

Chromium(VI) reduction in residues such as ash, slag and dust

Introduction

Chromium was first identified as a chemical element in 1797. The name is derived from the multicoloured compounds it forms (from the Greek “χρωμα” or “chroma”, meaning “colour”). It occurs only rarely in nature in elementary form (native element), for instance in meteorites and a few types of rock. The most important mineral containing chromium is chromite, FeCr_2O_4 .

Metallic chromium and chromium compounds were and are used widely in technical applications. Common examples of past and present applications include:

- Chromium as an alloying element in corrosion- and temperature-resistant stainless steels and nonferrous alloys
- Chrome plating, i.e. electroplating a thin layer of chromium onto an object (including plastic components) for decorative purposes or to prevent wear

- As a catalyst to promote or accelerate chemical reactions
- Chrome tanning for leather production
- Pigments containing chromium
- Wood preservatives containing chromium

This results in a variety of different matrices in which chromium and its compounds occur. They include the products listed above, but also other (residual) substances generated during production of these materials or after their use. Chromium also occurs in various types of incineration ash and in the building material cement, which contain chromium from natural sources. All of these matrices are significant in terms of their overall volumes. Additional substances of interest are described in detail in Section 6.



Fig. 1: Steel manufacturing

2. Oxidation states of chromium

In compounds, chromium usually occurs in oxidation states +II, +III and +VI, the latter being the most stable and hazardous in terms of its toxicology. In chromates (CrO_4^{2-}), chromium occurs in oxidation state +VI. In this case, it is referred to as hexavalent chromium.



Fig. 2: Mineral chromite

The diverse industrial applications of metallic chromium and its salts all generally begin with the mineral chromite (FeCr_2O_4) (Fig. 2). In various processing steps, it can produce sodium chromate, sodium dichromate, chromium(III) oxide, ferrochromium and metallic chromium. Hexavalent chromium compounds are the direct cause of subsequent contamination, but they also can form by the oxidation of metallic chromium and from naturally occurring, trace amounts of trivalent chromium compounds. One example is wood with its trace content of chromium(III), which can be converted into problematic chromium(VI) by incineration. The same is true of cement manufacturing, where the chromium(III) naturally occurring in the limestone is partially converted to chromium(VI) by heat and the oxidative atmosphere inside the kiln and cooler.

Chromium(III), as an essential trace element, is said to be of physiological significance in glucose, protein and fat metabolism.

In contrast, hexavalent chromium, as found in chromium(VI) oxide and chromates, is toxic, corrosive to the skin and mucous membranes, and can trigger allergic reactions in contact with them. The contact dermatitis caused by handling cement containing chromium is proven to be attributable to chromate. Present in the body after inhalation or swallowing, chromium(VI) compounds cause in some cases irreparable damage to the lungs, stomach, intestines, liver and kidneys, and are classified as mutagenic, toxic to reproduction and carcinogenic. Extensive occupational health and safety measures must therefore be taken when handling substances which contain or release hexavalent chromium compounds.

Because toxicity is largely concentrated on the hexavalent chromium, element analysis of the starting material alone is not expedient for evaluating toxicity. Analysis must reliably identify the respective species (distinguished by the valence, i.e. Cr-0, Cr-III or Cr-VI). In the case of potential skin contact, as with cement, it further must be determined what portion of the Cr-VI is water soluble and thus capable of skin penetration. Similarly, when it comes to landfilling contaminated materials, it is important to know what portion could be separated (eluted) from the landfill body and thus act as a potential groundwater contaminant. For these reasons, there is no uniform standard procedure for measuring Cr-VI; instead, special, established methods are used which depend on the objective and matrix. Likewise, various, application-specific methods are used for elution (see Table 1).

Common to all extraction and elution methods is the final analysis of the filtrate. Because Cr(III) ions are only slightly soluble in a neutral to alkaline environment (as is usually the case with eluates) due to the formation of $\text{Cr}(\text{OH})_3$, they are retained in the filter cake so that only the water-soluble chromium(VI) ions pass into the filtrate. By means of reaction with diphenyl carbazide, they can be specifically detected and quantified photometrically from a coloured complex. An alternative method is mass spectrometry (ICP-MS) or atomic emission spectrometry (AES or OES) based on the filtrate. While these methods cannot distinguish the valence of the chromium, it is known from the reasons described above that the filtrate contains almost exclusively chromium(VI). A relatively complex combination of high performance liquid chromatography (HPLC) and ICP-MS further makes it possible to distinguish between chromium(III) and chromium(VI).

