14th Arab International Cement Conference

21-23 November - Cairo

Determination and Reduction of Cr(VI) in cement

Davide Padovani & Matteo Magistri

Determination and reduction of Cr(VI) in cement

CONTENT OF THE SPEECH

1. What is “Cr (VI)” and why it is dangerous ?
2. Why we do have Cr (VI) in cement ?
3. European regulations and EN 197-10 : how to determine Cr(VI) ?
4. How to reduce Cr(VI) in cement ?
5. Liquid solutions for reducing Cr(VI)

1.400 Million €

turnover 2006

46 Plants

in 23 different countries

4.500 Employees

12% of workforce dedicated to R&D

MAPEI Group

D.A.M.

R & D Laboratories

Mapei S.p.A.
Milan - Italy

Vinavil SpA
Villadossola
Verbania - Italy

Rescon Mapei AS
Sagstua - Norway

Mapei France SA
Saint Alban (Tolosa)
Francia

Mapei Inc.
Laval (Montreal)
Canada

Mapei Corp. (Headq.)
Deerfield Beach
USA

Sopro Banchemie GmbH
Wiesbaden
Germany

What is Cr(VI) and why it is dangerous?

Cr(VI) is an oxidation state of the Cr element; this particular oxidation state allows Cr(VI) to form water soluble compounds.

The Cr(VI) which is released into solution during cement hydration is reported to be dangerous for human health when coming into contact with a person's skin.

Other oxidation states of Cr are Cr(0) metallic, and Cr(III). They are considered less dangerous because their solubility can be considered as insignificant.

EU Directive 2003/53/EC limits the content of Cr(VI) to 2 ppm

Determination and reduction of Cr(VI) in cement

The Cr(VI) issue interests even countries where there is still no regulation on this subject!

First of all because *human health* is a major issue; any information at this regard should be welcome!

Secondly because if you, as cement producers, need to export cement to Europe, you have to satisfy the EU directive; and as far as clinker is concerned, it should be taken into consideration that in Europe clinker price is strongly influenced by Cr(VI) content.

Cr(VI) reduction costs from 0,6 to 2,5 €/t of cement

Why we do have Cr(VI) in cement ?

During clinker burning we introduce into the kiln a certain amount or Cr (in all oxidation states), coming from:

Raw materials; Cr in nature is associated with iron minerals, usually clay contains a certain amount of Cr……

Secondary raw materials: generally used because cheaper, but if containing Cr…

Kiln refractory parts, raw milling etc.

We can say that clinker contains 50-150 ppm of total Cr

Why we do have Cr(VI) in cement ?

During clinker burning part of the total Cr introduced into the kiln is oxidised to Cr(VI) due to the oxidising atmosphere and high temperatures.

Cr from Raw materials

Cr from refractory

Cr from others....

Cr(0) + Cr(III)

50-150 ppm

Cr(VI)

5-15 ppm

From initial 50-150 ppm of total Cr, 5-15 ppm transform in Cr(VI)

How to determine Cr(VI) ?

According to the EN 197-10 standard the amount of soluble chromates in cement is determined by spectrophotometry on the filtered solution obtained while preparing mortars.

Some observations:

1. This way we measure the Cr(VI) released in solution during cement hydration: *we do not measure the real amount of Cr(VI) contained in the cement*

Determination and reduction of Cr(VI) in cement

How to determine Cr(VI) ?

According to the EN 197-10 standard the amount of soluble chromates in cement is determined by spectrophotometry on the filtered solution obtained while preparing mortars.

2. The Cr(VI) determination is made by using an indicator (diphenylcarbazide) acting at acid pH: we need to introduce reagents and change the pH.

Hydration water from cement	Diphenylcarbazide addition	pH adjustment to 1-2	Cr(VI) determination

How to determine Cr(VI) ?

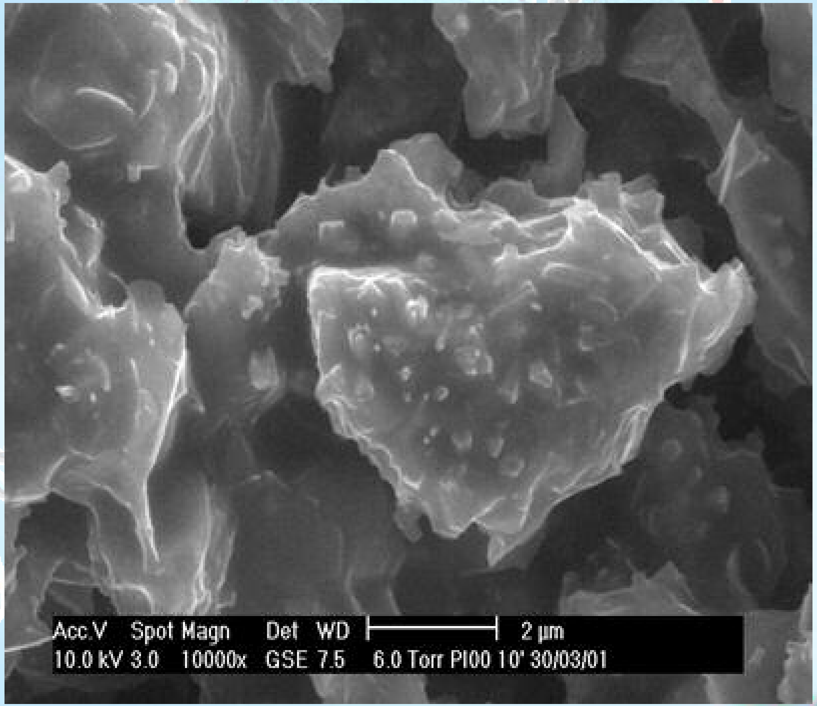
According to the EN 197-10 standard the amount of soluble chromates in cement is determined by spectrophotometry on the filtered solution obtained while preparing mortars.

