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It is not sulphur

The formation of carcinogenic and environmentally toxic chromates (chromium (VI) compounds) through the use of high-temperature insulation containing alkali and/or alkaline earth metals (insulation)

Chromates in the workplace

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Chromates in the workplace

Formation of carcinogenic and environmentally toxic chromium (VI) compounds (calcium and/or sodium chromate) through the use of high-temperature insulating materials and systems (insulation) containing alkali or alkaline earth metals

Fig.1: Thermally insulated gas engineFig.

Fig.2: Stripped turbocharger

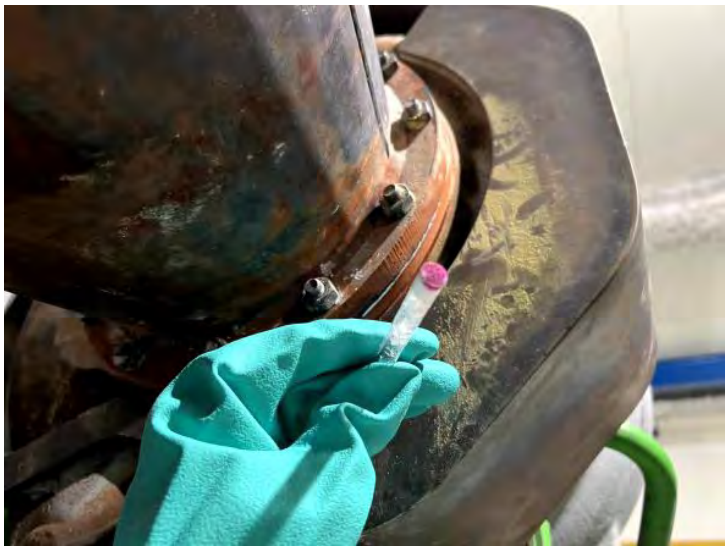

Fig.3: Positive Cr(VI) rapid test after stripping a turbocharger

Foreword
It is not sulphur

Chromates are chemical compounds that contain the chromate ion (CrO_4^{2-}). This anion consists of a chromium atom in the +6 oxidation state, surrounded by four oxygen atoms.

Chromates are typically brightly coloured and are used in dyes, pigments and in the industry for anti-corrosion coatings.

All chromates and other chromium(VI) compounds (with the exception of the water-insoluble barium chromate) are highly toxic, hazardous to water, carcinogenic and in some cases mutagenic or reprotoxic.

While chromate was used specifically in paints and coatings and is still used with special protective measures, the formation of chromate when using high-temperature insulating materials containing alkali and/or alkaline earth metals (ugs.
"insulations" or "insulation systems") is unintentional and is based on a logical and scientifically comprehensible, but so far rather unnoticed and therefore unfortunate thermo-chemical high oxidation of chromium (III) compounds, which are mainly found in alloys of stainless steels, with alkali and/or alkaline earth metal oxides, which are part of almost all common insulating materials and have been used since the ban on asbestos as insulating material for temperature ranges from approx. 250°C to 750°C, to hexavalent chromium compounds, i.e. chromates.

The yellowish powdery deposits produced by this process were often mistaken for sulphur in the past.

Despite intensive network research, there is no evidence of sulphur deposits in the use of insulation, which in turn leads to the conclusion that this is not the case.
"makeshift diagnosis" sounded logical and acceptable; on the one hand, sulphur powder cannot be considered to be very hazardous to health and, since there was always an internal combustion engine in the vicinity of isolated areas, the industry was satisfied with this explanation.

The fact that sulphur, which has a melting point of 112.8°C and a boiling point of 444.6°C, was also found in applications whose continuous operating temperature was far above the boiling point of sulphur did not necessarily lead to critical enquiries.

It is not known exactly when it was discovered that the residues released when used isolates are handled are not sulphur powder, but the carcinogenic and environmentally toxic calcium chromate (CaCrO4) or sodium chromate (Na2CrO4).

Chromates are hexavalent chromium compounds (also known as chromium (VI) compounds), often referred to simply as "chromium (VI)" and few people realise that a chromate is always the result of a chemical combination of two elements that first have to find each other and should be described as such (CALCIUM chromate, SODIUM chromate, etc.).

To this day, however, chromates are associated more with chromium than with its compounds.

With today's knowledge, it might have been possible to react earlier to the health and environmental damage, because the first indications of chromates in connection with high-temperature insulation materials were already available in the 1990s, in the form of a special communication from the American company Babcock and Wilcox, writing in 1994:

"The original version of this "Plant Service Bulletin (PSB-43)" was issued in April 1990 to warn owners and operators of boilers and steam generators that certain chromium-containing materials may produce hexavalent chromium chromium (Cr+ 6), a carcinogen, under certain operating conditions.

...

The original edition of PSB-43 referred only to chromium-containing refractory materials. This updated bulletin also covers other chromium-containing materials such as plastics, insulation and textiles". (*Annex CAA_001*)

The use of a "chromium-containing material" therefore led to the formation of "chromium (VI)". The culprit was quickly found, as the insulating material used also contained "up to 3% Cr2O3", the classic chromium (III) compound, which is also found in commercially available stainless steel alloys.

However, the insulating materials in question also contain refractory materials, fibres and aluminosilicate ("refractories, fibres, aluminosilicate"), a mixture of materials for which the well-known and globally operating manufacturer has even had its own "CAS number" created.

If you take a closer look at this CAS number, this material complex consists of 45-80% "...amorphous glass fibres made of silicon dioxide and aluminium oxide and a number of oxides such as zirconium dioxide, iron oxide, titanium oxide, magnesium oxide, calcium oxide, other alkaline earth oxides including sodium oxide, potassium oxide and barium oxides".

The resulting "chromium (VI)" was not named as a chromium (VI) compound (chromate) and if it was, then it was minimised to the chromium content of the insulating material, while the content of alkali and/or alkaline earth metals was (and still is) ignored.

Although the insulating materials used at that time are now available without chromium (III) compounds, chromate formation still occurs today when the above-mentioned "amorphous glass fibres" are used on hot parts containing chromium, as the proportion of alkali and alkaline earth metals, especially calcium oxide, has not changed!

However, final clarity about the formation of chromate in insulation materials containing alkali and/or alkaline earth metals in combination with chromium-containing hot parts should have been achieved at the latest with the publication of the patent "Heating equipment structure" by the Japanese company Toshiba in 2015 (Annex CAA_002).

Here the patent description states, among other things:

"Traditionally, asbestos was used as a heat-insulating material for a combustion chamber.

Asbestos is widely used because it is excellent for thermal insulation (heat retention), heat resistance, corrosion resistance, electrical insulation and the like, and is inexpensive.

However, it is no longer used because of the high probability of damage to health.

At present, a heat-insulating material consisting mainly of calcium silicate (a mixed oxide of calcium oxide and silicon oxide) is used as a heat-insulating material for a combustion chamber or the like.

The reason for this is that calcium silicate is safe and has excellent thermal insulation (heat retention), heat resistance and corrosion resistance and is cost-effective.

However, it has been pointed out that hexavalent chromium can form when a heat-insulating material comes into contact with a chromium-containing metal such as stainless steel in a combustion chamber or similar (e.g. non-patent literature).

This means that the surface layer of Cr2O3 of stainless steel or similar and the calcium component of the thermal insulation material react as follows and form hexavalent chromium.

$$2Cr2O3 + 4CaO + 3O\,2 \rightarrow 4CaCrO\,4$$

The formation of hexavalent chromium is not limited to biomass incinerators, but occurs in many high-temperature plants, e.g. in waste incineration plants, thermal power generation plants, high-temperature parts of pipework and chemical plants.

This means that if a component containing chromium comes into contact with a calcium-containing thermal insulation material, hexavalent chromium can form. This phenomenon (formation of hexavalent chromium) occurs more frequently with a metal component with a high chromium content.

This phenomenon is not limited to a calcium-containing thermal insulation material, but is also observed with a thermal insulation material containing potassium, magnesium, sodium and sodium.

The internationally renowned turbine manufacturer Toshiba recognised as early as 2011 what is still often doubted today, namely the formation of chromate when insulating materials containing alkali and/or alkaline earth metals come into contact with hot parts containing chromium.

In order to demonstrate this claim, a number of tests were carried out and documented, naming the insulation materials used, such as

Calcium silicate insulation material (containing calcium),

mineral wool (containing calcium and sodium) and

perlite (containing sodium)

All three insulation materials were heated together with a chromium-containing metal plate over a longer period of time and then the contact surface between the insulation material and the metal plate was analysed. In all three cases, chromates were detected in yellowish powder form, which had formed from the alkali or alkaline earth metal and chromium compounds.

The aim of the above-mentioned patent was to provide a process that coats hot parts containing chromium in such a way that no chromates are formed!

It may be attributed to the "old days" and the still limited research possibilities at that time that the findings did not lead to the realisation much earlier that the contact of hot parts containing chromium with insulating materials containing alkali and/or alkaline earth metals sooner or later leads to the formation of problems that are harmful to health and the environment.

In their various fields of work, the authors of this publication have been endeavouring for years, with varying degrees of intensity, to give the necessary attention to the formation of chromates when using today's insulating materials, especially on engines, turbines and exhaust elements, and are particularly committed to protecting people and the environment.

It is to be hoped that, as knowledge grows, there will also be an understanding that, after decades of ignorance, but also with a certain and unfortunately deliberate ignorance on the part of insulation, engine and turbine manufacturers and their associated service companies, measures must now finally be taken to minimise, or at best even prevent, the future formation of chromate.

It can be assumed that tens of thousands of combined heat and power plants, small and large power plants, stationary and mobile power generation plants are contaminated worldwide.

In Germany alone, over ten thousand combined heat and power plants are in operation, including in public buildings and institutions, residential complexes and as local energy suppliers. The number of steam and gas turbines in Germany alone is also in the four-digit range. All these plants are insulated with at least calcium, and in many cases also with sodium and potassium.

As the fine chromates can also be easily swirled around, it is not yet possible to estimate which areas outside the plants have also been contaminated.

It should also be noted that contaminated insulation materials, especially in textile form, have been disposed of incorrectly for decades, as waste containing chromate must be labelled and disposed of as special waste.

May this paper serve to give the chromate problem the necessary attention that will lead to the result that personnel and the sites are protected from further chromate exposures and immissions in the short term and that future chromate formation is minimised or at best prevented.

The current version of the European Directive 2004/37/EC, the Hazardous Substances Ordinance (GefStoffV) based on it and various TRGSs must finally be applied, whether the manufacturers of today's insulating materials, engines and turbines like it or not.

The asbestos scandal a few decades ago should have shown what happens when initial indications are ignored for whatever reason and a problem always comes at the wrong time, because there is no such thing as the ideal moment for a problem.

Occupational safety and environmental protection is an obligation for the future and must begin today.

The authors in December 2023

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Summary

Foreword - It is not sulphur

1) (thermo-)chemical background
2) Characteristics of today's insulation materials
3) High-temperature insulation in energy generation
4) Chromate formation on engines/turbines
5) Differentiation between large power plant/cogeneration plant
6) Chromates in the workplace
7) Insufficient information from manufacturers
8) Substitution
9) Characteristic Substitute
10) Unsuitable substitutes
11) Damage to health due to chromates
12) Environmental damage caused by chromates
13) Measures in the workplace
14) Decontamination
15) Clarification/prevention
16) Sources, picture credits, legal information
17) Imprint

Chapter 1
(thermo-)chemical background

The chromium (VI) compounds at the centre of attention here

Calcium chromate (CaCrO4) or sodium

chromate (Na2CrO4)

are formed, as already mentioned in the foreword, due to a thermo-chemical high oxidation of chromium (III) compounds (Cr2O3) with the alkali metal compound sodium oxide (Na2O) or the alkaline earth metal compound calcium oxide (CaO) in a certain temperature window between 250°C and 800°C. At temperatures between 900°C and 1,200°C, the chromates formed dissolve again (thermally) (Fig. 4):

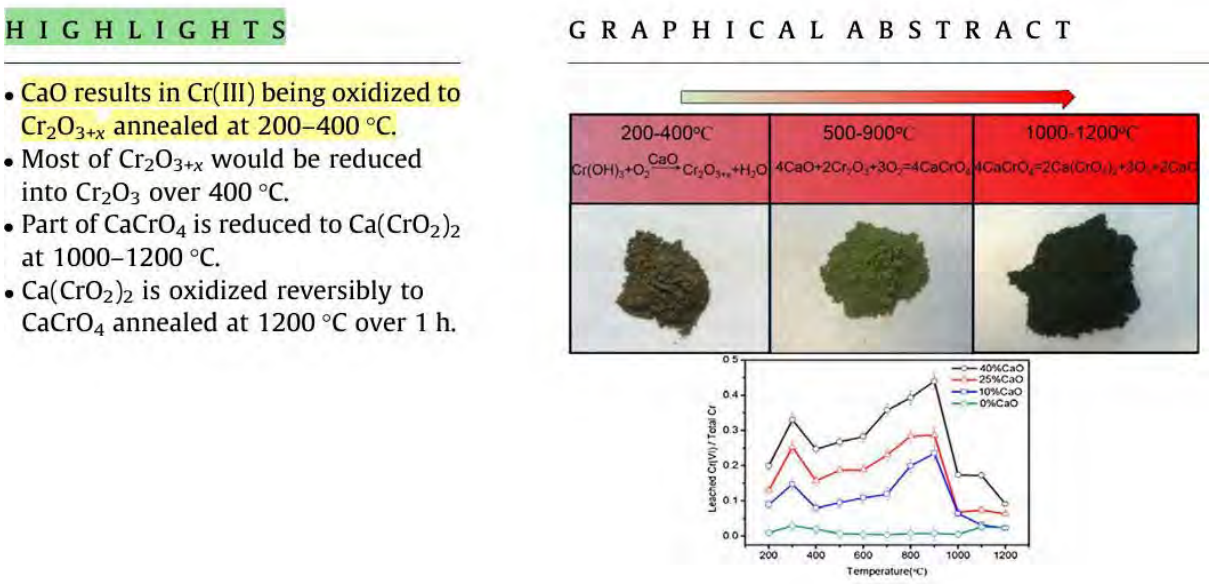


Fig. 4: Temperature-dependent calcium chromate formation.

Mao, Gao, Deng et al. letter in "The role of temperature on Cr(VI) formation and reduction during heating of chromium-containing sludge in the presence of CaO" (*Annex CA003*) et al:

"**The result showed that CaO promoted Cr(III) oxidation, but its influence is strongly dependent on the heating temperature, with the extent of the e!ect varying with temperature**. **From 200-400 C, the presence of CaO facilitated the formation of the Cr(VI)-containing intermediate Cr2O3+x** in the dehydration of chromium hydrate, while at temperatures above 400 C, Cr2O3+x decomposed, reducing part of Cr(VI) to Cr(III). **At 500 to 900 C, Cr(III) reacted with CaO to form a leachable CaCrO4 product**. This product was stable, and **a longer heating time did not significantly reduce the amount of Cr(VI).**"

Verbinnen, Billen et al. write on the same topic in "Heating Temperature Dependence of Cr(III) Oxidation in the Presence of Alkali and Alkaline Earth Salts and Subsequent Cr(VI) Leaching Behaviour" (*Appendix CAA004*) as follows:

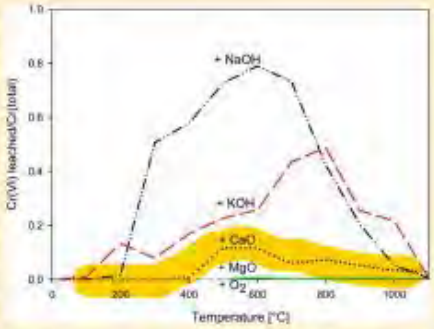
"In this paper, the temperature dependence of Cr(III) oxidation in high-temperature processes and the subsequent Cr(VI) leaching were investigated using synthetic mixtures. It was shown experimentally **that in the presence of alkali and alkaline earth metal salts an oxidation of Cr(III) takes place,** which agrees with the thermodynamic calculations.

The heating of synthetic mixtures of Cr2O3 and Na, K or Ca salts led to increased leaching of Cr(VI); in the presence of Na **at 600-800 °C more than 80 % of the original Cr(III) amount** was **converted into Cr(VI)**.

Fig. 5 shows the different levels of Cr(VI) leaching with the various alkali and alkaline earth metals:

Fig.5: Different Cr(VI) leaching, depending on the alkali/alkaline earth metal

ABSTRACT: In this paper, the temperature dependence of Cr(III) oxidation in high temperature processes and the subsequent Cr(VI) leaching was studied using synthetic mixtures. It was experimentally shown that in the presence of alkali and alkaline earth salts, oxidation of Cr(III) takes place, consistent with thermodynamic calculations. Heating of synthetic mixtures of Cr_2O_3 and Na, K, or Ca salts led to elevated leaching of Cr(VI); in the presence of Na, more than 80% of the initial Cr(III) amount was converted to Cr(VI) at 600–800 °C. Kinetic experiments allowed explanation of the increase in Cr(VI) leaching for increasing temperatures up to 600–800 °C. After reaching a maximum in Cr(VI) leaching at temperatures around 600–800 °C, the leaching decreased again, which could be explained by the formation of a glassy phase that prevents leaching of the formed Cr(VI). By way of illustration, Cr(VI) formation and leaching was evaluated for a case study, the fabrication of ceramic material from contaminated sludge. Based on the proposed reaction mechanisms, countermeasures to prevent Cr oxidation (addition of $NH_4H_2PO_4$, heating under inert atmosphere) were proposed and successfully tested for synthetic mixtures and for the case study.



The two studies above on the formation of chromates in the presence of sodium and/or calcium, among other things, which arose from different points of view, are supported by the scientific elaboration

"The formation of Cr(VI) compound at the interface between metal and heat-insulating material and the approach to prevent the formation by sol-gel process" by Sayano, Kanno et al. (*Annex CAA005*) was not only confirmed, but explicitly specified for insulation materials containing alkali or alkaline earth metals.

