Why the formation of alkali or alkaline earth chromates, in particular calcium and/or sodium chromate, can be scientifically proven under power plant conditions and why chromate formation can be regarded as "insulation material-dependent"

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Summary

This literature study investigates the material-dependent formation of chromium(VI) compounds – in particular calcium and sodium chromate – on hot stainless steel components in power plant environments.

Numerous experimental and thermodynamic studies show that alkali and alkaline earth metal oxides such as CaO and Na_2O, as contained in conventional insulating materials, contribute decisively to Cr (VI) formation.

The reaction can start as early as approx. 250–300 °C, with a significant amplification in the range between 500 and 800 °C.

The reactivity is clearly dependent on the chemical composition of the insulation material and its surface structure. Studies with non-alkaline fibers show significantly less or no chromate formation.

The results also show that the reaction chain is scientifically explainable and comprehensibly documented by independent studies.

Widespread assumptions that the glass core ofdampening agents or stainless steel are to be classified as "inert" and therefore no release of CaO or Na_2O have also been refuted by the available studies.

There is therefore no longer any objective doubt that Cr (VI) formation is to be expected to a high degree under typical power plant conditions and is influenced by the insulating material used.

1. Introduction

Chromium(VI) compounds such as calcium chromate and sodium chromate are considered carcinogenic, skin-absorbing and harmful to the environment. Their formation in technical plants, especially in power plants, has been intensively studied for several years. The role of insulation materials and their chemical composition is increasingly coming into focus, as dangerous chromates can form under the influence of temperature and humidity.

Several current information letters – including from the Federal Department of the Federal Chamber of Commerce (2023), the European Industrial Insulation Foundation (2025) and the Kassel Regional Council(2023) – address this issue. While the WKSB points out possible dangers and calls for protective measures, the EiiF assesses the formation of Cr (VI) as independentof the insulating material used. This assessment contradicts numerous scientific studies that prove a clear material-dependent formation of chromates.

The Kassel Regional Council (2023) also expressly recognises that chromium(VI) compounds are preferably formed when chromium-containing steels come into contact with materials containing alkali and alkaline earth metals, such as mineral wool or assembly pastes. Although the letter refers to another conceivable reaction pathway without these substances, this remains unspecific and without reliable evidence. Thus, despite the restrained language, the publication represents an assessment that is factually in line with the specialist literature.

This discrepancy between official restrained assessment and the statements of current research forms the starting point of this literature study. The aim is to systematically process the scientific evidence on insulation-material-dependent Cr (VI) formation. In particular, the role of alkali and alkaline earth metal oxides – such as CaO and Na_2O – as well as the temperature and humidity-related conditions under which chromates are formed in power plant environments are considered.

2. Evidence for the temperature-dependent formation of Cr(VI)

Verbinnen et al. (2013), *Heating Temperature Dependence of Cr (III) Oxidation in the Presence of Alkali and Alkaline Earth Salts and Subsequent Cr (VI) Leaching Behavior*, experimentally show that in the presence of NaOH, KOH or CaO, a significant conversion of Cr (III) to Cr (VI) already occurs at temperatures of 250–300 °C. In NaOH-containing systems, the first Cr (VI) leaching effects have already been observed at 300 °C. Cr (VI) release increases with temperature to a maximum in the range of 600–800 °C and then decreases as a result of glass phase formation. The study specifically sheds light on the direct influence of calcium oxide on the oxidation of Cr (III) and thus allows clear conclusions to be drawn about power plant conditions with oxidizing atmospheres.

Mao & Gao (2015), *The Role of Temperature on Cr (VI) Formation and Reduction During Heating of Chromium-Containing Sludge in the Presence of CaO*, complement these findings with an investigation of the role of temperature in combination with CaO. The authors show that unstable Cr (VI) precursors such as Cr_2O_{3+x} are formed at 200–300 °C , which increasingly change into stable calcium chromate ($CaCrO_4$) with increasing temperature. Between 500 and 900 °C, the preferred and largely irreversible formation of this stable Cr (VI) compound takes place. A thermal reduction of $CaCrO_4$ by MgO was only observed at temperatures above 1000 °C – a scenario that has no relevance in the practice of power plant insulation.

