Chromates at the workplace through the use of thermal insulation containing (earth) alkaline metal oxide

SUBSTITUTING TO PROTECT LIFE

SAFETY FOR PEOPLE AND THE ENVIRONMENT

6. Dezember 2024

Revision: 1.0

Foreword

This paper is dedicated to a highly topical and explosive topic: the **formation** and **effects** of **chromium (VI) compounds in the workplace** through the **use of thermal insulation containing (earth) alkaline metal oxide**.

It is aimed at all those responsible in industry, occupational health and safety, and research and development.

The aim is to clear up existing misunderstandings and show the way to long-term solutions.

A common misconception concerns the occupational exposure limit, which is often mistakenly perceived as a kind of safe threshold.

In fact, for chromium (VI) compounds, as for all carcinogenic substances, there is no toxicological threshold below which a hazard can be ruled out.

It is therefore essential to minimise any possible exposure as far as technically and organisationally feasible.

Another misunderstanding concerns the protective measures.

Personal protective equipment, such as protective suits or respiratory protection, must never be seen as the sole or long-term solution. It can only be a temporary solution, while more sustainable approaches are developed and implemented.

At the heart of all efforts is **the substitution of hazardous substances**, which is not only **a regulatory obligation**, but also **the ultimate goal** to **permanently prevent exposure to chromates**.

Although this path is complex and challenging, **it remains the only truly sustainable approach**.

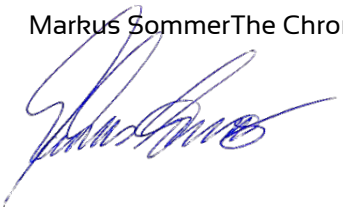
However, substitution is a process that cannot be implemented overnight. Short-term measures, such as neutralization or technical protection solutions, must therefore be pursued in parallel, without losing sight of the end goal.

This publication aims to raise awareness of the existing challenges, but also to show solutions on how **both** the health of employees **and** the environment can be sustainably protected **through** the consistent implementation of the STOP principle (Substitution, Technical, Organizational and Personal Protective Measures).

With this foreword, we invite you to take a critical look at the findings and recommendations for action presented and to work together to create a safe, sustainable and responsible working environment.

Olesnica, December 2024

Markus SommerThe Chromate Experts



Introduction

The history of industrial insulation is marked by innovations, but also by mistakes, the consequences of which often only became clear years later.

After asbestos insulation was recognized as carcinogenic and finally banned, substitute products such as mineral fibers, glass fabrics and calcium silicate products were long considered harmless.

However, current findings and warnings show that this assumption is wrong.

High-temperature insulation materials containing (earth) alkaline metal oxides such as calcium oxide or sodium oxide can form carcinogenic and chronically environmentally harmful chromium (VI) compounds (chromates) in thermochemical reactions with chromium (III) compounds contained in stainless steel alloys or incorporated stainless steel reinforcements, **including calcium and/or sodium chromate**, in particular **calcium** and/or **sodium chromate**.

Particularly affected are high-temperature insulation of so-called **combined heat and power plant engines** or other **energy-generating units**, as well as their inlets and outlets, but also **components of the exhaust gas aftertreatment** of **combustion engines**.

The automotive industry **is inevitably also affected by this** , because almost all thermally insulated vehicle-owned hot parts have chromium components and are oxygen-open with insulation containing (earth) alkaline metal oxide, and the permanent temperature is in the temperature ranges in which the high oxidation of trivalent chromium compounds in particular can take place (300-800°C).

Gas **or** steam turbines **in power plants** or **waste incineration plants** are **also** equipped with the named insulation materials.

The problem of chromate formation therefore exists **worldwide** and includes **transport vehicles** as well as **shipping or rail traffic**, provided that the propulsion **is carried out with** combustion engines.

This paper deals with the basics of the thermochemical **formation of chromium (VI) compounds**, **substantiates them** with technical or **scientific studies** of recent years, describes health damage caused by dermal and inhalation contact with chromium (VI) and then goes on to the **occupational and environmental assessments** on the basis of **Directive 2004/37/EC** which is implemented in Germany on the basis of the German **Hazardous Substances Ordinance** (GefStoffv) and the associated "**Technical Guidelines for Hazardous Substances**" (TRGS) (for the UK: **COSHH** "Control of Substances Hazardous to Health").

All sources used are state-of-the-art and can be accessed directly from the following authorities and institutions:

EU:

UK:

1. Warnings from manufacturers and authorities (excerpt)

The urgency of this issue is underscored by a series of alerts from leading companies and institutions:

- **Innio Jenbacher Ges. mbH & Co. Jenbach, Austria**
  Technical Instruction TA 2300-0025 dated 31.10.2023

  "... Chromium-6 (chromium in oxidation state 6, Cr-6 for short) is formed from chromium-containing steels in the presence of calcium (e.g. from the insulation material) and oxygen at temperatures above 400 °C.

  Cr-6 can ... can be found as a yellowish powder on the engine parts in question or in the insulation material. Cr-6 is in the form of a non-volatile powder.

  In order to keep the pollution of the breathing air as low as possible, the working methods described in this instruction must be strictly adhered to (e.g. the stirring up of dust when working with used insulation material must be prevented at all costs)."

- **MAN Trucks & Bus SE, Augsburg, Germany**
  Technical Information Service Notice 8339SM dated 13.12.2023

  "... Under certain conditions, calcium chromate CaCrO4 can be formed from existing components during operation. These are:

  - Chromium-containing steels (e.g. on exhaust systems) in contact with
  - Calcium-containing compounds (e.g. in insulating mats or assembly pastes)
  - at temperatures > 300°C and in the presence of oxygen

  Due to these conditions, the occurrence of chromium (VI) compounds is to be expected preferably on – but not limited to – components in the area of the exhaust tract or exhaust gas aftertreatment.

  Appropriate protective measures must be taken, especially when working on these components as part of repair or maintenance."

- **BG ETEM**
  Summary of Product Specifications dated 10.03.2023Possible Chromium (VI) Exposure through Contact of Chromium-Alloyed Steels with Materials Containing Alkali and Alkaline Earth Metals in Power Plants Chromium(VI)

  Problem:

  The contact of chromium-alloyed steels with alkaline and alkaline earth metals (calcium, magnesium, sodium and potassium) mineral wool insulation materials or assembly pastes leads to the formation of carcinogenic chromates (chromium(VI) compounds) at temperatures between approx. 350 – 800 °C.

  Hazard:

  These carcinogenic chromium(VI) compounds (category 1B) can irritate the respiratory tract and sensitize the skin. In acute skin injuries, some chromium(VI) compounds can lead to severe skin ulcers after contact. A possible risk to employees can therefore exist both inhalation, via the air at the workplace and dermal, through direct contact with the skin.

  For example, power plants (coal-fired power plants, woodchip power plants, gas and biomass power plants, combined heat and power plants and heating plants), waste incineration plants and chemical industrial plants, but also industrial furnaces and parts of stationary emergency power generators can be affected. Emphasizes the need to avoid calcium-containing materials to prevent the formation of carcinogenic chromates.

  Further warnings from engine manufacturers, such as Zeppelin Power Systems (CAT) or regional associations, can be found in the bibliography

2. Chemical basis of chromate formation

2.1 Experimental confirmations and chemical background

The formation of chromium (VI) compounds such as calcium chromate ($CaCrO_4$) and sodium chromate (Na_2CrO_4) occurs under specific thermodynamic conditions.

The formation of chromates occurs through the oxidation of chromium (III) compounds in the presence of calcium oxide or sodium oxide and oxygen:

- **Oxidation of chromium**:

Chromium in the alloy of stainless steels is oxidized at high temperatures by oxygen to chromium (III) oxide (Cr_2O_3):

$$4Cr + 3O2 \rightarrow 2\,Cr_{2O3}$$

- **Formation of calcium chromate**:

The chromium (III) compounds react thermochemically at high temperatures to form calcium chromate:

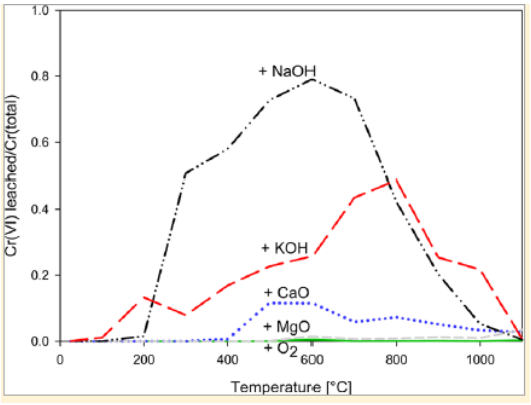
$$2Cr3+ + 3CaO + O\tfrac{3}{2}_2 \rightarrow 2\,CaCrO_4$$

- **Formation of sodium chromate:**

The chromium (III) compounds react thermochemically at higher temperatures to form sodium chromate:

$$2Cr3+ + 3Na2O+ + O\tfrac{3}{2}_2 \rightarrow 2Na2CrO4$$

Oxidizing environments promote these reactions, especially in the temperature range of 300–800 °C.



2. Chemical basis of chromate formation

2.2 Scientific findings and industrial research

- **The study**

  "The formation mechanism and thermal stability of $CaCrO_4$"

  proves that calcium chromate can be used at temperatures from approx. **300 °C** and remains thermally stable above **800 °C**; this stability makes it particularly problematic as the connection remains persistent in the working environment.

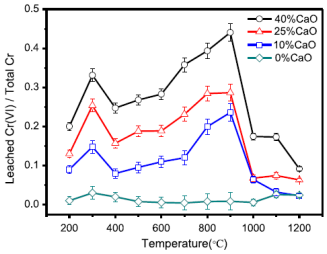
  Source: Yingjiang Wu et al. 2020, IOP Conf. Ser.: Earth Eviron. Sci. 514052024

- **The study**

  "The role of temperature on Cr (VI) formation during heating of Cr in the presence of CaO"

  shows that the formation of chromium (VI) compounds is directly proportional to temperature and oxygen content; high temperatures and an oxidizing atmosphere are the main drivers of the reaction.