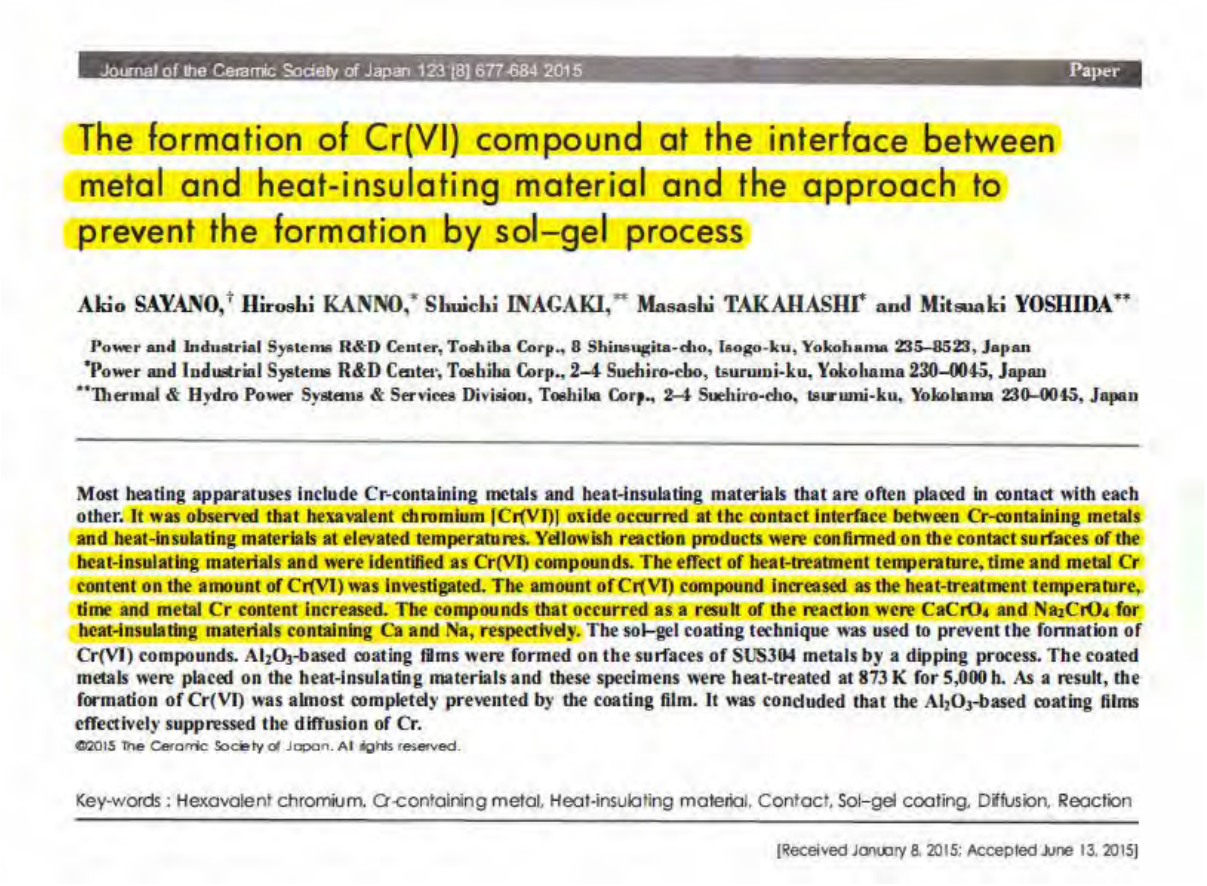
It is summarised as follows:

It has been observed that hexavalent chromium [Cr(VI)] oxide is formed at the contact surface between Cr-containing metals and heat-insulating materials at elevated temperatures.

Yellowish reaction products were confirmed on the contact surfaces of the heat-insulating materials and identified as Cr(VI) compounds.

The influence of heat treatment temperature, time and metal Cr content on the amount of Cr(VI) was investigated.

The amount of Cr(VI) compound increased with heat treatment temperature, time and metal Cr content. **The compounds formed as a result of the reaction were $CaCrO_4$ and Na_2Cr0_4 for calcium- and sodium-containing thermal insulation materials respectively**.



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The formation of Cr(VI) compound at the interface between metal and heat-insulating material and the approach to prevent the formation by sol–gel process

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Most heating apparatuses include Cr-containing metals and heat-insulating materials that are often placed in contact with each other. It was observed that hexavalent chromium [Cr(VI)] oxide occurred at the contact interface between Cr-containing metals and heat-insulating materials at elevated temperatures. Yellowish reaction products were confirmed on the contact surfaces of the heat-insulating materials and were identified as Cr(VI) compounds. The effect of heat-treatment temperature, time and metal Cr content on the amount of Cr(VI) was investigated. The amount of Cr(VI) compound increased as the heat-treatment temperature, time and metal Cr content 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. The sol–gel coating technique was used to prevent the formation of Cr(VI) compounds. Al_2O_3-based coating films were formed on the surfaces of SUS304 metals by a dipping process. The coated metals were placed on the heat-insulating materials and these specimens were heat-treated at 873 K for 5,000 h. As a result, the formation of Cr(VI) was almost completely prevented by the coating film. It was concluded that the Al_2O_3-based coating films effectively suppressed the diffusion of Cr.

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Key-words : Hexavalent chromium, Cr-containing metal, Heat-insulating material, Contact, Sol–gel coating, Diffusion, Reaction

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Fig.6: Insulating material containing calcium and sodium give rise to chromates

To summarise, it can therefore be concluded that there is no doubt that both scientifically and technically **the formation of carcinogenic and environmentally toxic chromium (VI) compounds** such as e.g.

Calcium chromate (CaCr04) and/or

Sodium chromate (Na2CrO4)

is to be expected due to the use of insulating materials containing alkali and/or alkaline earth metals, which are used **on hot parts containing chromium** such as engines, turbines, pipelines or other apparatus **at temperatures between 250°C and <750°C** over a longer period of time, and that these chromates are mostly found in yellowish dusts, whereby the chromates were also detected even if no yellowish deposits had yet formed.

Chapter 2
Characteristics of today's insulation materials

The best-known insulation material is certainly the widely used **mineral wool,** which is also used **as high-temperature insulation.**

Mineral wool can be found in every power station on pipelines, machines and other technical equipment.

It is often applied to the hot parts in several layers and then covered with a sheet metal jacket:

Fig. 7: Power station

insulationFig. 8: Power station insulation

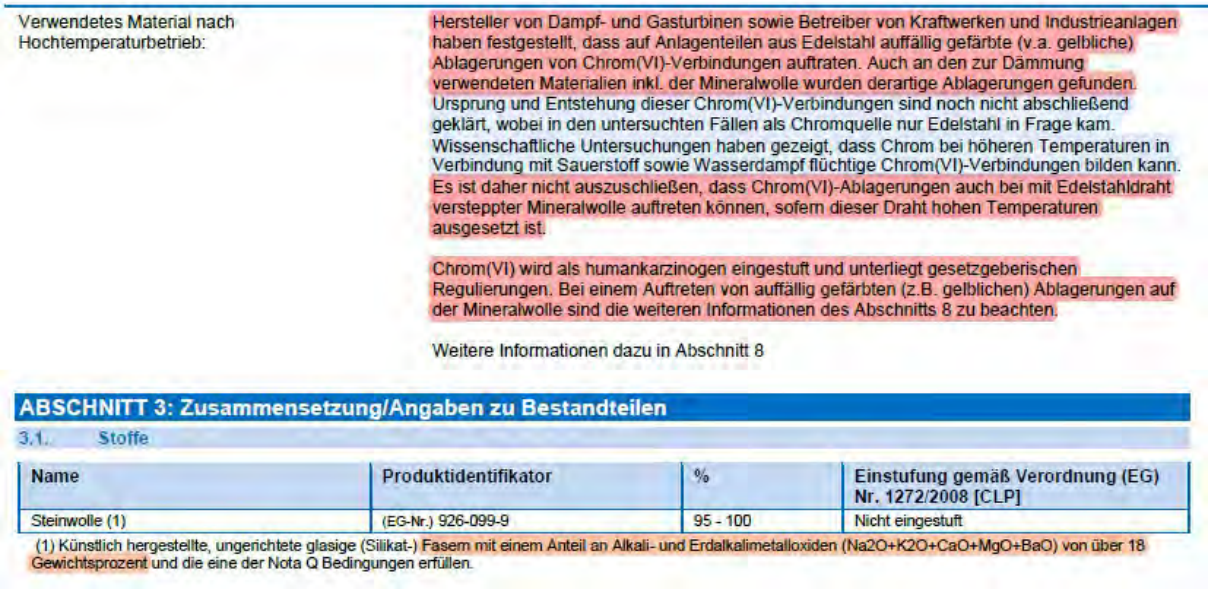
On the website of a major manufacturer (www.isover.de) we read:

How is mineral wool manufactured?

Mineral wool is manufactured using 95% mineral raw materials such as quartz sand, lime, soda and iron ore as well as recycled materials such as used glass. The latter makes up the largest proportion of the glass wool mix and comes from container glass and flat glass recycling. In the case of ISOVER glass wool, for example, the proportion of used glass can be up to 80 per cent.

Fig.9: Production of mineral wool

The technical data sheet of another manufacturer (www.rockwool.de) contains the chemical composition of its mineral wool:



Verwendetes Material nach Hochtemperaturbetrieb:	Hersteller von Dampf- und Gasturbinen sowie Betreiber von Kraftwerken und Industrieanlagen haben festgestellt, dass auf Anlagenteilen aus Edelstahl auffällig gefärbte (v.a. gelbliche) Ablagerungen von Chrom(VI)-Verbindungen auftraten. Auch an den zur Dämmung verwendeten Materialien inkl. der Mineralwolle wurden derartige Ablagerungen gefunden. Ursprung und Entstehung dieser Chrom(VI)-Verbindungen sind noch nicht abschließend geklärt, wobei in den untersuchten Fällen als Chromquelle nur Edelstahl in Frage kam. Wissenschaftliche Untersuchungen haben gezeigt, dass Chrom bei höheren Temperaturen in Verbindung mit Sauerstoff sowie Wasserdampf flüchtige Chrom(VI)-Verbindungen bilden kann. Es ist daher nicht auszuschließen, dass Chrom(VI)-Ablagerungen auch bei mit Edelstahldraht versteppter Mineralwolle auftreten können, sofern dieser Draht hohen Temperaturen ausgesetzt ist. Chrom(VI) wird als humankarzinogen eingestuft und unterliegt gesetzgeberischen Regulierungen. Bei einem Auftreten von auffällig gefärbten (z.B. gelblichen) Ablagerungen auf der Mineralwolle sind die weiteren Informationen des Abschnitts 8 zu beachten. Weitere Informationen dazu in Abschnitt 8

ABSCHNITT 3: Zusammensetzung/Angaben zu Bestandteilen

3.1. Stoffe

Name	Produktidentifikator	%	Einstufung gemäß Verordnung (EG) Nr. 1272/2008 [CLP]
Steinwolle (1)	(EG-Nr.) 926-099-9	95 - 100	Nicht eingestuft

(1) Künstlich hergestellte, ungerichtete glasige (Silikat-) Fasern mit einem Anteil an Alkali- und Erdalkalimetalloxiden (Na2O+K2O+CaO+MgO+BaO) von über 18 Gewichtsprozent und die eine der Nota Q Bedingungen erfüllen.

Fig.10: Data sheet mineral wool (extract)

The composition is defined as follows:

"Artificially produced, non-directional vitreous (silicate) fibres with a content of **alkali and alkaline earth metal oxides** (**Na2O+K2O+CaO+MgO+BaO**) of more than **18 percent by weight...**"

The authors are aware that the manufacturer, who himself writes that "conspicuously coloured (especially yellowish) deposits of chromium (VI) compounds appeared on the inside of his products during disassembly", is well aware of the investigation (Annex CAA005), but prefers to describe the formation process as "not yet conclusively clarified", but this reference should only be understood here as a side note.

However, after studying the website of the first mentioned manufacturer and analysing the above-mentioned data sheet, we can summarise that **mineral wool**, as the main **insulation material used worldwide, consists of** almost **one fifth alkali and alkaline earth metal oxides**!

The old or recycled glass mentioned is also the usual "**soda-lime glass**" and **lime is** nothing other than **calcium** and **sodium is** nothing other than **sodium**.

Another form of insulation system is the so-called "insulating mattress", which is usually made of glass fabric and actually resembles a mattress in its finished form.

After cutting and stitching, the glass fabric sheathing is filled with various insulating materials and then mounted in one or more layers, e.g. on turbines.

Insulating mattresses were manufactured over a hundred years ago; the two pictures show the production of asbestos mattresses. It was only years later that it was discovered that although asbestos was an excellent insulating material, it was unfortunately also very harmful to health, costing the lives of thousands of people who came into direct or indirect contact with asbestos fibres:

Fig11: Production of asbestos mattresses around 1920

Fig11: Production of asbestos mattresses around 1920

Until the 21st century, some manufacturing techniques and tools have not changed significantly and are still in use.

With the ban on asbestos, the previous asbestos-containing materials have been replaced (substituted) by other materials, the insulating fibres, i.e. insulation wool, have largely been replaced by the above-mentioned mineral wool and the current sheathing fabric now consists of glass fibres and no longer of the dangerous asbestos fibres. "Glass fabric".

Insulation mattresses made of glass fabric are used to insulate gas and steam turbines (with insulation thicknesses of up to several hundred millimetres in multi-layer designs), as well as motors and units with smaller and often only single-layer designs:

Fig12: Motor insulation with insulating mats

Fig13: Insulating mattresses exhaust area

But the same chemical composition also applies to the insulating fabrics as to the mineral wool already described, because the base material, the so-called "E-glass", also consists of 15-20% calcium oxide, among other things!

For example, "baunetzwissen.de" writes:

"Silicate glass is used almost exclusively in the construction industry. Mostly **soda-lime-silicate glass**, which was already used by the Egyptians and essentially consists of the basic materials **quartz sand**, **lime** and **soda.**

The molten glass is composed of silicon oxide (SiO_2), **calcium oxide** (CaO), **sodium oxide** (Na_2O), **magnesium oxide** (MgO) and aluminium oxide (Al_2O_3)." It goes

on to say:

"The composition has a significant influence on the viscosity of the melt and therefore on how the glass can be processed. Depending on the composition, the glass batch is melted at between 1,300°C and 1,600°C."

The sentence

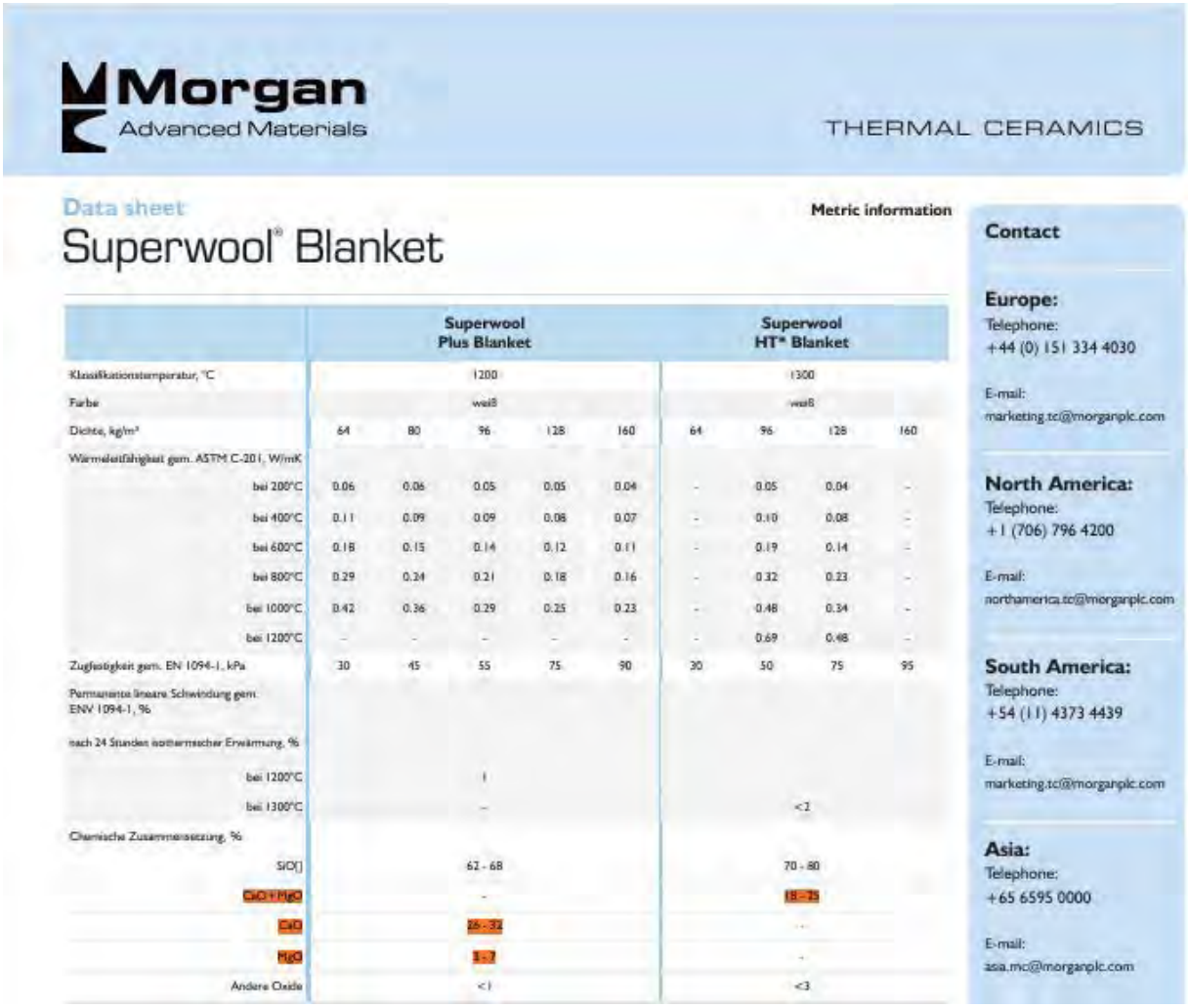
"***The melting temperature is lowered with the alkalis, because the melting temperature of pure SiO_2 is approx. 1,700°C***."

The addition of alkalis and alkaline earths allows manufacturers to mass produce at **much better conditions and costs** if, for example, **calcium and/or sodium are added** to the actual main component of the insulating products, namely **silicon oxide,** in the so-called "**glass melt"** required for the production of insulating materials.

Put simply, it could be said **that the manufacture of insulating products becomes much more favourable when alkaline or alkaline earth oxides are used**.

So-called "calcium silicate products" are used in the high-temperature range, also known as "CMS fibre" (calcium-magnesium-silicate fibre) or "EAS wool" (alkaline earth silicate fibre).

The chemical composition (Annex: *CAA_007*) is as follows:



Morgan Advanced Materials — THERMAL CERAMICS

Data sheet

Superwool® Blanket

Metric information

	Superwool Plus Blanket					Superwool HT* Blanket			
Klassifikationstemperatur, °C	1200					1300			
Farbe	weiß					weiß			
Dichte, kg/m³	64	80	96	128	160	64	96	128	160
Wärmeleitfähigkeit gem. ASTM C-201, W/mK									
bei 200°C	0.06	0.06	0.05	0.05	0.04	-	0.05	0.04	-
bei 400°C	0.11	0.09	0.09	0.08	0.07	-	0.10	0.08	-
bei 600°C	0.18	0.15	0.14	0.12	0.11	-	0.19	0.14	-
bei 800°C	0.29	0.24	0.21	0.18	0.16	-	0.32	0.23	-
bei 1000°C	0.42	0.36	0.29	0.25	0.23	-	0.48	0.34	-
bei 1200°C	-	-	-	-	-	-	0.69	0.48	-
Zugfestigkeit gem. EN 1094-1, kPa	30	45	55	75	90	30	50	75	95
Permanente lineare Schwindung gem. ENV 1094-1, %									
nach 24 Stunden isothermischer Erwärmung, %									
bei 1200°C			1						
bei 1300°C			-				<2		
Chemische Zusammensetzung, %									
SiO2			62 - 68				70 - 80		
CaO + MgO			-				18 - 25		
CaO			26 - 32				-		
MgO			1 - 7				-		
Andere Oxide			<1				<3		

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asia.mc@morganplc.com

Fig.15: Superwool, technical data

To summarise, this means that **all insulation materials used today for the temperature range from 250°C to >750°C**

with at least **15-20%** by mass of **alkaline or alkaline-earth metal-containing materials**!

Chapter 3
High-temperature insulation in energy generation

Whether the gas engine in a combined heat and power plant, the diesel engine in an emergency power generator or the gas or steam turbine in utility power plants, energy generation means heat and heat should be utilised, because heat loss means energy loss and energy is expensive.

Wherever conventional energy is generated, we will find thermal insulation, sometimes more and sometimes less, but without the so-called "insulation", energy generation would not be effective, apart from "renewables".