3. Objective

The toxicity of chromium(VI) has led to extensive legal restrictions and requirements for handling contaminated materials. Apart from total bans on certain applications, restrictions exist in many areas based on chromium(VI) limits, e.g. in classifying waste for landfills or selling incineration ash as an ingredient for fertilizer. Furthermore, chromium(VI) plays a significant role in the occupational safety requirements for many types of (filter) dust and residue in industrial processes.

Depending on the further use of such residues, currently valid regulations must be taken into account. On the European level, the REACH (EC 1907/2006) and CLP (EC 1272/2008) regulations are the foundation for all chemical legislation on chromium and its compounds. EU regulations are directly applicable in all Member States and therefore require no further national implementation procedures.

Tab. 1: Overview of possible extraction and elution methods for determining soluble chromium(VI)

Regulations	Method	Water-to-solids ratio
DIN EN 196-10	Standard mortar extraction	0.5
DIN 12457-1 and DIN 19529	2:1 shake test	2
DIN 12457-4 and DIN 38414-4	10:1 shake test ("S4")	10
DIN 19528	Column test	2 - 10
DIN 19730	Ammonium nitrate extract	2.5
BBodSchV	Soil saturation extract	0.25 - 0.5

On the national level in Germany, the following regulations for chromium(VI) exist:

- Chemicals Prohibition Order (ChemVerbotsV - Chemikalien-Verbotsverordnung)
- German Hazardous Substances Ordinance (GefStoffV - Gefahrstoffverordnung), where practical implementation is supported by various Technical Rules for Hazardous Substances (TRGS - Technische Regeln für Gefahrstoffe)
- Federal Soil Protection and Contaminated Sites Ordinance (BBodSchV - Bundes-Bodenschutz- und Altlastenverordnung)
- Landfill Ordinance (DepV - Deponieverordnung), limit values e.g. for disposing of ash and dust containing chromium
- Fertilizers Ordinance (DüMV - Düngemittelverordnung), relevant e.g. for the agricultural use of wood ash

Occupational safety requirements are defined in various, individual national regulations, such as for dust exposure. In future, limit values will likely be further tightened and regulations harmonized throughout Europe.

The objective for handling, using or recycling materials containing chromium(VI) is to reduce hexavalent chromium to chromium(III), thereby achieving detoxification and immobilization, so that the materials reliably comply long-term with corresponding limits. The chemistry of reduction is explained in the following section.

4. Reduction of chromium(VI) to chromium(III)

The oxidation of chromium(III) to chromium(VI) mentioned above is fully reversible using a reducing agent. In other words, the technical option exists of converting hazardous hexavalent chromium (e.g. chromate) to a safer, trivalent form, which in addition is sparingly soluble and thus largely immobilized:



Divalent iron acts as the reducing agent for chromium(VI). The reduction of chromate can only be effective and complete in the presence of water, i.e. with considerable material moisture content and simultaneous, intensive mixing. Furthermore, purely stoichiometric metering, i.e. an added quantity that corresponds exactly to the ratio in the chemical equation, is often too low in practice for total reduction. Some of the added reducing agent usually is consumed by competing reactions, chiefly by oxidation with dissolved atmospheric oxygen in an alkaline environment, or by increased consumption of the reducing agent by other substances that are present and can be reduced. Therefore, stoichiometric metering generally is not sufficient. Rather, the actual reducing agent demand must be calculated in each individual case based on laboratory trials. This step should be included in any applications planning.

In most applications, the reducing agent is a divalent iron salt or a solution containing iron(II), because these substances are effective and significantly lower in cost than other reducing agents.

5. Reducing agents

Reducing agents are substances which, prior to application, are present in a reduced state and can very readily oxidize in the presence of a reaction partner, i.e. donate electrons. The electrons donated by the reducing agent are simultaneously accepted by the target species [in this case: chromium(VI)], which is converted from a previously oxidized to a reduced state [in this case: conversion of chromium(VI) to chromium(III)].

