Possible Release of Chromium(VI) Compounds during Door Openings and Overhauls of Waste Incineration Plants

To operators of waste incineration and thermal recovery plants, plant and power station management, maintenance, occupational safety specialists and environmental officers

1. Occasion

During door openings in ongoing operation, during overhauls and during maintenance work on waste incineration plants, exposure of employees to carcinogenic chromium(VI) compounds cannot be ruled out. The contamination is carried by the crust that has grown on the grate components and by the ash and fly dust on the grate substructure, boiler passes, hoppers, flue gas ducts and filter levels.

The chromium does not come from the waste, but from the material of the plant.

2. Situation: formation in the furnace

In normal operation, four factors are permanently and simultaneously present: chromium-alloyed, heat-resistant grate and furnace components; alkaline ash constituents of calcium, sodium and potassium; oxygen from the combustion air; and metal surface temperatures in the range in which chromates form and remain stable. At the interface between the ash layer and the chromium oxide layer, the firmly bound trivalent chromium of the component becomes a water-soluble, carcinogenic chromium(VI) salt, as calcium chromate or as sodium chromate.

None of these four factors can be chosen in normal operation. If the grate is chromium-alloyed and the fuel contains calcium or sodium, the reactions take place. Even ordinary common salt is sufficient as a reaction partner, and household waste always contains table salt.

The alkaline constituents do not come from the waste alone. In dry and semi-dry flue gas cleaning, calcium hydroxide or calcium oxide is injected into the flue gas stream in excess; in wet scrubbing, caustic soda is used. Unused sorbent settles together with the fly ash on all downstream surfaces. The alkaline fraction is therefore part of the process and does not depend on the waste composition. In parallel, a volatile chromium compound forms in the moist, oxygen-rich flue gas and condenses on cooler plant parts. Boiler deposits, hoppers and filter dust therefore also carry chromate, although no chromium steel is involved there.

Chromate builds up not only on the visible surface, but also on undersides, joints and support points and on the load-bearing surfaces below the grate, which are made of the same material. These surfaces cannot be seen in the installed state and are regularly missing when the scope of cleaning is planned.

Shutdown is the formation maximum: the fuel has been consumed, the air supply continues, and the plant slowly passes through exactly the temperature range in which the conversion is fastest and the products are stable. The plant forms chromate with the greatest efficiency in the hours immediately before the inspection.

When the furnace is opened, moist ambient air enters. Chromates attract moisture and dissolve. The material thereby becomes both dust-forming and able to pass through the skin.

Loose ash layer on a component in the furnace area. Detection in ash in the furnace area, sample tube with colour change.

3. Legal classification

- Risk assessment under § 6 GefStoffV (German Hazardous Substances Ordinance) and TRGS 400; protective measures and minimisation requirement under § 7 GefStoffV and TRGS 500.
- TRGS 561 section 5.9.3 "Thermally stressed chromium-alloyed industrial components": paragraph 5 links the protective measures solely to the fact that chromium(VI) contamination is present or cannot be ruled out. In that case, the measures under sections 4.1 and 4.2 must be implemented.
- TRGS 561 section 5.9.3 paragraph 4: "Particularly during plant overhauls (maintenance work), dismantling and troubleshooting, exposure of employees to chromium(VI) compounds cannot be ruled out."
- TRGS 561 section 4.1: if the concentration of 1 µg/m³ for chromium(VI) compounds is foreseeably exceeded on a permanent basis, the establishment of a spatial black-white separation, for example by an airlock system connected to the work area for putting on and taking off work and protective clothing, must be examined and implemented if necessary.
- Exposure register under § 10a GefStoffV for employees for whom exposure to category 1A or 1B carcinogens cannot be ruled out.
- Operating instructions and instruction under § 14 GefStoffV; information of contractors under § 15 GefStoffV (overhaul, cleaning and scaffolding companies).
- Occupational medical care under ArbMedVV (Ordinance on Occupational Health Care). The annex of TRGS 561 lists chromium(VI) with target organs lung and nose, matrix urine, a BAR of 0.6 µg/l and an EKA correlation.
- Assess the hazard from skin contact separately under TRGS 401.

This text does not replace a site-specific risk assessment. Quotations from German sources are our translations.

4. What air measurement does not answer

For chromium(VI) compounds, Germany has neither an occupational exposure limit nor an acceptable or tolerable concentration. TRGS 561 states in section 5.7: "No ERB has yet been derived for chromium(VI) compounds. The concentration of 1 µg/m³ for the inhalable fraction is to be applied." The excursion factor is 8. If this concentration is complied with over an entire working life, according to TRGS 561 an additional statistical lung cancer risk in the order of approx. 4:1000 remains.

