Kassel Regional Council

Specialist center for product safety and hazardous substances

Hessian state measuring point for hazardous substances

HESSEN

information letter

Chromate exposures in power plants

Formation of carcinogenic chromium(VI) compounds on surfaces of thermally stressed chromium-containing steels through contact with alkali/alkaline earth metals insulating materials and assembly pastes

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situation

In power plants, chromium(VI) compounds (chromates) have been detected on the surfaces of plant components made of chromium-containing steels that are exposed to high process temperatures during operation and have direct contact with materials containing alkali/alkaline earth metals (insulation made of mineral wool and assembly pastes). Industrial insulators and other employees can be exposed to these chromates when the relevant components are stripped or dismantled.

Since the spring of 2022, a nationwide working group from several federal states and accident insurance institutions has been investigating this problem by means of metrological and empirical investigations at the workplaces affected and specialist research. The first results are already available.

chromate formation

In the temperature range from approx. 150 to 1100 °C, in the presence of atmospheric oxygen, a solid-phase reaction can occur on the contact surfaces of chromium-containing steels with materials containing alkali/alkaline earth metals such as insulating materials made of mineral wool or assembly pastes, in which the chromium contained in the steel reacts with the alkali and alkaline earth metals to form carcinogenic chromates. The two chromate-forming main players are the alkali metal sodium and the alkaline earth metal calcium, which occur as oxides and silicates in varying proportions in mineral wool. Lime soap containing calcium is the main component of assembly pastes. However, the other alkali/alkaline earth metals magnesium and potassium also form chromates classified as carcinogenic. The resulting chromates can become visible as a yellow deposit on the surfaces of affected components, although the absence of a yellow deposit is no guarantee of the absence of chromates. Likewise, the chromates can be deposited on the fibers of the adjacent insulating materials, although it should be noted that many types of mineral wool appear yellowish on their own.

Hazardous substance chromates

Chromates (with the exception of barium chromate, which is irrelevant here) are classified as carcinogenic category 1B (H350). They are also skin and respiratory sensitizers. If the solid penetrates even very small skin injuries, local ulcers can occur. They are acutely toxic when ingested orally. Due to the assumed exposure situations, the chronic effects of the chromates on the respiratory organs and direct contact via the skin are the main hazards considered here for workers.

Happen

In power plants, on generators and large engines, process plants in the chemical industry and generally wherever the four initial conditions

- chromium steel
- Insulating materials or assembly pastes containing alkaline/alkaline earth
- metal thermal stress
- oxygen in the ambient air

come together over long periods of operation, the undesirable formation of chromates must be expected. Direct material contact between the steel surface and the material containing alkali/alkaline earth metals is absolutely necessary for the formation of the chromates. The longer this contact lasted, the further this undesirable reaction can have progressed.

Due to the higher costs compared to conventional steel, chromium-containing steels are only installed where the thermal, physical or chemical requirements for the plant components require it. Therefore, only a plant-specific part of the components of a plant is affected. All relevant system components can be affected, such as turbine housings, pipes, connectors, flanges, valves, heat shields, exhaust gas ducts, manifolds and catalytic converters. The chromium content of the steels varies greatly. The extent of chromate formation increases with the chromium content.

Assembly pastes are used to seal mating surfaces that are under pressure and to reduce the tightening values of screw connections in order to meet the high demands on the tightness of these component connections, which are made when processing hot or supercritical phases. Due to their volume requirements, the chromates formed from the assembly pastes can swell out of the gaps in the mating surfaces, crystallize on the system surface and be released during disassembly.

Affected employees and exposure situations

Stripping and dismantling, which can lead to chromate exposure, is often carried out in the power plants by employees of industrial service providers, i.e. external companies. Since the removal of thermally aged mineral wool is expected to release chromate-laden fiber dust into the air we breathe, it is assumed that industrial insulators in particular may be exposed. After the insulation has been stripped, other employees, such as employees of technical testing organizations, can be exposed by working on components with surfaces contaminated with chromate. If fibers and dust contaminated with chromate remain in the work area or if they are transported to other work areas, the plant operator's permanent staff may also be called upon

charged after completion of the actual maintenance and repair work.