The thermal insulation sometimes only serves as heat and combustion protection, but usually it ensures that the heat is utilised in the best possible way.

In modern exhaust gas technology in particular, the implementation of today's exhaust gas standards would be inconceivable, because the operating temperature is also a component of the so-called
"SCR technology" (selective catalytic reduction), because the pollutants in the exhaust gases are burned and filtered in accordance with the regulations and the temperatures required for this come directly from the combustion system and the insulation ensures that the temperatures also remain in the system.

Combined heat and power plants utilise the so-called "CHP technology", the "cogeneration of heat and power", the gas engine drives generators that produce energy and the waste heat from the engines can be used to heat entire factories and housing estates.

Turbines and engines reach temperatures of over 500°C at maximum operation, and gas turbines can reach temperatures of around 1,000°C.

If turbines were not optimally insulated, the housing materials would "warp" far too quickly when they cooled down after being switched off, because the drop in temperature would stress the materials previously expanded by heat and more or less destroy the important inner workings within the turbines.

To make the cooling effect as gentle and long as possible, turbines are insulated with a wide variety of insulating materials and thicknesses.

Today's gas engines and turbines will at best be converted to water-fuelled operation over the next few decades, but regardless of the supply medium - the operating temperatures will not change and therefore neither will the thermal insulation.

Chapter 4
Chromate formation on engines/turbines

In 2022, "gas.info" presents Austria's ambitious transformation plans:

"By 2040, natural gas is to be completely replaced by climate-neutral energy sources in energy generation in Vienna. **One of Austria's largest gas turbines is** therefore currently being converted at the Donaustadt power plant site.

In 2023, Wien Energie, RheinEnergie, Siemens Energy and VERBUND want to add hydrogen for energy generation for the first time as part of an operational trial.

This test is the first of its kind worldwide on a commercial **gas and steam turbine plant** in this power class.

With this trial, the co-operation partners want to gain important insights for the conversion of **combined heat and power plants** to green sources.

The conversion of the turbine is the first milestone in the project. The gas turbine itself is now ready for the addition of hydrogen."

Fig.16: Gas turbine in Austria

In 2021, "MAN Energy" announces that it is "H2-ready" (Fig. 17)

Fig. 18: MAN's "H2-ready" gas engine (source: https://www.man-es.com/de/unternehmen/pressemitteilungen/press-details/2021/11/04/h2-ready-man-gas-engines-make-hydrogen-use-in-power-plants-possible)

And one of the world market leaders for gas engines in Austria, INNIO Jenbacher, has already announced that it will be launching in 2019:

Bild: E&M

zurück

KWK

Jenbacher setzt auf Wasserstoff

Der BHKW-Hersteller Innio Jenbacher arbeitet an Motoren, die mit reinem Wasserstoff oder Methanol betrieben werden können. Bis 2021 sollen die ersten Aggregate betriebsbereit sein.

Schon jetzt gilt Jenbacher als Spezialist für die Verbrennung von Sondergasen und hat auch viele Aggregate in Biogasanlagen installiert. Jetzt will man diese Kompetenz auf die Verbrennung von

Wasserstoff und anderen aus Strom gewonnenen Treibstoffen (sogenannter E-Fuels) erweitern. Details dazu präsentierte das Unternehmen in seinem Werk in Jenbach. Zur Realisierung gibt es eine For

Regardless of whether gas, steam or hydrogen is fed into the grid, engine and turbine technology is constantly evolving and moving with the times.

However, this is clearly recognisable for the expert in the pictures:

Insulation technology has - intentionally or unintentionally - NOT evolved since the 1980s, unlike all other components, because the same materials are still used today as were used 40 years ago:

Insulation materials containing alkali and/or alkaline earth metals

and their use leads, as described on the previous pages, to the formation of carcinogenic and environmentally toxic chromium (VI) compounds, in particular calcium and/or sodium chromate, because the insulation materials release oxides containing alkali and/or alkaline earth metals over time due to abrasion and ageing, which trigger the formation of chromate.

The temperatures described above, which support the formation of chromate, correspond to the continuous temperatures of the insulated machines, turbines and motors!

The findings described so far have now also been confirmed by machine and turbine manufacturers; the following images show positive chromium(VI) tests from a wide range of industrial sectors.

The so-called "chromium (VI) test" is considered relatively safe because it uses a special chemical discolouration effect.

There is a mixture of chemicals that only reacts in colour in combination with chromates, resulting in a purple discolouration (colorimetric test/spectrophotometry).

In the Encyclopedia of Analytical Science (Second Edition), 2005, we read about

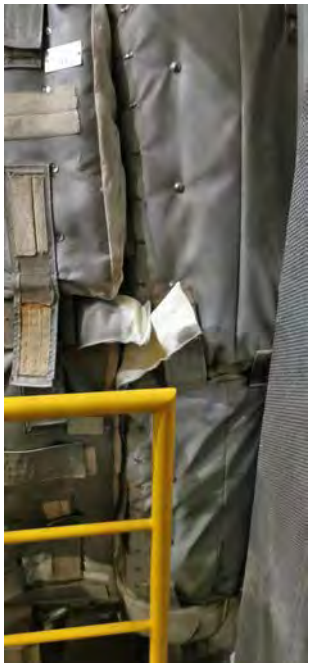
this: UV-visible spectrophotometry

UV-visible spectrophotometry is an established technique for the selective determination of Cr(VI) with good detection performance. The standard method for the selective determination of Cr(VI) is based on the formation of a red-violet coloured complex with 1,5- diphenylcarbazide under acidic conditions, which is detected spectrophotometrically at 540
nm can be detected .

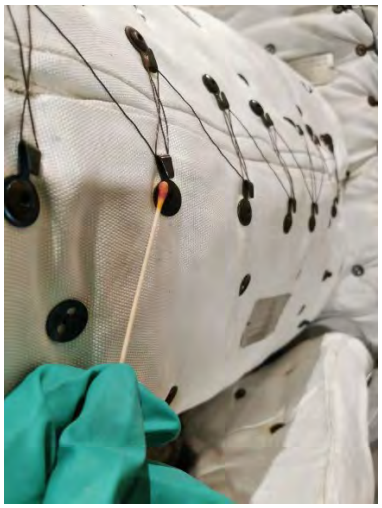
Practice has shown that false negative Cr(VI) tests are more likely to occur than false positive Cr(VI) test results; false negative tests can occur if, for example, other substances are superimposed on the chromium (VI) dusts and no chemical compound can be established.

Chromium (VI) detection when using thermal insulation containing alkali/alkaline earth metals:

gas turbines (Fig. 21-23):



steam turbines (Fig. 24-26):

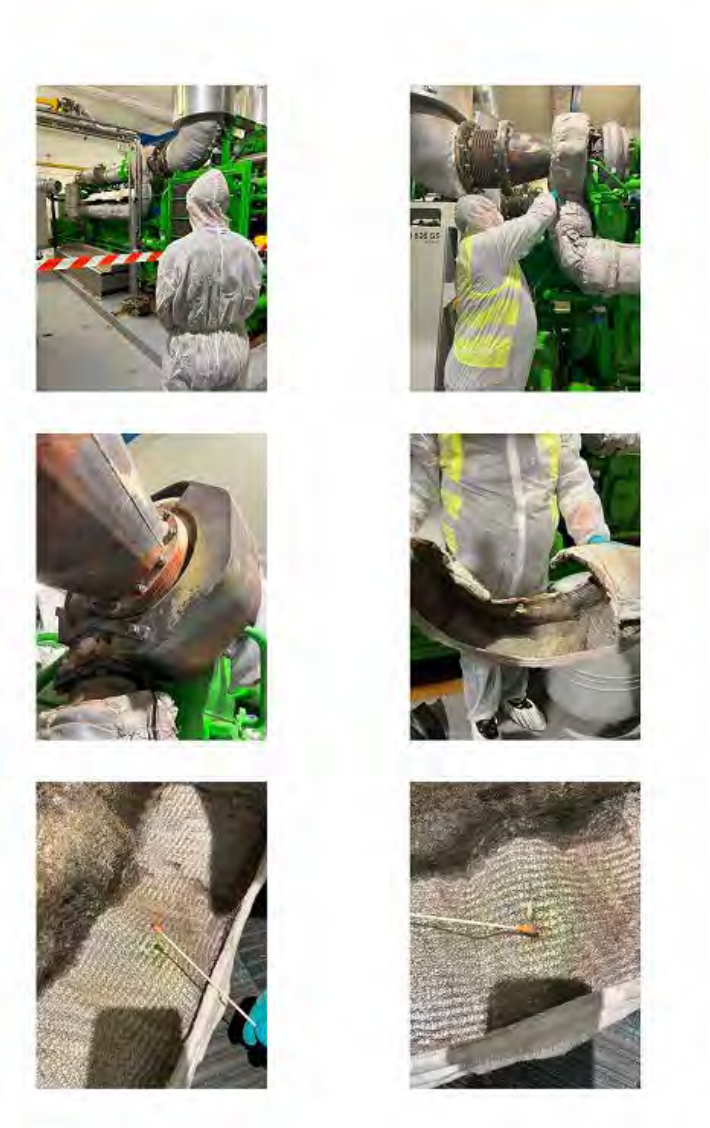


Boat and industrial engines (Fig. 27-29):

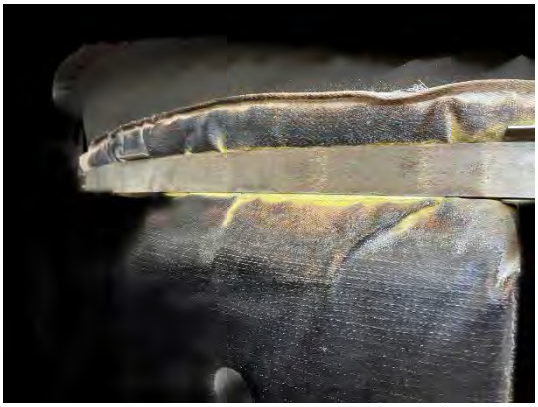
Gas engines (combined heat and power plants; Fig. 36-37, 39-40):

Glass fibres removed from the insulating elements also show chromate contamination, although no yellowish dusts are visible. (Fig. 42)

Fig. 43 shows impressions from a combined heat and power plant. After removing the insulation elements that were in use, very large exposures of calcium chromate can be seen:



Heat-dissipating holders/carriers, which are directly connected to the hot part, conduct the object temperature directly to the outside and heat even the surface of the insulating elements to such an extent that carcinogenic alkali metal particles can form on the outside of the insulation.
/Alkaline earth metal chromates (depending on the alkali or alkaline earth metal content of the insulating material (Fig. 41)



The following pictures show that chromate formation, especially with vibrating parts, is not a rare problem, but is to be expected almost everywhere where heat, chromium compounds and oxides of alkali and/or alkaline earth metals come into contact; this problem occurs on a large scale and worldwide!

Once you have internalised and understood the formation process, you will always find a chromium alkali/alkaline earth metal and a heat source when chromium (VI) compounds occur, especially calcium chromate, at first glance, but sometimes only at second glance.

Calcium and/or sodium chromate do not occur independently in nature, they are ALWAYS the result of a preceding thermochemical reaction!

High calcium chromate concentration on almost all hot engine parts of a gas engine (Fig. 44)

Chapter 5
Differentiation between large power plant/cogeneration plant

While the thermally insulated areas in large power plants are located in spacious buildings, combined heat and power plants are often installed in containerised rooms.

Although chromate formation is a given wherever hot parts containing chromium are insulated with insulation materials containing alkali or alkaline earth metal, the concentrated air pollution from chromates will be different than in smaller and narrower rooms due to the high and wide spaces.

In combined heat and power plants, which are often built in closed containers, it can happen that the workplace limit value, which has been set at just 1 microgram/m³ for chromates and thus almost all chromium (VI) compounds, is often exceeded ten thousand times over!

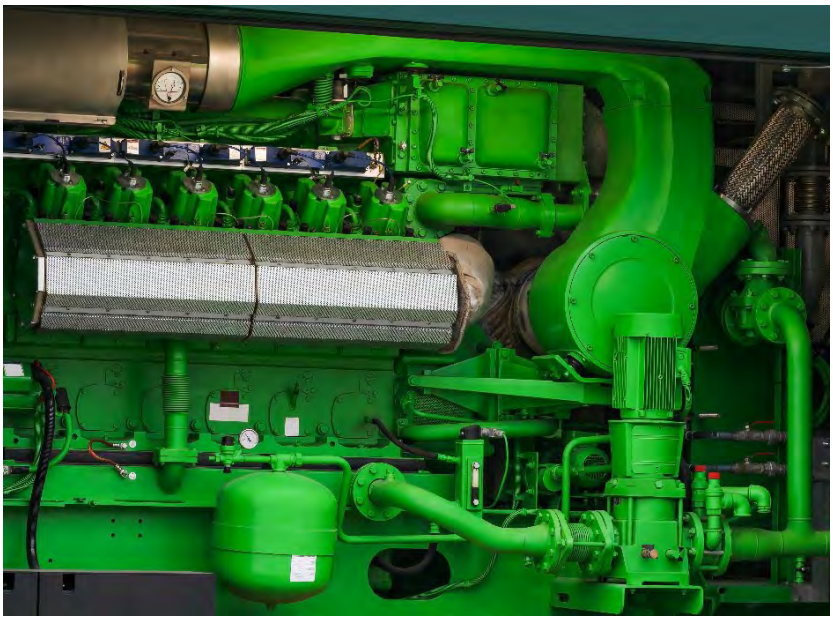


Fig.45: Gas engine in a narrow container installation (combined heat and power plant)

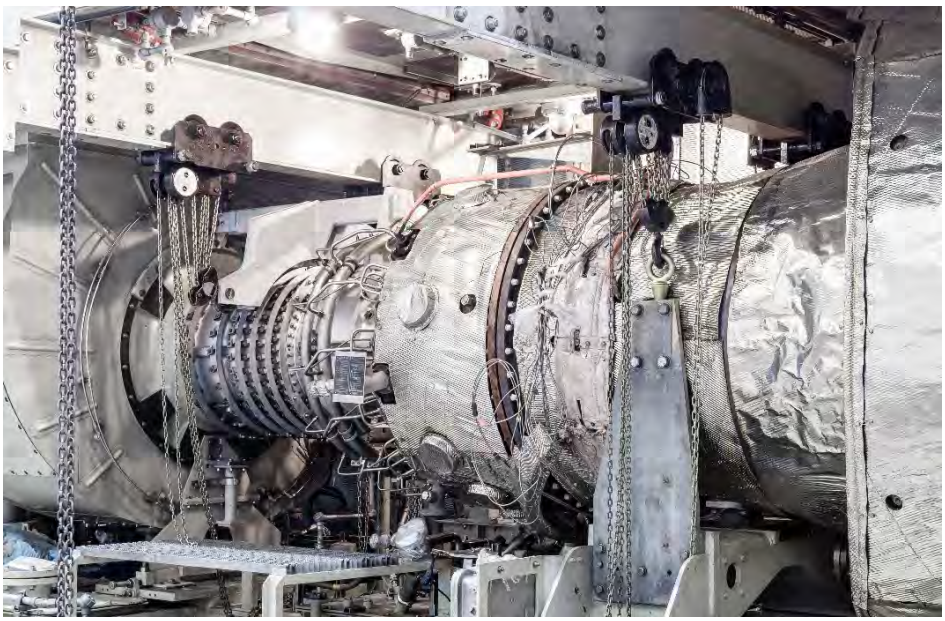


Fig.46: Gas turbine in the building (large power plant)

Chapter 6
Chromates in the workplace

Chromates can be formed wherever there are thermally insulated hot parts and the information provided by many manufacturers, who are now somewhat more open about the problem and admit the formation of chromates at least "under certain circumstances" "in small quantities in isolated systems", constantly endeavour to point out that the chromates are only released when the insulating elements are handled.

Unfortunately, these statements are wrong!

If chromates are trapped between the thermal insulation and the hot part, the release of carcinogenic dust at the workplace during engine or turbine operation is virtually pre-programmed.

The so-called "thermodynamics" or "heat conduction" alone (the flow of thermal energy (heat) due to a temperature difference) and according to the second law of thermodynamics, the flow of heat always takes place in the direction of lower temperature.

In this case, experts refer to the motor or turbine as "blowing", also for the simple reason that the insulating elements do not form a hermetic jacket and there are gaps between the individual elements.

Fig. 47 clearly shows how yellowish chromates have already formed on burst seams of the outer insulating fabric layer, but the image also shows the possibility of pure heat leakage in the transition area between the metallic and textile insulation, which is insufficiently insulated. Fig. 48 shows fibre abrasion on the turbocharger insulation, the loosened fibres can be found at the top left of the motor frame.

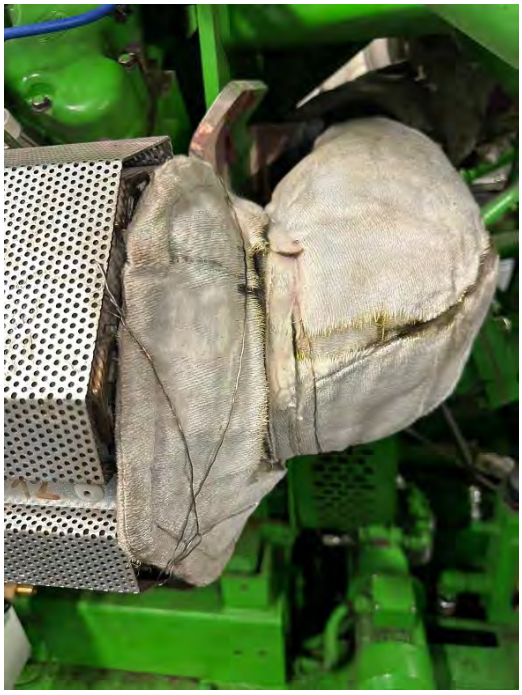


Fig.47: Chromates on the surface of textile insulationsFig.

48: Thermodynamic fibre turbulence

As can be clearly seen in Fig. 49, chromate contamination is present everywhere on the CHP plant; in Germany alone, over 10,000 CHP plants are in operation!