3. Ionic Chromatography (IC) constitutes a valid alternative because it is able to “read” directly the Cr(VI) content in water.

Determination and reduction of Cr(VI) in cement

How to determine Cr(VI) ?

In order to summarise: according to the standards, we measure and we are interested in the Cr(VI) released into solution after 15 min of cement hydration, not in the Cr(VI) really contained in cement. In this sense all factors able to “reduce” Cr(VI) release into solution are welcome.



Determination and reduction of Cr(VI) in cement

How to reduce Cr(VI) in cement ?

1. By producing a clinker without Cr(VI):
   - reducing Cr by selecting raw materials
   - changing the method of burning clinker…

2. By reducing Cr(VI) to Cr(III) through redox reactions, by adding to the cement iron or tin salts

Note: reducing agents act when water is added, so at the moment of cement use

Iron sulphate

It's available in powder form, hepta or mono-hydrated; it's the most common solution; generally added during cement grinding.

$$Fe^{2+} = Fe^{3+} + e^{-}$$

Determination and reduction of Cr(VI) in cement

Iron sulphate

AVANTAGES

- cheap material
- available

DISAVANTAGES

- expensive dosage system and storage needed
- difficult to dose
- hygroscopic material
- high dosage (~0,3% by cement weight)
- side effects: spots on concrete
- short lasting Cr(VI) reduction

Cost: 0,4-0,6 €/t of cement for reducing 10 ppm of Cr(VI)

MAPEI

Tin sulphate

It's available in powder form; it may be added during or after cement grinding

$$Sn^{2+} = Sn^{4+} + 2e^-$$

Determination and reduction of Cr(VI) in cement

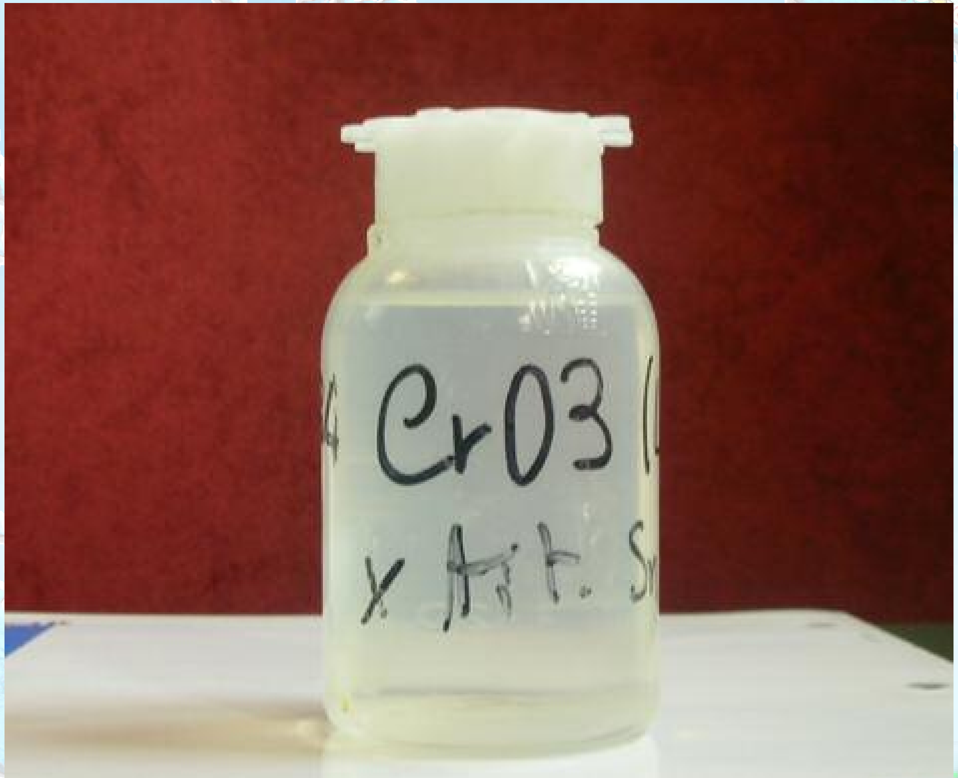
Tin sulphate

AVANTAGES	DISAVANTAGES
- long lasting Cr(VI) reduction	-expensive dosage system and storage needed
- Light colour hydration/oxidation products: no spots	-difficult to dose: (very low dosages 15-20 g/t ppm)
	- very expensive material

Cost: ~1,0 €/t of cement for reducing 10 ppm of Cr(VI)

Liquid solutions: MA.P.E./Cr 03

MA.P.E./Cr is a family of liquid reducing agents for Cr(VI). They can be used as normal "grinding aids": just a dosing pump is needed. MA.P.E./Cr 03 dosage: 30-40 g/t ppm.



MA.P.E/Cr 03

DIFFERENCES VS POWDER SOLUTIONS

- Liquid product; low viscosity
- Easy to dose
- No expensive storage and dosage system required
- long lasting Cr(VI) reduction
- Flexible solution for cement exportation

Conclusions

1) Cr is "naturally" present in cement; part of the total Cr transforms into Cr(VI) during clinker burning.

More documents and articles on Cr(VI) in cement on:

2) According to the European standards we measure Cr(VI) in cement by spectrophotometry analysing the hydration water: we do have to consider that we are measuring the Cr(VI) actually released into solution.

www.mapei.it/dam

3) Cr(VI) in the cement can be reduced through redox reactions, by using powders (iron, tin salts) or more advantageously liquids (MA.P.E./Cr 03) easy to store and to use. Other solutions are under investigation……..

14th Arab International Cement Conference

21-23 November - Cairo

Thank you