vehicle transporting the goods;
- Proper training to all relevant members of staff including special provisions for training vehicle drivers;
- Provision of documentation and emergency information for use by the driver and emergency services in the event of an accident in transit.

The regulations for supply and transport are quite specific and very extensive, such that a detailed description cannot be provided here. The reader is referred to the international regulations above, and their own national regulations for the various modes of transport for more detail.

A key point to remember however, is that the regulations for all modes of transport to be used must be fully complied with, so that where a given mode has a special requirement, this must be met along with other requirements for other transport modes in use.

- Hazardous Waste

There are extensive rules governing the consigning and disposal of hazardous wastes in most countries derived from international treaties. The transport rules will also apply where these materials are classified for transport purposes.

- Alloys - a special case

A decision in the European Union has resulted in alloys being recognised as a special case within the Dangerous Preparations Directive.

This means that inappropriate classification by the use of the current rules for preparations on alloys, which are not simple physical mixtures, can be avoided.

The responsibility for this however, rests with the supplier who must provide a body of evidence to prove the case for non-classification of their alloy.

• USA

All hexavalent chromium-containing substances and mixtures and some other chromium-containing substances must be labelled as hazardous.

Massive alloys are also considered as mixtures and as such have to be labelled. Hexavalent compounds should contain a cancer hazard warning. Under the OSHA Hazard Communication Standard (HCS), the manufacturer, importer or distributor shall ensure that each container of hazardous substances and mixtures is labelled, tagged or marked with the following information:

- Identity of the hazardous substance;
- Appropriate hazard warning;
- Name and address of the substance manufacturer, importer or other responsible party

5.4.2 Material Safety Data Sheets (MSDS)

These documents are of prime importance for exporters, importers and users of chromium-containing products. They are compulsory in some, but not all, countries. ICDA has produced a generic MSDS for ferrochromium. This document is available on request.

• EU Requirements

- Directives 91/155/EC, 93/112/EC and 2001/58/EC lay out the MSDS format which must contain information under the following obligatory headings:
- Identification of the substance/preparation and of the company;
- Intended/recommended uses;
- Composition (information on ingredients);

- Hazards identification;
- First-aid measures;
- Fire-fighting measures;
- Accidental release measures;
- Handling and storage;
- Exposure controls/personal protection;
- Physical and chemical properties;
- Stability and reactivity;
- Toxicological information;
- Ecological information;
- Disposal considerations;
- Transport information;
- Regulatory information;
- Other information;

MSDS are adhered to by the EAA (European Economic Area) countries.

• USA Requirements

The MSDS is of prime importance in the OSHA Hazard Communication Standard (HCS). The most important rules can be summarised as follows:

- Chemical manufacturers and importers (and this includes the metallurgical industries) shall obtain or develop a Material Safety Data Sheet for each hazardous chemical they produce or import.
- Users will have an MSDS for each hazardous chemical they use.
- Under the HCS, the definition of the label and MSDS (see below) must be the result of an assessment made by the manufacturer, importer or distributor, based on literature or other toxicological data. This decision is said to be “performance orientated”. A written assessment must be kept available. Each MSDS will contain the following information:

- Identity of the product (either single substance or compound)
- Physical and chemical characteristics of the hazardous chemical
- Physical hazards linked with the hazardous chemical: fire, explosion, reactivity
- Health hazards linked with the hazardous chemical: symptoms linked with exposure to the said substance and to the other substances, which may be emitted during processing
- Primary routes of exposure
- The OSHA Permissible Exposure Limit (PEL) or the ACGIH Threshold Limit Value (TLV)
- Whether the hazardous chemical is listed in the National Toxicology Programme (NTP) Annual Report on Carcinogens or has been found to be a potential carcinogen in the International Agency for Research on Cancer (IARC) monographs or by OSHA
- Any generally applicable precautions for safe handling and use which are known to the chemical manufacturer, importer or employer preparing the MSDS, including appropriate hygienic practices, protective measures during repair and maintenance of contaminated equipment and procedures for clean-up of spills and leaks
- Any applicable control measures, which are known to the manufacturer, importer or user preparing the MSDS such as engineering controls, work practice or personal protective equipment.
- Emergency and first-aid procedures
- Date of preparation of the MSDS or the latest modification
- Name, address and telephone number of the manufacturer, importer, user.

5.4.3 Induction and Training of Employees

Training of workers exposed to hazardous chemicals is obligatory in the USA (Hazard Communication Standard), in the EU (Directive 90/394/EEC) and most other countries.