While these basic criteria for a reducing agent apply to any number of substances, technical suitability and expedience are defined by the toxicity, availability, effectiveness, good handling properties and price of the reducing agent. In view of these aspects, iron(II) products mainly have become established in the market as reducing agents. They are available either in the form of solid ferrous sulfate of various types, or ferrous chloride solution.

Tab. 2: Overview of suitable KRONOS ecochem products

Product	Chemical formula	Active ingredient	Form supplied	Bulk weight / density
QUICKFLOC Ferrous sulfate	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (heptahydrate)	178 g Fe/kg (3.19 mol/kg)	Moist salt	approx. 1.0 t/m ³
FERROGRANUL 30 Ferrous sulfate monohydrate	$\text{FeSO}_4 \cdot \text{H}_2\text{O}$	304 g Fe/kg (5.44 mol/kg)	Granules	approx. 1.7 t/m ³
FERROPOWDER 30 Ferrous sulfate monohydrate	$\text{FeSO}_4 \cdot \text{H}_2\text{O}$	304 g Fe/kg (5.44 mol/kg)	Powder	approx. 1.4 t/m ³
KROnoCHROME Ferrous sulfate monohydrate	$\text{FeSO}_4 \cdot \text{H}_2\text{O}$	144 g Fe/kg (2.47 mol/kg)	Powder	approx. 0.8 - 1.1 t/m ³
FERROFLOC Ferrous chloride solution	FeCl_2	86 g Fe/kg (1.54 mol/kg)	Solution	1.36 g/cm ³
KRONOFLOC Ferrous chloride solution	FeCl_2	87 g Fe/kg (1.56 mol/kg)	Solution	1.37 g/cm ³

While the chloride-containing liquids are associated with good availability, easy storage and simple metering via variable speed pump, the free-flowing sulfates are preferred for applications in which chloride would cause disruptions or the treated matrix must remain dry (e.g. in the building materials industry).

Ferrous sulfates can have different water of crystallization contents:



Heptahydrates with 7 water of crystallization molecules dissolve more quickly in water and are therefore somewhat more effective for chromate reduction. Monohydrates dissolve slightly more slowly. They consequently have to be added in slightly higher quantities than heptahydrates, but offer the advantage in processing of higher temperature resistance.

Technical Information 2.03 provides information on the on-site storage and metering of liquid products. Technical Information 2.02 provides information on the storage and metering of free-flowing ferrous sulfates.

6. Practical examples

Chromium(VI) reduction in cement

One example of an application, which has been very successful and used widely for over 20 years, is chromium(VI) reduction in cement (see Technical Information 6.01). In Germany alone, over 25 million tonnes of low-chromate cement are produced annually by the addition of roughly 0.1% to 0.5% ferrous sulfate and sold on the market. In European Union Member States, marketing cement with more than 2 mg soluble chromium(VI) per kg cement is prohibited.

As long as cement containing added, free-flowing ferrous sulfate is stored in dry conditions, the chromium(VI) and iron(II) are both present in unchanged form. Only when the cement is used, e.g. as ready-mixed concrete or mortar, is the chromium(VI) reduced to chromium(III) once the cement is thoroughly mixed with water. The same occurs when the extraction method is carried out in the laboratory (standard mortar method to EN 196-10) to determine the content of soluble chromium(VI). Given correct metering, the limit value of 2 mg/kg soluble chromium(VI) has proven to be stable in the chromate-reduced cement even over a storage period of 12 months.

Remediating chromium-contaminated soil / contaminated sites

In the past, long-term industrial and commercial property and land use often led to the soil underneath roads and buildings being contaminated with pollutants from operating materials, this being due in part to the lack of environmental awareness. With regard to chromium(VI) contamination, this is seen particularly frequently in the case of old electroplating businesses. To prevent long-term

threats to groundwater, the soil in such areas must either be disposed of as hazardous waste or remediated by means of soil washing. If the contaminants mainly include chromium(VI) and other substances easily washed out, then soil washing can be effective and much of the soil can continue to be used after successful cleaning.

