Influence of alkaline and/or alkaline earth metal containing insulation materials on the passive layer of chromium-containing hot metal parts at surface temperatures up to 600°C

1. Introduction:

This study examines the chemical processes that take place on the surface of a thermally insulated stainless steel hot part made of material 1.4301 when the component has been exposed to temperatures of up to 600°C. The release of gaseous chromium compounds, which can lead to the formation of chromium(VI) oxide (CrO_3), is not expected at these temperatures, but yellowish deposits were detected during the dismantling of the plants.

These deposits have been identified as carcinogenic and environmentally harmful chromates and, due to their discoloration, indicate that they were formed by reactions with alkali and/or alkaline earth metals:

Fig. 1-4: Chromate deposits between metal hot part and thermal insulation[11]

As a literature review, coupled with practical experience, the study investigates which reactions and interactions occur when insulation materials consisting mainly of a SiO2-Al2O3 complex and contain alkali and/or alkaline earth metal oxides such as calcium oxide (CaO) and/or sodium oxide (Na_2O) and compares these results with analyses if the insulation materials are alkali and/or alkaline earth metal oxide-free products Is.

The aim is to evaluate the potential effects of these interactions on the passive layer of chromium-containing metal hot parts and to identify the conditions under which such reactions become significant, leading to legally prescribed measures in occupational health and safety and environmental protection.

Finally, measurement results and practical experience are analysed and compared with the provisions of EU Regulation 2004/37, which leads to the conclusion that the minimisation requirement can only be complied with if previous insulation systems (with alkali and/or alkaline earth metal oxides) are replaced by alkali and alkaline earth metal-free systems.

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Case study:

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Case study:

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2. Materials and conditions

2.1 Stainless steel hot parts:

The stainless steel hot parts examined consist of the material 1.4301, whose chemical composition typically includes about 17-19% chromium (Cr), 8-10% nickel (Ni), up to 2% manganese (Mn) and the residual iron (Fe) content. This stainless steel is often used due to its good corrosion resistance and mechanical properties at elevated temperatures. The study can also be applied to other stainless steels that have a higher chromium content.

Examples of such materials that have a chromium content of at least >5% and are suitable for continuous temperatures of up to 500/600°C include:

Material 1.4404 (AISI 316L): Contains about 16.5-18.5% chromium and 10-13% nickel and 2-2.5% molybdenum (Mo), which gives it improved corrosion resistance.

Material 1.4571 (AISI 316Ti): Contains approximately 16.5-18.5% chromium, 10.5-13.5% nickel and up to 2.5% molybdenum and titanium (Ti) for stabilization.

Material 1.4541 (AISI 321): Contains about 17-19% chromium, 9-12% nickel and is also stabilized by titanium (Ti).

Material 1.4845 (AISI 310S): Contains about 24-26% chromium and 19-22% nickel and is used specifically for high-temperature applications.

The above materials are particularly suitable for applications where high temperatures and corrosion resistance are critical.

However, the low levels of manganese and molybdenum do not prevent the basic attack that can be caused by substances such as calcium hydroxide ($Ca(OH)_2$) or sodium hydroxide (NaOH).

Although manganese and molybdenum improve overall corrosion resistance, they do not provide specific protection against the chemical reactions described above, which can destabilize the passive layer.

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2.2 Insulation materials:

2.2.1 E-glass products:

In particular, E-glass products such as insulating glass fabrics and insulating glass fibre needle mats, which contain about 15% calcium oxide (CaO) in addition to the described SiO_2-Al_2O_3 complex, are being investigated.

These materials are often used to provide thermal insulation in high-temperature environments.

In some cases, the glass fabric on the contact side is additionally provided with a silica coating that improves the wearability, even if these coatings do not fully persist at the high operating temperatures due to abrasion and aging.

