KRONOS
ecochem®

Chromate reduction in cement using ferrous sulfates

Depending on the origin of the raw materials used and the clinker production conditions, cement contains up to 100 ppm hexavalent chromium (chromate). In this water-soluble form, chromium is capable of penetrating the human skin and can cause an allergic reaction known as chromate dermatitis, depending on the intensity and duration of exposure.

Since Directive 2003/53/EC came into effect, all EU Member States have been obliged since 17 January 2005 to reduce the chromate content in cement and cement-containing preparations.

Among other things, Regulation (EC) No. 1907/2006 defines the following restriction regarding the production, marketing and use of cement and cement-containing preparations:

Cement and cement-containing preparations may not be used or placed on the market, if they contain, when hydrated, more than 0.0002% (2 ppm) soluble chromium (VI) of the total dry weight of the cement.

1

Chromate reduction

By adding a reducing agent, such as ferrous sulfate, the water-soluble hexavalent chromium can be converted into a hardly soluble, trivalent form that is no longer capable of penetrating the skin:

$$CrO_4^{2-} + 3\ Fe^{2+} + 4\ OH^- + 4\ H_2O \longrightarrow Cr(OH)_3 + 3\ Fe(OH)_3$$

Accordingly, the resultant stoichiometric bivalent iron demand is

3 mol Fe^{II} per 1 mol Cr^{VI}

or 3.22 mg Fe^{II} per 1 mg Cr^{VI}/kg cement [ppm].

The chemical reaction does not start until immediately after addition of the mixing water. Owing to the highly alkaline environment, the iron is subject to competing reactions, such as hydrolysis and oxidation due to dissolved atmo-spheric oxygen, meaning that corresponding overdosing is necessary, regardless of the product.

Ferrous sulfate has demonstrated its worth as a reliable chromate reducer in many years of practical application. The customary quantities added need not be expected to have any impact on the properties of the concrete. When using high dosages of more than 0.5%, it may be sensible to optimise the sulfate carrier in order to reliably exclude any effects on the setting behaviour.[1]

Poor storage stability of the cement can often be observed when using stannous sulfates as chromate reducers. This is because the effectiveness of tin sulfates declines in the course of time as a result of chemical reactions occurring in the cement matrix. Oxygen, moisture, and also an elevated content of free lime, can accelerate this loss of activity.[2] Consequently, larger quantities of added tin sulfate are often necessary to prevent the limit being exceeded, making chromate reduction with tin compounds even more expensive.

The use of antimony(III) compounds, e.g. Sb_2O_3, must be viewed critically owing to the possible toxicological risk of these substances, which are suspected of being carcinogenic.

2

KRONOS ferrous sulfate: properties and forms

Ferrous sulfate containing residual moisture is known as copperas and is obtained in large quantities during production of titanium dioxide by the sulfate process. Because of its complex handling requirements, the salt containing residual moisture is hardly used at all in the cement industry – free-flowing products suitable for pneumatic conveying are preferred for chromate reduction in cement.

Depending on the drying method chosen, the free-flowing ferrous sulfate types differ not only as regards their active-substance content and their particle size distribution, but also in terms of their physical and chemical properties. The different particle size distributions in the end-products essentially derive from the crystallite size of the moist iron sulfate and the drying method used (chemical or thermal drying).

The content of water of crystallisation is of decisive importance for the handling and effectiveness of the dried products:

$$FeSO_4 \cdot 7\,H_2O \xrightarrow{>40\,^\circ C} FeSO_4 \cdot 4H_2O \xrightarrow{>80\,^\circ C} FeSO_4 \cdot H_2O$$

(Heptahydrate) (Tetrahydrate) (Monohydrate)

← Water solubility increases

Thermal stability increases →

All free-flowing ferrous sulfate types are available in bulk or packed in IBCs. The optimum product for a particular field of application can be determined on the basis of the following criteria:

- Metering point (upstream of the cement mill, upstream of the classifier, downstream of the classifier, before cement shipping)
- Temperature conditions at the metering point/metering equipment
- Storage conditions (temperature)
- Availability/logistics.

