

Chromate reducing agents

by **Matteo Magistri and
Davide Padovani,**
Mapei SpA, Italy

A few months after the obligation to reduce Cr(VI) in cements has become law it is a useful time to review the situation regarding the use of chromate reducing agents and their relative efficiency, the method for the determination of Cr(VI) in cements and to present a new range of liquid chromate reducing additives.

Operators and workers in the building and construction industry when working with hydraulic binders may come into contact with soluble Cr(VI) ions potentially present in cements and cement-based materials. It has been recognised that Cr(VI) can cause irritation to the skin (dermatitis) and that it is dangerous to people's health. As a result, the European directive 2003 has become law in the majority of European states as of 17 January 2005, limiting the presence of the Cr(VI) ions to <2ppm. A method for the determination of soluble chromate ions in cement (prEN 196-10 2004) has been defined and the cement industry has adopted different measures in order to comply with the obligations imposed by the standard, by adding reducing agents for Cr(VI) to the cement.

In this article we will address the following issues:

- Chromate ion reducing agents and their efficiency.
- Methods for the determination of Cr(VI) ions in cements.
- Use of chromate ion reducing agents in liquid form.

The most commonly used chromate reducing agents are ferrous sulphate and stannous sulphate. Other reducing agents have been tested but with poor results: we will analyse the reasons from a technical point of view.

As regards the method for the determination of the Cr(VI), we present the results, confronting the different methods and establishing the advantages and disadvantages of each, taking into account the materials analysed (cements and cement-based materials) and the eventual presence of reducing agents.

Finally, we will present a new range of Mapei's liquid products based on pioneering technology.

Cr(VI) presence in cements

Concerns about Cr(VI) in cements was first highlighted in the countries of Northern Europe (where there is a higher presence of people with fair skin and more sensitive to the problem) and since then studies have been carried out in order to evaluate the effects on human health and the techniques for reducing the presence of Cr(VI) in cements.

It has been proven that when soluble chromates come into contact with human skin they are capable of provoking dermatitis and in some cases irritation and more serious diseases. The low number of cases has limited the introduction of restrictive measures, but the seriousness of the potential disabilities has resulted in a European legislation which limits the maximum permissible level of chromates to 2ppm.

The presence of Cr(VI) in cement derives principally from the presence of Cr (in various oxidation states) in the raw materials of cement, which are oxidised to Cr(VI) in the oxidising atmosphere and the high temperatures of the kiln.

In order to avoid the operators of the sector coming into contact with soluble hexavalent chromium, the following possibilities exist:

1. Produce cement without Cr(VI)
2. Reduce the Cr(VI), as the cement is used, by means of suitable reducing agents

The first approach, which in theory is the more secure, is seldom used as it is very difficult and expensive to introduce into the kiln, materials which are free of chromium (deriving from the raw materials or from the raw meal grinding) or else to cook the clinker in a reducing atmosphere.

The second solution is has been more commonly adopted by the cement industry. The Cr(VI) is reduced once it has

entered into solution in the mixing water, by means of an appropriate reducing agent (principally ferrous sulphate). In this way the operators or end-users of cement are protected; on the other hand operators involved in the production of cement, who can come in to contact with Cr(VI) by inhaling cement dust, are not protected.

Also the use of individual protection equipment, while always useful, only protects enduser operators rather than the workers in the cement production plant.

The reduction of Cr(VI) using reducing agents in the cement

The reduction of hexavalent chromium to trivalent chromium fits in with the general theory of redox reactions, in which two chemical compounds react together exchanging electrons. In our specific case, the oxidant Cr(VI) is reduced to Cr(III) by oxidising the reducing agent, ie strapping away a certain number of electrons from the reducing agent.

When choosing a possible reducing agent, it is necessary to take into account various factors, amongst which is their reducing power, the pH at which the reaction should take place and the speed of the reaction itself.

Redox potential, pH and reaction kinetics

From a thermodynamic point of view, the ability of a chemical species to lose or to acquire electrons, hence the ease with which it is oxidised or reduced, is expressed by the redox potential which is measured in volts and is indicated by E.

The higher the E value of a chemical species the more likely it is to be reduced, oxidising contemporarily other chemical species having lower redox potentials.

The redox potential does not have a

fixed value; it is greatly influenced by various factors (the concentration of the various chemical ions in solution which interact, pH and temperature). In order to confront the redox potential of various chemical ions, it is necessary to do so under the same conditions (same concentration, same acidity of solution and the same temperature), using therefore the concept of standard redox potential (E°), ie measured under standardised conditions. It is therefore possible to define the standard potential of a certain chemical compound which will be our reference as zero and then order the other chemical compounds in accordance with the value of their standard potentials. The redox couples at the higher potential can be reduced, under standard conditions, by all of those at lower potentials.

