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Newsletter 1/2004

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Chromate Reduction in Cement and Concrete

The new European Directive 2003/53/EC and its consequences for process and analytics

According to the European Directive 2003/53/EC cements and cement-containing preparations may not be used or placed on the market if they contain more than 2 ppm of soluble chromium(VI). This does, however, not apply, when the cement or the preparations are handled in controlled, closed and totally automated processes, where the possibility of skin contact is not given. The aim of the Directive on market restrictions for cements is to decrease skin diseases due to chromium(VI). However, the future success of this measures is questionable: it is well known that irritating allergies can not be reduced by lowering the chromium content of cement and cement containing preparations. Also, it has turned out that skin diseases due to chromate in leather gloves play an important role which has not been taken into account at all when issuing the Directive. It is not clear if these findings can be used to change the spirit of the Directive. Up to now it seems to be unavoidable, that the Directive must be complied with beginning of next year. As a consequence the European cement industry prepares to reduce chromate in cements.

Reducing agents

Most of the European cements contain more than 2 ppm of chromate i.e. water-soluble chromium(VI). If a reduction agent is used the reduction must be as effective and durable as possible. Ferrous sulfate is the most often used reducing agent for cement and cement containing preparations. Various products from different sources are available on the market. Their properties may vary widely, even for different ferrous sulfates, which leads to consequences for the product and its analytical examination. The requirements concerning storage, handling and dosing depend strongly on the different materials as well.

As an alternative, tin sulfate could also be used as a chromate reducing agent. However, the available quantities are limited and the price is extremely high compared to ferrous sulfate.

Stability of ferrous sulfate

In the Scandinavian countries the addition of ferrous sulfate to cement during grinding has been practised

for about twenty years up to now. However, this experience can not be transferred easily to other countries, because the grinding process affects the reactivity of the reducing agent. Ferrous sulfate is quite reactive and quickly dehydrates already at temperatures exceeding 60 °C. This lowers the reducing potential tremendously because the monohydrate is less water soluble than the penta- or hepta-hydrate for example (Fig. 1).

Also the grain size of the reducing agent is important. Although the solubility of ferrous sulfate improves when its specific surface is increased - as it happens by inter-grinding with cement -, a faster dehydration is induced. This can be seen from laboratory examinations.

Fig. 2 shows the chromate in cement samples to which ferrous sulfate had been added in different particle sizes. The chromate content in the unreduced cement was 17 ppm, the ferrous sulfate was 30 times overdosed, the cements were stored at 20 °C.

As critical as its particle size is the temperature when the ferrous

sulfate is added to the cement and the storage conditions. The loss of reactivity which the ferrous sulfate experiences under storage will be ultimately responsible for the time period in which the 2 ppm limit can be complied with.

To achieve a prolonged activity of the reducing agent the addition of granulated ferrous sulfate with a grain size of about 300 µm is preferred to a combined grinding of cement and reducing agent. This was confirmed by examinations on industrial bagged cements. Fig. 3 shows some ferrous sulfate aggregates of about 300 µm grain size after 3 months storing under plant conditions. The brown and rounded surface indicates thermal and chemical reactions in the cementitious environment.

In Fig. 4 a section through one of these grains is shown. It can be seen that unreacted ferrous sulfate remains under an inert surface.

Ground – and therefore much finer – material would have reacted completely without any reactive components remaining.