It is in line with today's practice that the fabrics in the warp and weft are additionally twisted with a stainless steel wire core, which usually consists of the material 1.4301 or 1.4571, and/or that the E-glass fabrics are hot-sided reinforced with an additional, so-called knitted mesh, here too the materials 1.4301 or 1.4571 are customary on the market. The knitted wire mesh is often sewn onto or connected to the E-glass fabric.

Thus, both in the case of stainless steel wire reinforcement and the use of knitted wire, a stainless steel-insulating fabric combination is provided even if hot parts that do not contain chromium are insulated with E-glass products.

2.2.2 Mineral wool products:

Mineral wool products that consist of a similar SiO2-Al2O3 complex as E-glass insulation, but contain not only calcium oxide, but also about 18% by mass of CaO, Na2O and other alkali or alkaline earth metal oxides. This higher proportion of oxides results from the use of "soda-lime glass", which comes from waste glass recycling and is used in fibre production.

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2.2.3 Calcium Silicate Products:

"Calcium silicate products" consist of a SiO2-Al2O3 complex, like E-glass or mineral wool thermal insulation, but contain a particularly high mass content of over 40% calcium oxide (CaO).

These products are known in the industry as "**superwool"** or "**organic wool".** In the maritime sector, the term "**Firemaster**" has become established, as these materials are often used in fire protection due to their high fire resistance.

2.2.4 Insulation materials without alkali and/or alkaline earth metal oxides:

In addition, the effect of insulating materials on hot parts made of stainless steel consisting of a SiO2-Al2O3 complex is investigated, but **does not contain alkaline and/or alkaline earth metal oxides**. These materials are particularly stable and are being studied to understand how their inertness positively affects the behavior of the passive layer at high temperatures and prevents the formation of chromium (VI) compounds.

2.3 Operating temperatures:

500 to 600°C under normal atmospheric conditions in terms of oxygen content and humidity.

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3. Mechanisms of chromium release and reaction

3.1 Use of fluxes in insulation fiber products

3.1.1 CaO (calcium oxide) as flux
Melting temperature reduction:

CaO is widely used in glass fiber manufacturing, especially in E-glass products, as a flux to lower the melting temperature of the glass.

This facilitates the processing and shaping of the glass fibers.

Chemical reactivity:

While CaO as a flux makes the production of the fibers more efficient, it also increases chemical reactivity, especially at high temperatures or in humid environments where it converts to calcium hydroxide ($Ca(OH)_2$).

The basic properties of CaO, and $Ca(OH)_2$ in particular, are strong and contribute to the destabilization of the passive layer, which can lead to the formation of calcium chromate (CaCrO4) when it interacts with released chromium(III).

3.1.2 Na2O (sodium oxide) as flux
Use in mineral wool:

Na2O is also used as a flux in glass fiber production, especially for mineral wool.

It lowers the melting temperature and facilitates fiber formation, but has a high chemical reactivity, especially in humid environments.

Alkaline environments:

Na2O contributes to the formation of a very strong alkaline environment that can increase the reactivity of chromium (III) and lead to the formation of sodium chromate (Na2CrO4) when it interacts with released chromium(III).

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3.2 Release of chromium compounds - Chromium(VI) and chromium(III): -

Rare release of gaseous chromium(VI):

The release of gaseous chromium(VI) oxide (CrO3) is relatively rare under normal conditions. CrO3 is only produced under strongly oxidizing conditions and high temperatures.

Even at temperatures of 500 to 600°C, the conversion of chromium (III) to chromium (VI) in the gas phase is a rare process.

More frequent release of chromium (III):

The release of chromium (III) is more likely, especially if the passive layer (chromium(III) oxide) is damaged by mechanical abrasion or chemical attack.

Chromium (III) usually remains in solid or dissolved form and does not enter the gas phase, but can be the starting point for chemical reactions that lead to the formation of chromates.