Van Leeuwen et al. (2024), *Reactive Condensation of Cr Vapor on Aluminosilicates Containing Alkaline Oxides*, additionally demonstrate that even below 500 °C, condensed formation of Cr (VI) preferably occurs on CaO-containing ceramic fibers (AES wool). In the experiments, Cr_2O_3 powder was evaporated at 800 °C in an atmosphere containing water vapor and the reactive chromium compounds were condensed on various types of fibers below 500 °C. The thermodynamic modelling shows that $CaCrO_4$ in particular forms as a stable condensation compound from around 150 °C on these materials – with increasing stability as the temperature drops. Fibers without alkali or alkaline earth metal content (e.g. quartz or pure Al_2O_3 fibers), on the other hand, show significantly less Cr (VI) load.

3. Detection of Cr (VI) formation on insulation materials

Sayano & Kanno (2015), "The formation of Cr (VI) compound at the interface between SUS304 stainless steel and calcium silicate insulation at high temperature", were able to show experimentally that when CaO-containing insulation comes into contact with stainless steel (SUS304) under power plant conditions (500–600 °C), yellow deposits are formed, which have been identified as calcium chromate. The amount of Cr (VI) increased with temperature and duration. The selected boundary conditions are explicitly oriented towards drier industrial situations, such as those realistic in turbine or boiler areas.

4. Role of insulation materials and their chemical composition

Van Leeuwen (2024), Dissertation "Condensation of Chromium Vapor and Interactions with Aluminosilicate Surfaces", documents on the basis of practical experiments with ceramic insulation materials that in particular fibers containing CaO, Na_2O or MgO (e.g. AES wool) promote the formation of Cr (VI) on their surfaces. Under air with 3–10 % water vapour, a significantly increased Cr (VI) deposition was measured at temperatures of 500–800 °C. More neutral materials (e.g., high-purity quartz) showed significantly less deposition. The investigations are particularly practical, as they simulate typical humidity levels in technical environments and still show clear material-related differences.

5. Evidence of material-dependent reactivity

Tatar & Gannon (2018), "Investigation of surface interactions between volatile chromium species and high temperature insulation materials", show in surface analyses using XPS that Cr (VI) preferentially adsorbs to aluminosilicate fibers with alkali/alkaline earth metal components. Cr (VI)-typical spectra were only detected for certain fiber types, which proves the material dependence. The supplementary study in the parallel study "XPS Characterization of Aluminosilicate Fibers" is specifically dedicated to moisture dependence – oriented towards the conditions of high-temperature fuel cells (SOFCs). These studies thus provide important insights into the influence of hydrogen, humidity and temperature on chromate formation.

6. Thermodynamic Models and Reaction Mechanisms

Karlsson et al. (2021) complement these findings by looking at the high-temperature corrosion of stainless steel in the presence of alkali salts such as NaCl, KCl and $CaCl_2$. This shows that alkali compounds not only act as oxidation partners for Cr (III), but can also promote the release of Cr from the metal matrix.

This Cr (III) release represents a crucial precursor for subsequent oxidation reactions in which Cr (VI) is formed. Thus, alkali oxides contribute not only to the oxidation but also to the initial mobilization of the chromium, which significantly increases the risk of chromate formation.

Verbinnen et al. (2013) and Van Leeuwen (2024) also use reaction equations and Gibbs energy models to prove that the formation of Na_2CrO_4, K_2CrO_4 and $CaCrO_4$ at 500–800 °C is thermodynamically favored. The oxidizing atmosphere in power plant environments promotes these reactions especially when chromium vapor or Cr_2O_3 comes into contact with CaO-containing surfaces.