Table 1: Overview of ferrous sulfate types for chromate reduction in cement

Trade name	Chemical formula	Active substance	Form supplied	Bulk density
QUICKFLOC Ferrous sulfate	$FeSO_4 \cdot 7\,H_2O$	178 g Fe/kg (3.18 mol/kg)	Moist salt	Approx. 1.0 t/m^3
FERROGRANUL 20 Free-flowing ferrous sulfate	$FeSO_4 \cdot 6\text{-}7\,H_2O$	195 g Fe/kg (3.49 mol/kg)	Fine granules	Approx. 0.8 t/m^3
KROnoCHROME Ferrous sulfate monohydrate	$FeSO_4 \cdot H_2O$	144 g Fe/kg (2.58 mol/kg)	Powder	Approx. 0.9 t/m^3
FERROGRANUL 30 Ferrous sulfate monohydrate	$FeSO_4 \cdot H_2O$	304 g Fe/kg (5.44 mol/kg)	Granules	Approx. 1.7 t/m^3
FERROPOWDER 30 Ferrous sulfate monohydrate	$FeSO_4 \cdot H_2O$	304 g Fe/kg (5.44 mol/kg)	Powder	Approx. 1.4 t/m^3

2.1

Ferrous sulfate heptahydrate

QUICKFLOC

The so-called copperas is produced in the form of a crystalline salt containing approx. 2 to 6% by weight seepage liquid. Owing to the residual moisture, it is not expedient to store (and use) QUICKFLOC in as-delivered condition, since the product hardens (much like wet snow), oxidises, and acidic drainage liquid can seep out. In other fields of application, copperas is therefore dissolved in water immediately after delivery, only the saturated solution being stored and used.

For chromate reduction in cement, there are two options for using QUICKFLOC as a reducing agent:

1. Addition to the cement mill as a saturated solution; in this case, the water introduced represents the limiting factor. This is only expedient when dealing with very low chromium(VI) contents of up to 5 ppm.
2. Addition in the form of free-flowing copperas; blending with a drying agent permits adsorptive binding of the seepage liquid.

In both cases, addition must take place upstream of the cement mill, in order to reduce the amount of moisture introduced by the copperas. However, water of crystallisation is also dried out during the joint grinding of clinker and copperas, as a result of which the ferrous sulfate is present in the finished cement in the form of the monohydrate.

FERROGRANUL 20

Thermal drying of copperas permits removal of the seepage liquid in order to obtain a free-flowing product. Since a small proportion of the water of crystallisation is also removed during drying, the average water of crystallisation content is 6-7 molecules H_2O per formula unit. The result is fine granules with very good free-flowing properties and a powerful chromate-reducing action, provided it is added to the fine-ground cement. As the temperature rises, the first three molecules of the water of crystallisation become mobile and can lead to initial agglomeration phenomena in the product upwards of about 40 °C.

FERROGRANUL 20 should preferably be stored and conveyed at temperatures well below 40 °C. The problem is specifically familiar when storing FERROGRANUL 20 in bins and can be mastered by taking appropriate technical measures in the bin.

With the very low quantities of FERROGRANUL 20 customarily added in practice, the individual iron sulfate grains are ”isolated“ in the dry cement meal environment. Any potential migration of water of crystallisation is immediately stopped and no unwanted reactions take place.

The situation is different in the presence of partial excess concentrations of FERROGRANUL 20 in the cement. Upwards of concentrations of approx. 20% and temperatures of about 70 °C, the mobility of the water of crystallisation becomes so great that a neutralisation reaction sets in. The acidic ferrous sulfate combines with the alkaline cement, forming hydrated iron oxide and calcium sulfate. The resultant encrustation phenomena of the ferrous sulfate agglomerates can cause serious operating malfunctions due to ”hard“ lumps:

$$FeSO_4 \cdot 7H_2O + \text{"Cement"} \xrightarrow{> 70\ °C} FeO(OH) + CaSO_4 \cdot x\ H_2O$$

Attention should be paid to good incorporation and the most homogeneous possible dispersion of FERROGRANUL 20 in the cement meal to avoid partial excess iron sulfate concentrations. Moreover, high transport speeds in combination with small pipeline radii can result in grain fracture in the case of FERROGRANUL 20. In conjunction with a high material pressure, the resultant increasing fines can lead to the formation of ”soft“ lumps in the bin, thereby impairing discharge.

2.2

Ferrous sulfate monohydrate

Monohydrate is the most thermodynamically stable modification of the ferrous sulfate types, demonstrating good storage stability and free-flowing properties even at temperatures higher than 150 °C.