Chromium(VI) compounds have no threshold. If airborne contamination above the detection limit is determined, the measured area can no longer be entered without concern.

Lifting off the components and breaking up the crusts are events lasting minutes; averaged over eight hours, they disappear mathematically. What must be checked is therefore the short-term peak against the excursion factor, not the eight-hour average alone.

Air measurement also covers only one of three routes of uptake. Article 3(3) of Directive 2004/37/EC states: "In risk assessment, all other routes of exposure, such as absorption into and/or through the skin, shall be taken into account." Chromium(VI) compounds are classified as H350 and carry the skin resorption notation "H" in the MAK and BAT values

list. For a carcinogenic substance with this notation, the assessment scheme of TRGS 401 already leads to the classification “high hazard” for small quantities and short contact times.

A value complied with in the furnace proves that the protective equipment of the persons deployed is effective. It proves nothing about the persons without protective equipment in the area in front of it, and it does not prevent carry-over to the outside as long as no airlock is set up and neither the protective clothing nor the tools used in the furnace are decontaminated in the passage area.

5. The area in front of the doors

This is currently the largest gap in the protection concept. In practice, many operators are not aware of the hazard from chromate-containing dust in the door area; zoning often does not take place there because the area is considered safe. However, floor samples from such door areas show that the deposited ash dust is contaminated with chromate.

This results in two hazards that an air measurement in the furnace does not reflect. First, resuspension: every movement of persons, vehicles and industrial trucks and every door opening stirs up the deposited dust again, precisely where persons work without protective equipment and are not listed in the exposure register. Second, carry-over via footwear into workshops, break rooms, changing rooms, control rooms and vehicle cabs. The route is short, uncontrolled and daily.

Detection in ash dust on a traffic route outside the furnace. Scaffolding material and work preparation in the area in front of the furnace door.

A separate protection concept is required for this area:

- The door area belongs to the controlled area, not to the transition: delimitation, signage, access rules.
- Define and mark zone boundaries, including a transition with change of footwear or footwear cleaning. Sticky mats alone are not sufficient for this. Effective are mats moistened with reducing agent in the walkways and in the airlock; extraction alone is not sufficient.
- Floor and wipe samples in the door area and in the adjacent areas as part of the risk assessment. They answer the question of the dust layer, which an air measurement does not answer.
- A defined decontamination regime instead of cleaning: chromate-binding treatment of the surfaces, collection of the bound material, extraction with a dust extractor of dust class H, at defined intervals and documented. No dry sweeping, no blowing off. Cleaning moves the dust; it does not remove the chromate.
- Airlocked access instead of an open transition: airlock with separate storage for used protective clothing, cleaning of footwear and washing facilities. This is where carry-over is actually interrupted.
- A defined transfer point for components, containers and tools; no setting down and no storage in the door area.
- Stationary measurement in this area in addition to the personal measurement in the furnace.

6. Protective measures during door opening and overhaul

Technical, with priority:

- Zoning and low-dust working are the key measures. Doors as controlled openings with a curtain or intermediate zone, not permanently open.
- Point extraction at the point of origin, dust extractor of dust class H. No blowing off with compressed air, no dry sweeping or brushing without extraction.
- Bind dust rather than moisten it. Moisture only binds as long as it lasts; wetness dissolves the chromate and transfers it into the water. Effective is a binding and reducing treatment that converts the hexavalent chromium into the trivalent state, followed by collection of the material.
- Wet grate components from above and in the joint area before lifting, lift them off horizontally rather than tilting them, place them directly in a closed container; only enter the area underneath after wetting and extraction.
- Clean components in a closed enclosure with extraction or by a wet process with water collection, not outdoors and not in the open workshop. The focus is on the underside. Transport between furnace and cleaning area covered or in closed containers.

Wetting before starting work on the grate. Full face mask, disposable protective suit with hood, gloves.

Personal:

- Powered air-purifying respirator TH3/TM3 P or full face mask P3 for crust removal and component cleaning. Filtering half masks are not sufficient for these activities.
- Disposable protective suit type 5/6 with hood, overshoes, eye protection, chemical-resistant gloves with a tight transition between sleeve and glove, change whenever soaked through.
- Washing facilities and shower in the exit area, shower before leaving the area. No private cleaning of work clothing, no taking it home.