3.3 Reaction of CrO3 and chromium (III) with insulation materials - With mat containing calcium and/or sodium oxide -

Reaction with CaO/Ca(OH)$_2$:

If CrO3 is nevertheless released, it can be released in an alkaline environment caused by CaO or Ca(OH)$_2$ reacts to calcium chromate (CaCrO4) instead of volatilizing.
This reaction is accelerated by the high reactivity of Ca(OH)$_2$ favored.
The same applies to Na2O or Na2(OH)$_2$ and the resulting formation of sodium chromate (Na2CrO4)

Chromium (III) and CaO or Ca(OH)$_2$/Na2O or Na2(OH)$_2$:

It is much more likely that released chromium(III) in the presence of Ca(OH)$_2$ and/or Na2(OH)$_2$ is oxidized to hexavalent chromium, i.e. converted into calcium chromate and/or sodium chromate.

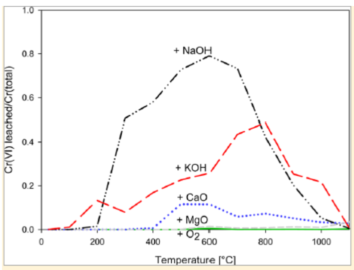

Fig. 5: Percentage leaching Cr(III) as Cr(VI)<2>

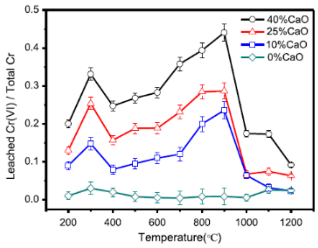

Fig.6: Cr(VI) leaching curve<3>

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3.4 With calcium oxide-free mat: Inertness of SiO_2 and Al_2O_3:

In a calcium oxide-free mat, both gaseous chromium compounds such as CrO_3 and chromium(III) would not undergo any significant chemical reactions.
SiO_2 and Al_2O_3 are very stable and unresponsive.

Fig. 7: No chromate formation after 10,000 hours of operation <11>

Barrier effect and filter effect:

The insulation mat could serve as a physical barrier or filter that slows or reduces the spread of gaseous CrO_3 . CrO_3 does not react with SiO_2 or Al_2O_3, but these materials, due to their physical structure, could hinder the diffusion of CrO_3 and thus reduce its concentration on the pipe surface.

3.5 Note on the supposed inertness of the glass core:

It is often argued that the calcium oxides in E-glass and mineral wool cannot dissolve from the matrix due to the inertness of the glass core, as they theoretically cannot be released from the solid glass structure. This assumption leads to the belief that the release of calcium or sodium ions is not possible under normal conditions.

However, such assumptions mainly refer to solid glasses.

However, the production of glass or mineral wool fibers produces fibers and filaments with an average diameter of 6-10 micrometers.

These continuous fibers are twisted and woven, but are exposed to mechanical stresses such as vibrations and temperature fluctuations, especially in the case of industrial insulation.

In addition, external influences or the start-up and shutdown of the systems can lead to condensation, which can also promote the release of ions.

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3.6 Potential diffusion of calcium ions by silica coating:

Despite the protective properties of the silica coatings of fabrics mentioned in the introduction, calcium ions can succeed in diffusing through the coating under certain conditions.
The porosity, thickness, and also any defects in the silica coating can serve as pathways for ion migration, but especially in humid or ionic environments.
The attraction of calcium ions to negatively charged areas, such as the stainless steel passive layer, can further promote this diffusion process.

3.6 Mention of a closed system study and differentiation from open systems:

In a study frequently cited by insulation manufacturers and insulation companies (Tatar, B., et al. (2018)<1>) It was investigated whether gaseous chromium compounds such as chromoxy hydroxide can be released during the heating of stainless steel under certain conditions and subsequently achieve a hexavalent chromium status. In this experiment, stainless steel was vaporized with water at 700°C in a closed system for many hours to create the necessary conditions for the release of gaseous chromium compounds.