Thus the conditions (reagent concentration, pH, etc) are of fundamental importance when one wishes to discuss the effective possibility of reducing (or oxidising) certain substances by other ones. Let us consider a real example such as Cr(VI). The reduction reactions of Cr(VI) to Cr(III) are as follows:

- 1) $\text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 6\text{e}^- = 2\text{Cr}^{3+} + 7\text{H}_2\text{O}$
(valid at acidic pH values)
- 2) $\text{CrO}_4^{2-} + 3\text{e}^- + 4\text{H}_2\text{O} = \text{Cr}^{3+} + 8\text{OH}^-$
(valid at alkaline pH values)

In both cases each chromium atom (in the +VI oxidation state) acquires 3 electrons (supplied by the reducing agent) and is reduced to Cr^{3+} (+III oxidation state), involving hydrogen ions (in an acidic environment) or hydroxide ions (in a basic environment). Alongside this reaction a second one is taking place, in which one or more molecules of the reducing agent lose three electrons which are acquired by the chromium.

The standard potential of Cr(VI) is E° ($\text{Cr}_2\text{O}_7^{2-}/\text{Cr}^{3+}$) = 1.3 V. Thus in an acidic environment this strong oxidising agent can be easily reduced by a long list of reducing agents. The effective potential however varies as the pH changes and

this variation is described by the Nernst equation which links the potential E to all the variables which influence it.

For reaction 1) the Nernst equation may be written as follows:

$$3) E = E^\circ + \frac{RT}{nF} \ln \frac{[\text{Cr}_2\text{O}_7^{2-}]}{[\text{H}^+]^{14}[\text{Cr}^{3+}]^2}$$

where:

- E° is the standard potential;
- n is the number of electrons exchanged in the redox process;
- R and F are physical constants;
- T is the temperature;
- $[X]$ is the concentration of the solution (in moles/litre) of the chemical ion X ;

By substituting the values of the constants, passing to base 10 logarithmic scales and considering that the $\text{pH} = -\log_{10}[\text{H}^+]$, the equation may be expressed as follows:

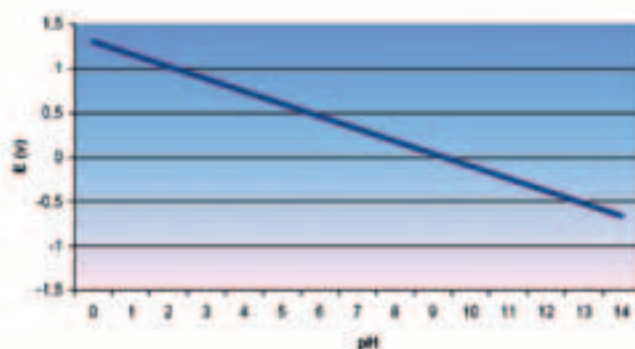
$$4) E = E^\circ + 0.01 \text{ Log} \frac{[\text{Cr}_2\text{O}_7^{2-}]}{[\text{Cr}^{3+}]^2} - 0.14\text{pH}$$

If for simplicity we consider the concentration of the Cr(VI) and Cr(III) to be the same at 1 mole/litre the equation becomes:

$$5) E = E^\circ - 0.14\text{pH}$$

which is an equation of a straight line with a negative slope. In the following diagram equation 5 is represented graphically: one can clearly see that as the pH increases the redox potential lowers drastically. This means that Cr(VI), while easily reduced by numerous agents in acidic environments, *at alkaline pH it is not easily reduced and*

Figure 1: variation of redox potential in function of the pH



only highly efficient reducing agents are capable of reducing it to Cr(III).

In order to evaluate if a chemical ion is capable of reducing Cr(VI), other than thermodynamic aspects relative to the redox potential, the kinetics of the reaction should also be considered, i.e.

the speed at which the equilibrium is reached. It is common that while certain chemical reactions are possible from a thermodynamic point of view, in reality they do not occur being kinetically inert. The kinetics of a chemical reaction can also be linked to the pH.

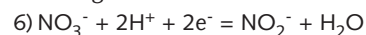
Reducing agents

We will try to explain through some examples the concepts so far expressed by analysing the performance of various reducing agents.

Sodium Nitrite

In various industrial sectors (waste water treatment, hide tanning processes and metal surface treatment) Cr(VI) is easily reduced by different types of reducing agents; however these processes take place at acidic or neutral pH values and these same reducing agents are ineffective at eliminating the chromates present in the water of a cement mix which typically occurs at alkaline pH values.