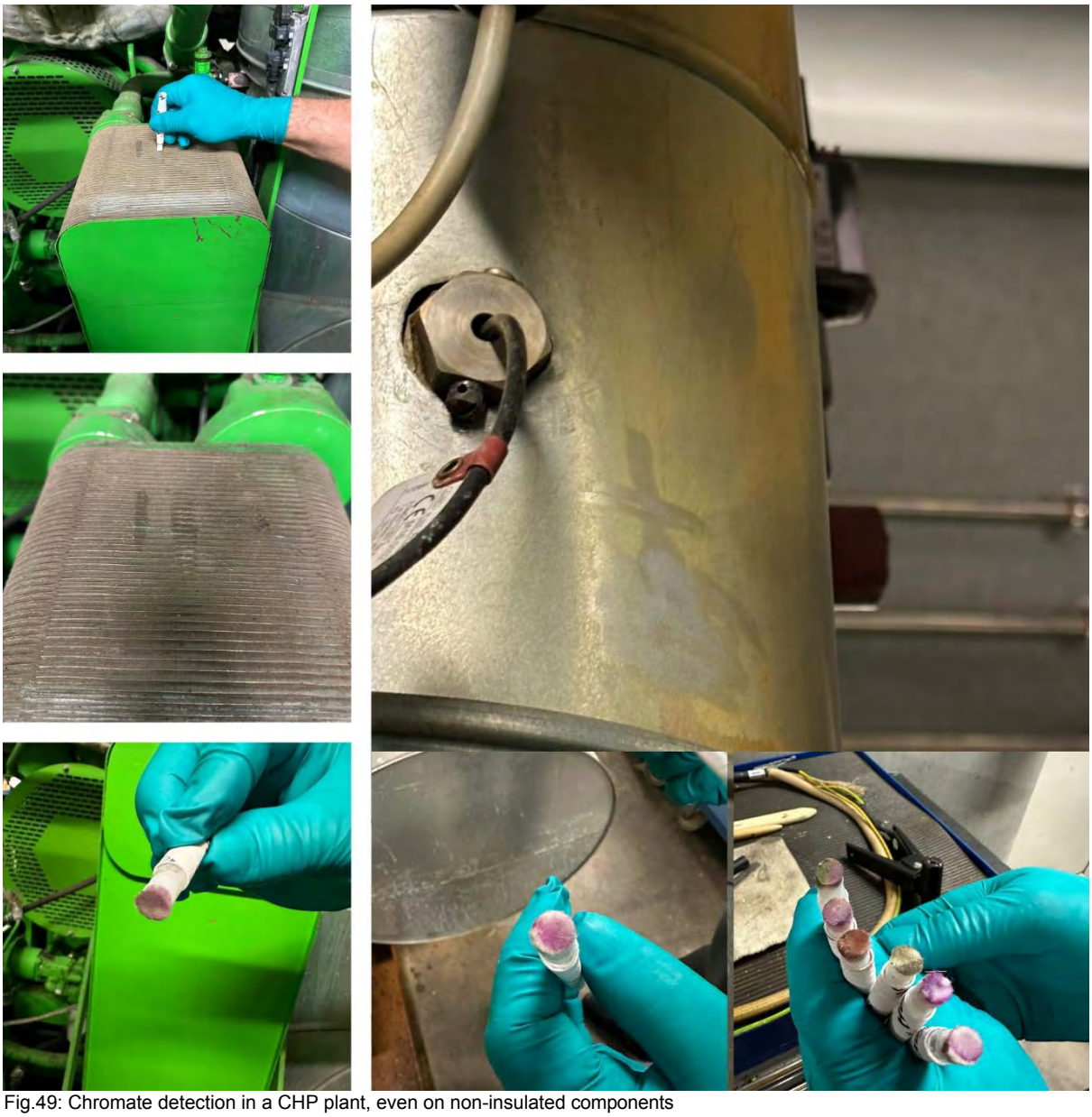


Fig.49: Chromate detection in a CHP plant, even on non-insulated components

Chapter 7
Insufficient information from manufacturers

The formation of calcium chromate when using auxiliary or operating materials containing calcium that come into contact with components containing chromium at temperatures above 250°C is known to manufacturers and operators.

Chromates were found on screws, nuts and all kinds of flange connections after a certain period of time, particularly in the case of so-called "assembly pastes" containing calcium. Since sealing material containing calcium is also used between two bolted components or in gaps, it is logical that chromates, especially calcium chromate, are also deposited in these areas.

However, the manufacturers of such pastes quickly recognised and understood the problem and reacted just as quickly.

The two market leaders "Molyslip" and "DuPont" have already launched calcium-free assembly pastes on the market in 2021/2022 and have partially withdrawn their calcium-containing pastes.

Engine manufacturers and service companies have accepted the changes and implemented them in the meantime.

MOLYSLIP

MOLYSLIP BRINGT KALZIUMFREIE ANTI-SEIZE-REIHE AUF DEN MARKT, UM NEUE INDUSTRIESTANDARDS FÜR GESUNDHEIT UND SICHERHEIT ZU ERFÜLLEN

Der globale Schmierstoffführer Molyslip hat alle Kalziumverbindungen aus seinem gesamten Sortiment an Anti-Seize-Schmiermitteln entfernt, um sicherzustellen, dass seine Produkte für den Bediener in allen Umgebungen sicher sind*.

Durch die Entfernung von Kalzium aus Ceramslip und Ferroslip ist Molyslip das erste Unternehmen, das ein 100 % kalziumfreies Anti-Seize-Sortiment anbietet. Der Schritt beseitigt jedes Risiko der Exposition gegenüber Karzinogenen aus Anti-Seize-Verbindungen, die bei Hochtemperatur-Betriebsbedingungen gefunden wurden, während die hohe Leistung, die Molyslip-Kunden mit seinen Produkten verbinden, beibehalten wird.

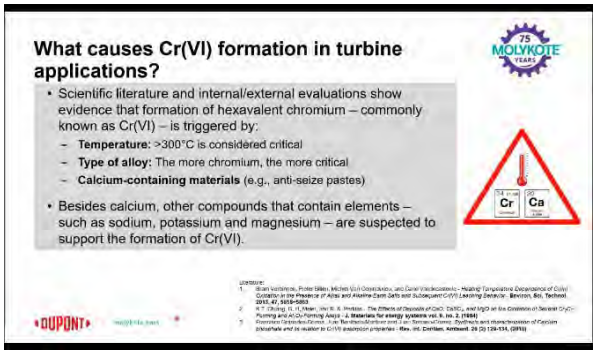
„Unser Hauptziel ist immer die Sicherheit unserer Kunden." Andrew Cunningham, kaufmännischer Leiter „Wir bei Molyslip haben das große Glück, hochmoderne Labors mit Chemikern zu haben, die auf dem Gebiet der Schmierstofftechnologie führend sind. Wir können daher schnell reagieren, wenn Sicherheitsprobleme wie Cr(VI) auftauchen. Unsere Prioritäten sind zweifellos – das bestmögliche Produkt für den Job, aber niemals auf Risiko für unsere Benutzer." Er fügt hinzu: „Viele Anti-Seize-Schmiermittel auf dem Markt enthalten immer noch Kalzium, aber ich bin stolz darauf, dass unsere Kunden unser Molyslip-Sortiment beruhigt verwenden können."

Calcium wurde traditionell als Antihaftfeststoff bei hoher Temperatur verwendet. Sowohl Ceramslip als auch Ferroslip profitieren von der Änderung der Formel, bei der Kalzium durch neuere Additivechnologie ersetzt wurde, was unseren Produkten eine höhere Leistungsfähigkeit verleiht.

* Wie im jüngsten Safety Bulletin von Energy UK hervorgehoben, kann krebserregendes sechswertiges Chrom Cr(VI) auftreten, wenn 3 spezifische Parameter gleichzeitig erfüllt sind:

Calciumbasiertes Produkt ist vorhanden
Temperaturen über +300 °C
Chromstahl ist vorhanden
Energy UK, Sicherheitsbulletin für sechswertiges Chrom, September 2019

Fig. 50: Information letter from MolyslipFig. 51



What causes Cr(VI) formation in turbine applications?

- Scientific literature and internal/external evaluations show evidence that formation of hexavalent chromium – commonly known as Cr(VI) – is triggered by:
  - **Temperature:** >300°C is considered critical
  - **Type of alloy:** The more chromium, the more critical
  - **Calcium-containing materials** (e.g., anti-seize pastes)
- Besides calcium, other compounds that contain elements – such as sodium, potassium and magnesium – are suspected to support the formation of Cr(VI).

75 MOLYKOTE YEARS

Cr Ca

DUPONT

: Chromate formation in assembly pastes (Dupont)

In December 2023, MAN informs its customers about the "...presence of calcium chromate ... in the exhaust tract, exhaust gas aftertreatment, and components for insulation and heat protection..." (*Annex CAA_008*)

It goes on to say, "The dust or deposits are caused by chromium-containing stainless steels in contact with calcium-containing substances such as insulating materials or anti-seize pastes and high thermal loads."

We read on:

"Under certain conditions, calcium chromate CaCrO4 can be formed from existing components

during operation. These are

· Cr-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

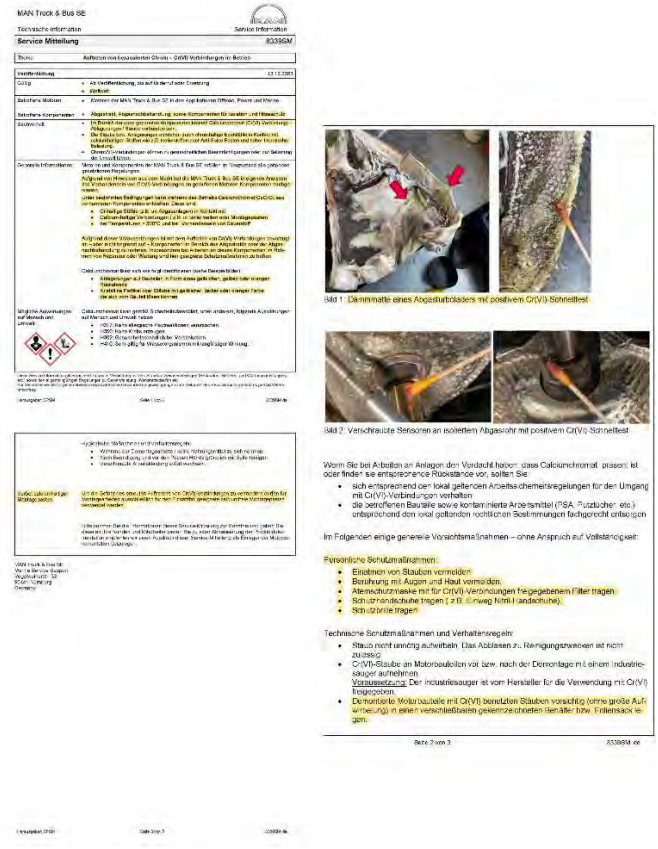
Due to these conditions, the occurrence of Cr(VI) compounds is to be expected preferably on - but not limited to - components in the area of the exhaust tract or exhaust gas aftertreatment.

Suitable protective measures must be taken, especially when working on these components during repair or maintenance.

Calcium chromate can be identified as follows (see example pictures):

· Deposits on components in the form of a yellowish, yellow or orange residue

· Crystalline particles or dusts with a yellowish, yellow or orange colour that can detach from the component"


MAN Truck & Bus SE

Service Mitteilung 8339SM

Bild 1: Dämmmatte eines Abgasturboladers mit positivem Cr(VI) Schnelltest

Bild 2: Verschraubte Sensoren an isolierten Abgasrohr mit positivem Cr(VI) Schnelltest

Wenn Sie bei Arbeiten an Anlagen den Verdacht haben, dass Calciumchromat präsent ist oder finden sie entsprechende Rückstände vor, sollten Sie:

- sich entsprechend den lokal geltenden Arbeitsschemeisregelungen für den Umgang mit Cr(VI)-Verbindungen verhalten
- die getroffenen Bauteile sowie kontaminierte Arbeitsmittel (PSA, Putztücher etc.) entsprechend den lokal geltenden rechtlichen Bestimmungen fachgerecht entsorgen

Im Folgenden einige generelle Vorsichtsmaßnahmen – ohne Anspruch auf Vollständigkeit:

Persönliche Schutzmaßnahmen:

- Einatmen von Stauben vermeiden
- Berührung mit Augen und Haut vermeiden
- Atemschutzmaske mit für Cr(VI)-Verbindungen freigegebenem Filter tragen
- Schutzhandschuhe tragen (z.B. Einweg Nitril Handschuhe).
- Schutzbrille tragen

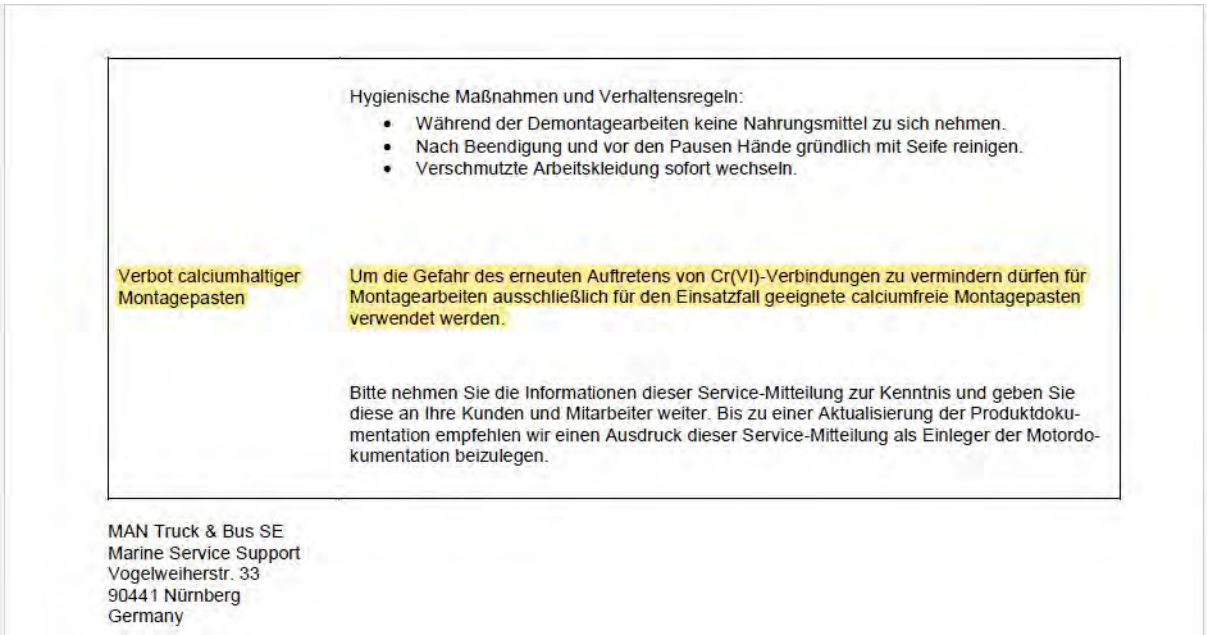
Technische Schutzmaßnahmen und Verhaltensregeln:

- Staub nicht unnötig aufwirbeln. Das Ablasen z.. Reinigungszwecken ist nicht zugelassig
- Cr(VI)-Stäube an Motorbauteilen vor bzw. nach der Demontage mit einem Industriesauger aufnehmen.
  Voraussetzung: Der Industriesauger ist vom Hersteller für die Verwendung mit Cr(VI) freigegeben.
- Demontierte Motorbauteile mit Cr(VI) beinhalten Stäuben vorsichtig (ohne große Aufwirbelung) in einer verschließbaren gekennzeichneten Behälter bzw. FolienSack legen.

Fig.52: Warning about CaCrO4, MAN SE

The warning message concludes with the request:

*"In order to minimise the risk of re-occurrence of Cr(VI) compounds, only **calcium-free assembly pastes** suitable for the application may **be used** for assembly work."*



Hygienische Maßnahmen und Verhaltensregeln:

- Während der Demontagearbeiten keine Nahrungsmittel zu sich nehmen.
- Nach Beendigung und vor den Pausen Hände gründlich mit Seife reinigen.
- Verschmutzte Arbeitskleidung sofort wechseln.

Verbot calciumhaltiger Montagepasten

Um die Gefahr des erneuten Auftretens von Cr(VI)-Verbindungen zu vermindern dürfen für Montagearbeiten ausschließlich für den Einsatzfall geeignete calciumfreie Montagepasten verwendet werden.

Bitte nehmen Sie die Informationen dieser Service-Mitteilung zur Kenntnis und geben Sie diese an Ihre Kunden und Mitarbeiter weiter. Bis zu einer Aktualisierung der Produktdokumentation empfehlen wir einen Ausdruck dieser Service-Mitteilung als Einleger der Motordokumentation beizulegen.

MAN Truck & Bus SE
Marine Service Support
Vogelweiherstr. 33
90441 Nürnberg
Germany

Fig.52: MAN warning to use only calcium-free assembly paste.

The user is faced with the question of why there is a ban on assembly pastes containing calcium, but why insulation containing calcium should continue to be used.

Without wishing to minimise the danger posed by chromate-containing screw connections, what is the relationship between partial and low-dust-intensity stoving and easily released inhalable dusts?

Chromates resulting from the use of calcium-containing pastes can be easily localised, which is unfortunately not the case for calcium-containing isolations (extensive exposure and contaminated fibre dusts / local deposits).

Unfortunately, there are no recommendations for overcoming the much larger problem. One of the largest manufacturers of CHP engines, takes a slightly different approach, but also has no solution to prevent the formation of dangerous chromates.

The engine manufacturer from confirms the formation of chromate through the already thermochemical high oxidation of chromium (III) compounds to the carcinogenic chromium (VI) compound calcium chromate:

"*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 be found in very low concentrations as a yellowish powder on the relevant motor parts or in the insulation material. Cr-6 is present in the form of a non-fugitive powder.*"

With the illustrations on the so-called "technical instructions", the engine manufacturer contradicts itself, the "low concentrations" of yellow powder are more than clearly recognisable, both on the inside of the insulating element and on the outside of the insulated component.

4 Zusätzliche Informationen

Allgemeine Hinweise

Das Isolationsmaterial an Gasmotoren unterliegt aufgrund der mechanischen und thermischen Beanspruchung im Motorbetrieb einem Alterungsprozess. Dies zeigt sich zum einen daran, dass bei der Demontage von Isolationsmaterial nach längerem Betrieb feine Glasnadeln an den entsprechenden Motorteilen (z.B. Abgasstrang, Turbolader, ...) sichtbar werden. Zum anderen kann es im Laufe der Zeit zu chemischen Reaktionen kommen, die zur Bildung des Gefahrstoffes Chrom-6 führen können.

Chrom-6 (Chrom in der Oxidationsstufe 6, kurz Cr-6) bildet sich aus chromhaltigen Stählen in Gegenwart von Kalzium (z.B. aus dem Isolationsmaterial) und Sauerstoff bei Temperaturen über 400 °C. Cr-6 kann in sehr geringen Konzentrationen als gelbliches Pulver auf den betreffenden Motorenteilen oder im Isolationsmaterial gefunden werden. Cr-6 liegt in Form eines nicht flüchtigen Pulvers vor.

Um die Belastung der Atemluft möglichst gering zu halten, müssen die in dieser Anweisung beschriebenen Arbeitsweisen genau eingehalten werden (z.B. das Aufwirbeln von Stäuben bei Arbeiten mit gebrauchtem Isolationsmaterial muss unbedingt verhindert werden).

Cr-6 Ablagerungen auf einem Kompensator (gelbliches Pulver)

Cr-6 Ablagerungen im Isolationsmaterial (gelbliches Pulver)

Alle sechswertigen Chromverbindungen sind toxisch und auch krebserregend.