  Source: Mao et al. 2015, 0045-6535, Chemosphere 138 (2015) 197-204



2.3 industrial research

- **The study**

  "The formation of Cr (VI) compounds at the interface between metal and heat-insulating material"

  investigates the formation of chromium (VI) compounds at the contact surface between chromium-containing metals and thermally insulating materials at elevated temperatures.

  The results show that **yellowish reaction products**, identified as **chromium (VI) compounds**, form on the contact surfaces of the insulation materials.

  The amount of chromium (VI) compounds formed increases with

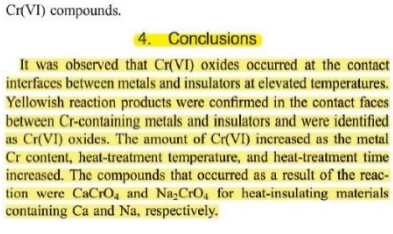
  increasing temperature,

  longer treatment time and

  higher chromium content of the metal!

  Specifically, **calcium chromate ($CaCrO_4$)** and/or **sodium chromate (Na_2CrO_4)** were detected between metal parts heated over a longer period of time that were directly connected to insulation materials containing **calcium (oxide)** and/or **sodium (oxide).**

  Source: Journal of the Ceramic Society of Japan 123 [8] 677-684 2015


Cr(VI) compounds.

4. Conclusions

It was observed that Cr(VI) oxides occurred at the contact interfaces between metals and insulators at elevated temperatures. Yellowish reaction products were confirmed in the contact faces between Cr-containing metals and insulators and were identified as Cr(VI) oxides. The amount of Cr(VI) increased as the metal Cr content, heat-treatment temperature, and heat-treatment time increased. The compounds that occurred as a result of the reaction were $CaCrO_4$ and Na_2CrO_4 for heat-insulating materials containing Ca and Na, respectively.

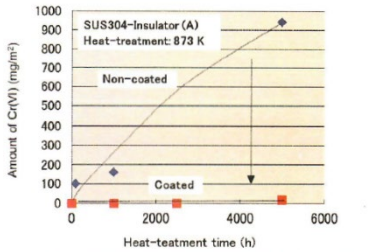


Fig. 10. Relationship between heat-treatment time and amount of Cr(VI) that occurred at 873 K for the combination of coated SUS304 and insulator (A) and the combination of non-coated SUS304 and insulator (A).

3. Chromium (VI) compounds – classifications, health and environmental hazards

Chromium (VI) compounds are CMR substances and are therefore classified as hazardous substances for humans and the environment according to the CLP Regulation and the GESTIS databases:

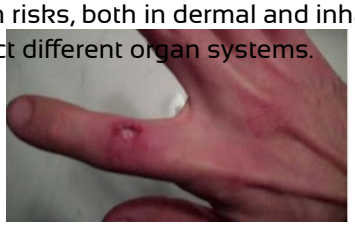
- H350 (carcinogenic): Even small levels of exposure can cause cancer.
- H410 (hazardous to the environment): Persistent, hardly degradable and toxic to aquatic systems.
- H (skin resorptive): Absorbable through the skin and sensitizing.

Sources:

- CLP Regulation (EC) No 1272/2008, Annex VI.
- List of MaK and BAT values of the DFG (2024).

3.1 Health effects of chromium (VI) compounds

Contact with chromium (VI) compounds poses significant health risks, both in dermal and inhalation exposure. These hazards are both acute and long-term and affect different organ systems.



❖ **Acute effects:**

1. **Dermal exposure:**
   - **Skin irritation and dermatitis:**

     Chromium (VI) compounds often cause severe skin irritation, which manifests itself in inflammation and redness.
   - **Skin sensitization:**

     Repeated contact can cause allergic contact dermatitis. Individuals can become sensitized, which means that even the slightest exposure can cause allergic reactions.
     - **Classification:**
       H317 (May cause allergic skin reactions).
2. **Inhaled exposure:**
   - **Irritation of the respiratory tract:**

     Inhalation of dust or gases containing chromium (VI) causes acute irritation of the respiratory tract, including coughing, shortness of breath and pharyngitis.
     - **Classification:**
       H334 (May cause allergy, asthma-like symptoms or breathing difficulties if inhaled).

3. Chromium (VI) compounds – classifications, health and environmental hazards

3.1 Health effects of chromium (VI) compounds

❖ **Long-term effects:**

1. **Dermal exposure:**
   - **Chronic skin conditions:**

     Long-term exposure leads to irreversible skin damage, including "chromium ulcers", deep, poorly healing skin lesions.

2. **Inhaled exposure:**
   - **Lung cancer:**

     Regular inhaled exposure to chromium (VI) compounds significantly increases the risk of lung cancer.

     - **Classification:**
       H350 (May cause cancer).
   - **Chronic respiratory diseases:**

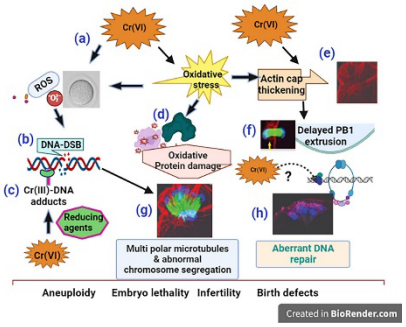
     Asthma, chronic bronchitis and, in severe cases, destruction of the nasal septum (nasal perforation) are typical consequences.

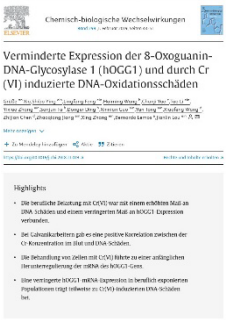
3. **Systemic effects:**
   - **Liver and kidney damage:**

     The reduction of chromium (VI) to chromium (III) in the body releases reactive oxygen species (ROS), which cause oxidative damage to organs.
   - **DNA damage:**

     Chromium (VI) interacts directly with DNA, causing mutations and increasing the risk of cancer.
   - **Immune system:**

     Chronic exposure weakens the immune system and increases susceptibility to infections.




Chemisch-biologische Wechselwirkungen

Verminderte Expression der 8-Oxoguanin-DNA-Glycosylase 1 (hOGG1) und durch Cr (VI) induzierte DNA-Oxidationsschäden

Highlights

4. Chromium (VI) compounds in the workplace

4.1 Tolerance concentration/acceptance concentration:

- **Exposure-risk relationship (ERB):**

  In contrast to other harmful substances in the workplace, there is no occupational exposure limit value for chromium (VI) compounds due to the health risks described, below which it justifies action-free action.

  The **Risk-Related Concept of Measures for Activities with Carcinogenic Substances (TRGS 910)** defines the risk of cancer as follows:

- **Tolerance risk:**

  A cancer risk of **4:1,000** (i.e. one additional cancer per 250 exposed persons) is considered a tolerance concentration, but compliance with it already requires special measures to minimise risk.

- **Acceptance risk:**

  A cancer risk of **4:10,000 | 4:100,000** (i.e. four additional cancer cases per 10,000 | 100,000 exposed persons) is considered an acceptance concentration at which the risk is considered sufficiently controlled.

  Below the acceptance risk, no additional measures are necessary, provided that the state of the art is complied with.

Risk-related concept of measures:

TRGS 910 obliges employers to take measures to further minimise exposure in **the event of exposures above the acceptance risk** but **below the tolerance risk**.

Exposure-risk relationship (ERB):

For chromium (VI) compounds, TRGS 910 specifies this ERB value.

This exposure value is estimated to be **0.001 mg/m³ or 0.001 mg/m³** . **1ug/m³** (4:1,000).

Based on this classification, the

the **tolerance concentration** of **chromium (VI) compounds** at the **workplace**

0.001 mg/m³ or **1ug/m³**

and the **acceptance concentration** of **chromium (VI) compounds** in the **workplace**

0.0001 mg/m³ or **0.1 ug/m³**

4. Chromium (VI) compounds in the workplace

4.2 Connection between TRGS 910 and chromium (VI) compounds:

- **Chromium (VI) compounds** fall under the regulations of TRGS 910 because they **are classified** as carcinogenic (H350).
- **For activities with chromium (VI) compounds, compliance with the acceptance and tolerance concentrations is mandatory**.
- **Measures to reduce exposure must** already **be taken** if the **risk is above the acceptance concentration**.

TRGS 910 in the latest version of 10.10.2024 describes the "relationship between risk areas and measures" as follows:

The low-risk area covers the area up to the Akzeptanzrisiko.In this area there is little need to implement additional measures.

The medium risk range includes the range **from acceptance to tolerance risk. In this area, the need for additional measures increases significantly** the closer the concentration is to the tolerance concentration.

The high-risk range begins above the tolerance risk. In this area, there is an immediate need for additional measures to reach at least the medium risk range.

In the risk assessment of chromates in the workplace, the range of the medium risk is therefore in the concentration range of **0.0001 mg/m³** or **0.1 ug/m³** **to** **0.001 mg/m³** or **1ug/m³**

However, the operator (employer) may not make the (non-)implementation of protective measures dependent on exposure measurements that have not yet been carried out.

Visible CMR substances and their detection by rapid tests are sufficient to assume a potential danger.

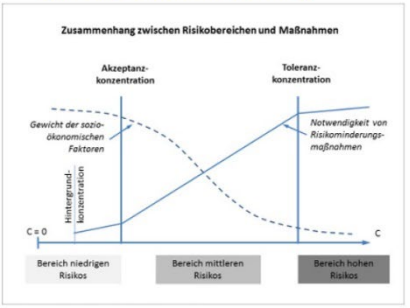
The assessment must be carried out according to the **precautionary principle** , with **conservative assumptions** and **immediate implementation of the S-T-O-P principle**:

- **Substitution**
- **Technical measures**
- **Organizational measures**
- **Personal protective equipment**

5. Chromium (VI) compounds in the workplace

4.2 Connection between TRGS 910 and chromium (VI) compounds:

Abbildung: Zusammenhang zwischen Risikobereichen und Maßnahmen



C: Konzentration in der Luft am Arbeitsplatz

Der Bereich niedrigen Risikos umfasst den Bereich bis zum Akzeptanzrisiko.In diesem Bereich ist die Notwendigkeit der Durchführung zusätzlicher Maßnahmen gering.

Der Bereich des mittleren Risikos umfasst den Bereich vom Akzeptanz- bis zum Toleranzrisiko. In diesem Bereich steigt die Notwendigkeit zusätzlicher Maßnahmen deutlich an, je näher die Konzentration bei der Toleranzkonzentration ist.