For example in a number of old leather production processes in which the untreated leather hides were impregnated with an acidic solution of sodium dichromate (a Cr(VI) salt), Cr(III) was obtained (which is the effective tanning agent) by reduction with sodium nitrite (NaNO_2), reacting according to the following reaction:



The standard redox potential is E° ($\text{NO}_3^-/\text{NO}_2^-$) = 0.94 V, which is

lower than the couple $\text{Cr}_2\text{O}_7^{2-}/\text{Cr}^{3+}$ ($E^\circ = 1.3$ volt). Thus in acidic environments nitrite easily reduces the dichromate to trivalent chromium.

Applying the Nernst equation to reaction number 6), the following reaction is obtained which describes the variation of the redox potential with pH.

$$7) E = E^\circ - 0.06\text{pH}$$

By displaying equations 5 and 7 on the same diagram one may clearly see that

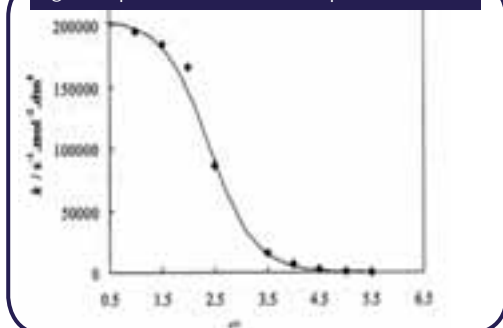
as the pH increases the potential of the chromium decreases more rapidly than that of the nitrite and once a certain value has been passed the potential of the redox couple $\text{NO}_3^-/\text{NO}_2^-$ becomes greater than that of the $\text{Cr}_2\text{O}_7^{2-}/\text{Cr}^{3+}$ couple: *beyond this pH value it is thermodynamically*

impossible to reduce Cr(VI) with sodium nitrite.

Sulphur compounds

In some waste-water treatment processes Cr(VI) is eliminated by reduction through the use of certain sulphur compounds (such as metabisulphite $S_2O_5^{2-}$, sulphite SO_3^{2-} and thiosulphate $S_2O_3^{2-}$). The redox potential of these compounds in an alkaline environment in various cases is very low (eg the couple SO_4^{2-}/SO_3^{2-} , $E = -0.92$), which means that from a thermodynamic point of view and under these conditions the reduction of the chromate is possible. In Figure 3, the variation of the kinetic constant (measures the speed of a reaction) in function of pH of the reaction between sulphite and Cr(VI) is shown. While at acidic pH values the constant is very high, at pH = 5 the constant is already reduced to zero: *this means that while the reaction is thermodynamically*

Figure 3: pH reaction between sulphite and Cr(VI)

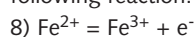


possible, from a kinetic point of view the reaction is inert.

Divalent iron and tin salts

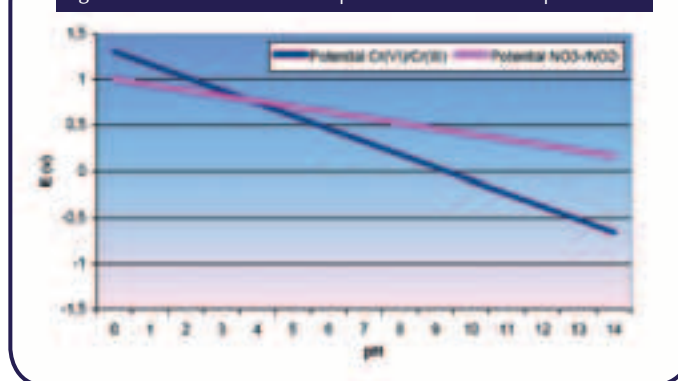
The efficiency of divalent iron salts is well known (of which the most commonly used is ferrous sulphate).

Iron is oxidised according to the following reaction:



the standard potential of which is $E^{\circ} = 0.77$ V. Given that this reaction does not involve the exchange of H^{+} or OH^{-} ions, it would seem that the pH should not have any influence on the potential. Even though the redox potential of Cr(VI) in alkaline conditions is close to zero or negative, one may ask why is it possible

Figure 2: variation of the redox potential in function of pH



that the iron sulphate is in fact effective. The answer lies once more in the Nernst equation for equation 8 where the relationship between the concentration of Fe^{2+} and Fe^{3+} ions is shown.

$$9) E = E^{\circ} + 0.06 \text{ Log } [Fe^{3+}]/[Fe^{2+}]$$

Both Fe^{2+} and Fe^{3+} react with the hydroxide (OH^{-}) ions forming poorly soluble hydroxides, which precipitate directly at relatively low pH values. While the hydroxide of Fe^{3+} , $Fe(OH)_3$ is much less soluble than the hydroxide of Fe^{2+} , $Fe(OH)_2$, this means that as the pH is increased the former precipitates much more rapidly than the latter and the Fe^{3+} ion is subtracted much quicker from the solution than the Fe^{2+} ion: as the concentration ratio of the two ions lowers drastically, the value of potential falls and at pH = 13 one may calculate that the potential reduces to approximately -0.50 V. The divalent salts of iron are therefore, at alkaline pH, strong reducing agents.