A supplementary look at the two Tatar studies (2018) shows that Cr(VI)-containing surface compounds can also form in the downstream cooling area, these results come from experiments under SOFC-like conditions with higher humidity and complex surface chemistry of porous insulation materials.

The Cr(VI) spectra observed there are based, among other things, on temporary monochromate formations as a result of esterification or polymerization processes on porous, non-alkali-containing fiber surfaces. In the technical context of power plant environments with a small air gap and normal humidity, less porous geometries and cyclic temperature curves, such processes are much less likely and are not relevant for an assessment.

In addition, it could be assumed that these chromate forms would largely evaporate during reheating due to their instability, or would not form at all due to the lack of water vaporization.

The Tatar results should therefore not be interpreted as general evidence for insulation-independent Cr (VI) formation, but as an indication of a very specific scenario with a high water vapor content, but offer important insights for SOFC environments.

In this context, it is particularly noteworthy that the EiiF letter (2025) refers to the Tatar study "XPS Characterization of Aluminosilicate Fibers Post Interaction with Chromium Oxyhydroxide at 100–230°C ", in which ferritic stainless steel of the type **FSS 409** was used – a material that is preferably investigated in SOFC systems, but does not play a significant role in classic power plant applications or large engines.

In contrast, the study by Sayano & Kanno (2015) is based on investigations with austenitic stainless steel (SUS304), which is typically used in power plant components.

In addition, the release of volatile chrome oxy hydroxide in Tatar's investigations was only possible with the targeted use of high temperatures in combination with a strong flow of water vapor – two conditions that are not met in this form under real power plant conditions.

In the energy-generating industry, there are also no typical SOFC cooling zones for thermally insulated stainless steel hot parts, in which only 100°C to 230°C prevail. The area relevant for chromate formation in engines, turbines, pipelines and other components is mainly the thin air gap between the chromium-containing hot part and the mainly alkaline insulation layer. In this area, artificially generated water pressure vaporization is not physically possible, because only a short-term condensation of humidity can occur in this area; even a somewhat stronger evaporation of formed condensation will not be able to trigger the formation of the volatile chromium(VI) compounds.

7. Conclusion

The analysed literature consistently proves on the basis of independent experimental and thermodynamic studies:

Cr(VI) formation can start at about 250–300 °C, as the Verbinnen study (2013) shows, but typically reaches its thermodynamic and reaction kinetic peak in the range between 500 and 800 °C.

The conversion is carried out by alkaline and alkaline earth metal oxides (esp. Na, K, Ca).

Insulation materials with CaO/Na_2O components contribute directly to chromate formation.

Chromate formation is therefore dependent on both temperature and insulation material.

Against the background of the available studies – including material-related investigations under power plant conditions, analyses from the field of fuel cell technology and thermodynamic modelling – the statement that the formation of chromate triggered by alkali-containing insulation materials has been **sufficiently scientifically investigated and proven** can be considered technically justified.

Both the experimental repeatability and the mechanistic plausibility of the reaction chain (Cr release, oxidation, binding as chromate) are documented. The material composition of the insulation is therefore a controllable, safety-relevant factor.

The studies complement each other by different humidity limit conditions: While Tatar (2018) mainly investigates humid conditions that are typical for fuel cells, Sayano (2015) and van Leeuwen (2024) take a closer look at the real operating conditions in power plants.

Verbinnen (2013), on the other hand, analyzes the temperature-dependent reactivity between Cr (III) and CaO in a very targeted manner. Together, a consistent picture emerges: The formation of calcium and sodium chromates is not only possible under conventional technical conditions but can also be controlled by the choice of insulation material and can be scientifically explained and understandable.

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Version history

Version	Date	Change
1.0	May 2025	First edition
1.1	November 2026	New layout in the design system of the Chromate Experts; spelling of chromium(VI) standardized.