Der Bereich des hohen Risikos beginnt oberhalb des Toleranzrisikos. In diesem Bereich besteht eine unmittelbare Notwendigkeit zusätzlicher Maßnahmen, um zumindest den Bereich mittleren Risikos zu erreichen.

Tabelle 1: Besondere Maßnahmen bei Exposition gegenüber krebserzeugenden Gefahrstoffen in Abhängigkeit der jeweiligen Risikobereiche

1. Substitution			
	I. Niedriges Risiko	**II. Mittleres Risiko**	**III. Hohes Risiko**
Substitutionsprüfung	**Ja**	**Ja**	**Ja**
Erläuterung	Der Arbeitgeber muss regelmäßig die Möglichkeit einer Substitution durch Gefahrstoffe mit geringerer Gesundheitsgefährdung prüfen, siehe TRGS 600		
Umsetzung der Substitution (Stoff und Verfahren), expositionsmindernde Verwendungsform, siehe auch TRGS 600, Anlage 3	**Ja,** wenn im Rahmen der Verhältnismäßigkeit möglich.	**Ja,** im Rahmen der Verhältnismäßigkeit verpflichtend (wenn technisch möglich), unter Berücksichtigung von wissenschaftlichen Erkenntnissen und Zumutbarkeit).	**Ja,** prioritäre, verpflichtende Maßnahme gemäß Ergebnis der Substitutionsprüfung
Erläuterung	Das Ergebnis der Substitutionsprüfung ist in der Gefährdungsbeurteilung zu dokumentieren.		

2. Technische Maßnahmen			
	I. Niedriges Risiko	**II. Mittleres Risiko**	**III. Hohes Risiko**
Technische Maßnahmen	-	**Ja**	**Ja**
Erläuterung	Durch regelmäßige Kontrolle ist sicherzustellen, dass keine Verschlechterung der Expositionssituation eintritt, zusätzliche Maßnahmen sind nicht erforderlich.	Der Arbeitgeber hat technische Maßnahmen nach dem Stand der Technik unter Beachtung der Verhältnismäßigkeit zu ergreifen.	Der Arbeitgeber hat technische Maßnahmen nach dem Stand der Technik verpflichtend zu ergreifen.
Räumliche Abgrenzung nach § 10 Absatz 3 GefStoffV	**Ja,** im Rahmen der Verhältnismäßigkeit	**Ja**	**Ja,** bevorzugt durch bauliche Maßnahmen
Erläuterung	Die räumliche Abgrenzung eines Arbeitsbereichs durch bauliche Maßnahmen hat das Ziel, eine Belastung von Beschäftigten in anderen Arbeitsbereichen durch freigesetzte krebserzeugende Stoffe zu verhindern.		
Reduzierung expositionsrelevanter Mengen	**Ja,** im Rahmen der Verhältnismäßigkeit	**Ja**	**Ja**
Erläuterung	Die Reduzierung der verwendeten, expositionsrelevanten Stoffmengen ist ein Mittel zur Minimierung der resultierenden Exposition. Unabhängig von der tatsächlichen Expositionshöhe und dem damit korrespondierenden Risikobereich hat der Arbeitgeber eine Minimierung der verwendeten, expositionsrelevanten Stoffmenge stets zu veranlassen		
Warn- und Sicherheitszeichen nach § 10 GefStoffV	**Ja,** im Rahmen der Verhältnismäßigkeit	**Ja**	**Ja**

3. Organisatorische Maßnahmen			
	I. Niedriges Risiko	**II. Mittleres Risiko**	**III. Hohes Risiko**
(Grund)Hygienemaßnahmen	**Ja**	**Ja**	**Ja**
Erläuterung	Unabhängig von der tatsächlichen Expositionshöhe und dem damit korrespondierenden Risikobereich hat der Arbeitgeber stets die Maßnahmen nach § 8 GefStoffV zu veranlassen.		
Minimierung der Expositionsdauer	**Ja**	**Ja**	**Ja**
Erläuterung	Der Arbeitgeber hat stoff- und tätigkeitsspezifisch eine Optimierung hinsichtlich minimaler Expositionsdauer vorzunehmen Die Minimierung der Expositionsdauer ist wünschenswert. Hierzu können betriebliche Vereinbarungen getroffen werden.	Die Minimierung der Expositionsdauer ist verpflichtend. Hierzu können betriebliche Vereinbarungen getroffen werden.	
Minimierung der Anzahl exponierter Beschäftigten	**Ja**	**Ja**	**Ja**
Erläuterung	Die Minimierung der Exponiertenzahl ist wünschenswert.	Die Minimierung der Exponiertenzahl ist verpflichtend. Dabei hat der Arbeitgeber stoff- und tätigkeitsspezifisch eine Optimierung hinsichtlich minimaler Exponiertenzahl und minimaler Expositionsdauer vorzunehmen.	
Risikotransparenz und Risikokommunikation	**Ja**	**Ja**	**Ja**
Erläuterung	Der Arbeitgeber hat die Expositionshöhe und den zugeordneten Risikobereich zu ermitteln und die Beschäftigten hierüber im Rahmen der Unterweisung zusätzlich zu unterrichten.		
Betriebsanweisung, Unterweisung, Schulung	**Ja**	**Ja**	**Ja**
Erläuterung	Der Arbeitgeber hat sicherzustellen, dass den Beschäftigten eine schriftliche Betriebsanweisung zugänglich gemacht wird, dass sie in den Methoden und Verfahren unterrichtet werden (Schulung), die im Hinblick auf die Sicherheit bei der Verwendung der betreffenden Gefahrstoffe angewendet werden müssen und dass sie anhand der Betriebsanweisung über auftretende Gefährdungen und entsprechende Schutzmaßnahmen mündlich unterwiesen werden. Im Rahmen der Unterweisung muss eine allgemeine arbeitsmedizinisch-toxikologische Beratung erfolgen.		

4. Atemschutz			
	I. Niedriges Risiko	**II. Mittleres Risiko**	**III. Hohes Risiko**
Atemschutz	_	**Ja**	**Ja**
Erläuterung		Der Arbeitgeber hat den Beschäftigten Atemschutz zur Verfügung zu stellen. Bei Tätigkeiten mit Expositionsspitzen wird während der Dauer der erhöhten Exposition dringend empfohlen Atemschutz zu tragen.	Der Arbeitgeber hat den Beschäftigten Atemschutz zur Verfügung zu stellen, der von den Beschäftigten getragen werden muss. Beim Tragen von belastendem Atemschutz: siehe Anforderungen Nr. 5

5. Administrative Maßnahmen des Betreibers			
	I. Niedriges Risiko	**II. Mittleres Risiko**	**III. Hohes Risiko**
Maßnahmenplan nach § 6 Absatz 8 Satz 1 Nr. 4b GefStoffV	-	**Ja**	**Ja**
Erläuterung		Der Arbeitgeber stellt im Rahmen der Gefährdungsbeurteilung einen Maßnahmenplan auf, in dem er konkret beschreibt, aufgrund welcher Maßnahmen, in welchen Zeiträumen und in welchem Ausmaß eine weitere Expositionsminderung erreicht werden soll. Die Dokumentation der Gefährdungsbeurteilung ist nach § 18 Absatz 2 GefStoffV der zuständigen Behörde auf Verlangen zu übermitteln.	

4.3 Legal basis and obligations for hazard assessment (risk assessment)

4.3.1 Hazardous Substances Ordinance (GefStoffV):

- **§ 6 – Risk assessment:**
  - The risk assessment must take into account all available information, including visible contamination and rapid test results.
  - Measures to protect employees and the environment must be implemented immediately on the basis of the known risks.
- **§ 7 – Minimization requirement:**
  - Visible CMR materials require immediate action, regardless of whether measurements are available. Exposure must be reduced to the lowest technical and organisational level.
- **§ 10 – Substitution obligation:**
  - CMR substances must be replaced by less hazardous alternatives, where technically feasible.

4.3.2 TRGS 400 – Risk assessment:

- Employers must work based on the best available data, including visual cues and rapid tests.
- The unavailability of measured values is no reason to delay measures.

4.3.3 TRGS 910 – Risk-related concept of measures:

- For carcinogenic substances, a potential hazard is automatically assumed if the substance is present.
- In the absence of exposure data, the operator must make conservative assumptions and assume the maximum possible exposure.

Other TRGS to be used in connection with chromium (VI) compounds are:

- **TRGS-401:** Hazard from skin contact Investigation – Assessment – Measures
- **TRGS 402:** Determination and Assessment of Hazards in Activities with Hazardous Substances - Inhalative Exposure
- **TRGS 410:** Exposure Directory
- **TRGS 510:** Storage of hazardous substances
- **TRGS 561:** Activities with carcinogenic metals
- **TRGS 600:** Substitution

4. Chromium (VI) compounds in the workplace

4.4 Procedure for risk assessment

1. **Immediate measures based on visible contamination:**
   - **Visible deposits or dust are considered potentially dangerous**.
   - **The mere visibility and the rapid test detection require classification as a high risk.**

2. **Conservative assumptions:**
   - The operator must assume that the exposure is above the tolerance concentration (e.g. 4:1,000 risk for chromium (VI) compounds).
   - Risk mitigation measures must be initiated immediately, even without measured values.

3. **Risk minimization according to the STOP principle:**
   - **Substitution:** Replace CMR substances with less hazardous substances where possible.
   - **Technical protective measures:** Use of closed systems, improved ventilation or filter technologies.
   - **Organisational measures:** access restrictions, adaptation of work processes.
   - **Personal protective measures (PPE):** respiratory protection, protective clothing, gloves until the hazard is eliminated.

4. **Documentation and transparency:**
   - Visible contamination and test results must be documented in the risk assessment.
   - Provisional measures and further planned steps are to be recorded.

4. Chromium (VI) compounds in the workplace

4.5 Practical consequences

1. **Protective measures:**
    - Even without measured values, comprehensive protective measures such as PPE, access restrictions and technical protection must be implemented immediately, even before substitution.

2. **Proactive planning:**
    - At the same time, the operator must arrange for exposure measurements to validate the risk assessment and optimise long-term measures.

