



Practice Report: Appropriate dosing of chromate reducers

A new approach to the detection and targeted correction of overdosing

Because of the better mixing obtained, chromate reducers are generally added either upstream of the cement mill or immediately downstream, before the material enters the classifier. Later addition to the fin-finished cement before loading or bagging is only rarely still to be encountered today. This results in a situation where the non-reduced, original content of water-soluble chromium(VI) can often no longer be determined, or only at great effort, e.g. by joint milling of clinker and sulphate carrier in the laboratory.

Without accurate knowledge of the original content of water-soluble chromium(VI), it is more difficult to assess whether a particular cement batch contains a sufficient quantity of reducing agent to ensure long-term stability of several months. While the quantity actually added is documented, it is hardly possible to exactly determine and assess fluctuations in the original Cr(VI) content that can result from different raw materials or calcining conditions, for example.

A measured value to EN 196-10 that is below the detection limit merely indicates that the quantity of reducing agent added is still sufficient, at least if determined immediately. It does not permit conclusions to be drawn regarding the degree of overdosing or the long-term stability to be expected. So, a measured value below the detection limit can stand for two extreme situations. First: the reducing agent dose is just enough to completely eliminate the content of water-soluble Cr(VI) at the time of measurement. Depending on the product and the point of addition, a storage period of several months could then result in the maximum limit later being exceeded. Second: it is equally possible that a high overdose is already present if a measured value below the detection limit is obtained. In the event of the lowest possible measured value being obtained (e.g. < 0.1 ppm), it is impossible to distinguish between these two extreme situations.



Previous approach to solving the problem

To eliminate this uncertainty, Annex E of standard EN 196-10 (Methods of testing cement) describes a method for estimating the chromate-reducing capacity by increasing the Cr(VI) content by means of a standard solution of potassium dichromate that is added to the mixing water prior to extraction. It has, however, been found that this type of addition often yields greatly fluctuating recovery rates, since a substantial portion of the chromate ions added in this form is directly incorporated into the cement matrix and thus not detected when measuring the water-soluble content. This makes it very difficult to assess the chromate-reducing capacity present in order to determine any overdosing.

New approach to solving the problem

An innovative method consists in increasing the water-soluble content of chromate ions in controlled fashion by mixing a defined quantity of a non-reduced cement with a known content of water-soluble Cr(VI) into the cement to be tested, prior to extraction. This can be done in the following way, for example:

The quantity of 450 g cement required by EN 196-10 is prepared using 300 g of the cement to be tested (which contains the chromate reducer) and 150 g of a non-reduced cement with a known content y of water-soluble Cr(VI) and mixed thoroughly. The content z of water-soluble chromium(VI) determined in this mixture corresponds to:

$$z = \frac{2}{3}x + \frac{1}{3}y$$

where x stands for the chromate-reducing capacity of the cement to be tested. For a meaningful assessment, the measured value z should be greater than 0.5 ppm.

Transposition of the equation yields:

$$x = \frac{3}{2}z - \frac{1}{2}y$$

In this context, the non-reduced cement should have a water-soluble Cr(VI) content y of at least 10 ppm, in order to cover the widest possible range of overdosing. A lower Cr(VI) content restricts the measuring range and the value of the information obtained.

Should you not have a suitable cement at your disposal, the Technical Service of KRONOS ecochem will be more than pleased to help you find a supplier.

As a general rule, the value of x is negative; the more negative the value, the higher the overdose of chromate reducer and the remaining chromate-reducing capacity.

Experience shows that a value of x in the range of approximately -1 ppm to -4 ppm should be targeted for long-term stability of several months. Higher negative values are indicative of overdosing, which is only needed in special cases (e.g. for 12-month stability of preparations).

The following advantages characterise this new method :

- Determination of overdosing of the chromate reducer, estimation of the remaining chromate-reducing capacity, assessment of the long-term stability to be expected.
- Detection of major fluctuations in the original content of water-soluble Cr(VI), e.g. owing to raw materials or calcining conditions. This permits more targeted adjustment of the quantity of added chromate reducer to fluctuations of this kind.
- Protection against exceeding maximum limits as a result of insufficient addition of chromate reducer owing to fluctuations in clinker production.
- Cost savings thanks to the detection and avoidance of unnecessarily high overdoses of chromate reducer.

The information in this publication is intended to serve as a guide, but is not necessarily complete and is given without warranty. Caution must be exercised to comply with statutory obligations and to avoid infringing rights of third parties. Please consult our Safety Data Sheets before using any of our product.

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