KROnoCHROME

To produce this powder-type monohydrate, the acidic seepage liquid in the ferrous sulfate is neutralised chemically. Because of its fineness, this product is suitable for universal use, both before and after grinding. Its great thermal stability and the residual moisture content of approx. 0.5%, which is extremely low for a chemically dried monohydrate, rule out the possibility of caking and agglomeration, enabling problem-free storage and metering. The low residual moisture content is achieved by a downstream drier.

FERROGRANUL 30
FERROPOWDER 30

Spray-drying of a copperas solution at elevated temperatures leads to a further two ferrous sulfate monohydrate types:

FERROGRANUL 30 and FERROPOWDER 30.

The two products differ only in terms of particle size distribution. Both the active-substance content of approx. 30% Fe^{2+} and the chemical composition of the two grades are comparable. The thermal stability of these products is similar to that of KROnoCHROME.

While FERROPOWDER 30 powder can be used at any conceivable metering point, FERROGRANUL 30 granules should always be added at a metering point upstream of the cement mill or the classifier.

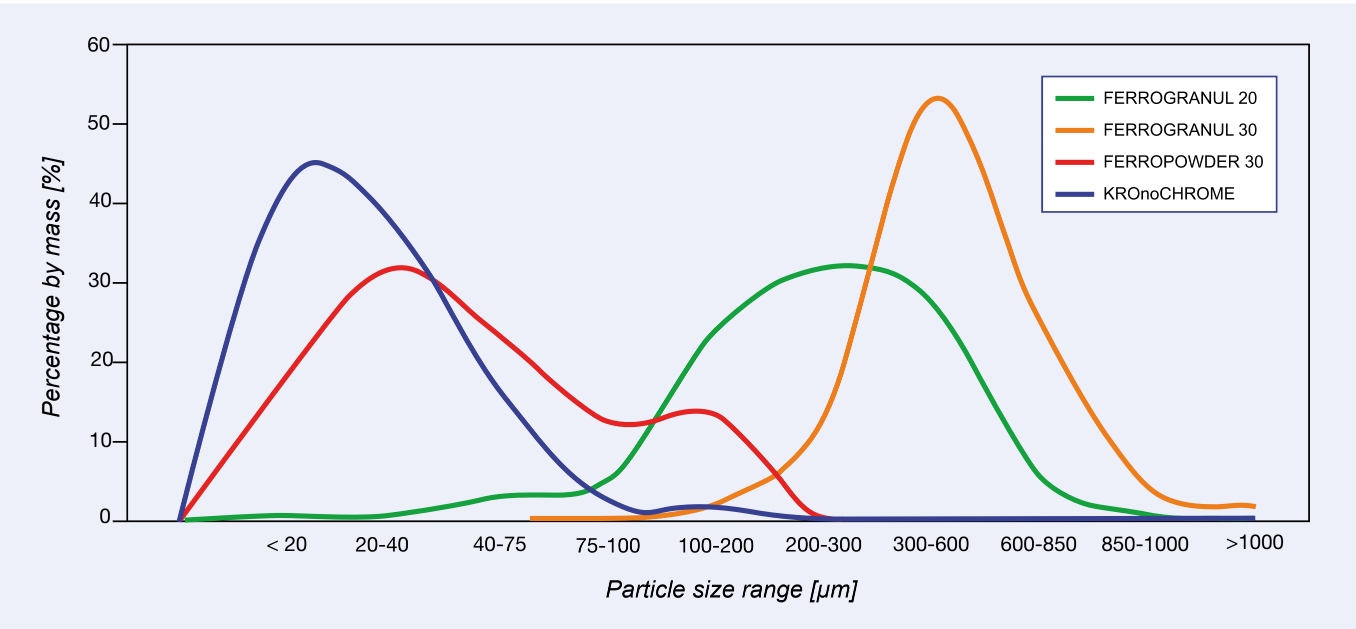

Fig. 1: Typical particle size distribution of free-flowing ferrous sulfate types

3.0

Dosage

Although all ferrous sulfate types are basically suitable for chromate reduction in cement, the level of unreduced chromium(VI) and the required metering point determine the optimum product. Moreover, it must be borne in mind that the slightly poorer water solubility of the monohydrate has to be compensated for by adding a slightly higher quantity. In contrast, the thermal stability of the monohydrate can offer greater operating reliability, e.g. in plants without a cement cooler. Following joint grinding of the clinker with the reducing agent, the ferrous sulfate is always present in the cement meal in the form of powder-type monohydrate.