Fig.54: Calcium chromate on components and insulating elements

The following information is therefore more than accurate:

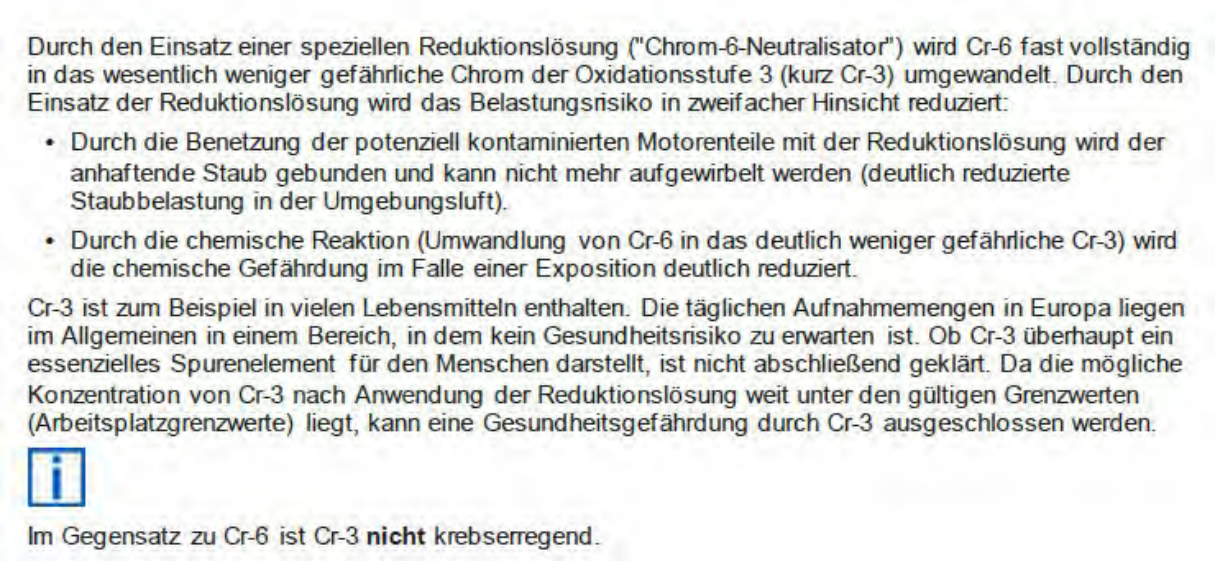
"In order to minimise exposure to breathing air, the working methods described in these instructions must be strictly adhered to (e.g. the stirring up of dust when working with used insulation material must be avoided at all costs)."

In the further course of the instructions to end users, the so-called "neutralisation" of chromates is presented as if there were nothing more normal and commonplace than neutralising carcinogenic and extremely environmentally toxic heavy metal compounds with the aid of a spray bottle.

Chapter 8) "Decontamination" deals with this topic in more detail.

The "instructions", which can certainly be considered negligent, are in stark contrast to the applicable occupational health and safety regulations, in particular on the basis of EU Directive 2004/37/EC, which is the basis for the German Hazardous Substances Ordinance (GefStoffV), as well as the nine(!) applicable "Technical Guidelines for Hazardous Substances" (TRGS) with regard to calcium chromate.

While all workplace safety regulations stipulate that work processes and measures must be designed in such a way that the risks for directly and indirectly affected employees and external persons are not only minimised, but at best eliminated, and there is also an obligation to carry out a substitution test as part of a prescribed risk assessment, the recipient of the guide gets the feeling that measures that are a little reminiscent of daily window cleaning are completely sufficient to achieve the best working conditions again:


Durch den Einsatz einer speziellen Reduktionslösung ("Chrom-6-Neutralisator") wird Cr-6 fast vollständig in das wesentlich weniger gefährliche Chrom der Oxidationsstufe 3 (kurz Cr-3) umgewandelt. Durch den Einsatz der Reduktionslösung wird das Belastungsrisiko in zweifacher Hinsicht reduziert:

- Durch die Benetzung der potenziell kontaminierten Motorenteile mit der Reduktionslösung wird der anhaftende Staub gebunden und kann nicht mehr aufgewirbelt werden (deutlich reduzierte Staubbelastung in der Umgebungsluft).
- Durch die chemische Reaktion (Umwandlung von Cr-6 in das deutlich weniger gefährliche Cr-3) wird die chemische Gefährdung im Falle einer Exposition deutlich reduziert.

Cr-3 ist zum Beispiel in vielen Lebensmitteln enthalten. Die täglichen Aufnahmemengen in Europa liegen im Allgemeinen in einem Bereich, in dem kein Gesundheitsrisiko zu erwarten ist. Ob Cr-3 überhaupt ein essenzielles Spurenelement für den Menschen darstellt, ist nicht abschließend geklärt. Da die mögliche Konzentration von Cr-3 nach Anwendung der Reduktionslösung weit unter den gültigen Grenzwerten (Arbeitsplatzgrenzwerte) liegt, kann eine Gesundheitsgefährdung durch Cr-3 ausgeschlossen werden.

Im Gegensatz zu Cr-6 ist Cr-3 **nicht** krebserregend.

Fig.55: "Neutralisation of Cr6"

"Almost completely" is just as vague as "significantly reduced" and the food information on chromium (III) compounds ignores the fact that chromium (III) compounds in the industrial sector have little in common with the trace elements of everyday life and that work with chromium (III) compounds must be carried out "drain-free" and must not be disposed of in normal waste or in normal waste water.

As with MAN, Innio also lacks the reference to substitution testing of the chromate-causing source (calcium-containing insulation), "Worn or damaged insulation material should be replaced as soon as possible", but even the reuse of contaminated insulation elements is not necessarily discouraged, although anyone who now understands the formation of calcium chromate when using calcium-containing insulation elements should quickly realise that the renewed (and presumably increased) formation of chromate occurs again.

The "neutralisation" may therefore be conceded at most to alleviate the working conditions a little, but it does not in any way comply with the provisions of the above-mentioned EU directive regarding measures to prevent hazardous pollutants in the workplace.

As part of a network search on the occupational exposure limits for chromium compounds, we read, among other things

"AMENDMENT OF **THE OCCUPATIONAL EXPOSURE LIMIT FOR CHROMIUM COMPOUNDS ACCORDING TO ACGIH**

The American Conference of Governmental Industrial Hygienists (ACGIH) announced in March 2018 that it had adopted its proposed change to the occupational exposure limit for chromium compounds. The change was published in the 2018 edition of the publication Occupational Exposure Limits and Biological Exposure Indices (BEIs). The new OEL is 0.0002 mg/m3 for inhalable hexavalent chromium compounds, which is a 250-fold reduction from the previous OEL of 0.05 mg/m3. The new occupational exposure limit value for chromium compounds contains a limit value of 0.003 mg/m3 for inhalable chromium(III) compounds, which represents a 167-fold reduction compared to the previous occupational exposure limit value of 0.5 mg/m3."

Despite all efforts to argue in favour of compliance with occupational exposure limits, one point in particular must not be forgotten:

"Compliance with the occupational exposure limit value (OEL) does not release you from the minimisation requirement of the Hazardous Substances Ordinance (GefStoffV). The aim of occupational health and safety is to reduce or eliminate exposure to hazardous substances as far as possible and not just to comply with the OEL." (Source: kom.net - Arbeitsschutz NRW)

According to TRGS 900 (Annex: CAA011) and TRGS 910 (Annex: CAA012) the following occupational exposure limits apply:

Calcium oxide: 1 mg/m³

Chromium (III) compounds: 2mg/m³

Chromium (VI) compounds: 1µg/m³

Although "neutralisation" converts Cr (VI) compounds into less hazardous Cr (III) compounds, the source of the formation of carcinogenic dusts is the thermochemical reaction of chromium (III) compounds with calcium oxides.

Just how little the gas engine manufacturer trusts its own statements is shown by the instruction that all work before and after dismantling should only be carried out in full protective clothing:

5 Arbeitsanweisung

Vorgeschriebene persönliche Schutzausrüstung für Arbeiten mit Cr-6 (PSA Cr-6)

- Schutzmaske (staubdichte Atemschutzmaske, FFP-3)
- Schutzhandschuhe
- Einweg-Overall
- Schutzbrille

Anmerkung zu den Schutzhandschuhen

Für die (De-) Montagearbeiten müssen die Handschuhe einen mechanischen Schutz aufweisen. Der Chemikalienschutz ist in diesem Fall von untergeordneter Bedeutung. Um Kontaminationen zu vermeiden, müssen diese Handschuhe vor Beginn der Arbeiten an den gereinigten Maschinenteilen gegen neue Schutzhandschuhe ausgetauscht und entsorgt werden.

Demontage von gebrauchtem Isolationsmaterial

Vorgeschriebene persönliche Schutzausrüstung (PSA): PSA Cr-6

Bei der Demontage von gebrauchtem Isolationsmaterial ist darauf zu achten, dass eine Staubbildung so weit wie möglich vermieden wird. Das Isolationsmaterial muss vorsichtig entfernt werden, um Staubbildung zu vermeiden. Um die Staubbildung zu reduzieren, kann das Isolationsmaterial bereits während der Demontage mit einer Reduktionslösung besprüht werden.

Behandlung des Isolationsmaterials bei geplanter Wiederverwendung

Vorgeschriebene persönliche Schutzausrüstung (PSA): PSA Cr-6

Wenn das Isolationsmaterial nach Abschluss der Wartungsarbeiten wiederverwendet werden soll, wird das Material abgelegt und großflächig mit Reduktionslösung besprüht. Anschließend wird das Material zusammengelegt, in einen großen PE-Sack verpackt und bis zur Wiederverwendung idealerweise außerhalb des Arbeitsbereichs gelagert.

Soll das Isolationsmaterial entsorgt werden, ist das gleiche Verfahren wie oben beschrieben anzuwenden. Der PE-Sack muss gemäß den lokalen Vorschriften als Abfall gekennzeichnet werden.

Die Bodenfläche, auf der das Isolationsmaterial zur Behandlung abgelegt wurde, muss mit feuchten Tüchern gereinigt werden.

Reinigung der kontaminierten Motorteile

Vorgeschriebene persönliche Schutzausrüstung (PSA): PSA Cr-6

Alle potenziell kontaminierten Motorenteile werden mit der (Druckpump-) Sprühflasche ausreichend mit der Reduktionslösung benetzt. Nach einer Einwirkzeit von 15 Minuten werden die Teile mit feuchten Tüchern gereinigt. Diese Tücher können über den Restmüll entsorgt werden.

Beseitigung von Staub, der bei der Demontage von Isolationsmaterial entsteht

Vorgeschriebene persönliche Schutzausrüstung (PSA): PSA Cr-6

Haben sich bei der Demontage des Isolationsmaterials Staub oder Glasfasernadeln in der unmittelbaren Umgebung abgesetzt, werden diese ebenfalls mit Reduktionslösung benetzt und anschließend mit feuchten Tüchern aufgewischt. In diesem Fall muss die Reaktionszeit nicht abgewartet werden. Soll der Staub mit einem Staubsauger aufgesaugt werden, muss dieser der Klasse H entsprechen.

Fig.56: No maintenance work without protective clothing

How contradictory all well-intentioned advice is is shown in particular by the point

"Treatment of the insulation material with planned reuse

Mandatory personal protective equipment (PPE): PPE Cr-6

If the insulation material is to be reused after the maintenance work has been completed, the material is laid down and sprayed with reducing solution over a large area. The material is then folded up, packed in a large PE bag and stored, ideally outside the work area, until it is reused.

If the insulation material is to be disposed of, follow the same procedure as described above. The PE bag must be labelled as waste in accordance with local regulations.

The floor surface on which the insulation material was placed for treatment must be cleaned with damp cloths."

On the one hand, the dismantled parts should therefore be well packaged and stored outside the workplace, if possible, after they have been "sprayed" beforehand and thus, according to the company, "almost completely" "significantly reduced", i.e. decontaminated, but on the other hand, the same material can also be reused, but still wearing full protective clothing.

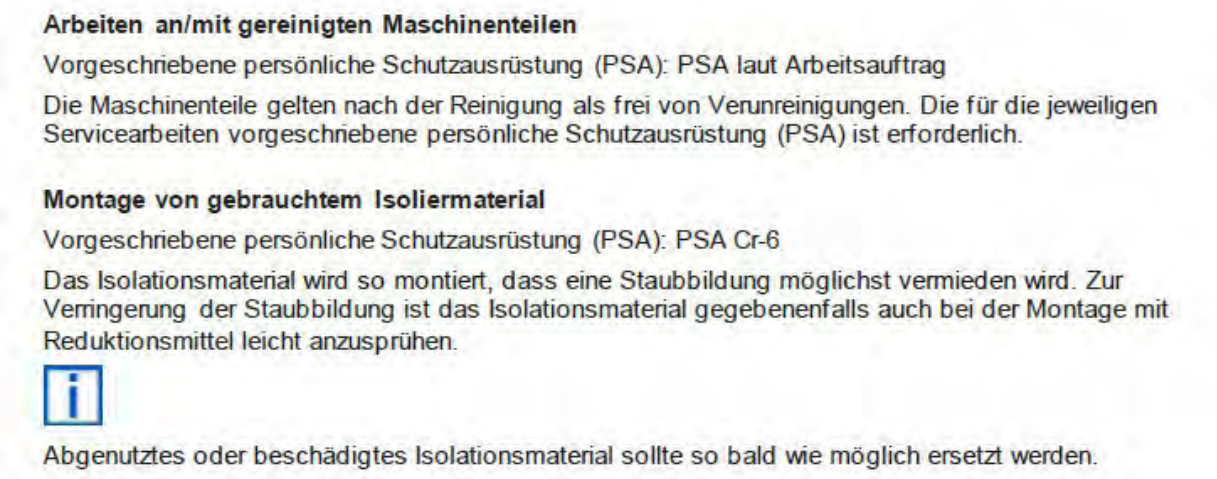


Fig. 57: Reassembly of chromate-contaminated parts

Insulation elements that may still be partially contaminated are therefore reassembled on extensively cleaned hot engine parts. The elements still contain calcium, are no longer as resistant due to ageing and use and are once again exposed to chromium (III) compounds in the alloys.

To make matters worse:

On the insides of the used insulation parts there are now even o!ene chromium(III) compounds from the "neutralisation", calcium oxide is still contained in the insulation material to 20% and the renewed formation of calcium chromate will repeat itself.

The objective of the Hazardous Substances Ordinance is not achieved!

The American engine manufacturer **Caterpillar** also **reports chromate deposits** on its website or offers the download (attachment: *CAA013 (English)/CAA014(German)*) of the warning notices (for Germany: Zeppelin):

Illustration 1 g06515618
Exhaust system examples of yellow residual deposits

If such yellow residual deposits are found on the engine, engine component parts, or associated equipment or package, Caterpillar recommends following local regulations and guidelines and good hygiene and safe work practices. Precautionary examples are listed below:

- Avoid creation of airborne dust containing the yellow deposits. If generation of airborne dust cannot be avoided, it is advisable to use a face shield or goggles and a negative pressure half mask respirator with P-100 cartridges (or equivalent).
- Wear personal protective equipment to prevent skin and eye exposure. Wear cut proof nitrile gloves and a disposable protective suit.
- Wash hands and face with soap and water prior to eating, drinking, smoking or during rest room breaks to prevent ingestion of any yellow powder.
- Avoid release of the residual deposits to the environment. All waste generated during the repair process including cleaning towels, and used Personal Protective Equipment (PPE) need to be collected and stored in a proper container pending disposal as hazardous waste.

In the event that hexavalent chromium is discovered, Caterpillar recommends following all local guidelines and wearing the correct PPE during the decontamination and removal process.

There are multiple methods of cleaning material that can be considered. Once such method is to utilize a solution consisting of 10% citric acid, 10% ascorbic acid and 80% distilled water to convert the hexavalent chromium powder to a trivalent chromium state.

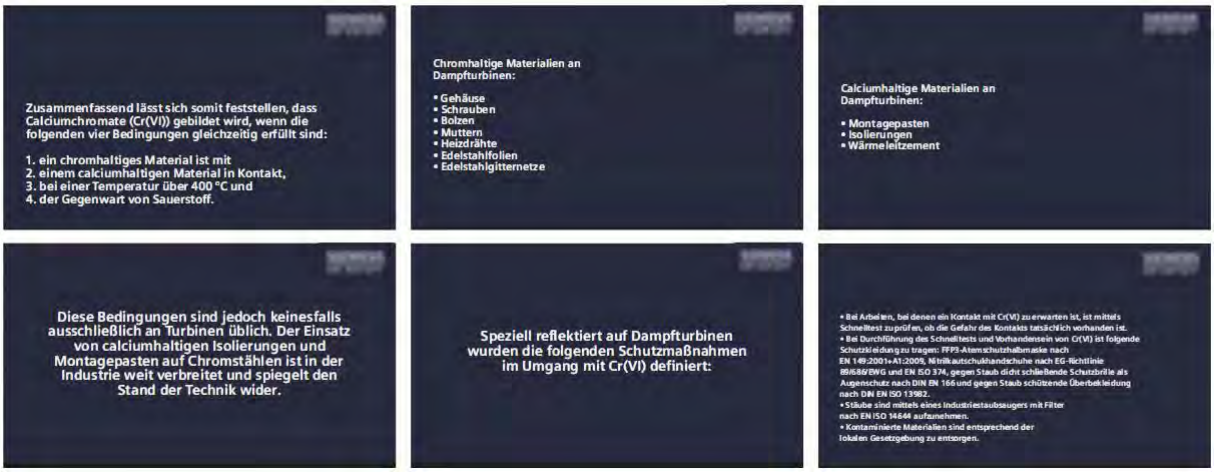
Special care should be taken to prevent agitating the powder and creating airborne dust.

Fig.58: *Caterpillar notice "Chromium (VI)"*

The American company, which also owns the **turbine manufacturer SOLAR** and whose **construction machinery** is known worldwide, produces **gas, diesel and, more recently, H2-ready engines, all of which are equipped with calcium-containing insulation systems**.

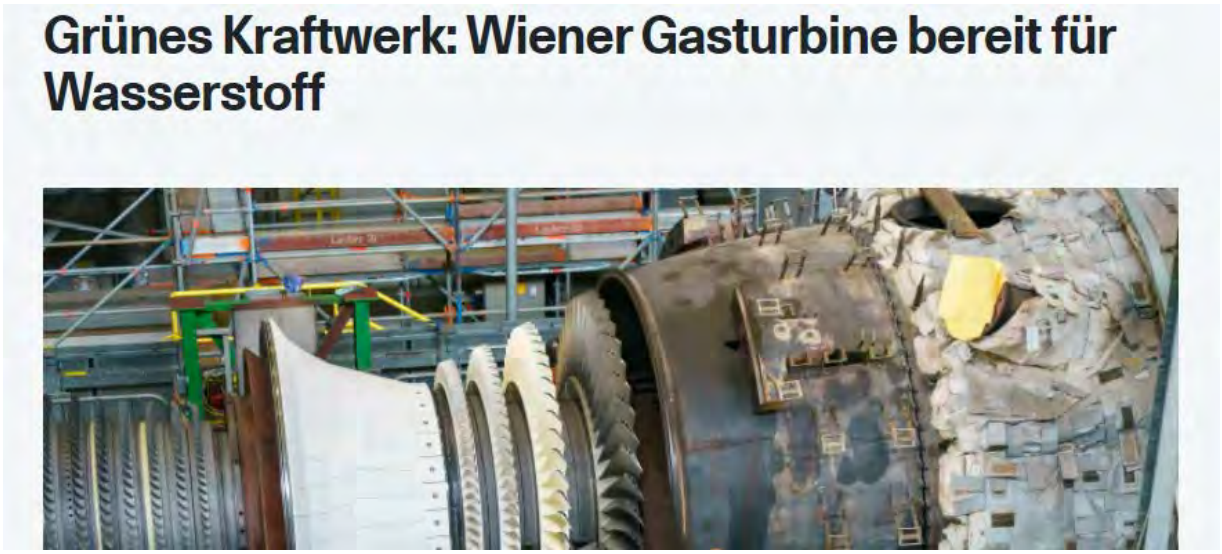
Textile systems have the same audau as already described, metallic systems have a modular structure, here the abrasion of the inner **protective foils made of stainless steel (containing Cr3)**, which encase **different insulating materials (containing CaO)**, inevitably leads to the **formation of the hexavalent chromium compound calcium chromate**.