This study shows that while it is technically possible to produce small amounts of unspecified chromium(VI) compounds that can settle on insulating materials, the release of these gaseous chromium compounds was only possible in this particular scenario because the closed reaction system combined several crucial factors:

the increased pressure due to external water vaporization,
the high temperature
and the trapped atmosphere, which maximized the oxidation potential of the environment.

These extreme conditions caused the normally stable chromium(III) oxide passive layer to form chromium(VI) oxide (CrO_3), which then changed to the gas phase and precipitated on the insulation materials.

However, this scenario corresponds to **not** the normal external conditions that prevail in open systems.

In an open system, pressures and temperatures are typically lower, and atmospheric oxygen concentration is significantly lower, reducing the potential for oxidation.

In addition, in an open system, the resulting water vapor would escape into the environment instead of accumulating in a closed space to lead to more intense reactions.

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In industry, hot parts containing chromium are usually coated with an insulating material. Although the evaporation of condensation, which may be between stainless steel surfaces and the insulation system, cannot be ruled out, the small quantities of water are not sufficient to depict the continuous water evaporation caused in the Tatar study, which also examines a stainless steel surface not covered with an insulation layer.

Especially in the case of insulation materials that contain calcium oxide and/or sodium oxide in higher mass proportions, the moisture is more likely to be absorbed by the insulation material, as both calcium oxide and sodium oxide are hygroscopic substances that react chemically with water (reactivity with water).

Calcium oxide, also known as burnt lime, is highly reactive with water and forms calcium hydroxide, also known as slaked lime, regardless of temperature.

This process is called hydration and is exothermic, which means that heat is released.

Sodium oxide also reacts very easily with water, creating sodium hydroxide, a very strong base that attracts water strongly, known as caustic soda.

The hygroscopic sodium hydroxide can absorb water from the air.

Therefore, the release of later gaseous chromium(VI) compounds, which were observed only to a small extent in the closed system study, is extremely unlikely under the normal conditions of a thermally insulated open system and thus in practice in the case of thermal insulation of chromium-containing hot parts.

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4. Effects on corrosion under insulation (CUI):

4.1 Influence of CaO and Na_2O on CUI -

Alkaline Conditions and Passive Layer Destabilization:

In an insulation mat containing CaO and/or Na_2O, highly alkaline environments can develop in the presence of moisture, as CaO is converted to $Ca(OH)_2$ and Na_2O to NaOH. These basic substances can destabilize the protective chromium oxide layer of stainless steel.

Promotion of corrosion:

Once the passive layer is damaged, the stainless steel underneath becomes more susceptible to corrosion. In the presence of moisture, which acts as an electrolyte, this can lead to increased local corrosion, including pitting corrosion and intergranular corrosion. These mechanisms contribute significantly to corrosion under insulation (CUI).

Chromate formation and CUI:

The highly alkaline conditions also promote the oxidation of released chromium (III) to chromium (VI), resulting in the formation of chromates such as calcium chromate ($CaCrO_4$) and sodium chromate (Na_2CrO_4). These chromates are not only corrosive, but also harmful to the environment and toxic.

Water vapor attack on CaO and Na_2O-containing materials:

When condensation has formed between the stainless steel hot part and the insulation and the stainless steel hot part is heated, water vapor is produced. This water vapour, in contact with insulation materials containing calcium and/or sodium oxide, such as E-glass, mineral wool and calcium silicate products, can lead to a chemical reaction that produces calcium hydroxide ($Ca(OH)_2$) and sodium hydroxide (NaOH). These basic compounds can degrade the structure of the insulation material over long periods of time and attack the protective passive layer of the stainless steel, resulting in accelerated corrosion.

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Influence of polyurethane coatings:

Some glass fabrics, which are used as the first insulation layer on the stainless steel hot parts, are coated with polyurethane to improve the ready-to-wear ability. However, at high temperatures, such as those examined in the study, polyurethane decomposes, resulting in the release of toxic fumes and residues. These residues could be deposited on the surfaces of the hot stainless steel part and change the chemical environment, which could indirectly affect the stability of the passive layer.