The special advantage of a heptahydrate, its good water solubility, is lost as a result of the grinding process. From the point of view of economics, the active-substance content of the reducing agent is the only decisive factor when using this metering point. If the reducing agent is only added to the finished cement downstream of the classifier, the necessary added quantity is lowest when using FERROGRANUL 20. However, a cement temperature in excess of 50 °C at the metering point requires special consideration.

To avoid caking and agglomeration in the chromate-reduced cement, the addition of FERROGRANUL 20 has to be exactly matched to the cement flow in this case, i.e. premature dosing and run-on of the heptahydrate, e.g. in the hot cement trough conveyor, must be ruled out. An immediate and thorough blending needs to be achieved. If the cement temperature is above 60 °C, the application of a temperature-stable ferrous sulfate monohydrate is recommended. Given correct storage, the reducing effect of the ferrous sulfate in the cement is preserved over a period of more than six months, which may be prolonged by an increased dosage.

The handling of free-flowing ferrous sulfate requires compliance with general safety and hygiene measures, as customary for chemicals and described in the Safety Data Sheet.

Table 2: Typical dosages (guide values) for a chromium(VI) content of 10 ppm in the cement for addition downstream of the mill

Product	Typical surplus*	Typical dosage
FERROGRANUL 20	Approx. 8-fold	0.13%
KROnoCHROME	Approx. 14-fold	0.34%
FERROGRANUL 30	Approx. 20-fold	0.22%
FERROPOWDER 30	Approx. 20-fold	0.22%

** Referred to the stoichiometric demand (3 mol Fe/mol Cr)*

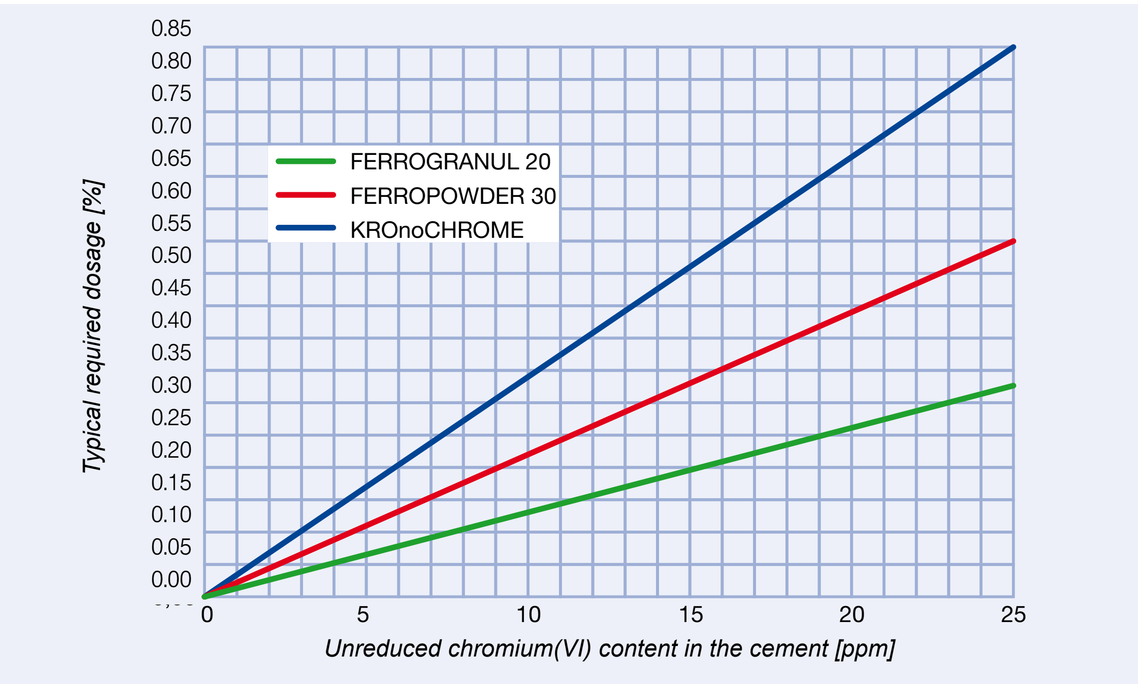

Fig. 2: Typical necessary dosages (guide values) for addition downstream of the mill

3.1

Special notes on dosing

The chromate-reducing effect of a ferrous sulfate added to the cement is also governed by the active-substance content (% Fe^{2+}), in addition to other influencing factors, such as the content of water of hydration, particle size, dissolving power, metering point, storage period and extraction method.