The criteria for the success of remediation and subsequent use of the soil are defined in the Federal Soil Protection and Contaminated Sites Ordinance (Bundes-Bodenschutz- und Altlastenverordnung) and in the Technical Regulations LAGA M 20. Based on residual contamination with the individual tested parameters, a "soil class" from Z0 to Z2 is assigned as a quality criterion for further use of the soil, similar to a landfill waste classification. Soil in the strictest class Z0, which is intended for subsequent use, can contain max. 12.5 µg/L total chromium in the eluate, although even class Z2 specifies a limit of 60 µg/L total chromium. The Federal Soil Protection and Contaminated Sites Ordinance (BBodSchV) distinguishes between playgrounds, residential zones, parks and recreational facilities, industrial and commercial properties and grasslands, and defines different, strict limits for each.

For soil washing, the chromate reducing agent, e.g. ferrous chloride solution or free-flowing ferrous sulfate, can be mixed with the soil as homogeneously as possible prior to, or during, the washing process, e.g. with a screw or compulsory mixer, typical added quantities being in the range from 0.5% to 5%. The required stability of chromate reduction has also been demonstrated in this case in many years of practical application.

Chromate reduction in fly ash

To lower the waste class of chromate-containing fly ash and thus optimize the costs of disposal, this type of ash can be industrially pre-treated, e.g. in a screw mixer, to reduce the chromium(VI) content. In this application example, a liquid product (KRONOFLOC ferrous chloride solution) and a free-flowing ferrous sulfate monohydrate (KROnoCHROME) were used with added water. In both cases, a lower waste class was achieved thanks to successful and sustainable reduction of the chromium(VI) content. Depending on the degree of chromate contamination in the ash, the required added quantity typically is between 0.5 and 5%.



Fig. 3: Soil removal as part of remediating a contaminated site

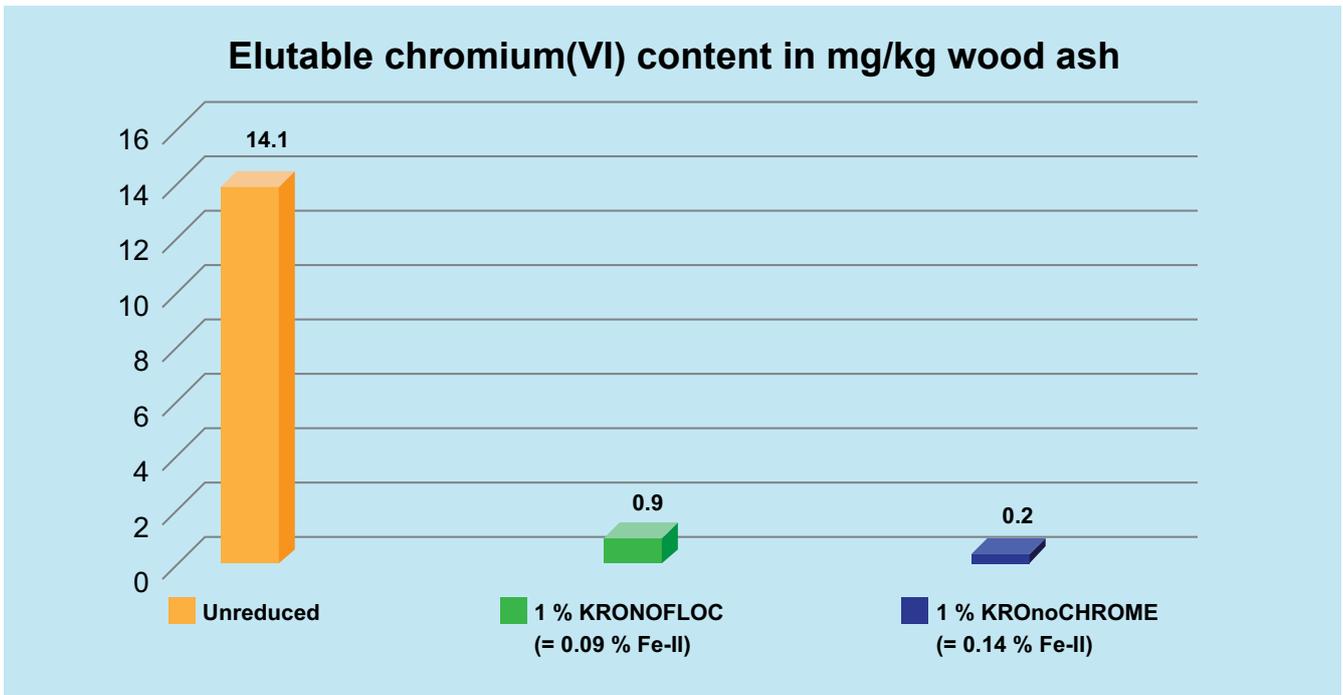


Fig. 4: Elutable chromium(VI) content to EN 12457-4 (S4 shake test) in wood ash with and without added iron salt products