Organisational:

- Limit the number of persons in the furnace, keep an access list, no parallel work on top of each other.
- No eating, drinking or smoking in the area; breaks exclusively outside the controlled area.
- One-way routing via the airlock; tools remain in the controlled area or are decontaminated at the material airlock; containers are closed and cleaned on the outside before being passed out.
- Decontaminate or vacuum scaffolding material before passing it out; dispose of planks that cannot be cleaned as contaminated material. Dismantle scaffolding only after rough cleaning has been completed.
- Check effectiveness by wipe samples at defined points in the clean area: break room, changing room, control room, door handles, vehicle cabs.

The periphery must also be included: ash hoppers, primary air ducts, deslaggers and conveyors, boiler passes and heating surfaces, soot blowers, flue gas ducts and expansion joints, cyclones and filter levels, rotary valves, silos,

induced draught fans, inspection openings and the porous refractory lining. Deposits from operation are sufficient, even without crust cleaning.

7. Decontamination

Cleaning removes dust from one place and carries it to another. Decontamination changes the substance: hexavalent chromium takes up three electrons and changes to the trivalent state, which is not carcinogenic. For this purpose, the chromate is first bound, then reduced and collected together with the carrier material. Three points belong to this:

- **Work without run-off.** The liquid used must not leave the surface uncontrolled. Drip trays or sealed edges, no run-off into yard drainage, sewers or soil.
- **Prove effectiveness.** The treatment is only reliable when wipe samples afterwards no longer give a positive result. It is not the agent that proves success, but the measurement afterwards.
- **Know the limits.** On oily or heavily dust-laden surfaces, the reducing agent does not fully reach the chromate, and it does not prevent new formation in the next operating cycle. Decontamination does not replace a technical and organisational protection concept; it closes its gaps.
- **Decontamination point for personnel.** The exit from the controlled area should be designed as a decontamination point: delimited cabin or airlock chamber with extraction, floor mat moistened with reducing agent, storage for contaminated disposable clothing and washing facilities.

Implementation and the process from zoning through treatment to disposal belong in the hands of personnel trained for this.

8. Environment, waste and transport

In addition to the carcinogenicity classification, chromium(VI) compounds carry the hazard statement H410, very toxic to aquatic life with long-lasting effects. For sodium chromate and for calcium chromate, this is laid down in the harmonised classification. This classification is independent of carcinogenicity and justifies a separate chain of measures that is regularly overlooked in practice.

- **Water.** Cleaning, shower and firefighting water contains dissolved chromate. Discharge into yard drainage, storm water sewers or the sewer system without treatment is not permitted; the German Wastewater Ordinance, the local drainage statutes and the AwSV (German Ordinance on Facilities for Handling Substances Hazardous to Water) are decisive. Required are separate collection, sealed interim storage and treatment by reduction to chromium(III) with precipitation.
- **Soil and precipitation.** Chromates are water-soluble. Open storage of removed material and unprotected placement of contaminated components outdoors lead to leaching into the soil when it rains. Storage under a roof, on an impermeable surface and in closed containers.
- **Waste classification.** Bottom ash and boiler ash are listed in the German Waste Catalogue Ordinance as mirror entries (19 01 11* / 19 01 12; filter dusts 19 01 13* / 19 01 14). HP7, carcinogenic, and HP14, ecotoxic, must be examined. HP14 is directly linked to H410, with a significantly lower concentration threshold than HP7, and is therefore the more likely trigger for classification as hazardous waste.
- **Transport.** With classification as H410, ADR labelling as an environmentally hazardous substance applies, with the corresponding carriage and transport document obligations.

The overhaul residue is a concentrate; the bottom ash from regular operation is diluted. If both are mixed, the examination shifts to the large volume. Separate collection at the source is therefore the most effective single measure of the concept. Separate streams are: crust removal, deposits from component undersides and load-bearing surfaces, boiler deposits, vacuum cleaner contents, used filter elements, sweepings, disposable suits, wiping cloths and respiratory protection filters.

9. Forwarding

Please forward internally to plant and power station management, occupational safety specialist, environmental officer, maintenance and overhaul planning.

References:

TRGS 561, version 4 May 2026, sections 2, 5.7 and 5.9.3 [4.1 and 4.2]
TRGS 400, 401, 402, 500, 910; GefStoffV §§ 6, 7, 10a, 14, 15; ArbMedVV
Directive 2004/37/EC, Article 3(3) and Article 5(3); Regulation (EC) No 1272/2008 (CLP); Regulation (EU) No 1357/2014 (HP7, HP14)
German Waste Catalogue Ordinance (AVV); Wastewater Ordinance, AwSV; ADR. Further reading: paper "Chrom(VI) in der Abfallverbrennung" (Chromium(VI) in waste incineration)

Kind regards

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