KROnoCHROME is a co-product of titanium dioxide production. Even the raw material, a sulphuric salt, is subject to unavoidable fluctuations in its content of Fe^{2+} ions for production-related reasons.

During the production of KROnoCHROME, the sulphuric acid in the filter salt is completely neutralised by adding a lime product, the moisture content being reduced to below 0.5% in a downstream drier. The dosage of the lime product is adapted to the likewise slightly fluctuating sulphuric acid concentration, and this automatically results in further variation of the iron content in the end product.

Figure 3 shows the resultant fluctuation range during a month of real production. The Fe^{2+} content is checked several times per day at our production facility in Nordenham, Germany, as part of quality control. The KROnoCHROME Data Sheet indicates a typical iron(II) concentration of 14.4%. This figure represents more the lower end of the typical fluctuation range and was deliberately chosen in order to guarantee the reliability of chromate reduction at all times in practical use.

In general, however, it is recommendable to use an appropriate, slight overdose. Since the raw materials and processes used are similar, the production-related fluctuations described above affect not only our KROnoCHROME product, but all filter salt-based iron sulfates available on the market (monohydrates with an iron(II) content of approx.10-15% according to the supplier).

3.2

Test methods

Depending on the temperature, moisture content and storage period of the chromate-reduced cement, a thin crust of hydrated iron oxide can form around the individual ferrous sulfate particles, protecting the interior of the particle against oxidation.

To test the effectiveness of the reducing agent used, particularly in trials for determining the storage stability after tempering, this protective shell first has to be mechanically broken up in order to expose the reactive iron(II). Reference is made to ”passive“ solubility in this context. In practice, the necessary shear forces are generated directly when mixing the cement with sand.

The practice-oriented standard EN 196-10:2006 for determining water-soluble chromate has proven successful for assessment of a chromate reducing agent. In-house studies have shown that varying the prescribed stirring times brings about changes in the chromate content measured. Consequently, exact compliance with the stirring times is essential in order to obtain comparable results that conform to the standards.