First insights

Workplace measurements according to TRGS 402 of the GefStoffV have already been able to prove by the measuring points involved in the working group that industrial insulators are exposed to chromates when stripping the insulation from corresponding system components. The currently applicable risk-related assessment standard for chromium(VI) of 1 µg/m³ in the shift average was also exceeded. It should be noted that the employees were wearing suitable personal protective equipment including class 3 particle-filtering half masks (so-called FFP3 masks) due to the handling of mineral wool. Stationary measurements showed the spread of dust contaminated with chromate through air currents. Wipe and material samples from affected surfaces also tested positive for chromates.

The problem of chromate formation is well known to the manufacturers of the power plant, but not necessarily to all plant operators. Various manufacturers provide information internally, directly to their customers or publicly, which, in addition to pointing out the possible risk, describes measures for removing chromate deposits and protecting employees. There is currently no knowledge of the awareness of the problem in the chemical industry or other trades that may be affected, such as shipping companies whose ship engines may be affected.

Current recommendations for protective measures

Regardless of a complete risk assessment by the employer and the protective measures to be derived from this, the following information is given if exposure to fibers and dust contaminated with chromate is to be expected. Most of the measures already result from the measures that have to be taken to protect against the release of fiber dust from mineral wool. When handling mineral wool, the requirements of TRGS 521 must also be observed, depending on their age.

substitution

Of the four initial conditions mentioned above plus the contact time, there is only an influence on the choice of the insulating materials and assembly pastes used. The chromium content of the system components results from the technical requirements. Mineral wool and assembly pastes that have already been installed and are exposed as a result of current work cannot be substituted either. If other products are to be selected in the future, a new risk assessment is required for their use and it must be ensured that they demonstrably pose a lower or no other risk.

Technical and organizational measures

- Application of low-dust working techniques
- Moistening of the mineral wool to avoid dust formation Removal of visible
- deposits and cleaning of the construction site areas with suitable industrial vacuum cleaners of dust class H, no cleaning by sweeping or sweeping

- Foil enclosures of the construction site areas to prevent the spread of dust, covering of grating floors

-Some power plant manufacturers recommend treating surfaces contaminated with chromate with acidic solutions of citric and ascorbic acid to reduce the carcinogenic chromium(VI) to chromium(III) compounds, which are still classified as toxic. The working group has no knowledge of the effectiveness of this procedure. It is pointed out that appropriate occupational safety measures must also be taken when handling acids.

Personal protective equipment (PPE)

- Suitable respiratory protection, at least class 3 particle-filtering half masks (so-called FFP3 masks)
- Protective suit type 5 (EN ISO 13982-1) with a hood, which is to be worn in such a way that it adequately protects the skin and clothing of the workers from dusts that may be contaminated with chromate

- appropriate goggles, the the penetration the possibly Suitable protective gloves according to TRGS 401 effectively prevent
- chromate-loaded dusts from reaching the eyes
- When taking off the PPE, the respiratory protection must be taken off as the last step in order not to inhale the dust that is thrown up when taking off. Suit and gloves are to be disposed of after one use due to suspected contamination. The shoes should be vacuumed with an industrial vacuum cleaner. The glasses should be cleaned wet.

Working group activities

The working group will continue to deal with the topic in 2023 and 2024 with the following tasks.

- Metrological determinations regarding the exposure of employees and the work areas
- Determination of the chemical identity of the formed chromate compounds
- Determination of the system-specific conditions for chromate formation (chromium content of the affected components, composition of the insulating materials and assembly pastes, process temperatures, contact times of the reactants)
- Survey of the current state of knowledge of the trades concerned and their current handling of plant components and insulating materials that may be contaminated with chromate
- Description of the necessary level of protection

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Sources

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