Experience shows that for a

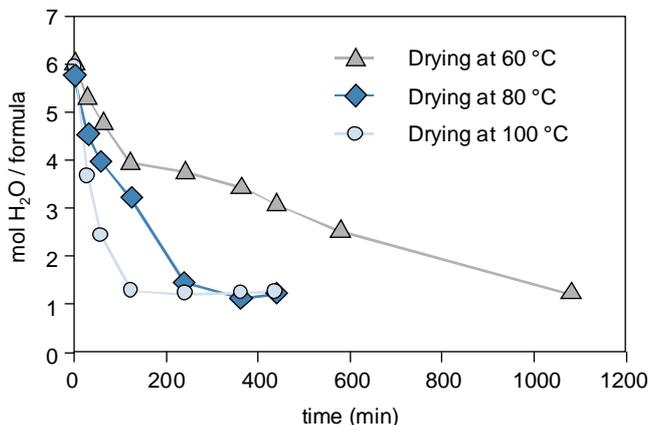


Fig. 1: Thermal behaviour of ferrous sulfate

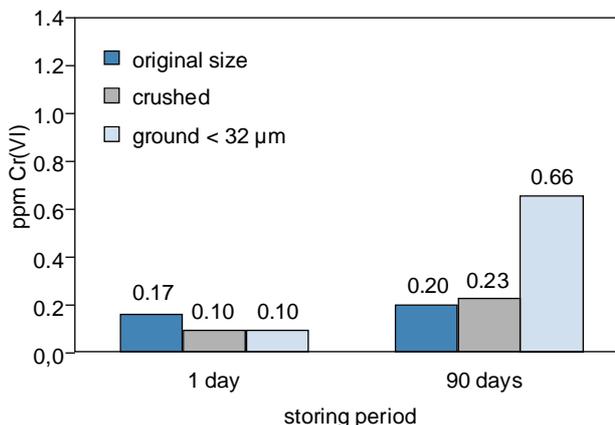


Fig. 2: Influence of fineness on the reactivity of FeSO₄

cement treated with 300 µm ferrous sulfate a minimum shelf life of about six months can be guaranteed under proper storage conditions.

Analytical aspects

Practical experiences show that the speciation of chromium(VI) in cement is an analytical challenge. Systematic investigation showed that each kind of reducing agent and the way of adding it to the cement requires an appropriate test

method including sample preparation. Comparative examinations of the chromate content in pure cements as well as of mortars and concretes produced with these cements showed significantly higher values in the pure cement samples.

In the practical use of cementitious materials, the influence of additives is important as well. Organic matter may also have a strong influence on the quality of the test result, because it often leads to

cloudy solutions. Reducing agents like sulfide from, e. g., ground granulated slag in CEM II-S and CEM III cements can provoke lower test results simply due to the adjusted test conditions (lower pH value) for the spectrophotometric determination of chromium(VI). The European standard, which is in preparation for the determination of chromium(VI), will take these experiences into account.

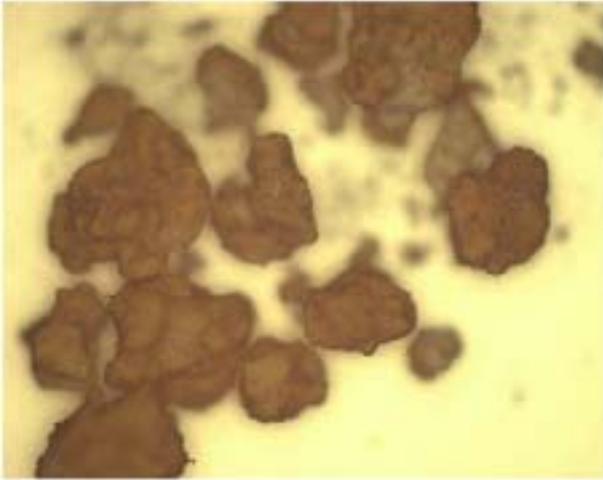


Fig. 3: Ferrous sulfate particles after 3 months storage in bagged cement



Fig. 4: Section through a ferrous sulfate grain after 3 months storage in bagged cement

NO_x Reduction in the Cement Industry

European Legislation as driving force for effective reduction measures

Burning of cement clinker is a high-temperature process, which requires gas temperatures of up to 2,000 °C to form the clinker phases. As a result of it the formation of thermal NO is more or less unavoidable. Additionally, the formation of fuel NO contributes to the total NO_x emissions. In the course of a more and more demanding European legislation, the cement industry is challenging the need for improved NO_x abatement. The main driving forces are the European "Directive on the Incineration of Waste" and the IPPC process resulting in the description of Best Available Techniques (BAT) for all relevant industrial sectors.

The European cement industry is facing pressure from different sides to achieve a more extensive NO_x reduction. On the one hand, very strict air quality limits have been specified by the European Union. As a consequence, licensing procedures are becoming increasingly complicated, especially when air quality limits for NO₂ are already exceeded in the vicinity of the plants. On the other hand, the European BREF Document (Best Available Techniques Reference Document) for the cement and lime manufacturing industries defined an emission level of 200 – 500 mg/m³ for NO_x, which should be achievable with the use of so-called Best

Available Techniques (BAT). However, there was also an opposing view within the BAT experts group that the emission level associated with the use of BAT should be 500 – 800 mg/m³ (as NO₂). Furthermore, the European Directive on the Incineration of Waste stipulated NO_x emission limit values for cement plants co-incinerating waste, namely 800 mg/m³ for existing plants and 500 mg/m³ for new plants. As a consequence of all these developments, the individual NO_x emission limits have been tightened in most countries so that there is a need to apply effective NO_x abatement measures.

The BREF Document contains a

series of primary and secondary measures, which have been successfully applied for NO_x reduction in the cement industry. Flame cooling, low-NO_x burners, mineralizers and staged combustion have been identified as appropriate process-integrated measures. Experience shows that the NO_x reduction potential of those measures depends on the special situation at each individual kiln and also on the initial NO_x level. However, primary measures have been widely implemented in the cement industry.