3. **Employers' liability insurance association and authorities:**
    - It should be checked whether visible CMR substances and test results should be reported to the competent authorities or employers' liability insurance associations, also to give the authorities the opportunity to assess the responsibility of OEMs.

Violations of rules or delays can result in legal consequences, especially in the case of carcinogenic substances such as chromium (VI) compounds.

These practical consequences mean in detail:

4.6 Practical consequences and recommendations

The findings on the formation and hazard of chromium (VI) compounds as well as the risks of reoxidation of chromium (III) compounds require concrete measures that go beyond existing legal requirements.

Both manufacturers and operators must assume their responsibility to ensure the health of employees and the protection of the environment.

The following consequences and recommendations result from this for

- Manufacturers of insulation materials or companies that equip them with such materials at the factory,
- Operators of installations whose components are equipped with such thermal insulation and
- Authorities and supervisory bodies whose task it is to monitor and, if necessary, monitor compliance with the regulations

4. Chromium (VI) compounds in the workplace

4.6 Practical consequences and recommendations

- **For manufacturers of insulation materials, as well as**
- **Manufacturers of technical systems with pre-installed thermal insulation:**

1. **Development of alternative materials:**

   Manufacturers and users of high-temperature insulation materials should invest more in the development and testing of alkaline and alkaline earth metal-free products in order to prevent the formation of chromates (chromium (VI) compounds).

2. **Transparency and communication:**
   - Clear disclosure of the risks of existing products, including potential reactions under thermal conditions, is essential.
   - Users should receive detailed instructions on how to safely handle affected products.

3. **Refraining from misinformation:**

   Technological innovations that completely prevent the release of chromates should be prioritized and implemented as soon as possible; inadequate decontamination and disregard of applicable regulations harm people and the environment!

- **For operators of technical plants, in particular CHP/CHP plants, as well as**
- **Operators of power plants:**

1. **Update of the risk assessment:**
   - Operators are obliged to immediately adapt their risk assessments to the latest findings and in particular to take into account the risks posed by thermochemical reactions in the vicinity of insulation materials and chromium-containing alloys.

2. **Immediate implementation of the STOP principle:**
   - **Substitution: Use of safe insulation materials that do not contain oxides containing (earth) alkaline metals.**
   - **Technical measures: Use of closed systems and improved extraction systems to minimise dust emissions.**
   - **Organizational measures: Regular training for employees and clear access restrictions to endangered areas.**
   - **Personal Protective Equipment (PPE): Provision of respirators, protective suits and gloves to avoid dermal contact and inhalation.**

4. Chromium (VI) compounds in the workplace

4.6 Practical consequences and recommendations

- **For operators of technical plants, in particular CHP/CHP plants, as well as**
- **Operators of power plants:**

3. **Runoff-free handling:**

   Work with contaminated materials or neutralising liquids must be carried out without drainage, as chromium (III) compounds are also hazardous to water.

4. **Disposal of contaminated materials:**
   Contaminated insulation materials or surfaces must be treated as hazardous waste, disposed of properly and must not be reused under any circumstances – not even after treatment with neutralising fluids.

- **For authorities and supervisory bodies:**

1. **Stricter monitoring and control:**
   - Authorities should check compliance with the substitution obligation and the requirements for risk assessments more closely and consistently sanction violations.
2. **Promotion of safe technologies:**
   - Public funding programs could create incentives to promote the development of safe materials and processes.
3. **Education and awareness-raising:**
   - National campaigns could help to raise awareness of the risks posed by chromium (VI) compounds and raise awareness among both operators and employees.

Result:

The responsibility for handling chromium (VI) compounds lies equally with manufacturers, operators and authorities.

Preventive measures, such as the substitution of hazardous substances, as well as strict compliance with existing legal requirements are essential to ensure the health of employees and the protection of the environment in the long term.

Only through joint efforts can the risk from chromium (VI) compounds be sustainably reduced.

5. Legal obligations

The legal requirements for the handling of chromium (VI) compounds are clearly regulated and include both the obligations to minimise exposure and to substitute hazardous substances.

5.1 Hazardous Substances Ordinance (GefStoffV):

5.1.1 § 6 Risk assessment

Content:

- Employers must assess hazards from hazardous substances in the workplace. This assessment includes:
    - Identification of all hazardous substances and mixtures.
    - Examination of possible routes of exposure: inhalation, dermal, oral.
    - Consideration of the specific properties of CMR substances (e.g. carcinogenic, mutagenic, toxic for reproduction).

Special features for CMR substances:

- **The highest care is always required for KMR fabrics:**
    - **Even the smallest exposures can be harmful to health.**
    - **The risk assessment must take into account current scientific findings (e.g. exposure-risk relationships).**
    - **Dermal risks:**
        - **Substances that can be absorbed through the skin (skin resorptivity "H") require special protective measures as they can cause systemic damage.**
        - **KMR substances, such as chromium (VI) compounds, can cause allergies, dermatitis and cancer when they come into contact with the skin.**

Documentation obligation:

- **The risk assessment must be carried out in writing and updated regularly, especially in the case of new findings (e.g. detection of CMR substances by rapid tests or measurements).**

5. Legal obligations

5.1 Hazardous Substances Ordinance (GefStoffV):

5.1.2 §7 General protective measures

Content:

- Employers must minimise or completely avoid exposure to hazardous substances as far as technically possible.

Special features for CMR substances:

1. **Exposure minimization:**
    - **CMR fabrics require special protective measures that go beyond general standards.**
    - **Technical measures (e.g. closed systems, negative pressure work areas) have priority over organisational and personal measures.**
2. **Dermal exposure:**
    - **Skin protection is particularly important for skin-resorptive CMR substances:**
        - **Provision of suitable gloves, protective clothing and skin protection products.**
        - **Regular review of the effectiveness of the protective measures.**
3. **Inhaled exposure:**
    - **Technical measures such as extraction and filter systems must be implemented as a priority.**

STOP principle:

The GefStoffV requires the application of the STOP principle, the order is to be applied in a binding manner:

- **Substitution.**
- **Technical protective measures.**
- **Organizational measures.**
- **Personal protective equipment.**

5. Legal obligations

5.1 Hazardous Substances Ordinance (GefStoffV):

5.1.3 § 8 Additional protective measures for activities with hazardous substances

Content:

- Employers must take additional measures if general protective measures are not sufficient.

Special features for CMR substances:

1. **Workplace restrictions:**
    - **Activities with CMR substances may only be carried out by trained personnel.**
    - **Unauthorized persons must be excluded from the work area.**
2. **Dermal risks:**
    - **Skin contact with CMR substances must be excluded by special measures, e.g. double gloves and protective creams.**
3. **Labelling obligation:**
    - **Areas where CMR substances are used must be marked. Example: "Attention! Working with carcinogenic substances."**

5.1.4 § 9 Occupational Exposure Limit Values and Exposure-Risk Relationship (ERB)

Content:

- For certain substances, in particular CMR substances, there are no fixed occupational exposure limits, but exposure-risk relationships (ERB).
- **The ERB indicates the concentration of a CMR substance associated with a tolerable or acceptable risk of cancer:**
    - **4:1,000 (risk of tolerance): Additional cancer cases in 4 out of 1,000 exposed individuals.**
    - **4:100,000 (risk of acceptance): Additional cancer cases in 4 out of 100,000 exposed people.**

Special features for CMR substances:

- **In the case of exposures above the risk of acceptance, measures must be taken to reduce them.**
- **In the case of exposures above the tolerance risk, activities are usually prohibited.**
- **Employers must ensure that dermal exposures are excluded even when complying with the ERB.**

5. Legal obligations

5.1 Hazardous Substances Ordinance (GefStoffV):

5.1.5 § 10 Substitution

Content:

- **Substitution obligation:**
  Employers are obliged to replace hazardous substances with less hazardous substances, mixtures or processes, if this is technically possible.

Special features for CMR substances:

1. **Priority:**
   - **The substitution of CMR substances is a top priority, as no exposure is considered safe.**
2. **Technical feasibility:**
   - **Employers must prove that there are no technically feasible alternatives if substitution is not implemented.**
3. **Documentation:**
   - **The examination of substitution options must be documented in a comprehensible manner in the risk assessment.**
4. **Dermal risks:**
   - **If substitution is not possible, measures must be taken to exclude both dermal and inhaled exposures.**

Example of a successful substitution of calcium-containing insulation elements by calcium-free insulation elements:

Calcium-containing insulation elements:

Yellowish deposits show the carcinogenic and environmentally harmful Cr (VI) compounds

Calcium-free insulation elements:

no yellowish deposits; presence of the chromium (VI) rapid test remains negative and confirms the successful substitution

5. Legal obligations (GefStoffV)

- **Section 10 of the Hazardous Substances Ordinance aptly summarises the above-mentioned provisions as follows:**

If the occupational exposure limit value cannot be complied with in activities with carcinogenic or germ cell mutagenic hazardous substances of category 1A or 1B despite exhaustion of the technical protective measures, or if activities in the medium-risk range are carried out, the employer must immediately draw up an action plan.

The action plan must set out how the goal of complying with the occupational exposure limit or getting into the low-risk range is to be achieved.

The following shall be listed:

- the measures envisaged,
- the targeted reduction of exposure, and
- the planned time frame.

The action plan shall be retained together with the documentation of the risk assessment in accordance with Section 6 (8).

If, even if the action plan pursuant to subsection (5) is implemented, the occupational exposure limit value cannot be complied with in the case of activities involving carcinogenic or germ cell mutagenic hazardous substances of category 1A or 1B, or if activities in the high-risk range are carried out, the employer must ensure that these activities are carried out only in accordance with a rule announced in accordance with Section 20 (4).

- **Section 10a Special Record-Keeping, Notification and Notification Obligations for Activities with CMR Substances of Category 1A or 1B**

In order to be able to understand the amount and duration of an exposure in the event of a later illness, the employer must keep a register of employees who carry out such activities with CMR substances of category 1A or 1B for which the risk assessment shows a risk to their health.

The list must indicate the activity as well as the amount and duration of exposure of the employees. (...)

The list must be kept up-to-date at all times during the duration of the exposure and kept for at least **the following periods after the end of the exposure**:

for activities with CMR materials of category 1A or 1B, 40 years... On termination of the employment relationship, the employer must provide the employees with an extract from the register containing the information concerning them. **The employer must keep proof of the handover like personnel documents**.