Wood ash from incinerating fresh beechwood chips

A portion of the chromium(III) naturally occurring in wood as a trace element is oxidized during incineration to chromium(VI), which is then contained in the incineration ash. Ash from fresh, untreated beechwood can contain as much as 20 mg chromium(VI) per kg. As a renewable and CO₂-neutral fuel, wood will become increasingly important in future as an energy source. Against this backdrop, the chromate contamination of wood ash poses a problem for the disposal and recycling of the ash, and with regard to occupational safety when handling it.

Reducing chromium(VI) to chromium(III) can make it possible to lower the waste class of such waste and is therefore more economical. Direct recycling of the ash as an ingredient in fertilizer frequently is prevented by the Fertilizers Ordinance, which permits a limit of max. 2 mg chromium(VI) per kg dry mass, or even max. 1.4 mg/kg for product not subject to mandatory labelling. Here, too, chromate reduction can lower the chromium(VI) content to below the limit value and thus enable economically and ecologically effective recycling in line with the principle of a circular economy (Fig. 4).



Fig. 5: Biomass power plant (wood-fired)

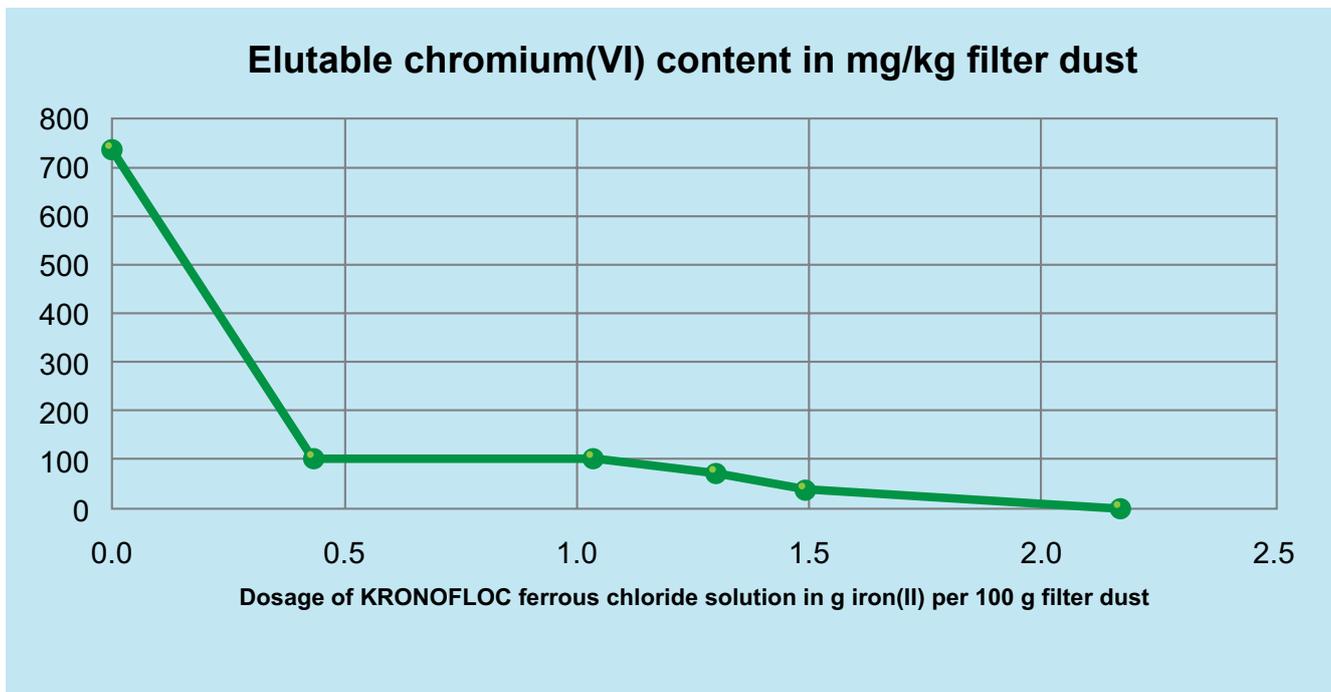


Fig. 6: Elutable chromium(VI) content in filter dust from a stainless steel plant at different dosage levels of KRONOFLOC ferrous chloride solution