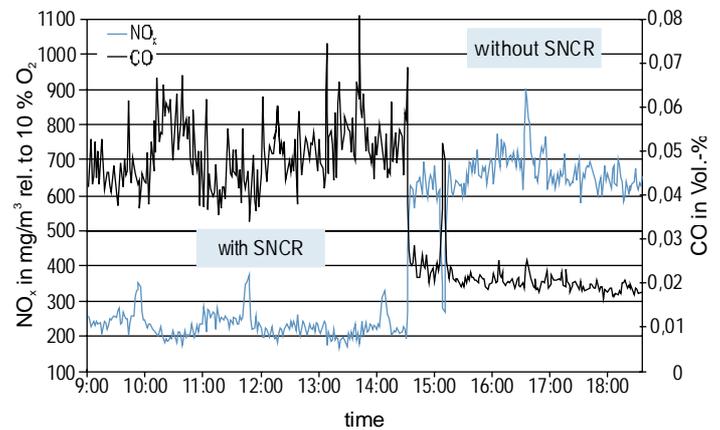
Plants, which were newly built in the last years, are equipped with precalciner and tertiary air duct so that the technique of staged com-

bustion can be applied. The reduction of NO_x by this technique in the precalciner can be improved by lowering the air ratio in the reduction zone. Furthermore, the fuel properties certainly have an effect on the NO_x reduction. Besides the nitrogen content, the reactivity of the fuel is assumed to play an important part in the formation and decomposition of NO . Operational trials showed that the potential of this technique is limited by process constraints, such as unacceptable increase of coating formation and reduced burnt clinker.

If high reduction rates are required for meeting new emission limits, the application of secondary measures is inevitable in many cases. The SNCR process (Selective Non-Catalytic Reduction) is the most promising technique to achieve significant NO_x reduction rates at moderate costs. Up to now, SNCR plants have been installed at more than 30 cement kilns in Europe, with rising tendency. One of the main advantages is that SNCR is applicable at most types of rotary kilns, provided the existence of the appropriate "temperature window" (900 – 1,000 °C). Depending on the initial NO_x level, reduction rates of more than 50 % are achievable. The standard reducing agent is a 25 % aqueous ammonia solution. However – especially for economic reasons - increasing use is being made of ammonium containing waste waters.

In the last years, operational trials were carried out in the cement industry to investigate the reduction potential of the SNCR process. It turned out that very low NO_x emission values could be achieved with

Fig. 2: Effect of the combination of staged combustion and SNCR process on NO_x and CO emissions



SNCR technology. However, high reduction rates are accompanied by high $\text{NH}_3/\text{NH}_4^+$ emissions and a notable build-up of ammonium compounds in the ESP dust. Though there are no NH_3 emission limit values in most European countries, SNCR trials are always aiming at a low NH_3 slip. This corresponds with the current environmental policy which is intending to reduce the input of acidifying nitrogen compounds into the ecological system. The objective of current investigations is to optimise the installed SNCR plants. A potential means to improve the performance could be the development of ingenious injection strategies. These investigations show that the optimisation has to take the plant specific conditions into account (fig. 1).

Even though no experiences about simultaneous application of SNCR and staged combustion had been documented so far, the BREF document considered the combination of both as "emerging technique". With this technique an attainable NO_x emission level of 100 - 200 mg/m^3 is assumed. Industrial trials showed that low NO_x concentrations could be achieved, but also increased CO emissions were ob-

served. A decisive role regarding a significant decomposition of NO is attributed to a sufficient residence time of the reacting species in the right temperature window. Furthermore, the combustion of the calciner fuel should be completed as far as possible. Besides, the injection of ammonia water also interacts with the oxidization of CO because the formation of NH_2 radicals requires OH radicals which are essential for the oxidization of CO (fig. 2) as well. Taking these open questions into account, the combined application of SNCR and staged combustion cannot be seen as BAT up to now.

According to the BREF Document, the SCR technique (Selective Catalytic Reduction) is supposed to provide the highest NO_x reduction potential. The first industrial scale SCR plant in the cement industry is in operation for more than 3 years. So far, the available test results seem to indicate good operability at the respective plant. The main goal is still to meet the current emission limit value. However, short-term trials showed that also lower NO_x concentrations are achievable. At the moment it is still too early for a comprehensive assessment of the plant, in which – apart from the reduction rate – operating safety, costs and potential side effects have also to be evaluated.



Fig. 1: SNCR process: Configuration of injection lances at a riser duct

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