5. Legal obligations (GefStoffV)

➢ **Paragraph 18 of the GefStoffV further states:**

Without prejudice to Section 22 of the Occupational Health and Safety Act, the employer must inform the competent authority of the following upon request:

- **the result of the risk assessment in accordance with Section 6 and the information on which it is based, including the documentation of the risk assessment,**
- **the activities in which employees have actually or may have been exposed to hazardous substances and the number of such employees,**
- **the persons responsible in accordance with Section 13 of the Occupational Health and Safety Act,**
- **the protective and precautionary measures carried out, including the operating instructions,**
- **a copy of the action plan in accordance with Section 10 (5) for activities in the medium or high risk sector.**

In the case of activities involving carcinogenic, germ cell mutagenic or reprotoxic hazardous substances of category 1A or 1B, the employer must also inform the competent authority of the following upon request:

- **the result of the substitution test,**
- **Of**
  a. activities carried out and industrial processes used and the reasons for the use of these hazardous substances,
  b. the quantity of hazardous substances produced or used,
  c. the type of protective equipment to be used,
  d. type and extent of exposure,
  e. substitutions carried out.

At the request of the competent authority, the specialist knowledge required by Annex II of Regulation (EC) No. 1907/2006 for the preparation of safety data sheets must be proven.

5. Legal obligations (summary)

The EU Directive 2004/37 EC on protection against CMR substances is implemented in Germany by the Hazardous Substances Ordinance (GefStoffV), which in turn forms the basis of the individual Technical Directives on Hazardous Substances (TRGS).

Chromium (VI) compounds are harmful to health and carcinogenic by inhalation, dermal and orally.

Due to the additional classification **H410 "chronically harmful to the environment with long-term damage to aquatic organisms", chromates or products contaminated with chromates must therefore also be stored separately and disposed of as hazardous waste, provided with the appropriate waste codes.**

Due to the warnings of the manufacturers and the information letters from the authorities, the owner or operator of the plant areas described at the beginning is aware of the risk that people and/or the environment are highly endangered by carcinogenic and chronically environmentally hazardous substances.

This knowledge obliges owners and operators of these systems to immediately initiate protective measures! In this context, the Europe-wide principle of minimisation applies to minimise the formation of harmful substances and the associated danger to employees, uninvolved third parties and the environment without delay, or at best to prevent it.

After initiating various immediate measures (demarcation, minimization of the persons to be endangered, spatial separation, etc., which result from the risk assessment, which is also to be changed immediately), **it must be examined how the hazard can be minimized or prevented by selecting suitable procedures or substitute products.**

Although the release of chromates due to the use of (earth) alkaline metal oxides has been known for several years (the first warnings were published in 2021), little has been done by engine and turbine manufacturers to remedy the technically solvable problem of chromate formation (by using (earth) alkaline metal oxide-free insulation products).

Since the engines, turbines, components of the exhaust gas aftertreatment and all other components affected later do not yet have chromates in the delivery state, they are now advertised as "chromium (VI)-free". In this way, the subsequent risk management is transferred from the manufacturer to the customer or consumer with full awareness; an examination of the extent to which the Product Safety Act (ProdSG) makes the seller liable has not yet been considered.

Product Safety Act (ProdSG):

- **Obligation of manufacturers:**
  Products must be designed in such a way that no disproportionate risks arise when used as intended.
    - Manufacturers who continue to use calcium-containing insulation materials in particular risk the formation of carcinogenic chromates at the expense of their customers and could thus be held responsible for potential damage to humans and the environment.

5. Legal obligations (summary)

REACH/CLP Regulation:

1. **Chromium (VI) compounds as SVHC:**

   As substances of very high concern (SVHC), chromium (VI) compounds are subject to strict requirements with regard to production, use and communication in the supply chain.

2. **H-phrases:**

   Chromium (VI) compounds are classified with the H-phrases **H350 (carcinogenic)** and **H410 (environmentally hazardous).**

6. Responsibility of manufacturers and operators

6.1 Responsibility of the manufacturers:

- **Material selection:**
  Manufacturers are obliged to develop and use alternative materials that do not promote the formation of chromates.
- **Substitution test obligation (TRGS 600):**
  According to the Hazardous Substances Ordinance, hazardous substances must be replaced by safer alternatives. This obligation should also apply to the manufacturer of the pre-insulated units.
- **Ethical responsibility:**
  Manufacturers who downplay risks or withhold alternatives are not only acting negligently, but could also be legally prosecuted.
- **Product liability:**
  Deliberate omissions that cause damage to health or the environment could be punished under the Product Liability Regulation.

6.2 Responsibility of the Operators:

- **Risk assessment:**
  Operators must not rely on assurances of safety from manufacturers, but are obliged to include new findings in their risk assessments.
- **Substitution obligation: Operators**
  must independently examine and implement alternatives, regardless of the manufacturer's decisions.
- **Legal and moral responsibility:**
  Passivity could be considered contributory negligence if known hazards are not addressed.

7. misleading recommendations for action

7.1 Reducing liquids (neutralizer)

Due to the fact that it is chemically possible to convert hexavalent chromium compounds into comparatively less dangerous trivalent chromium compounds by using a mixture of ascorbic and citric acid, manufacturers of engines and aggregates prefer to point out that this process can "as far as possible" eliminate the existing hazard from carcinogenic chromium (VI) compounds and also take the liberty of pointing out that that chromium (III) compounds are also found as trace elements in food and that the body even needs these "essential building blocks".

However, these indications are more than misleading, as there is a big difference between the chromium (III) compounds in food or dietary supplements and industrially produced or produced chromium compounds.

At first glance, this reasoning may seem coherent, but the two elements differ significantly.

➢ **Problem:**

Trace elements vs. industrial concentrations

- WHO recommendation:

  The maximum intake of chromium (III) as a trace element is 50–200 µg/day.

- Industrial reality:

  The neutralization of chromates formed on large areas of engines and/or turbines produces concentrations that are far above this range.

  According to TRGS 900, an occupational exposure limit of 2 mg/m³ applies to chromium (III) compounds.

➢ **No fight against the cause, only short-term immediate action, chromates return**

A **particular risk** is the potential **reoxidation of chromium (III) compounds to chromium (VI) compounds** under unfavorable conditions.

Upon re-exposure to high temperatures or oxidizing environments, as is often the case in industrial processes, chromium (III) can be oxidized by oxygen and converted back to its more toxic hexavalent form.

This applies in particular to surfaces that are already contaminated by chromate-containing residues or, for example, to calcium-containing (insulation) materials that are reused in thermal processes.

This reaction increases the risk of re-release of carcinogenic and environmentally hazardous chromium (VI) compounds and highlights the need to completely remove contaminated materials and replace them with suitable alternatives.

7. misleading recommendations for action

7.1 Reducing liquids (neutralizer)

Principle of operation of neutralizing fluid

1. **Aim of the reaction:**
   - The reduction to **chromium (III) compounds** (e.g. Cr^{3+} or $Cr(OH)_3$ reduces acute toxicity.

2. Role of components:

1. **Ascorbic acid (vitamin C):**
   - Acts as a powerful reducing agent.
   - Reduces Cr(VI) to Cr(III) by donating electrons.
2. **Citric acid:**
   - Creates a slightly acidic environment (pH≈3).
   - Provides protons (H^+) required for the reaction.
   - Stabilizes the resulting Cr(III) ions by forming soluble complexes (e.g. Cr(Citrate)).

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3. Chemical reaction equation

The reduction of chromate CrO to chromium (III) can be represented as follows:$\frac{2-}{4}$

1. **Redox reaction:**
   Ascorbic acid ($C_6H_8O_6$) gives up electrons while Cr(VI) absorbs electrons:

   $CrO + 3C\frac{2-}{4}_{6H8O6+8H^+} \rightarrow 2Cr^{3+} + 3C_6H_6O_6 + 4H_2O$

2. **Products:**
   Chromium(III) as Cr^{3+}, which may precipitate to **$Cr(OH)_3$** (chromium(III) hydroxide). Dehydroascorbic acid ($C_6H_6O_6$).

3. **Complex formation with citric acid:**

   Citric acid ($C_6H_8O_7$) can stabilize chromium (III):

   $Cr^{3+} + C_6H_8O_7 \longrightarrow Cr(Citrate)$

7. misleading recommendations for action

7.1 Reducing liquids (neutralizer)

4. Practical aspects

Advantages:

1. **Effective reduction:**
   - Ascorbic acid reliably reduces chromium (VI) in a short time.
2. **Easy to use:**
   - The mixture is easy to make and does not require complex technology.

Disadvantages and risks:

1. **Formation of new compounds that are harmful to health and the environment:**
   - **Chromium (III) compounds** such as **$Cr(OH)_3$** are less toxic, but still **hazardous to water (H412)** and **skin sensitizing (Sh)**.
   - Formation of soluble complexes (e.g. Cr(Citrate)) can increase the mobility and environmental distribution of chromium.
2. **Incomplete reduction:**
   - The spraying of contaminated plants and their components is not a professional pollutant control but only an immediate measure; however, it is to be expected that chromates will remain, albeit smaller.

Necessary measures:

- The treated residues must also be considered hazardous waste and disposed of accordingly.
- **Work with neutralizing fluids should be carried out drain-free,** as water-soluble chromium (III) complexes are potentially hazardous to the environment.

In summary, it can be concluded that **a misleading sense of security is suggested on the part of the manufacturers** and that the actual danger of chromium (VI) exposure is presented as controllable because it can be combated with a simple neutralization solution.

In particular, the reference to the "essential" trace elements gives the impression that it is sufficient to have a neutralisation solution ready so that the hazard can be sufficiently eliminated.

7. misleading recommendations for action

7.2 Chromium (III) compounds

In the so-called "Substance Evaluation Conclusion Document" 215-160-9 of the French ANSES on behalf of the French Ministry of the Environment, chromium (III) compounds are classified not only as skin sensitizing, but also as toxic with repeated administration.

Mutagenicity concerns are also confirmed and should lead to a different classification in the near future.