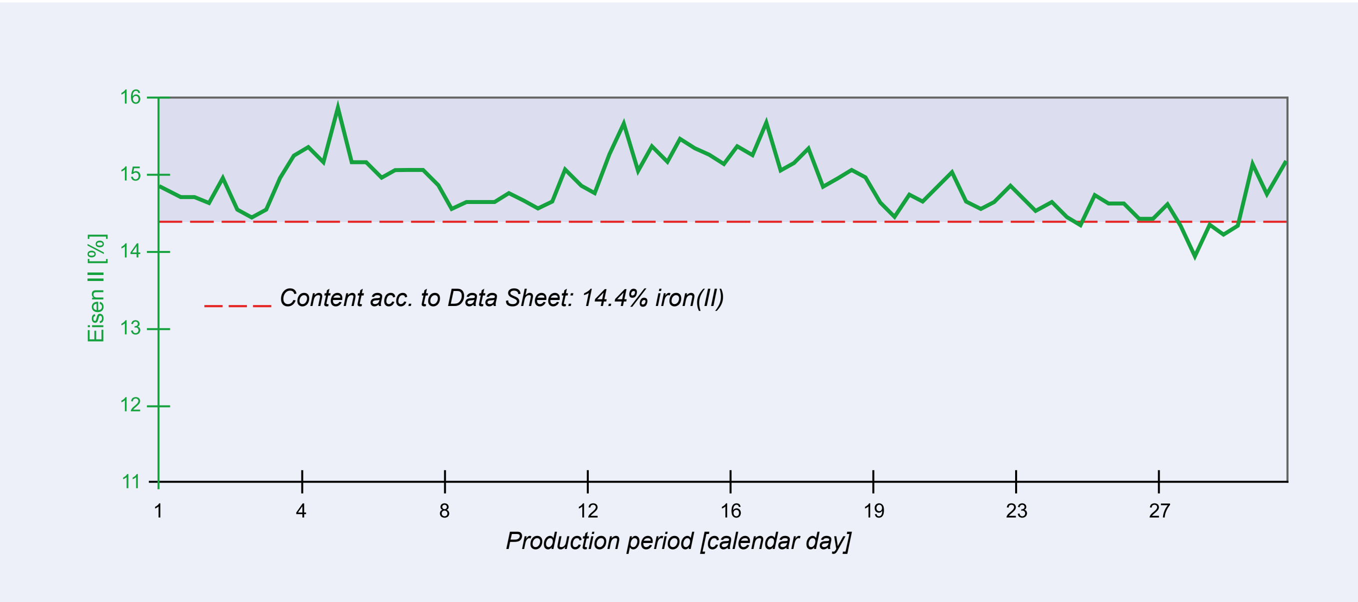

Fig. 3: Fluctuation range of the iron(II) content of KROnoCHROME during one month of production

4.0

Transport and storage / Equipment

Free-flowing ferrous sulfate is usually delivered as loose, bulk material in dry-bulk trailers or semi-bulk containers, using trucks having a compressor with air cooler. In the case of FERROGRANUL 20, this ensures that the product is not overheated when unloaded using the vehicle's dry compressed air.

(Flexible) lines with a diameter of DN 65 to 80 have proven successful for pneumatic conveying of the free-flowing products. The length of the conveyor line should preferably not exceed 60 m. A radius of between 800 and 1,000 mm is recommended when using arches or bends. The conveyor line should ideally be inclined. Diverter pots are not suitable for granular materials like FERROGRANUL 20, as they may cause undesired grain breakage. If the material has to be conveyed over relatively long, horizontal distances, appropriate intermediate air supply points (supporting air) should be provided to accelerate the volume flow. As a rule, it takes less than two hours to unload a 25-tonne batch.

Ferrous sulfate tends to form lumps in the presence of high moisture levels. Consequently, these products must always be kept dry during storage. Storage in bins does not impose any special requirements on the material, since iron sulfate is not corrosive when dry. Accordingly, even unprotected steel can be used as a material.

The following installations should be provided in order to ensure trouble-free product discharge:

- Sunshade, preferably in the form of a light-coloured jacket with free air circulation (only required for FERROGRANUL 20 to prevent temperature-induced formation of lumps)
- Discharge aid in the form of aeration jets or intermittent vibrator to ensure a steady flow
- Steep bin discharge cone of > 60 °
- Relieving troughs in the bin for avoiding material pressures in excess of 0.5 kg/cm².

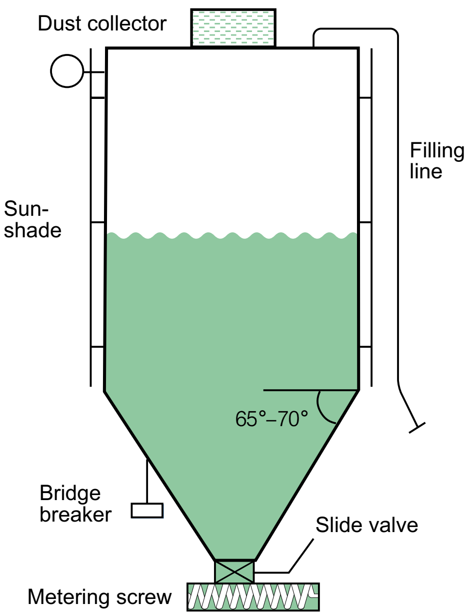

Fig. 4: Diagram of a bin facility for free-flowing ferrous sulfates

Literature

[1] R. Härdtl, M. Dietermann, G. Bolte; ZKG International 59 (2006), No. 10, p. 88-93

[2] S. Baetzner, J. Glöckler, D. Israel, M. Paul; Cement International 8 (2010), No. 5, p. 68-76

KRONOS INTERNATIONAL, Inc.
KRONOS ecochem
Peschstr. 5 • 51373 Leverkusen • Germany
Tel. +49 214 356-0 • Fax +49 214 44117
kronos.ecochem@kronosww.com
www.kronosecochem.com

KRONOS ecochem®