In autumn 2021, German **turbine manufacturer Siemens Energy** will be publicising the **chromate problem in turbine construction** at a power plant colloquium:



The sentence "**However, these conditions are by no means exclusive to turbines. The use of calcium-containing insulations and assembly pastes on chromium steels is widespread in the industry and reflects the state of the art."** there is nothing to add.

We recall Figure 16 and take a look at the quantities of calcium-containing insulation mats used:



It is not uncommon for thousands of so-called "insulating mattresses" to be in use in large power plants, and each mattress consists of calcium-containing fabrics that are in direct or indirect contact with hot parts containing chromium.

An additional complicating factor in turbine construction is that the energy generators also have a so-called "trace heating system", which is attached to the chromium-containing housing with calcium-containing "heat conductive cement".

Even if non-chromium-containing hot parts are insulated with calcium-containing insulating materials, the formation of calcium chromate cannot be ruled out, as the materials already containing calcium are often reinforced with stainless steel wire. The calcium-containing yarns and fibres are twisted around chromium-containing wires (cores) to give the fibres more stability.

Knitted wire mesh is also used to absorb vibrations in order to reduce abrasion of the more sensitive yarns and fibres.

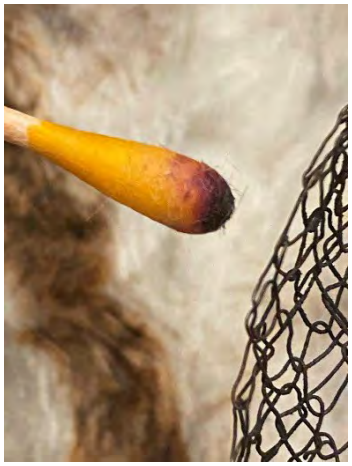


Fig. 60-64:
Chromate deposits on insulating mattresses

From the previous pages it is therefore recognisable that - in very simplified terms

calcium-containing products such as assembly pastes or thermal insulation, i.e. in contact with hot parts containing chromium (motors, turbines, exhaust pipes and systems, construction machinery, aggregates and other machines in the case of insulation; screws, nuts, screw connections, flange connections in the case of assembly pastes) at operating temperatures of over 250°C, preferably in the temperature range up to 750/800°C, lead to the formation of the carcinogenic and environmentally harmful chromium (VI) compound calcium chromate!

The "market", i.e. the manufacturers of insulation materials, assembly pastes, motor and turbine manufacturers, power plant and combined heat and power plant operators, as well as insulation companies, service companies and their associated subcontractors and service providers, must come to terms with this fact.

The manufacturers of assembly pastes have understood and accepted this thermochemical effect of chromate formation and have provided short-term substitutes in accordance with EU Directive 2004/37/EC and the Hazardous Substances Ordinance (GefStoffV) (calcium-free assembly pastes).

But why is it so difficult for engine and turbine manufacturers, insulation manufacturers and insulation and service companies?

a) to proactively address the problem and to fully clarify and
b) following "salami-slicing" tactics and, above all, providing inadequate information.
c) offer substitutes?

It can be assumed that the costs for decontamination and substitution associated with the chromate problem will be in the two- if not three-digit million range, as tens of thousands of turbines, combined heat and power plants and hundreds of thousands of commercial vehicles are in operation worldwide. Only time will tell who will have to pay for these costs.

The insulation industry worldwide is considered to be slow to innovate, all market activities and production lines do not provide for material changes, the "recipe" of insulation materials has hardly changed for more than four decades.

The "no calcium - no calcium chromate" solution in turn presents the current insulation material industry with unsolvable tasks, because as described in one of the previous chapters, the addition of alkali or alkaline earth metals lowers the temperature for the melting process of today's (calcium-containing) standard insulation materials! Today's manufacturers' melting plants are simply not designed for the production of alkali or alkaline earth metal-free insulating materials; an entire supply chain that has been self-sufficient for decades, cooperating well and advising each other in the process, would collapse. All the protagonists are in a proverbial dead end. Calcium-free insulating materials and systems in particular are available, so substitution would certainly be possible, but not within the established supply chains.

Chapter 8
Substitution

Alkali and alkaline earth metal-free insulating materials solve the chromate problem in motor and turbine insulation and are available as a substitute, they just cannot be produced by the current suppliers of the insulation materials currently in use.

However, engine and turbine manufacturers receive technical "advice" from today's insulation manufacturers and are constantly told that calcium-free insulation materials are not available. This statement is false and does not represent the current state of the art; it is merely a protective assertion by today's manufacturers to (still) prevent an imminent paradigm shift.

The manufacturer of assembly pastes previously containing calcium is changing its production and mixing system slightly and will subsequently present calcium-free assembly pastes.

The manufacturers and processors of calcium-containing insulation materials cannot change the "mixing system" because - as already described - the omission of calcium and/or sodium oxide would require a different melting process.

We remember the quotes from chapter 2:

"The composition has a significant influence on the viscosity of the melt and therefore on how the glass can be processed. Depending on the composition, the glass batch is melted at 1,300°C to 1,600°C.",

the sentence:

"***The melting temperature is lowered with the alkalis, because the melting temperature of pure SiO_2 is approx. 1,700°C***."

and the explanation:

"Silicate glass is used almost exclusively in the construction industry. Mostly **soda-lime-silicate glass**, which was already used by the Egyptians and essentially consists of the basic materials **quartz sand**, **lime** and **soda.**

The molten glass is composed of silicon oxide (SiO_2), **calcium oxide** (CaO), **sodium oxide** (Na_2O), **magnesium oxide** (MgO) and aluminium oxide (Al_2O_3)."

The substitute for the above-mentioned materials must therefore not contain the alkaline and alkaline earth metal ingredients

Calcium oxide (CaO),

sodium oxide (Na_2O) and

magnesium oxide (MgO)

to prevent the formation of calcium, sodium and/or magnesium chromate, but still consist of quartz sand (SiO2) and aluminium oxide (Al2O3).

Chromium-containing stainless steel wire reinforcement with Cr2O3 is also still possible, as the chromium (III) compounds no longer have any chromate-relevant reactants due to the absence of all alkali and/or alkaline earth metal compounds!

Chapter 9
Characteristic Substitute

In 2021, the Polish company Kavarmat, which has been manufacturing textile insulation for thirty years, will present a completely alkali- and alkaline earth metal-free material called "#Bergkristall" as a high-temperature fabric or fibre mat, which consists exclusively of a mixture of quartz sand and aluminium oxide.

In contrast to today's E-glass (with 15-20% CaO content) or ECR-glass (with 20-25% CaO content), the "#Bergkristall-Gewebe" is calcium and sodium-free, temperature-resistant up to 800°C and has another advantage, because it does not itch or create dust and, as the following pictures show, is suitable for insulating engines, turbines and pipelines without alkali or alkaline earth metals:

Fig. 66/Fig.67 CHP exhaust pipe insulated calcium-free

Fig. 68/Fig.69 Exhaust pipe CHP unit insulated calcium-free

Fig. 70/Fig.71 Exhaust gas pipe CHP insulated calcium-free

The #Bergkristall product line also includes fabrics with water- and oil-repellent coatings. The impregnations of the calcium-free textile insulations are usually in shades of green to distinguish them from calcium-containing insulation systems, which usually have grey coatings.

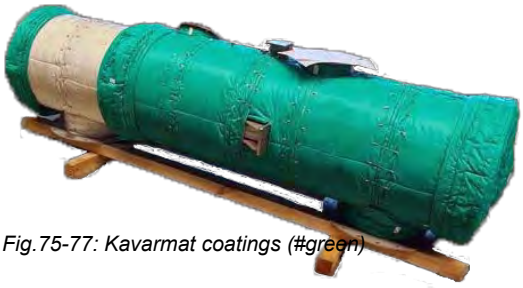


Fig.75-77: Kavarmat coatings (#green)

Parallel to the alkali- and alkaline earth metal-free insulating fabrics, quartz glass fibre mats have also been

ave also been developed in various insulation thicknesses.

Fig. 72: #Bergkristall, calcium-free

With a pure stainless steel fine mesh, which consists exclusively of woven wires, another completely alkali- alkali metal-free mesh is offered.

Fig.74: KavarSteel, stainless steel mesh

The #Bergkristall fibre is also a component of a composite felt that is marketed under the product name "#PROTEKTO".

It consists of two components; an alkali/alkaline earth metal-free fibre mat (#Bergkristall), needled with a glass fibre needle mat that was previously used as standard.

Here, the layer of #rockcrystal fibre acts as a so-called "chromate blocker", which can be mounted on stainless steel hot parts without the formation of chromates and can then be further insulated at low cost (with calcium).

Fig.78: #PROTEKTO

Fig.73: #PROTEKTO

System CAA016 - Technical features #pure by Kavarmat System CAA017

- Technical features #PROTEKTO by Kavarmat

The chromate blocker can be used in particular for multi-layer pipework insulation in power stations. Other areas of application include large-scale systems such as boilers and tanks, which were previously insulated with mineral wool containing calcium and sodium.

Since the calcium-containing insulating materials do not come into direct contact with hot parts containing chromium, as the alkali- and alkaline earth metal-free side of the material is in contact with the object, chromate formation is largely excluded, even if small quantities of calcium-containing glass fibres are present on the contact side due to needling and unrolling of the composite mat.

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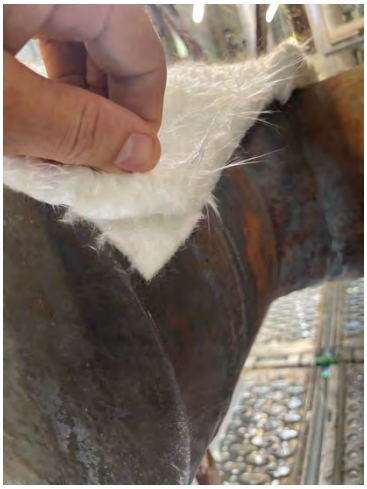


Fig. 80: Chromate blocker

Fig.79-80 clearly show the layer build-up; the fibre component, which is applied directly to the component and is free of alklai and alkaline earth metals, does not allow the formation of chromate, as it does not contain any chemical elements that can react (highly oxidise) with the chromium compounds.

The insulating felt composite can also be used where so-called "calcium silicate products" were otherwise used, by using a layer of a high-temperature insulating material, often with a calaium content of up to 40/45%, as the first insulating layer. As the contact layer is free of alkali/alkaline earth metals, it is possible to no chromate is formed.

Fig. 81: Industrial insulation with chromate blocker

To summarise, the substitution of current insulation materials containing alkali or alkaline earth metals is possible.

The new and innovative insulating materials do not contain any alkali and/or alkaline earth metal oxides, in particular calcium oxide and sodium oxide.

The assertion that there are no "calcium-free" insulation materials is therefore false, they are simply not available from the current market leaders.

The chromate problem was not treated with the necessary seriousness either by the engine and turbine manufacturers or by the producers of today's insulating materials.

It is reasonable to assume that all the protagonists involved have given each other bad advice and have probably failed to think outside the established supply chains.

In contrast to the already substituted assembly pastes, the substitution of calcium-containing insulation materials and insulation systems in particular was never seriously considered necessary.

On the one hand, the resulting chromates were kept as sulphur residues for far too long, and on the other hand, the thermochemical formation of chromate and the resulting consequences were probably not sufficiently scrutinised and taken into account.

Finally, it must be concluded that "the little yellowish powder" is not identified as the danger it really is.

Calcium chromate and sodium chromate are not only carcinogenic but also environmentally toxic substances (H350 - may cause cancer and H410 - chronically harmful to the environment with long-term effects on aquatic organisms); dangerous for humans and the environment.

It is not only the exposure risk, i.e. the inhalation or oral intake route, that must be considered, but also the dermal risk for humans - in all three forms, diseases can be triggered that may not even be associated with chromium (VI) compounds.

There is no threshold value, i.e. an acceptable exposure level, for chromates in the workplace, so - in accordance with the Hazardous Substances Ordinance, which is based on European occupational health and safety legislation, in particular EU Directive 2004/37/EC - the spread of dust and deposits must not only be minimised, but also prevented as far as possible, which is why the so-called "risk assessment" stipulates a mandatory substitution test.

If substitution is technically and economically feasible, it must be carried out in accordance with the universally applicable "S-T-O-P" principle.

It is irrelevant whether (to put it bluntly) the previous favourite supplier has a solution or not.

The previous behaviour at the workplace, such as lack of protective equipment or lack of substitution etc., must be changed immediately, whether it is the engine room of a boat, the combined heat and power plant in the basement of a hospital or an authority, the biogas plant or similar, because:

It's not sulphur!

Chapter 10
Unsuitable substitutes

Calcium-free insulating fabrics (silicate fabrics) are not new, but they have only ever been used as heat protection covers or similar for stationary parts and are therefore only suitable for such purposes.

Silicate fabrics are sold under the brand names "Siltemp" or "Hitemp" or "Silica fabric" and often come from Far Eastern countries.

The actual purity in terms of alkali or alkaline earth metal content is also not always confirmed by the suppliers.

The tear resistance and sewability and thus the suitability as a cover for insulating pillows and/or mattresses are simply not given in terms of material technology.

It is also not sufficient to encase calcium-containing insulation materials (superwool/biowool) with the above-mentioned standard fabrics to prevent the formation of chromate, even if an attempt is made to "protect" the silicate fabric with stainless steel wire gauze.

After just a few hours of operation, the fabric has worn out and the chromate formation process is even intensified, as the chromium content of the hot part and the chromium content of the stainless steel wire gauze now come into contact with the increased calcium content of the insulation material inside.

Fig.82: Siltemp/Superwool combination

The figure shows how the yellowish chromate compounds were formed despite the calcium-free contact side.

The reason for this is the burst seams, which are due to the weak mechanical resistance of the standard silicate fabric.

The calcium-containing (40% CaO) is now no longer protected and the fibres of the inlet can react with the chromium compounds from the knitted wire mesh and/or the hot part.

Another approach taken by the industry, especially today's market leaders, would be to impregnate the calcium-containing glass fabrics with calcium-free compounds, for example vermiculite compounds.

In principle, this approach is understandable, but one important aspect is not taken into account here; the abrasion caused by vibrating hot parts and the so-called "wear and tear" associated with this.
"Ageing".

As the impregnation is only minimal, it also only provides a minimal barrier between chromium and calcium/sodium.

If abrasion forces act on this impregnation, it will only be a matter of time before this barrier dissolves mechanically and the calcium components are released again.

Since it must always be expected that damage will occur on the inside of parts subject to heavy loads, it can only be described as negligent overall if only the inside of the insulating elements are provided with a light (alkali and alkaline earth metal-free) impregnation, while the fabric sheath and the first layer of the internal insulating material still contain calcium and/or sodium.

With stationary parts, this may be successful and reduce the formation of chromate, but with highly vibrating parts such as engines or turbines, we can only advise against such tests, because it will only be a matter of time before the inner jacket is damaged and thus exposes its own alkali/alkaline earth metal components, or can no longer protect the alkali/alkaline earth metal-containing inner insulating material from contact with the hot parts.

The trials to which the providers refer were only tested over a period of one week!

Chapter 11
Damage to health due to chromates

Chromium (VI) and its compounds (chromates) are classified as carcinogenic, partially mutagenic, reprotoxic and completely environmentally harmful hazardous substances in the following hazard classes:

Chromium (VI) as chromium trioxide (CrO3) (EC-No. 606-053-1; CAS 18540-29-9)

H317 - May cause skin irritation H350 - Carcinogenic 1B
H400 - very toxic to aquatic organisms
H410 - very toxic to aquatic life with long lasting effects

Source: https://echa.europa.eu/de/information-on-chemicals/cl-inventory-database/-/discli/notification-details/130199/658697

Chromium (VI) as calcium chromate (CaCrO4) (EC-No. 237-366-8; CAS 13765-19-0)

H302 - Harmful if swallowed H350 - Carcinogenic 1B
H400 - very toxic to aquatic organisms
H410 - very toxic to aquatic life with long lasting effects

Source: https://echa.europa.eu/de/information-on-chemicals/cl-inventory-database/-/discli/details/52650

Chromium (VI) as sodium chromate (CrNa2O4) (EC-No. 231-889-5; CAS 18540-29-9)

H330 - Fatal if inhaled H350 - Carcinogenic 1B
H340 - mutagenic 1B
H360 FD - repro 1B - May damage fertility. May damage the unborn child.
H400 - very toxic to aquatic organisms
H410 - very toxic to aquatic life with long lasting effects

Source: https://echa.europa.eu/de/information-on-chemicals/cl-inventory-database/-/discli/notification-details/69660/1708906

Chromium (VI) and its compounds therefore all belong to the category of so-called "CMR pollutants" (carcinogenic, mutagenic and/or reprotoxic), but above all uniformly classified as carcinogen 1B!

Diseases in connection with chromium compounds are summarised in the document "Merkblatt zur BK Nr. 1103: Erkrankungen durch Chrom oder seine Verbindungen (Bek. des BMA vom 25.2.1981 im BArbBl Heft 4/1981)" (Annex: CAA_021)

Studies on the carcinogenicity of chromium (VI) compounds were carried out as early as the 1970s; these have been confirmed by further studies in modern times.

The above-mentioned leaflet from the Federal Institute for Occupational Safety and Health (baua) states, among other things:

"II Pathophysiology

Chromium or its compounds are mainly absorbed via the respiratory tract, to a lesser extent via the skin and occasionally via the gastrointestinal tract.

According to current knowledge, hexavalent chromium is converted to the trivalent state immediately after absorption.

Most of the chromium absorbed is excreted relatively quickly, mainly via the kidneys.

Inhalation of hexavalent chromium compounds leads to irritation of the upper respiratory tract. Necrosis on uninjured skin is rare; however, poorly healing ulcers can occur if hexavalent chromium compounds penetrate small skin injuries.

Sensitisation leads to allergic contact eczema. The toxic effects are mainly due to the strongly oxidising properties of this substance in an acidic environment and the associated cell-damaging reactions.

Prolonged exposure to hexavalent chromates can cause malignant tumours of the respiratory tract; to date, these have mainly been observed in chromate-producing companies and in the chromate pigment industry.

Inhalation of the chromate dust produced in the process is probably the cause of cancer formation.

The carcinogenic effect seems to depend on the solubility of the respective chromium(VI) compound.

The less soluble compounds such as zinc chromate, calcium chromate, strontium chromate and chromium III chromate are attributed the carcinogenic effect.

Alkali chromates, lead chromate and chromic acid, on the other hand, are probably not or only weakly carcinogenic."

The health hazards caused by chromium (VI) compounds are explained very clearly in the elaboration

"The pathobiochemistry of

chromium" by Nele Schumacher (Münster University of Applied

Sciences; Annex: CAA_019).

Nele Schumacher is one of the VDI sponsorship award winners for her master's thesis in chemical engineering in 2016.

In chapter 3 "Chromium in the human body" we read:

3.1 Overview

In the body: Trivalent Cr[III] and hexavalent Cr[VI] elemental Cr not relevant

Cr[III] and Cr[VI] have different chemical and biological properties

General rule: Cr[VI] is far more toxic than Cr[III]

In the body: spontaneous reduction of Cr[VI] to Cr[III] Damage through oxidation
Cr[VI] can easily penetrate cell membranes Cr[III] cannot penetrate cell membranes

In chapter 4 "Toxic effects on humans - 4.1. Acute oral toxicity" the lethal dose of Cr[VI] is given as 50-70 mg per kilogram body weight.

For an adult human weighing approx. 80-90 kg, the lethal dose (oral) would be approx. 5.1 grams, which is alarmingly low.