4.2 Reduction of CUI by calcium oxide-free insulation:

Lack of basic foundations:

In a calcium oxide-free insulation mat composed primarily of SiO_2 and Al_2O_3 , there are no reagents that could lead to the formation of alkaline environments. Without these basic conditions, the susceptibility to corrosion of stainless steel remains low.

Long-term integrity of the insulation mat:

The chemical stability of SiO_2 and Al_2O_3 helps ensure that the insulation mat remains stable for an extended period of time without creating corrosive conditions that could promote CUI.

Prevention of electrolyte formation:

Because the mat is less hygroscopic and does not contain alkaline substances, the formation of electrolytes required for corrosion is reduced. This significantly reduces the risk of CUI and extends the life of the pipe.

Resistance to water vapour:

In contrast to calcium and sodium oxide-containing materials, SiO_2-Al_2O_3 complexes are chemically stable and do not react with water vapor. These materials maintain their structural integrity even under repeated exposure to water vapor and preserve the passive layer of the stainless steel because it does not release aggressive (basic) hydroxides that could attack the protective chromium oxide layer.

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4.3 Influences of the stainless steel passive layer:

Passive layer as a negatively charged area:

The passive layer on stainless steel, which consists mainly of chromium(III) oxide (Cr_2O_3), can develop a negative surface charge under certain conditions. This charge could attract calcium ions diffused by the silica coating, which could lead to the deposition of calcium on the passive layer and the possible formation of calcium chromate. This attraction could increase the likelihood that calcium ions will migrate to the passive layer despite the coating and contribute to chemical reactions there.

5. Flux dilemma: pros and cons

5.1 Advantages of fluxes in production

E-glass production:

In the production of E-glass, a complex of SiO_2, Al_2O_3 and about 15% CaO has proven to reduce the melting temperature and improve the mechanical properties of the glass fibers.

Mineral wool production:

In the production of mineral wool, the high proportion of waste glass, which consists of soda-lime glass, already provides the necessary fluxes such as CaO and Na_2O to lower the melting temperature and facilitate processing.

5.2 Disadvantages of fluxes:

Promotion of corrosion and chromate formation:

CaO and Na_2O, which are introduced into the fibers during the manufacturing process, can lead to the formation of chromates under certain conditions when they come into contact with chromium (III) from the passive layer of stainless steel.

Chromium (VI) compounds such as calcium chromate ($CaCrO_4$) and sodium chromate (Na_2CrO_4) are formed in highly alkaline environments created by the reaction of CaO and Na_2O with moisture.

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Promotion of stainless steel corrosion:

These basic compounds (NaOH, $Ca(OH)_2$) can attack the protective chromium oxide layer (Cr_2O_3) of the stainless steel, which leads to the destabilization of the passive layer and thus to corrosion.

This is particularly problematic in the case of corrosion under insulation (CUI), where corrosion often progresses unnoticed until significant damage occurs.

6. Knowledge of chromate formation by alkali/alkaline earth metal containing insulation materials on chromium-containing hot parts since 2011(!):

6.1 Japanese patent specification JP2012220174A "STRUCTURE OF HEATING APPLIANCES<10>"

In 2011, i.e. thirteen years before the preparation of today's study, the company Toshiba describes the state of affairs that insulation materials containing alkali and/or alkaline earth metal oxide and direct heat contact with chromium-containing hot parts promote the formation of alkali and/or alkaline earth chromates, in particular calcium chromate and/or sodium chromate.

Individual tests are described, in each of which samples of mineral wool (trade name: Rockwool), a calcium silicate product (trade name: Keical Ace Supersilica; calcium oxide content: approx. 45%) and an unspecified perlite product (calcium oxide-free, but containing sodium oxide) and heated to 600°C over a longer period of time (without increased water vapour influence).