Note: The geographical regions or countries referenced above represent those areas with the strictest

regulations in place. They can be used as guidelines with possible adaptation to the local regulatory trends or provisions.

In addition, reference to the International Labour Organisation (ILO) Convention No 170 and Recommendation No 177, published in June 1990 and entitled "Safety in the use of chemicals at work" is also recommended.

5.5 Environmental Control and Monitoring

Effective control and monitoring of all emissions to air, water and land is essential.

Wastes deserve special mention because of the potential for these to be moved from one region to another and the controls associated with this. The materials may include:

- Recyclable metallic scrap
- Slags or residues resulting from the manufacture of ferrochromium and stainless steel or chemicals
- Filter dust resulting from the production of ferrochromium and stainless steel (including used filter bags)
- Sludges from dust abatements
- Metal finishing effluents, slurries or wet cakes
- Used CCA treated wood
- Used packaging (bags, drums, etc.) that contained chromium chemicals
- Chromium-containing refractories
- Tanning process solid and liquid wastes
- End of life articles

On an international basis, the UNEP "Basel Convention" of 22 March 1989 on transboundary movements of hazardous wastes and their disposal was implemented in May 1992.

The OECD Decision of 30 March 1992 on the control of transfrontier movements of wastes destined for recovery operations classifies recyclable waste in three lists (green, amber and red) according to the degree of risk – the red list imposes the strictest procedures.

The lists are permanently under revision. (Refer to OECD Monograph No 34 "Monitoring and Control of Transfrontier Movements of Hazardous Wastes – Updated July 1993").

For the European Union, refer to the Council Regulation No 259/93 of 1 February 1993 on the "Supervision and Control of Shipments of Waste Within, Into and Out of the European Community". This text is also based on three categories and became applicable as of May 1994.

Under these regulations, it is obligatory for the contracting parties to declare such operations to all concerned authorities, expedition and destination and countries of transit.

5.5.1 European Union

The Integrated Pollution Prevention and Control (IPPC) Regulations (96/61/EC) set out requirements for industries to apply Best Available Techniques (BAT) to control emissions to all environmental media (air, water and land).

These Regulations are supported by Best Reference Technology (BREF) notes for various industrial sectors and by other Regulations or Directives which apply to air, water and waste classification, landfill and incineration.

- Water

See above under Water Framework Directive.

The Drinking Water Directive 98/83/EC lists limits for several metals.

- Waste

The Directives 78/319/EEC (The Hazardous Waste Directive) amended by Council Decision 2001/118/CE, 91/689 EEC and 94/31/EC along with Commission Decision 94/904/EC provide detailed lists of wastes and a systematic basis for classification of wastes consistent with the principles used for classifying products and preparations.

The Landfill Directive (1999/31/EC) sets out criteria for preparation, operation, monitoring and closure of landfill sites according to the type or class of waste deposited.

5.5.2 Japan

- Soil

Once soil is contaminated, the impacts last for a long time. Therefore Environmental Quality Standards are presently defined based on the Basic Environmental Law for 27 items including hexavalent chromium.

These EQS values are standards against which compliance is desirable for protecting human health and conserving the living environment and are reviewed according to accumulated scientific data on an as necessary basis.

The soil EQS stipulates standards considering water quality including purification of groundwater, and the farmland standard aims to conserve the production of food.

These two standards are used to judge whether soil is contaminated or not and give targets for designing measures to protect against pollution.

- Waste

The purpose of the Wastes Disposal and Public Cleansing Law is to preserve the living environment and improve public health through restriction of waste discharge, the control of appropriate sorting, storage, collection, transportation, recycling and disposal of wastes and the conservation of a clean living environment.

- Water

Under the Basic Environment Law, Environmental Quality Standards (EQS) for water pollutants are target levels for water quality to be achieved and maintained in public water.

These standards are established to achieve two important goals: to protect human health and conservation of the living environment.

Hexavalent chromium is included in a list of EQS values for 26 substances for the protection of human health.

An EQS for groundwater pollution was also established in 1997.

For the living environment, EQS values have been established for Biochemical Oxygen Demand (BOD), Chemical Oxygen Demand (COD), Dissolved Oxygen (DO), and other parameters. EQS values for nitrogen and phosphorus were established to prevent eutrophication of lakes and coastal waters.