Steel mill slag

Slag from steel or ferrochrome production, which has undergone uncontrolled solidification, often contains elutable chromate and poses a risk to groundwater depending on how it is stored or its route of disposal. This applies in particular to unprotected surface storage, such as an outdoor waste heap or drainage collector.

A material's particle size is of critical significance to the timeframe for elution of the chromium(VI). On account of the usually coarse structure of slag that has undergone uncontrolled solidification, elution is significantly slower and often still not complete after several hours. The low specific surface area of coarse slag results in the very slow release of the soluble chromium(VI) portion. Laboratory testing for this example showed that treatment with iron(II) was only effective when it was added to the seepage water of the slag heap. In contrast, when it was applied on top of the slag heap itself in conjunction with simulated rainfall, the reducing effect was inadequate because the elution of the soluble chromium(VI) is significantly slower than the oxidation of the iron(II) by atmospheric oxygen, a process which competes with the chromate reduction. One practical option for effective resolution of the problem is to treat the collected seepage water with iron salts in order to reliably rule out any risk to the environment.

Filter dust from a stainless steel plant

Chromium alloy steel processing often generates filter dust with a high chromate content. Hexavalent chromium reduction can be expedient not only for the disposal route, but also with regard to occupational safety when handling the dust.

As an example, filter dust from a steel plant with an elutable chromium(VI) content of 740 mg per kg dust (740 ppm) was treated with various iron salts to demonstrate the effectiveness of the method even with such highly contaminated dust (Fig. 6).

7. Sustainability of chromate reduction

Successfully reduced chromium can undergo a reverse reaction under certain circumstances, for example in a highly alkaline environment at high (air) humidity or in the presence of oxidizing accompanying substances. Thus, over time and under the right conditions, chromium(VI) can form again from chromium(III).

In this context, "sustainability" means that the unwanted reverse reaction is prevented long-term, and the treated matrix therefore continues to be in compliance with legal regulations over an extended period of time. Sustainability in this sense is also referred to as the long-term stability of chromate reduction. Taking cement as an example matrix, different requirements are imposed on long-term stability, which arise from the various, typical periods of use of the low-chromate cement.

For example, cement sold in bulk must maintain a maximum of 2 mg/kg chromium(VI) for only two months from the time it is made available on the market, while cement packed in bags usually has to remain low in chromate for 6 or even 12 months, because it often is stored for longer periods before use than bulk cement. Some regulations stipulate even as many as 24 months of storage stability for special cementitious binding agents. For this reason, bags of cementitious building materials generally show a date until which a chromium(VI) content of less than 2 mg/kg (referred to the cement content) is guaranteed if the bags are stored properly.

Better long-term stability can be achieved by adapting the dosage of the chromate reducing agent, which can be determined and optimized in laboratory trials. The rule of thumb is that dry materials like cement should be stored in a dry environment with no humidity, while in the case of already moist substances like wood ash, total chromate reduction should be ensured by thorough mixing and added moisture right when the reducing agent is introduced.

One example of a thoroughly desirable reaction during storage is the natural reduction of chromium(VI) in wood ash by the organic humic substances contained in forest soil, which frequently have a reducing effect.

By spreading the ash in a forest environment, a significant portion of the chromium(VI) can be converted to chromium(III) by natural reduction processes, and the ash decontaminated without an externally added reducing agent.

On the other hand, oxidizing species such as manganese dioxide (MnO_2) can also be present in soil, which can oxidize chromium(III) back to unwanted chromium(VI). This aspect should be kept in mind in individual cases (e.g. when the goal of reductive treatment in soil remediation is to reuse the soil).

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