After separation of the stainless steel/insulation structure, visible chromate deposits were detected on all three samples, which were subsequently confirmed by laboratory technology!

7. Literature and Practical Studies

7.1 Literature

Tatar et al. investigate in "Study on the Interaction of Chromium Oxide Volatiles with Aluminosilicate Fiber Materials at High Temperatures."<1> volatile chromium compounds and detect them, but the test setup and procedure do not correspond to the conditions in practice for the thermal insulation of engines, turbines and incineration plants in the temperature range up to 600°C.

On the one hand, the volatile chromium compounds are only dissolved at significantly higher temperatures and only by strong water vaporization, and on the other hand, the heated stainless steel samples are not directly bonded to the insulating materials. The small chromium (VI) compounds deposited on the insulation materials have

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no technical connection with the conditions prevailing in practice, also because they have not had any opportunity to evaporate in a more or less closed system (glass tubes).

In industrial applications, common insulation materials would absorb much of the moisture from water vaporization, resulting in less impact on the stainless steel passive layer. Furthermore, the insulation materials examined in the study do not contain calcium, but have a low sodium oxide content and therefore do not correspond to the typical application and are more likely to be used at temperatures above 750°C/800°C or in furnace construction.

The experimental setup in JP2012220174A (2011) "STRUCTURE OF HEATING APPLIANCES" <10> is much more practice-oriented, because it deals with the use of insulation materials, which are also used in the majority of common practice; moreover, these tests were carried out at normal humidity and thus without artificial and higher water vaporization.

The results confirm all the findings of chromates that have been made in the last months and years on engines, turbines and piping systems, as well as on components of the exhaust gas aftertreatment systems.

The patent application, coupled with the later study Sayano, Kano, Innagaki, et al. (2015). "The Formation of Cr(VI) in Metal and Heat-Insulating Materials under High Temperature Conditions."<4> describes the finds from the

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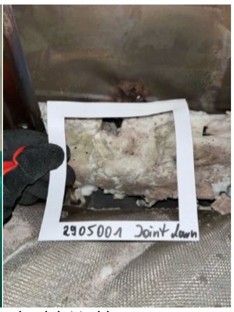
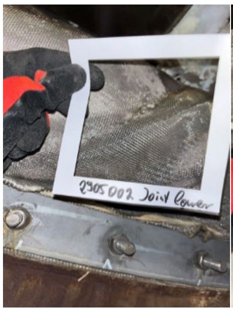
7.2 Practice

Fig.8: Mineral wool Fig. 9&10: Superwool/Firemaster

Figs.11&12: E-glass fabric Fig.13: Expansion joint turbine



Figs.14&15: Expansion joint of the turbine Fig.16: Laboratory samples positive

In recent years, chromium (VI) tests have been carried out in various European power plants on a wide variety of plant areas, of which more than 70% were tested Cr6-positive (rapid test) followed by a positive cross-sample (laboratory).

In the meantime, the interfaces of the thermal insulation on the exhaust system in the engine compartment of a car have also been tested positive for chromium (VI) (Fig.17).

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8.Rules and regulations

8.1 Legal basis

EU Regulation 2004/37/EC deals with the protection of workers from exposure to carcinogenic or mutagenic substances and calls for a general **principle of minimisation**.

This includes the application of the **S-T-O-P principle** , which is primarily used to minimise risk, whereby

"**S**" stands for substitution.

In view of the fact that calcium and sodium chromate as chromium (VI) compounds are classified as **SVHC (Substances of Very High Concern),** which are carcinogenic (H350) and chronically harmful to the environment (H410), and sodium chromate is also considered toxic to reproduction (H360FD), legal measures for substitution are particularly urgent.