- Air

The purposes of the Air Pollution Control Law are, firstly, to protect public health and preserve the living environment with respect to air pollution by controlling emissions of soot, smoke, and particulate matter from factories and other business establishments.

Secondly, to control emissions of particulates when buildings are being demolished.

Thirdly, to promote various measures limiting the emission of hazardous air pollutants and by setting maximum permissible limits for automobile exhaust gases etc.

5.5.3 South Africa

- Air

Air quality is legislated through the National Environmental Management: Air Quality Act of 2004 and has as its objective to protect the environment and to enhance ambient air quality to ensure the environment is not harmful to the health and well-being of people.

- Waste

Waste management must follow a hierarchical sequence of prevention, minimisation, resource recovery, treatment and finally disposal. Wastes are classified as either General or Hazardous. Classification implies determination of the properties and risks of waste. Properties include toxicity, ecotoxicity, carcinogenicity, mutagenicity, teratogenicity and persistence.

- Water

The Department of Water Affairs and Forestry is the custodian of South Africa's water resources. Its mission is i.e. to ensure that water quality remains fit for use and that the viability of the aquatic ecosystems is maintained and protected. The Department developed the South African Water Quality Guidelines for this purpose. The National Water Act (36 of 1998) is the primary piece of legislation.

5.5.4 USA

Maximum Achievable Control Technology (MACT) and Generally Available Technology (GACT)-based rules are being developed for major and area chromium emission sources on an industry by industry basis.

In most cases, different standards will be determined for trivalent and hexavalent chromium.

These regulations are based on the "Clean Air Act of 1990", which identifies "Chromium Compounds" in its listing of hazardous air pollutants. Sources not covered under EPA MACT or GACT standards are regulated at levels set by state agencies.

5.6 Chemicals Management

In an effort to improve the control and management of the widespread use of industrial chemicals, the OECD embarked upon a structured risk assessment review process for all chemicals.

For the EU this was set out in the Existing Substances Regulation 793/93/EC (ESR), under which producers or importers were required to submit Standardised Information Data Sets (SIDS) on a scheduled basis.

As a result of that process a group of five hexavalent chromium products has undergone a risk assessment review leading to some classification changes (captured in the 29th ATP of the Dangerous Substances Directive) and the conclusion that further risk reduction measures were required. The UK is currently developing a suitable risk reduction strategy on behalf of the EU.

Because of slow progress on ESR, the International Council of Chemicals Associations (ICCA) launched a voluntary initiative under which industry was encouraged to submit hazard data dossiers for its products.

In February 2001, the EU published a White Paper Strategy for a Future Chemicals Policy containing the following key elements:

- Making industry responsible for safety
- Extending the responsibility along the supply chain
- Authorisation of substances of very high concern
- Substitution of hazardous chemicals

The White Paper has been developed into the Draft EU Regulation known as REACH (Registration,

Evaluation, Authorisation (and Restriction) of Chemicals which is currently being considered by the EU Parliament. It is anticipated that this will come into force by mid-2007.

Alongside these, a series of End of Life Directives is emerging in the EU covering vehicles (ELVD) Electrical and Electronic Equipment (WEEED) and Building Materials and another on Restriction of Hazardous Substances.

Both ELVD and WEEED mention hexavalent chromium and restrict its presence in such new articles from 2007 and 2006 respectively.

Under the Precautionary Principle on the one hand and Sustainable Development on the other, collectively these activities mean the following for industries:

- Comprehensive characterisation of products and their uses to enable human and environmental risk assessments to be made
- Replacement of hazardous by less hazardous substances
- Best practice benchmarking to International Standards
- Waste minimisation, recycling of waste and end of life articles

In other words, Product Stewardship and Life Cycle Inventory/ Assessment.

6 Product Stewardship

Under this regime, companies take visible responsibility for ensuring that best practice considerations apply to their products throughout the product life cycle.

This includes addressing all of the features listed in sections 3 and 5 above.

- Provide comprehensive information regarding products via communications such as MSDS. This is particularly important for hazardous products and where identified uses of an otherwise non-hazardous product can result in the generation of hazardous products e.g. stainless steel and the formation of hexavalent chromium in stainless steel welding fumes.

- Discourage inappropriate use(s) of products.