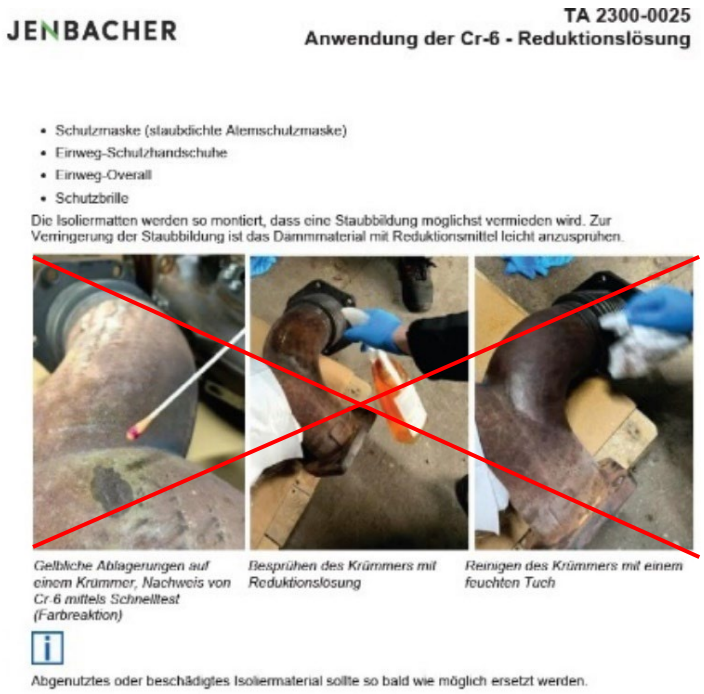
It can already be seen from the "ECHA" database that chromium (III) oxide with the CAS no. 1308-38-9 is classified as reprotoxic 1B in 278 entries; in addition, the following H-phrases are noted in the majority of cases:

H317H360H413

To describe such a substance as a vital trace element almost gives the impression that the uncontrolled use of neutralisation liquids is an almost harmless process, in which, according to experience, little caution is required. and encourages unsupervised measures by unqualified employees.

Anyone who presents this measure as sufficient and also shows pictures in their recommendations of how the soil on which the neutralisation work is carried out is unprotected, should perhaps be prohibited by the authorities from commissioning untrained personnel to combat highly carcinogenic and environmentally hazardous substances.

All recommendations given in the technical instructions do not coincide in any way with the described packages of measures for the handling of CMR substances at the workplace, nor with regulations regarding released chromium (III) compounds!



JENBACHER

TA 2300-0025
Anwendung der Cr-6 - Reduktionslösung

- Schutzmaske (staubdichte Atemschutzmaske)
- Einweg-Schutzhandschuhe
- Einweg-Overall
- Schutzbrille

Die Isoliermatten werden so montiert, dass eine Staubbildung möglichst vermieden wird. Zur Verringerung der Staubbildung ist das Dämmmaterial mit Reduktionsmittel leicht anzusprühen.

Gelbliche Ablagerungen auf einem Krümmer, Nachweis von Cr-6 mittels Schnelltest (Farbreaktion)

Besprühen des Krümmers mit Reduktionslösung

Reinigen des Krümmers mit einem feuchten Tuch

Abgenutztes oder beschädigtes Isoliermaterial sollte so bald wie möglich ersetzt werden.

8. Risk assessment

The risk assessment forms the basis for the safe handling of hazardous substances and is particularly important for carcinogenic, mutagenic and reprotoxic (CMR) substances such as chromium (VI) compounds. It enables employers to systematically assess risks and take appropriate protective measures. The legal framework is described in detail in § 6 of the Hazardous Substances Ordinance (GefStoffV) and the Technical Rules for Hazardous Substances (TRGS).

8.1 Implementation of the risk assessment

1. **Identification of hazards:**
    - Visible deposits or dusts with chromium (VI)-containing compounds must be classified as a potential hazard, even without exposure measurements.
    - Rapid tests and material analyses can provide an initial assessment of the hazard.
    - In addition, specific properties of the materials, such as skin resorptivity (H) or environmental hazard (H410), must be included in the assessment.
2. **Assessment of exposure:**
    - Exposure-risk relationships (ERB) according to TRGS 910 must be used to assess tolerable and acceptable risk.
    - Where measurements are lacking, conservative assumptions must be made that assume the maximum possible exposure.
3. **Documentation:**
    - The risk assessment must be comprehensively documented, including the risks identified, protective measures applied and the examination of alternatives.

8. Risk assessment

8.2 Special requirements for CMR substances

1. **Minimization requirement:**
    - According to § 7 GefStoffV, exposure to CMR substances must be minimised as far as possible. This requires:
        - Substitution of hazardous materials with less hazardous alternatives.
        - Technical measures such as closed systems and extraction systems.
        - Organisational measures, e.g. access restrictions and special working procedures.
2. **Precautionary principle:**
    - If a hazard cannot be completely ruled out, comprehensive protective measures must be implemented as a precautionary measure.
    - Work with substances or residues containing chromium (VI) must be classified as high-risk.
3. **Runoff-free handling:**
    - Work with potentially contaminated liquids, such as neutralizing liquids, or solid materials must be carried out without drainage. Residues must be treated as hazardous waste.

8.3 Regular review and adjustment

- New findings or changed working conditions make it necessary to update the risk assessment immediately (§ 6 GefStoffV).
- Regular reviews are mandatory, even if no new findings are available.

8.4 Involvement of experts

- External experts or employers' liability insurance associations should be involved in the preparation or updating of the risk assessment in order to increase the quality of the assessment.
- Especially in complex processes, such as the substitution of insulation materials or the decontamination of chromate-containing residues, cooperation with experts is essential.

9. Substitution test

The substitution test is a central component of the measures to protect health and the environment and is clearly prescribed by § 10 of the Hazardous Substances Ordinance (GefStoffV). It requires that hazardous substances and mixtures, in particular CMR substances, be replaced by less hazardous alternatives where technically possible. The sole use of neutralizing fluids is not a substitution, but merely a short-term emergency measure to reduce acute hazards. The long-term solution lies in the complete substitution of the problematic components.

9.1 Neutralizing fluid as an immediate measure

- **Conditions for use:**
    - The use of neutralizing liquids, consisting of ascorbic and citric acid, is a necessary immediate measure, but may only be carried out by specially trained personnel.
    - This measure is only permissible if all other protective measures, such as spatial separation and technical security of the work areas, have already been implemented.
- **Limited effect:**
    - Neutralizing fluids reduce the acute hazard of chromium (VI) compounds by reducing them to chromium (III) compounds. However:
        - There is no guarantee that the reduction will take place in full!
        - New chromium (III) compounds can form CMR substances again by re-oxidation when exposed to heat or oxygen again.
- **No long-term solution:**
    - Neutralization cannot be considered a substitute for substitution. It only serves to contain the acute risk in the short term.

9. Substitution test

9.2 Obligation to Substitution

1. **Control of existing chromates:**
    - The first step in substitution testing is the complete removal of existing chromium (VI)-containing residues in contaminated work areas.
    - These areas need to be thoroughly cleaned and dusted, as chromates can be deposited not only on surfaces, but also in hard-to-reach areas.
2. **Replacement of (earth) alkaline metal oxide-containing insulation materials:**
    - There is no doubt that chromium (VI) compounds are formed by the thermochemical reaction between chromium-containing metals and (earth) alkaline metal oxide-containing insulation materials.
    - The continued use of such insulation materials inevitably leads to the re-formation of chromates, which is neither technically acceptable nor legally permissible.
    - Substitution obligation: The GefStoffV requires the replacement of hazardous substances and components as soon as alternatives are available and technically feasible.
3. **Availability of safe alternatives:**
    - Contrary to the representation of some main suppliers, alkaline and alkaline earth metal-free insulation materials have been established in practice for years. These materials have proven to be not only safer, but also technically superior.
    - Operators should implement these alternatives immediately to permanently prevent the formation of CMR substances.

9. Substitution test

9.3 Cleaning and prevention

1. **Cleaning contaminated work areas:**
    - Entire work areas in which chromium-containing alloys and insulation materials containing (earth) alkaline metals were used are most likely contaminated.
    - Thorough cleaning of these areas is necessary to completely remove any remaining chromium (VI) residues.
2. **Prevention through substitution:**
    - The substitution of hazardous insulation materials not only reduces the risk of chromate formation, but also contributes to the long-term safety and sustainability of work processes.
3. **Technical and organizational measures:**
    - In addition to substituting insulation materials, operators should ensure that all technical and organizational protective measures are implemented. These include closed systems, access restrictions and continuous monitoring of work areas.

Result

The substitution test is an indispensable step in permanently minimizing the risk of chromium (VI) compounds.

The use of neutralizing fluids can only be considered as a temporary solution. In the long term, there is no way around the substitution of (earth) alkaline metal-containing insulation materials.

Safe and technically superior alternatives are available in sufficient quantities and must be implemented immediately.

Operators who do not act risk not only legal consequences, but also considerable health and environmental damage.

9. Conclusions for Dealing with Chromates in the Workplace

9.1 For the EU

- Directive 2004/37/EC **is to be applied** throughout **the European Union**, which prohibits a **clear minimisation requirement**, especially for **CMR substances in the workplace,** regardless of the existing occupational exposure limit value.

- From 2025, the uniform limit value for chromium (VI) compounds of 0.005 g/m³ will apply within the EU | 5 ug/m³This limit value represents a legally permissible maximum concentration, but does not represent a risk-free threshold.

Even if the limit value is complied with, employers are obliged to further reduce exposure where technically feasible (Article 5).

There is no toxicological threshold for chromium (VI) compounds, as even the smallest amounts can be harmful to health!

A toxicological threshold is the point below which a substance is considered safe and no damage to health is expected.

Since chromium (VI) compounds are classified as carcinogenic substances, the occupational exposure limit value must be viewed in a differentiated way, because even the smallest exposures to CMR substances can cause long-term damage to health.

If a workplace measurement result is below the limit value, there is a widespread misconception that the workplace is considered safe, but this assumption is wrong, because the minimisation requirement always and exclusively applies to CMR substances.