8.2 Chromium (VI) compounds vs. asbestos fibers

The measures to be taken and occupational safety and environmental protection measures to be observed in the case of chromium (VI) compounds are to be compared with those which are also to be applied in the case of asbestos fibres.

H-phrases (hazard statements) are known throughout Europe and are uniformly regulated. They are part of the **CLP (**Classification, Labelling and Packaging of Substances and Mixtures) Regulation, which applies throughout the European Union (EU). The CLP Regulation is based on the Globally **Harmonised System of Classification and Labelling of Chemicals (GHS),** which was developed by the United Nations.
The H-phrases are used for the **uniform classification of chemical hazards** and enable clear and understandable labelling of hazardous substances and mixtures. This labelling requirement applies to manufacturers, importers and users throughout the EU, so that the same H-phrases are used in all member states.

If one compares the classifications of asbestos and chromium (VI) compounds with each other, one probably expects a much more dangerous overall classification of asbestos compared to chromium (VI) compounds, but exactly the opposite is the case:

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Comparison of H-Phrases Asbestos Fibres | Chromium (VI) compounds

Chrom(VI)-Verbindungen	Asbestfasern	Gemeinsame H-Sätze	Erklärung
H350	H350	H350: Kann Krebs erzeugen	Beide Stoffe sind krebserregend.
H372	H372	H372: Schädigt die Organe bei längerer oder wiederholter Exposition	Bei chronischer Exposition können beide Stoffe Organ- und Gewebeschäden verursachen.
H335	H335	H335: Kann die Atemwege reizen	Beide Stoffe reizen die Atemwege, besonders beim Einatmen.

Unterschiedliche H-Sätze	Chrom(VI)-Verbindungen	Asbestfasern	Erklärung und Vergleich
Hautreaktionen	**H317**: Kann allergische Hautreaktionen verursachen	**H315**: Verursacht Hautreizungen	**H317** ist gefährlicher, da allergische Reaktionen langanhaltend sein können, während H315 auf vorübergehende Reizungen hinweist.
Augenschäden	**H318**: Verursacht schwere Augenschäden	**H319**: Verursacht schwere Augenreizung	**H318** hat ein höheres Gefahrenpotenzial, da es irreversible Augenschäden verursachen kann, während **H319** reversible Reizungen beschreibt.

Nicht gemeinsame H-Sätze	Chrom(VI)-Verbindungen	Asbestfasern	Erklärung
Umweltgefahr	**H410**: Sehr giftig für Wasserorganismen, mit langfristiger Wirkung	-	Chrom(VI)-Verbindungen sind stark umweltgefährdend, insbesondere für Wasserorganismen. Asbest hat keine vergleichbare Umweltgefahr.
Genetische Schäden	**H340**: Kann genetische Defekte verursachen	-	Chrom(VI)-Verbindungen sind mutagen, was Asbestfasern nicht nachgewiesen wurde.
Atembeschwerden	**H334**: Kann bei Einatmen Allergien, asthmaartige Symptome oder Atembeschwerden verursachen	-	Chrom(VI)-Verbindungen können starke allergische Reaktionen und Atemprobleme auslösen.

8.3 Substitution by alkaline and/or alkaline earth metal oxide-free insulation materials:

In view of the potential hazards and the legal obligations under EU Regulation 2004/37/EC and the
S-T-O-P principle, it is absolutely justified to conclude **that alkali and/or alkaline earth oxide-free insulation materials consisting of a pure SiO2-Al2O3 complex should be used in the future**.

These materials offer a safer alternative and meet the requirements for minimizing risks from hazardous substances. This substitution would significantly reduce or effectively eliminate the risk of chromate formation, thus complying with legal requirements and promoting the protection of the environment and the health of workers.