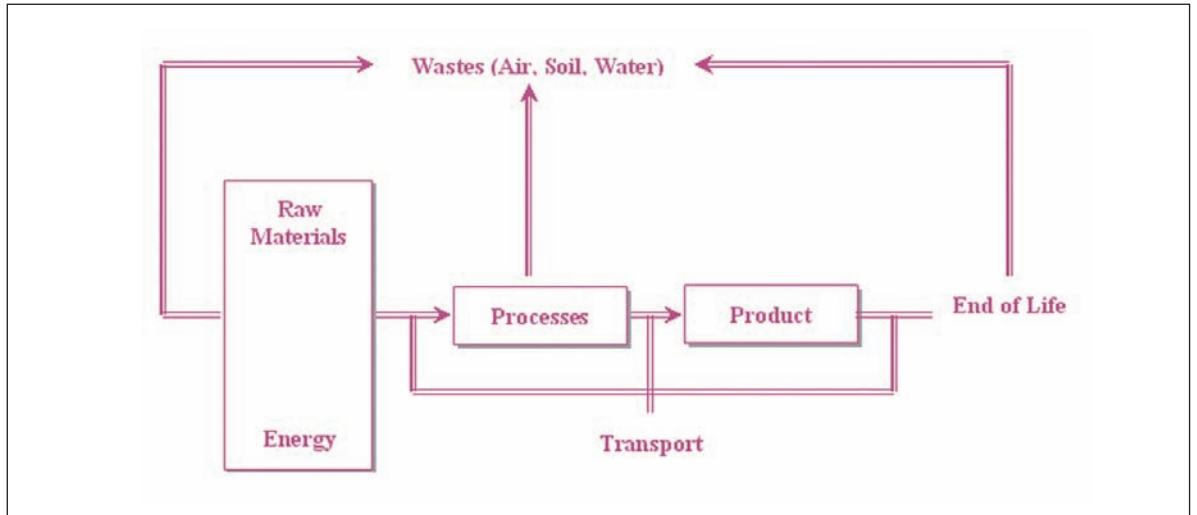
- Work in an open and transparent way with customers and regulators as appropriate to resolve issues of concern relating to products and their uses.

This may include advice on engineering standards, best practice standards for occupational exposure reduction and environmental controls, workforce education and training, waste minimisation/ recycling and end-of-life solutions in line with Sustainable Development.

7 Tools

7.1 Life cycle Inventory/Assessment (LCI/LCA)

LCI is essentially a technique for accounting for and evaluating all of the inputs and outputs throughout the life cycle of a product under ISO Standard 14040.



LCA assembles the above data for different players in the same industry enabling best practice benchmark values to be identified and it can also be used to compare alternative products which might be available for the same end use and gives:

- To the producers, a set of benchmark data to support or defend current and future business decisions particularly where there are alternatives
- To regulatory or other bodies, a set of current best practice data which can be used to formulate or influence regulations.

ICDA has completed an LCI for ferrochromium. This document in turn provides important inputs into the stainless steel LCI. As part of the ongoing process of updating information, ICDA will also update the LCI periodically to reflect the improvements in technology as well as to make the data more representative of the global ferrochrome production. Copies of the LCI study are available from ICDA on request.

7.2 International standards organisation (ISO)

Since 1993, several ISO standards have been developed and those relevant to the context of the Guidelines are:

Environmental Management Systems	ISO 14001, 14002, 14004
Environmental Auditing	ISO 14010 - 14012, 14015
Environmental Labelling	ISO 14020 - 14025
Environmental Performance Evaluation	ISO 14031
Life Cycle Assessment	ISO 14040 - 14043
Occupational Health and Safety Management Systems	ISO 18001, 18002

Members are strongly encouraged to set up and practice Health, Safety and Environmental Management Systems that include all of the features set out in Section 3 above and to seek corresponding ISO accreditation.

7.3 Ecolabelling

Ecolabelling is a tool to enable producers to indicate the environmental aspects of a product or service. It may take the form of statements, symbols or graphics on product or package labels, product literature, technical bulletins, etc.

An environmental aspect is an element of an organisation's activities, products or services, which can interact with the environment.

Ecolabelling forms part of the ISO 14000 Series of Environmental Management Standards:

- ISO 14020 Basic principles
- ISO 14021 Self-declaration environmental claims - terms and definitions
- ISO 14022 Self-declaration environmental claims environmental labelling symbols
- ISO 14023 Self-declaration environmental claims - testing and verification methodologies
- ISO 14024 Environmental labelling type 1 - guiding principles and procedures
- ISO 14025 Environmental labelling type 111 - guiding principles and procedures

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