It is easy to understand why there is no threshold value for chromium (VI) and its compounds, but rather the extremely low tolerance value of just one microgram per cubic metre of breathing air.

Due to the high oxidation potential of chromium (VI) compounds, there is a risk of "Chronic ulcers and acute contact inflammation" (dermal risk).

Skin diseases caused by dermal contact with chromium (VI) compounds are also the basis of so-called "bricklayer's scabies":

Wikipedia also describes masonry scabies as "...chromate allergy, also ...or cement scabies, is an allergic skin reaction that occurs on dermal contact with chemical compounds from the chromate group. This form of allergy is classified as allergic contact dermatitis."

Schumacher writes under "Effects of respiratory exposure":

- Inflammation of the nasal mucosa, bronchitis
- Irritation of the respiratory tract
- Ulcers on and perforation of the nasal septum,

seasonal cancer and an increased risk of lung cancer are reported as long-term effects.

Chapter 4 "Toxic effects on humans" continues:

4.4 Mutagenicity and carcinogenicity

- external Cr[III] intake: no genotoxic effects
- External Cr[VI] intake: **DNA damage**, **gene mutation**, **chromosonal deviations** and **mutations**
- But: Genotoxic effects only in the presence of reducing agents!

...

- **Latency period: 5- 58 years (on average 25 years)**

4.5 Inclusion reduction model

Cr[VI] can penetrate the cell walls as tetrahedral CrO42-

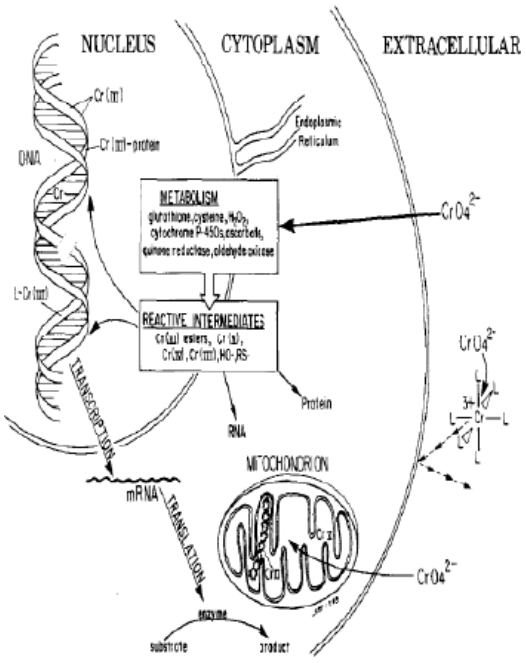


Fig.84: Intracellular penetration of Cr(VI)

What few people realise is that it is actually the chromium (III) compound that triggers the risk of carcinogenicity/genotoxicity.

These are the chromium (III) compounds that have penetrated intracellularly as chromium (VI) compounds and have been oxidised by the body first to chromium (V), then to chromium (IV) and finally to chromium (III) compounds.

While chromium (III) compounds cannot be absorbed intracellularly, which can be seen as a protective measure of the human body, it is precisely the tragedy of our own human defence system that bypasses natural protection.

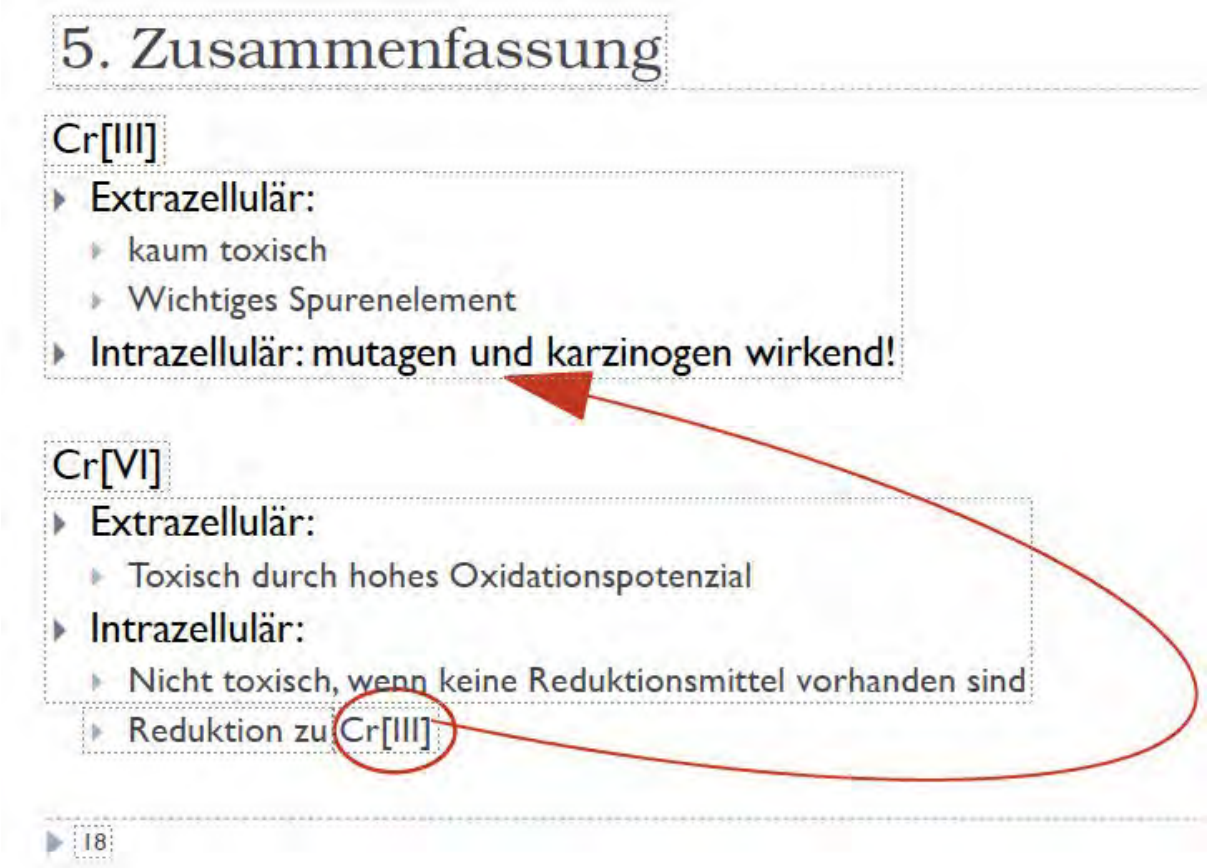


Fig.85_Summary Cr(III)/Cr(VI);extra- or intracellular

The intracellular uptake of Cr (VI) compounds and their reduction to Cr (III) compounds can lead to so-called "DNA double-strand breaks".

Although the body's own system also provides repair mechanisms here, these are impaired by the presence of reduced Cr (III) compounds and can thus have mutagenic and, above all, carcinogenic consequences!

The appendices CAA_021: Influence of manganese and chromate... and CAA_020: DNA fragmentation exposure... clearly describe how and which DNA damage is caused by the intake of Cr (VI) compounds.

The two scientific papers are clearly written, but also very complex, so that only a section from CAA021 is quoted for this guide and will serve as the conclusion of this chapter:

"After uptake, chromium (VI) is reduced to chromium(III) via one- and two-electron systems, whereby these reactions are carried out with the participation of the reducing agents ascorbate and glutathione. The resulting chromium intermediates (chromium (V), chromium (IV), chromium (III)) are able to form adducts with the DNA and thereby damage it. Chromium (III) shows a high amninity to DNA, whereby additional cross-links with molecules such as ascorbate, glutathione, histidine and cysteine can be formed.
The ternary chromium-DNA adducts with ascorbate show a high mutagenic potential. Chromium (III) mainly binds to the phosphate backbone of the DNA, whereby compounds via N7-guanine are also known (summarised in Eastmond et al. 2008 and Wise and Wise 2012).

The ternary DNA adducts lead to increased base mismatches during replication, whereby the protein complexes of the mismatch repair bind to these DNA adducts for repair, block the replication fork and a DNA DSB is generated.

It has already been established that mismatch repair-pro cient cells contribute to an increased induction of DNA-DSB, while mismatch repair-de cient cells do not generate DNA-DSB under the influence of chromate (Reynolds et al. 2007, summarised in Zhitkovich et al. 2005, Salnikow and Zhitkovich 2008 and Wise and Wise 2012).

The reduction of chromium(VI) to its intermediates also generates ROS, which can damage the cell (summarised in Zhitkovich 2005).

The resulting DNA DSBs can be repaired via the NHEJ, HR, SSA and MMEJ repair pathways, although there are already indications of inhibitory effects of chromium(VI) on the almost defect-free HR, which could jeopardise genomic stability (Browning et al. 2016).

In addition, it has already been shown that chronic exposure to chromium(VI) compounds leads to hypermethylation of repair genes, such as the hMLH1 gene of mismatch repair, and thus inhibits their expression (Takahashi et al. 2005, Hu et al. 2018).

The mismatch repair defect leads to microsatellite (MS) instability. MS are frequently repeating DNA segments of around 6 base pairs, whereby instability is triggered by mismatches and a defect in mismatch repair.

The consequences are the increased occurrence of mutations and the associated increased risk of tumour development (Hirose et al. 2002, Takahashi et al. 2005, summarised in Karran 1996 and Wise and Wise 2012).

In addition, chromium (VI) has been observed to cause chromosomal aberrations and micronuclei with whole chromosomes and fragments.

Chromium (VI) compounds can therefore be regarded as aneugenic and clastogenic (Benova et al. 2002, summarised in Salnikow and Zhitkovich 2008).

In addition to the genotoxic and mutagenic effects, reproductive toxicity and carcinogenic mechanisms of chromium (VI) have also been identified.

Occupationally exposed people in particular are exposed to chromium compounds, with chromium (VI) causing reduced fertility in workers in the steel industry (Hjollund et al. 2000). In addition, an increased incidence of lung carcinomas and tumours of the nasal epithelium and paranasal sinuses due to chromium (VI) was observed (summarised in Zhitkovich 2005 and Eastmond et al. 2008).

Based on these findings, the International Agency of Research on Cancer (IARC) categorised chromium (VI) as a Group 1 carcinogen in humans (IARC 1990).

Chapter 11
Environmental damage caused by chromates

The Federal Ministry of Health writes on its website:

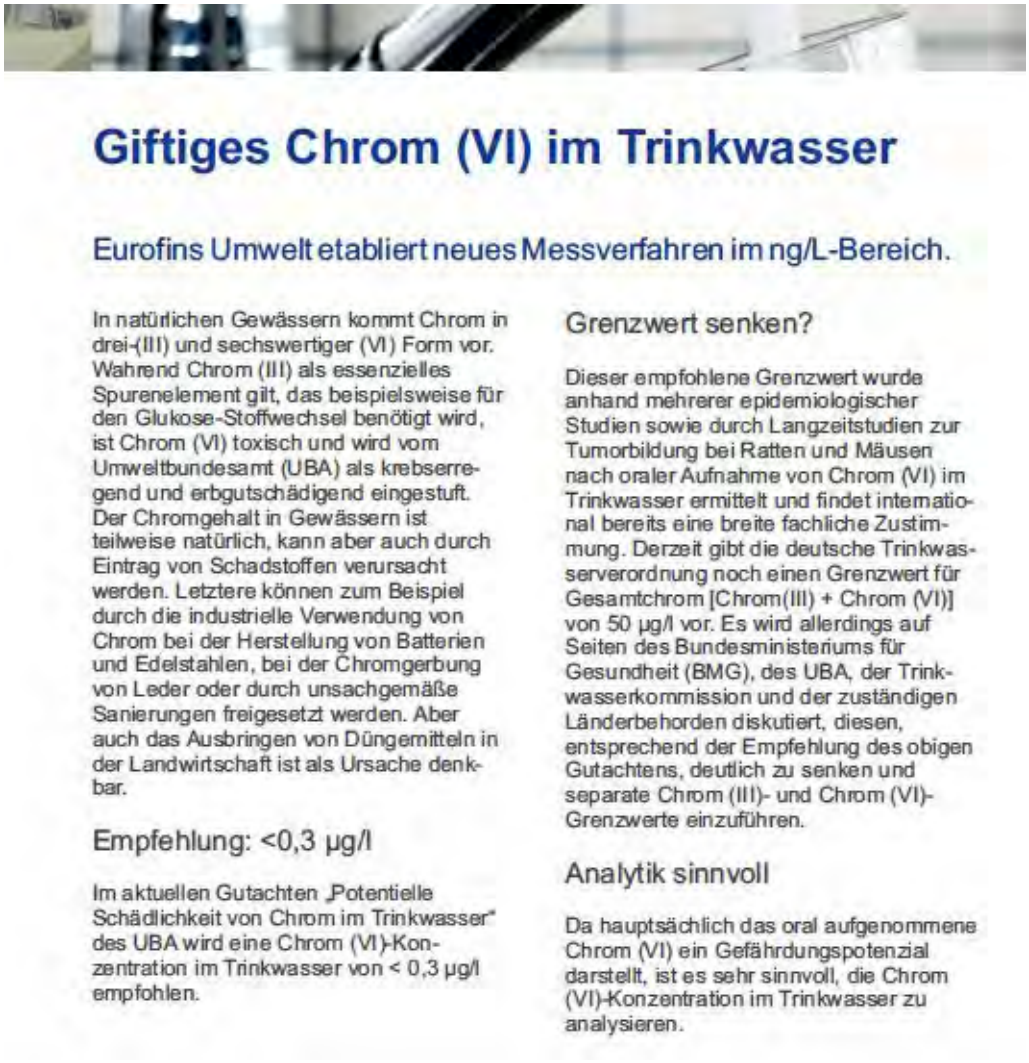
"Chromium of oxidation state VI (chromium (VI)) is of geogenic origin in drinking water and occurs in significant concentrations in several regions of Germany.

It is genotoxic and is classified as carcinogenic.

The limit value for chromium (total) in the Drinking Water Ordinance is currently 50 µg/l (0.050 mg/l).

Recent scientific findings suggest that the risk of additional cancer cases increases from a concentration of 0.3 µg/l of chromium (VI) in drinking water."

"Eurofins Umwelt" writes (Fig. 86: "Toxic chromium (VI) in drinking water"):



Giftiges Chrom (VI) im Trinkwasser

Eurofins Umwelt etabliert neues Messverfahren im ng/L-Bereich.

In natürlichen Gewässern kommt Chrom in drei-(III) und sechswertiger (VI) Form vor. Während Chrom (III) als essenzielles Spurenelement gilt, das beispielsweise für den Glukose-Stoffwechsel benötigt wird, ist Chrom (VI) toxisch und wird vom Umweltbundesamt (UBA) als krebserregend und erbgutschädigend eingestuft. Der Chromgehalt in Gewässern ist teilweise natürlich, kann aber auch durch Eintrag von Schadstoffen verursacht werden. Letztere können zum Beispiel durch die industrielle Verwendung von Chrom bei der Herstellung von Batterien und Edelstahlen, bei der Chromgerbung von Leder oder durch unsachgemäße Sanierungen freigesetzt werden. Aber auch das Ausbringen von Düngemitteln in der Landwirtschaft ist als Ursache denkbar.

Empfehlung: <0,3 µg/l

Im aktuellen Gutachten „Potentielle Schädlichkeit von Chrom im Trinkwasser" des UBA wird eine Chrom (VI)-Konzentration im Trinkwasser von < 0,3 µg/l empfohlen.

Grenzwert senken?

Dieser empfohlene Grenzwert wurde anhand mehrerer epidemiologischer Studien sowie durch Langzeitstudien zur Tumorbildung bei Ratten und Mäusen nach oraler Aufnahme von Chrom (VI) im Trinkwasser ermittelt und findet international bereits eine breite fachliche Zustimmung. Derzeit gibt die deutsche Trinkwasserverordnung noch einen Grenzwert für Gesamtchrom [Chrom(III) + Chrom (VI)] von 50 µg/l vor. Es wird allerdings auf Seiten des Bundesministeriums für Gesundheit (BMG), des UBA, der Trinkwasserkommission und der zuständigen Länderbehorden diskutiert, diesen, entsprechend der Empfehlung des obigen Gutachtens, deutlich zu senken und separate Chrom (III)- und Chrom (VI)-Grenzwerte einzuführen.

Analytik sinnvoll

Da hauptsächlich das oral aufgenommene Chrom (VI) ein Gefährdungspotenzial darstellt, ist es sehr sinnvoll, die Chrom (VI)-Konzentration im Trinkwasser zu analysieren.

Like arsenic, cadmium, cobalt and other pollutants, chromates are categorised as hazardous waste in group HP 7.

The "LAGA - Bund-/Ländergemeinschaft Abfall" writes among other things

"**Waste shall be classified as hazardous if it has one or more hazardous properties HP 1 to HP 15** (No. 2.2.1 of the introduction to the List of Wastes of the WSR) or contains certain persistent organic pollutants (POPs) above the concentration limits in Annex IV of the POP-V (cf. No. 2.2.3 of the introduction to the List of Wastes of the WSR)."

In the notice of the European Commission, (Annex: *CAA_023*)

Technical guidance on waste categorisation (2018/C 124/01)

it says

"This notice is a technical guidance document on certain aspects of Directive 2008/98/EC on waste (hereinafter referred to as the Directive).
'Waste Framework Directive') (1) and Commission Decision 2000/532/EC establishing a list of wastes (hereinafter 'Waste List'), as amended in 2014 and 2017 (2). It is intended in particular to provide explanations and guidance to national authorities, including at local level, and businesses on the correct interpretation and application of the relevant EU legislation in relation to the classification of waste, e.g. for authorisation issues. The guidance therefore addresses the identification of hazardous properties, the assessment of whether the waste has a hazardous property and ultimately the question of categorising the waste as hazardous or non-hazardous."

Until now, and thus for decades, textile insulation has been classified under the waste code "101103" has been disposed of.

However, the correct waste code for chromate-contaminated waste would be "160902"!

The two waste codes differ not only numerically, but also categorically; while "10 11 03" - "Glass fibre waste" is assigned to the category "**ANH**", the waste code "16 09 02" - "Chromates..." belongs to the category "**AH**".

ANH stands for "Absolutely Non Hazardous", which means AH "Absolutely Hazardous" - so absolutely dangerous!

Even if the chromate content were to be considered low, it cannot be determined exactly and fulfils at least the safety-relevant classification "MH" - "Mirror hazardous" - also due to the definitive content of calcium oxide.

Chromate-contaminated insulation materials, which also contain chromium (III)-containing compounds and open calcium oxide compounds, must be disposed of subject to labelling, which has not yet been done; an immediate instruction is recommended here, because so far all stripped insulation systems end up in normal construction waste, which is a deliberate environmental pollution!

Chapter 12
Measures in the workplace

The Hazardous Substances Ordinance (GefStoffV), which is based on the latest version of EU Directive 2004/37/EC, forms the basis for all workplace measures relating to the risks posed by carcinogenic and reprotoxic substances.

A revised version of the GefStoffV will be published in 2024 and will prioritise the protection of workers from carcinogenic and other hazardous substances in particular.

At the latest with the warnings from Innio, MAN, Caterpillar, Siemens and other companies and associations, it should be clear to every employer or operator of energy-generating plants that have insulation systems containing alkali and/or alkaline earth metals that the current practices must be changed immediately!

The "BG ETEM" trade association was the first German trade association to inform its members about chromate hazards in the workplace:

https://www.bgetem.de/arbeitssicherheit- health-protection/industry-information1/energy-supply/power-plants-and-heating-plants/specialist-publications/possible-chromium-vi-exposure

The technical information can be found under Annex: CAA_024: BG ETEM.