Date:

2024-09-03

Case study:

Chromates in the workplace

Case study:

Influence of alkali and alkaline earth metal insulation products on the passive layer of hot stainless steel parts and the resulting formation of carcinogenic and chronically environmentally harmful chromium (VI) compounds (chromates; in particular calcium and/or sodium chromate) and the resulting consequences for the protection of humans and the environment

Case group:

High-temperature insulationRelease of fibres and dusts

Authors:

Lloyd Hopes
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8.4 Raising awareness when using so-called "neutralization "solutions""

For some time now, so-called "neutralizing fluids" have been offered on the market and are also proposed by engine manufacturers as an effective means and more or less sufficient safety measure.

Some of the spray solutions are pure ascorbic acid dilutions, in some cases they are still mixed with citric acids.

It is true that ascorbic acid is able to convert chromium (VI) compounds into chromium (III) compounds (reduction; down-oxidation).

To put it simply, the manufacturers recommend loosening the insulation parts and then spraying the spray solution into the open area of the thermal insulation that has been partially loosened until then.

Here, the term neutralization is used in a user-deceptive way and suggests a quick solution. In particularly brazen "guidebooks", the resulting chromium (III) is even praised as an essential building block in the human organism and is probably intended to assume the harmlessness, i.e. the "neutralization" of the chromate problem.

It is not pointed out that simply by loosening the mounted insulation element, indeterminate amounts of chromate are released, which are then swirled around the workplace for a long time. Likewise, the users of the spray solutions are not informed that chromium (III) compounds also have a limit value at the workplace and that work with chromium (III) compounds must be carried out "drain-free"; here, in particular, the authorities must intervene and increasingly point out that work with the possible release of CMR substances, which are also chronically harmful to the environment, may only be carried out by trained personnel.

Even in the case of stationary engines, e.g. in energy generation by combined heat and power plants, chromium (VI) air measurements were carried out at several workplaces, which after evaluation showed that the values were 210% or 290% of the limit value, i.e. 2.1 times and 2.9 times as high.

Direct measurements were also carried out in the breathing area of service personnel, here workers were equipped with a mobile measuring device, which was worn during the execution of repair work and then evaluated; in these measurements, the values were 2900%(!) and 5100%(1) above the limit value!

Finally, it should be pointed out that, especially in Germany, chromium (VI) compounds are not a tolerable occupational exposure limit value, but an "exposure-risk relationship" of 1µg/m³ (4:1000) (TRGS 910).

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In the Netherlands and France, occupational exposure limits of 1µg/m³ also apply.

Regardless of the ERB or the AGW, the already mentioned minimization requirement according to 2004/37/EC applies, there is no tolerance value for chromium (VI) compounds, for which no action would have to be taken!

Wearing personal protective equipment (PPE), which is perceived by many as the best and only protective measure, is of course mandatory if contact with CMR substances cannot be prevented at all, but it is by no means the first or only protective measure, because it is the "P" in the "S-T-O-P" principle, i.e. the last measure if S, T and O have not yet been conclusively and successfully applied.

In principle, the workplace should be designed in such a way that the wearing of full personal protective equipment is at least temporarily appropriate.

A fundamental part of the risk assessment, which must always be carried out if contact with CMR substances cannot be ruled out, is the substitution test.

This study shows that substitution is technically possible without any problems and protects not only people but also the environment.

In this respect, the substitution must be carried out in accordance with the regulations for maintenance work of high-temperature systems that are operated with process temperatures between 250°C and 750°C.

New systems that have so far been equipped with alkaline and/or alkaline earth metal oxide-containing thermal insulation should be equipped with alkaline and alkaline earth oxide-free insulation at the factory in the future in order to follow the minimization principle of EU Regulation 2004/37 in new buildings as well!

Figs.18-21: Completely chromate-free insulation materials because they are free of alkali and alkaline earth metal oxide <11,12>

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Images (practice):

11. Kavarflex Polska Sp. z o.o. Sp.k., PL
12. Hopes Generation Ltd., UK

Test methods (practice):

MATInspired B.V., NL
HexChecks (Figure Engineering)
SEEF B.V., NL

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