A summary of 2004/37/EC follows on the following pages; important derivatives from this are marked in bold or yellow:

DIRECTIVE 2004/37/EC OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL

of 29 April 2004 in the latest version (2024)

on the protection of workers from the risks related to exposure to carcinogens, mutagens or substances toxic for reproduction at work (Sixth individual Directive within the meaning of Article 16(1) of Council Directive 89/391/EEC)

Article 1

➢ **Goal**

(1) The aim of this Directive is to protect workers against risks to their health and safety arising or likely to result from exposure to carcinogens, mutagens or substances toxic for reproduction at work, including prevention.

It lays down the relevant minimum requirements, including limit values.

...

(3) Directive 89/391/EEC shall apply in full to the entire field referred to in paragraph 1, without prejudice to more stringent and/or specific provisions of this Directive.

Article 2

➢ **Definitions**
For the purposes of this Directive:

a. "Carcinogen"

I. **a substance or mixture which meets the criteria for classification as a carcinogenic substance of category 1A or 1B set out in Annex I to Regulation (EC) No 1272/2008 of the EuropeanParliament and of the Council** (1);

II. a substance, mixture or process listed in Annex I to this Directive and a substance or mixture released by a process referred to in that Annex;

...

c. **'limit value'**,
unless otherwise specified, the limit value of the time-weighted average concentration for a carcinogen, mutagenic or reprotoxic substance in the air within a worker's breathing area within a reference period specified in Annex III;
...

e. **'health surveillance'**,
the assessment of an individual worker in order to determine his state of health in connection with exposure to certain carcinogens, mutagens or reprotoxic substances at work.

Article 3

➢ **Scope — Identification and assessment of hazards**

(1) **This Directive shall apply to activities in which workers are or may be exposed to carcinogens, mutagens or substances toxic for reproduction as a result of their work**.

(2) **For each activity that may involve exposure to carcinogens, mutagens or substances toxic for reproduction, the nature, extent and duration of the exposure of workers shall be determined in order to assess all risks to the safety and health of workers and to determine appropriate measures**.

(3) This assessment shall be carried out at regular intervals and in any event whenever there is a change in conditions which may affect workers' exposure to carcinogens, mutagens or substances toxic for reproduction.

(4) **The employer must inform the competent authorities of the criteria on which this assessment is based, upon request**.

(5) **The risk assessment shall take into account all other routes of exposure, e.g. absorption into and/or through the skin**.

(6) **When assessing the risk, employers pay particular attention to any impact on the safety or health of particularly vulnerable workers, taking into account, inter alia, whether it is advisable not to employ these workers in areas where they may come into contact with carcinogens, mutagens or substances toxic for reproduction**.

CHAPTER II

OBLIGATIONS OF EMPLOYERS

Article 4

➢ **Reduction and replacement**

(1) **The employer shall reduce the use of a carcinogen, mutagen or substance toxic for reproduction in the workplace, in particular by replaceing, as far as technically possible, it with substances, mixtures or processes which, when used or applied, are not or are less dangerous to the health or safety of workers.**

(2) The employer shall inform the competent authority of the result of its investigations upon request.

Article 5

➢ **Measures to avoid or reduce exposure**

(1) **If the results of the assessment provided for in Article 3(2) reveal a risk to the safety or health of workers, exposure of workers must be avoided**.

(2) If it is not technically possible to substitute the carcinogen, mutagen or substance toxic for reproduction by substances, mixtures or processes which, when used or applied, are not or are less dangerous to safety and health, the employer shall ensure that the carcinogen, mutagenic or reprotoxic substance is manufactured and used in a closed system as far as technically possible.

(3) If the application of a closed system is not technically possible, the employer shall ensure that the exposure of workers to the carcinogen, mutagenic or reprotoxic substance is reduced to the lowest technically feasible level without a threshold value.

(4) **Exposure shall not exceed the limit values for carcinogens, mutagens or substances toxic for reproduction set out in Annex III**.

(5) In all cases where a carcinogen, mutagen or reprotoxic substance is used, the employer applies all of the following measures:

(a) limiting the quantities of carcinogens, mutagens or substances toxic for reproduction in the workplace;

(b) limiting the number of workers who are or may be exposed to the minimum possible;

(c) (i) the organisation of working procedures and technical measures with a view to avoiding or minimising the release of carcinogens, mutagens or substances toxic for reproduction in the workplace;

(d) **removal of carcinogens, mutagens or substances toxic for reproduction at source, local extraction device or general ventilation system, all of which must be compatible with the necessary protection of public health and the environment**;

(e) **the use of appropriate measurement methods for carcinogens, mutagens or substances toxic for reproduction, in particular for the early detection of abnormal exposures resulting from an unforeseeable event or accident**;

(f) applying appropriate working procedures and methods;

(g) collective and/or individual protective measures where no other solution to avoid exposure is possible;

(h) **hygiene measures, in particular regular cleaning of floors, walls and other surfaces**;

(i) **informing workers**;

(j) **demarcation of hazard areas and the installation of appropriate warning and safety signs, including the 'no smoking' sign, in areas where workers are or may be exposed to carcinogens, mutagens or substances toxic for reproduction**;

(k) precautions for emergencies where abnormally high levels of exposure may occur;

(l) **ensuring safe storage, handling and transport, including through the use of hermetically sealed containers that are clear, clearly and visibly marked**;

(m) **To ensure the safety of the collection, storage and disposal of waste by workers, including through the use of hermetically sealed containers that are clear, clear and visibly marked**.

Article 6

➢ **Information to the competent authority**

If the results of the assessment provided for in Article 3(2) reveal a risk to the safety or health of workers, employers shall, upon request, provide the competent authority with relevant information on:

(a) activities carried out and/or industrial processes used, including the reasons for the use of carcinogens, mutagens or substances toxic for reproduction;

(b) quantity of substances or mixtures produced or used containing carcinogens, mutagens or substances toxic for reproduction;

(c) number of exposed workers;

(d) preventive measures taken;

(e) type of protective equipment to be used;

(f) type and degree of exposure;

(g) **Cases of substitution**.

Article 7

➢ **Unpredictable exposure**

(1) **In the event of an unforeseeable event** or accident that **could cause abnormal exposure of workers, the employer shall inform the employees**.

(2) **Until normal conditions have returned, and as long as the causes of abnormal exposure have not been eliminated**,
(a) **only the workers needed for repairs and other necessary work have access to the affected area**;

(b) **the workers concerned shall be provided with protective clothing and breathing apparatus which they must wear; the exposure shall not be of unlimited duration and shall be limited to the minimum strictly necessary for each worker**;

(c) **Workers are not allowed to work in the affected area without protective equipment**.

Article 8

➢ **Predictable exposure**

(1) In the case of certain activities, such as maintenance operations, where the possibility of a significant increase in the exposure of workers is foreseeable and for which any possibility of further technical preventive measures to limit such exposure has already been exhausted, the employer, after consulting the workers and/or their representatives in the undertaking or establishment, shall determine the necessary measures, without prejudice to the employer's responsibility: to reduce the duration of workers' exposure as much as possible and to ensure the protection of workers during these activities.

Pursuant to the first subparagraph, the workers concerned shall be provided with protective clothing and breathing apparatus to be worn for the entire duration of the abnormal exposure, which shall not be of unlimited duration and shall be limited to the minimum strictly necessary for each worker.

(2) **Appropriate measures shall be taken to clearly delineate and identify the areas in which the activities referred to in the first subparagraph of paragraph 1 are carried out or to prevent unauthorised access to those areas by other means**.

Article 9

➢ **Access to Hazardous Areas**

Employers shall take appropriate measures to ensure that the sectors in which the activities in respect of which the results of the assessment provided for in Article 3(2) reveal a risk to the safety or health of workers are carried out are accessible only to those workers who need to enter them in order to carry out their work or to perform certain tasks.

Article 10

➢ **Hygiene measures and individual protective measures**

(1) **Employers are required to take appropriate measures for activities where there is a risk of contamination by carcinogens, mutagens or reprotoxic substances to ensure that:**

(a) workers do not eat, drink or smoke in work areas where there is a risk of contamination by carcinogens, mutagens or substances toxic for reproduction;

(b) workers are provided with suitable protective clothing or other suitable special clothing;

(c) separate storage facilities for work or protective clothing on the one hand and street clothing on the other;

(d) provide workers with suitable and adequate toilets and washing facilities;

(e) **the protective equipment is properly stored in a designated place and, if possible, checked and cleaned before use, but in any case after each use**;

(f) **Damaged protective equipment must be repaired or replaced before reuse**.

(2) **The costs of the measures referred to in paragraph 1 shall not be borne by the workers**.

Article 11

➢ **Information and training of workers**

(1) The employer shall take appropriate measures to ensure that employees and/or their representatives in the undertaking or establishment, in particular in the form of information and instructions, receive sufficient appropriate training on the basis of all available information in relation to:

(a) **possible health hazards**, including the additional risks of tobacco use;

(b) **measures to be taken to prevent exposure**;

(c) **hygiene regulations**;

(d) **wearing and using protective equipment and clothing**;

(e) Measures to be taken by workers, in particular by rescue teams, in the event of incidents and for the prevention of incidents.

This instruction must be

— **take into account new or changed hazards**, especially if employees **in fact** or **probably new carcinogens, mutagens or substances toxic for reproduction or several different carcinogens, mutagens or substances toxic for reproduction, including those contained in dangerous medicinal products, or when circumstances related to work change**,

...

— **be repeated regularly in other settings if necessary**

...

9. Conclusions for Dealing with Chromates in the Workplace

9.1 For the EU

Directive 2004/37/EC establishes a primary principle of minimisation for carcinogenic or mutagenic agents.

This means that exposure to these substances must be reduced as much as technically possible in all EU member states – regardless of national specificities or limit values.

A fixed limit value is not to be understood as a "safety zone" in which further measures can be dispensed with below this value.

Rather, the goal always remains to further minimize pollution, even if the limit value is already undercut.

All EU member states must at least implement the EU directives, but can still tighten them with regard to limit values and additional regulations; thus, the minimization obligation applies in all EU countries.

In France and the Netherlands, an occupational exposure limit of 1 ug/m³ applies, for Germany the already described ERB (exposure-risk relationship) (4:1000) has been set at 1ug/m³, which thus sets the acceptance risk, i.e. the low risk range, at 0.1 ug/m³.