The German "Fachverband Biogas" also points out the dangers:

https://www.biogas.org/edcom/webfvb.nsf/id/de-bg-etem-chromvi-exposition

What does the state of knowledge in 2024 mean for the future handling of insulation containing alkali and/or alkaline earth metals and for entering facilities insulated with these materials?

The fact that combined heat and power plants, engines, emergency power generators, local energy suppliers, gas and steam turbines, as well as parts of the automotive sector (exhaust systems, SCR technology, catalytic converters, etc.) are more or less contaminated with carcinogenic chromium (VI) compounds (chromates, especially calcium chromate), depending on the extent of the alkaline and/or alkaline earth metal-containing insulation.Depending on the extent of the alkali and/or alkaline earth metal-containing insulation, it can now be assumed that they are more or less contaminated with carcinogenic chromium (VI) compounds (chromates, especially calcium chromate), even if all protagonists find it difficult to accept or admit this fact.

DIE CHROM TEXPERTEN
ARBEITSSCHUTZ | DEKONTAMINATION | SUBSTITUTION | ENTSORGUNG

Substitution (test) - The "S" of the STOP system

A problem always comes at the wrong time; there is no such thing as the perfect moment.

What has been described so far clearly shows that employers and operators are obliged to rethink their approach in future and take immediate action.

But what do these measures look like?

According to the Occupational Health and Safety Act (ArbSchG) and the Hazardous Substances Ordinance (GefStoffV), as well as the applicable Technical Guidelines for Hazardous Substances (TRGS), all measures must be carried out according to the so-called "S-T-O principle":

"BGN Branchenwissen" writes about the measures to be applied:

"In the case of additional protective measures, the employer must define the measures in accordance with the STOP principle so that the risk to the health and safety of employees caused by a hazardous substance is eliminated or minimised. To this end, substitution is to be prioritised. In particular, activities involving hazardous substances are to be avoided or hazardous substances are to be replaced by substances or mixtures or processes that are not hazardous or less hazardous to the health and safety of employees under the respective conditions of use. The examination of substitution options is described in TRGS 600."

S - Substitution

T - Technical measures

O - Organisational measures

P - Personal measures

The STOP principle describes the order of priority of protective measures.
"STOP hierarchy". **Substitution check**

and substitution

Substitution ("S") is the most effective protective measure. It describes the replacement of a hazardous substance or process by a hazardous substance or process with an overall lower risk.

It **is therefore the first priority of the STOP principle**. Further details are regulated by TRGS 600 and substance-specific TRGS on substitute solutions.

As part of the risk assessment, the employer must assess the possibilities of substitution in accordance with the Hazardous Substances Ordinance by carrying out a so-called substitution test.

The result of the test for substitution options must be documented in accordance with GefStoffV and TRGS 600.

The GefStoffV stipulates that the so-called "risk assessment" for the affected workplace must first be prepared or modified.

The risk assessment represents a pragmatic evaluation of the general working conditions and aims to identify hazards for people and the environment and to minimise them, or at best prevent them altogether.

These dangers are already mentioned in this brochure, namely to prevent the formation of carcinogenic and environmentally toxic chromates, especially calcium chromate.

Insulating materials containing calcium and/or sodium are responsible for the formation of calcium and/or sodium chromate, whose alkali or alkaline earth oxides react thermochemically with chromium compounds to form hexavalent chromium compounds.

The risk assessment, which is usually carried out by so-called "SiFa" specialists (SiFa: specialist for occupational safety), therefore comes to the conclusion that the hazard emanates from insulation systems that are installed on the energy-generating systems.

Since these calcium-containing isolates give rise to calcium chromate, the substitution test will lead to the question of whether the current calcium-containing isolates should be substituted by new, calcium-free isolates, so that the logical conclusion can be drawn.

No calcium - No calcium chromate No
sodium - No sodium chromate

is fulfilled.

As there are alkali-free and alkaline-earth metal-free insulation systems that are technically and economically feasible, the substitution test concludes that the insulation systems currently containing alkali and/or alkaline-earth metals should be replaced by alkali-free and alkaline-earth metal-free insulation systems in the near future.

However, until the substitution is carried out, i.e. the exchange or replacement of the calcium-containing isolation systems, the remaining "T-O-P" measures must be applied, because it is always important to prevent the risk of inhalation or dermal contact for employees and uninvolved third parties!

Technical measures - The "T" of the STOP system

As long as the energy generators contaminated by the current insulation systems are in operation, measures must be taken to reduce the inhalation exposure risk and the dermal contact risk for employees and service personnel until they are replaced by alkali and alkaline earth metal-free insulation.

One of these measures could be the creation of so-called "closed systems".

"The closed system must be designed in such a way that during operation of the system there is no operational open connection between the interior containing hazardous substances and the environment.

If a closed system is not technically possible and there is an increased risk to employees, further protective measures must be taken for these activities according to the state of the art and in accordance with the STOP principle, which eliminate the risk or, if this is not possible, reduce it as far as possible.

...

In the ranking of technical protective measures, ventilation measures and extraction systems are in second place after closed systems.

As extraction systems at the point of origin or discharge of hazardous substances are usually only effective in the immediate vicinity of the emission source, extraction systems are less effective than closed systems. The intended use must be ensured."

Organisational measures - the "O" of the STOP system

Organisational ("O") protective measures must be taken if the protection objective cannot (or could not) be achieved by (as yet) substitution or (despite exhausting all) technical measures.

Organisational measures ensure that protective measures are sufficient in the long term. These include, for example, maintenance plans and inspections as well as working time regulations to reduce exposure or minimise reciprocal stress.

Regardless of the STOP principle, organisational protective measures must be taken to reduce the risk to employees to a minimum, e.g. creation of operating instructions and implementation of instructions.

Personal protective measures - the "P" of the STOP principle

Personal ("P") protective measures, such as wearing respiratory protection, come **last in the STOP principle**.

They must be used if hazards cannot be sufficiently reduced by higher-ranking protective measures.

Personal protective measures are **used, for** example, for **short-term activities with high exposure or also for irregular or only occasional exposure or as a temporary measure until technical or organisational measures have been implemented.**

Source: https://vorschriften.bgn-branchenwissen.de/daten/tr/trgs500/5.htm

Even if the advice of engine and turbine manufacturers to wear full protective clothing when servicing power generators is absolutely correct, this measure cannot be declared permanent.

However, with these warnings, manufacturers are first of all fulfilling their duty to inform their customers.

However, when you consider that the installation of thermal insulation that has not been further developed in terms of construction and material composition since the 1980s means that engine compartments in which engines with a unit price of several hundred thousand euros are operated can, according to the latest findings, be described as contaminated with carcinogenic and environmentally toxic hazardous substances, then the question arises as to whether the dangers to people and the environment should not have been recognised a little earlier, despite the industry's inertia towards innovation and complacency.

The last chapter of this guide shows the consequences of thermochemical chromate formation.

Chapter 13
Decontamination

In order to prevent the risk of inhalation or dermal absorption of chromates, the motors and connected system parts that were insulated with insulation materials containing alkali/alkaline earth metals must be "stripped", i.e. the previously installed thermal insulation must be removed.

When dismantling begins, it is not yet known whether and where the chromates, especially calcium chromate, have formed.

In principle, it must be assumed that calcium chromate can also be released between any insulating element containing calcium and a hot part containing chromium.

It is therefore essential that full protective clothing is worn during all inspection work:

Safety goggles Respirator
mask FFP3
Full-body protective suit with taped seams Work shoe covers
Nitrile gloves

The transitions between the protective suit and the gloves or work shoes must also be taped:

Fig.87: Full protective clothing before starting the deinstallation and decontamination work

The following pages show more than clearly why protective clothing is so fundamentally important

To prevent further exposure, the floor area is covered with foil.

The foils are also used to wrap the dismantled insulation elements so that they can be safely stored in the labelled waste bags for later disposal.

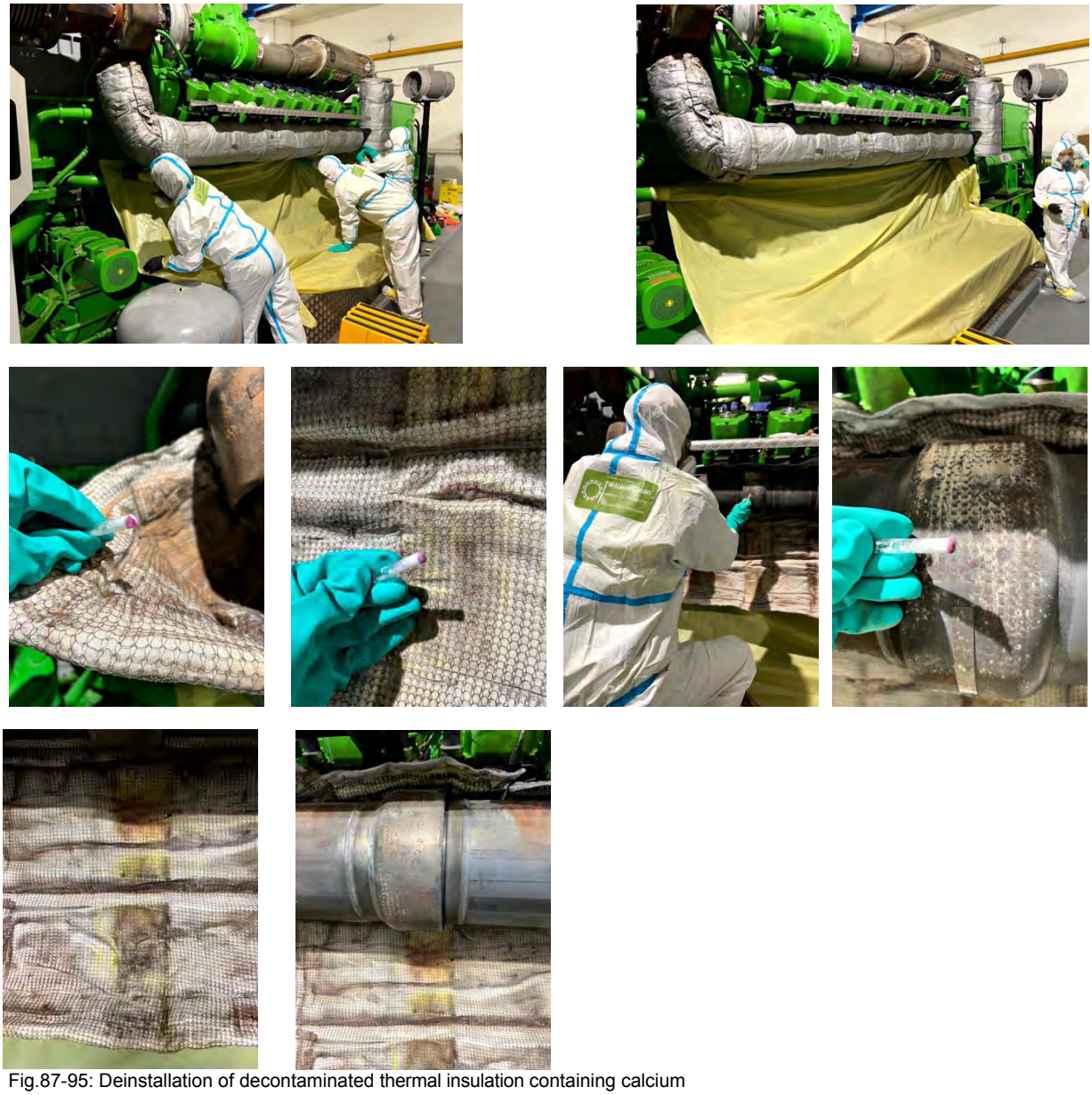


Fig.87-95: Deinstallation of decontaminated thermal insulation containing calcium

After all the insulating elements have been dismantled with a minimum of dust, the engine area, which is still contaminated, is thoroughly vacuumed (H vacuum cleaner).

All hot parts must then be thoroughly cleaned, as they still contain calcium oxide and, above all, carcinogenic chromate dusts.

If this cleaning process is not carried out, the chromates will reappear when the engine is started up!

It is being considered to treat the contaminated surfaces with laser technology so that there is no longer any open exposure; this will be reported on later in a special issue when initial experience with this technology is available.

The following pictures show the conventional method currently used with so-called "neutralisation liquid"

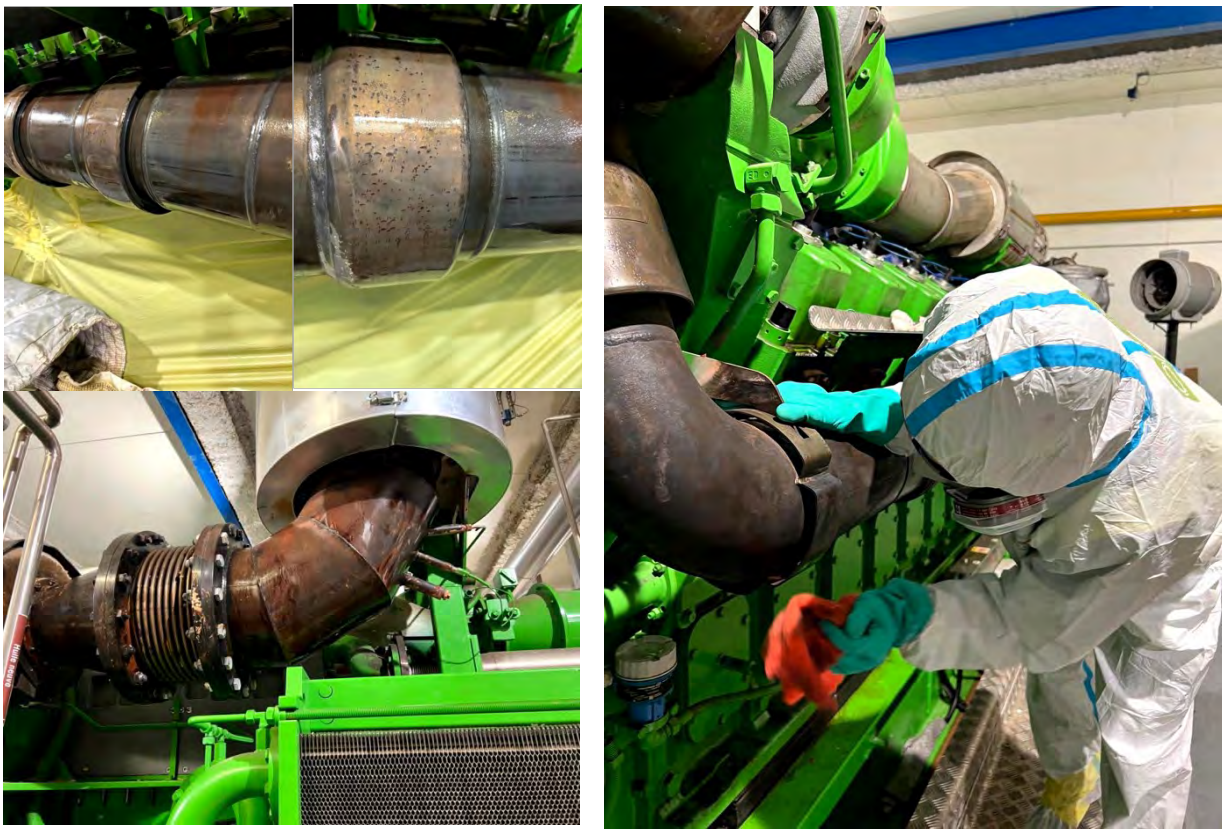


Fig.96-99: Decontamination of system components

Once all motor hot parts have been thoroughly cleaned and subsequent chromium (VI) tests are negative, and other components are thoroughly cleaned and dust-free, the motor is considered decontaminated and substitution, i.e. the installation of insulating elements containing alkali and alkaline earth metals, can begin.

Once the substitution has been completed, the workplace is considered accessible again and no longer poses a risk to people or the environment.

All dismantled old insulation elements, as well as all tools and the protective clothing worn, are disposed of professionally and thus labelled as hazardous waste.

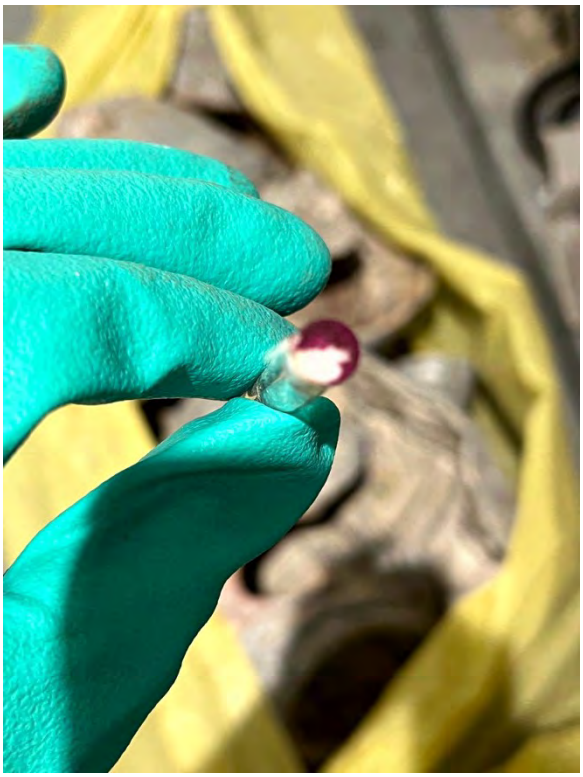


Fig.100: Disposal

The package of measures can be adapted again and the system can return to normal operation without endangering third parties.

Chapter 14
Clarification/prevention

Even today, very few of those affected, such as employees, service personnel and others who have direct contact with contaminated insulation elements, realise that they are or have been exposed to carcinogenic and environmentally toxic substances.

This guide attempts to appeal to the sense of responsibility of all protagonists to abandon the "salami tactics" practised to date and finally address the chromate problem openly.

Hexavalent chromium compounds are carcinogenic and toxic to the environment.

The diseases that can be associated with chromate exposure are insidious and can be manifold and the direct connection is not always recognised.

Chromate-induced DNA damage in particular can lead to mutagens and carcinogens, and the medical profession must be sensitised to this issue.

Personnel who have had (or still have) contact with chromates must be fully informed in order to be able to take precautions or initiate treatment.

However, it also goes without saying that every employee who has been or is still exposed to chromates is listed in an exposure register, also in order to minimise their exposure. to be able to document the "chromate years".

The current state of knowledge must lead to all those involved admitting that the time has come to carry out clarification and prevention, whether those who are and/or were knowingly or unknowingly responsible for the danger that has gone unrecognised for far too long like it or not, because:

It's not sulphur!

Chapter 15
Sources, picture credits, legal information

This guide will be available for download in January 2024 on the website chromatexperten.de under the menu item "Guide"; there you will also find all illustrations, as well as the cited sources, studies and other documents, including the warnings of the engine manufacturers or mentioned data sheets, regulations, etc.

With a few exceptions, all cited documents are freely available on the Internet.

As this guide does not pursue a commercial purpose, but is intended to serve as a training and information basis for further research, works protected by copyright may also be used without the consent of the copyright holder (e.g. §60c UrhG).

This report is updated and supplemented on an ongoing basis as new findings or information become available and therefore makes no claim to completeness.

The authors involved have contributed their expertise to the best of their knowledge and belief in order to provide a comprehensive guide for all those affected.

Questions, suggestions and corrections can be sent to info@chromatexperten.de at any time.

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