With regard to the 2004/37/EU Directive, the German ERB calculation comes closest to the minimisation requirement, but even in countries that adopt the "occupational exposure limit" of 5 ug/m³ from 2025, an exposure concentration below 5 ug/m³ does not mean that no further measures need to be taken on the part of employers or operators, because the pan-European minimisation or, at best, prevention requirement still applies.

It is to be expected that the "German model" will also be adapted in the other countries in the coming years.

For the manufacturers of engines, turbines, power units and exhaust components, the 2004/37/EU must also be considered on a pan-European basis, so it is mandatory to equip their own products in such a way that they do not produce carcinogenic and environmentally harmful chromates.

However, the fact that the technical systems do not contain any chromates in the delivery state can mean that they produce chromates from the time they are put into operation, and thus the binding minimization requirement also applies to the manufacturers.

9. Conclusions for Dealing with Chromates in the Workplace

9.1 For areas outside the EU

- **United Kingdom (GB/UK)**

Before Brexit, Great Britain, like all EU member states, was subject to the requirements of Directive 2004/37/EC.

After leaving the EU, the directive of the British Health & Safety Executive (HSE) applies, which is set out in the rulebook

"Control of substances hazardous to health

The Control of Substances Hazardous to Health Regulations 2002 (as amended) an Approved Code of Practice and guidance",

is written down and, just like the European 2004/37/EC, requires that the minimisation of exposure to carcinogenic and mutagenic substances (CMR substances), as far as technically and organisationally possible, has top priority in occupational health and safety and environmental protection.

Today, the UK continues to rely on a principle that is very similar to the idea of minimisation: the so-called ALARP principle (As Low As Reasonably Practicable).

This approach calls for the pollution of hazardous substances to be reduced to a level that is as low as reasonably achievable, taking into account technical, economic and organisational feasibility.

Thus, even after Brexit, there will remain a strong focus on reducing exposure to CMR substances, comparable to the requirements that were previously derived directly from 2004/37/EC.

The ALARP Principles are not written down as an independent "ALARP Act" for CMR substances, but result from the general legal and regulatory framework that applies in Great Britain to the handling of hazardous substances, in particular carcinogenic, mutagenic and reprotoxic substances. Fundamental here is the transfer of the minimisation obligations from the previously applicable EU Directive 2004/37/EC to British law after Brexit.

Specifically, information on the application of the ALARP principle can be found primarily in the publications and guidelines of the British Health and Safety Executive (HSE). Relevant sources include:

1. **COSHH (Control of Substances Hazardous to Health) Regulations** and associated HSE guidelines:

   Although these provisions and the associated guidance documents (e.g. the ACOP L5) do not explicitly refer to "ALARP rules" for CMR substances, the fundamental principle of minimisation and the obligation to reduce risk to an acceptable level (ALARP) is clear.

2. **HSE Guidance on ALARP (As Low As Reasonably Practicable)**:

   The HSE has published general explanations of the ALARP concept that apply across industries. These illustrate how employers assess the feasibility of protective measures against the risks posed by CMR substances and which measures make sense to achieve ALARP status.

3. **Reducing Risks, Protecting People (R2P2)**:This HSE policy document on risk assessment and decision-making describes in detail the principles that are also used for the handling of CMR substances.

In short:

ALARP as a principle can be found in the relevant HSE guidelines, in particular in the context of the COSHH regulations and the HSE's basic ALARP guidelines.

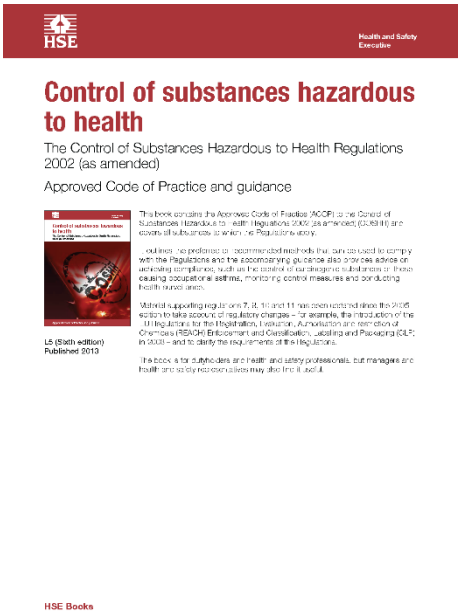
The actual location of the ALARP philosophy for CMR substances thus results from the interaction of the British hazardous substances law and the general HSE guidelines on the ALARP principle.

9. Conclusions for Dealing with Chromates in the Workplace

9.1 For areas outside the EU

➢ United Kingdom (GB/UK)

- **Control of substances hazardous to health (COSHH)**
  - **ACOP 7**



HSE

Health and Safety Executive

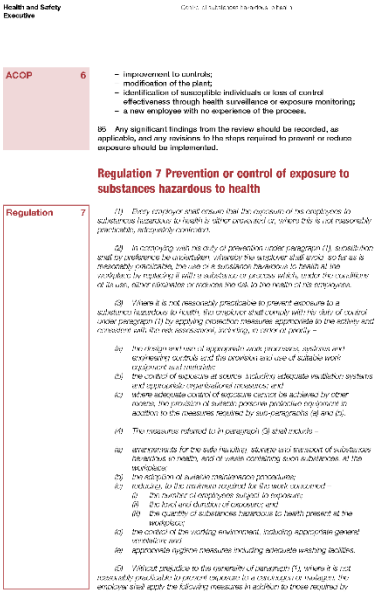
Control of substances hazardous to health

The Control of Substances Hazardous to Health Regulations 2002 (as amended)

Approved Code of Practice and guidance

L5 (Sixth edition)
Published 2013

HSE Books

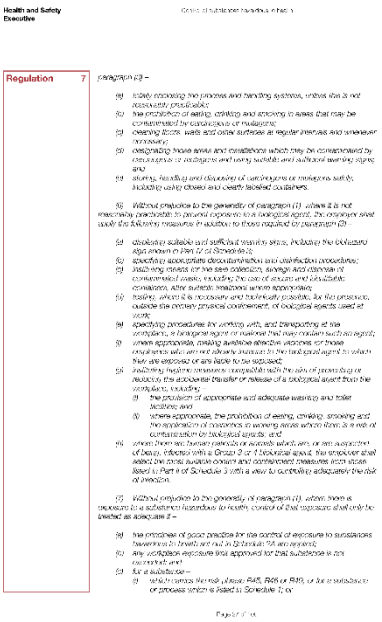


Health and Safety Executive

ACOP 6

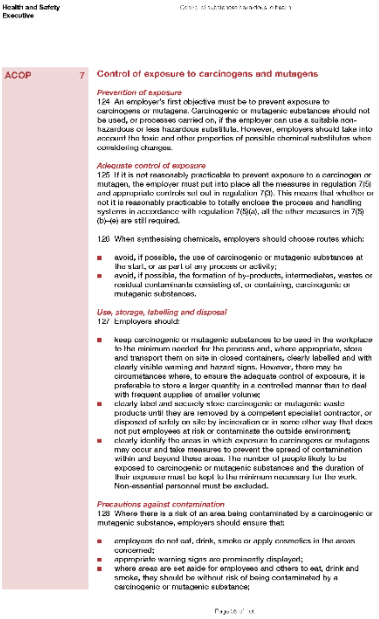
Regulation 7 Prevention or control of exposure to substances hazardous to health

Regulation 7



Health and Safety Executive

Regulation 7



Health and Safety Executive

ACOP 7

Control of exposure to carcinogens and mutagens

Prevention of exposure

Adequate control of exposure

Use, storage, labelling and disposal

Precautions against contamination

9. Conclusions for Dealing with Chromates in the Workplace

9.1 For areas outside the EU

- **United Kingdom (GB/UK)**
  - **Control of substances hazardous to health (COSHH)**
    - **ACOP 7**

Approved Codes of Practice (ACOPs) are documents issued by the UK Occupational Health and Safety Authority **(HSE)** that provide practical guidance on how to comply with specific regulations.

What are the 8 COSHH principles?

Principles of Good Control Practices

- **Minimizing emissions, releases, and spread.**
- **Consideration of routes of exposure.**
- **Selection of control measures that are appropriate to the risk.**
- **Selection of effective control options.**
- **Personal protective equipment – the last control option.**
- **Verification of the effectiveness of controls.**
- **Provision of information and training.**

The measure adopted worldwide and considered sufficient to simply use a protective suit (PPE) is based on incorrect interpretations of regulations and laws.

Personal protective equipment is to be used as a measure if all other measures have not (yet) led to success; However, the aim of all measures is to eliminate exposure (dermal and inhalative) and not to have to use the protective suit in the future!

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   - Mao, H. et al., *The role of temperature on CrVI formation during heating of Cr in the presence of CaO*, Chemosphere 138 (2015).
   - Miyauchi, H. et al., *The formation of Cr (VI) compounds at the interface between metal and heat-insulating material*, J. Ceram. Soc. Jpn. 123 (2015).

2. **Alerts:**
   - **Innio Jenbacher Ges. mbH & Co.:** Technical Instruction TA 2300-0025
   - **MAN Trucks and Bus SE:** Service Leaflet 8339SM CrVI
   - **Caterpillar Energy Solutions GmbH:** Technical Circular Chrome (VI)
   - **BG ETEM:** SmPC "Chromium(VI)"
   - **Free State of Thuringia, LV Consumer Protection:** Chromium(VI) Exposure during the Maintenance and Repair of Turbines and Engines

3. **Legal basis:**
   - CLP Regulation (EC) No. 1272/2008
   - REACH Regulation (EC) No. 1907/2006
   - Hazardous Substances Ordinance (GefStoffV), §§ 6, 7, 10
   - Product Safety Act (ProdSG)

4. **Technical rules:**
   - **TRGS 400:** Risk assessment
   - **TRGS 510:** Storage of hazardous substances
   - **TRGS 561:** Activities with carcinogenic metals
   - **TRGS 600:** Substitution
   - **TRGS 900:** Occupational Exposure Limits
   - **TRGS 910:** Risk-related Concept of Measures for Activities with Carcinogenic Hazardous Substances

5. **Gestis database:**
   - Data sheets for **calcium chromate**, **sodium chromate**, **chromium (VI)** and **chromium (III) compounds**.

6. **Further references:**
   - DFG MAK and BAT Value List (2024)
   - EU Directive 2004/37/EC