The same considerations may be also applied to tin salts. In this case, while the ions of Sn^{2+} and Sn^{4+} form hydroxides which are even less soluble than those of Fe^{2+} and Fe^{3+} , the redox potential is even lower as the pH is increased (at pH = 13 the calculated $E = -0.90$ V). This explains why tin salts are more efficient as reduction agents of Cr(VI), even at much lower dosages. The other advantages of the use of tin over iron are well known from the literature:

- superior stability and duration of the reduction with time
- absence of spots on the exposed surfaces of manufactured pre-cast units (thanks to the clear colours of hydration and oxidation products).

The principal disadvantage of tin salts

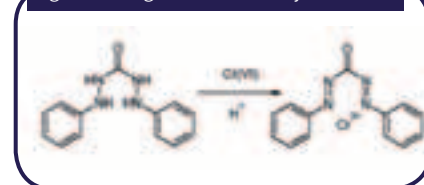
which limits their use in the field of cement, is the high cost of these materials and the reduced availability in certain markets.

Analytical methods for the determination of Cr(VI) in cement

Spectrophotometry

The methods of analysis presently in use for the determination of Cr(VI) in cement and cement based products, as a first step, envisage the extraction of the soluble chromates by means of the filtration of the water of a cement mortar or paste mix. The quantitative analysis of these chromates (EN 196-10) is based on the use of diphenylcarbazide. This reagent is oxidised by the Cr(VI) to diphenylcarbazone (see Figure 4), which forms a redviolet complex (maximum absorption at $\lambda = 540$ nm) on reaction with Cr(III) and the concentration of which (linked to the level of Cr(VI) present) can be measured to a high level of precision using photometric methods.

Figure 4: reagent is oxidised by Cr(VI)



The method is efficient but it is necessary to remember that this complex forms and is stable only in an acidic environment, and it is for this reason that in the methods already mentioned it is envisaged the acidification of the water containing the chromate extracted from the cement.

This change of pH does not influence the results obtained on the analysis of pure cements, but in the case of cements containing reducing substances there may be significant errors, because reducing agents which are inefficient at alkaline pH values may become active in acidic conditions and give the false impression of the reduction of the Cr(VI).

This method due to various interferences is also difficult to apply to cement-based products (such as mortars, adhesives etc.) which may contain, along with the cement, a vast range of organic and inorganic additives.

Table 1: analysis following elimination of reduction agents with peroxodisulphate

Standard test method	Elimination of reducing agents	ppm Cr(VI)
EN 196-10	-	0.00
EN 196-2.xx (provisional)	Peroxodisulphate/orthofosforic acid	20.34
TRGS-051	Bromine/sodium hydroxide	1.25

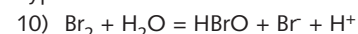
Notes on the analysis of diphenylcarbazide after the elimination of the reducing agents.

In order to use diphenylcarbazide and photometric analysis on cements

containing reduction additives, alternative methods were proposed (envisaged in the EN 196 standard or in the German TRGS 051 standard). These methods use oxidising agents (eg bromine solution

or peroxodisulfate) to eliminate before acidification the reducing agents present in the water containing chromates.

Besides further complicating the method of analysis, from a theoretical point of view, it is possible that these reagents are not inert with respect to the Cr(VI). Bromine for example, above pH = 7, reacts according to reaction (10) giving hypobromite and bromide.



Hypobromite is a strong oxidising agent, which in theory could possibly

Table 2: different cement types with and without reducing agents showing residual ppm Cr(VI)

Cement type	Reducing agent	Formula	Dosage	Residual ppm Cr(VI)	
				EN-196-10 (diphenylcarbazide)	Mapei/Unichim (Ion Chromatography)
CEM I 52.5 R	-	-	-	9.21	9.15
CEM I 52.5 R	Nitrite	NO ₂ ⁻	0.3 %	0.15	9.13
CEM I 52.5 R	Formaldehyde	HCOH	0.6 %	5.31	9.15
CEM I 52.5 R	Solphite	SO ₃ ⁻	0.6 %	0.00	9.05
CEM I 52.5 R	-	-	-	9.73	8.93
CEM I 52.5 R	Thiosulphate	S ₂ O ₃ ²⁻	0.3 %	0.02	8.52
CEM I 52.5 R	Hydrosulphite	S ₂ O ₄ ²⁻	0.3 %	0.01	7.79
CEM II/A-LL 42.5 R	-	-	-	9.29	8.67
CEM II/A-LL 42.5 R	Thiosulphate	S ₂ O ₃ ²⁻	0.3 %	0.02	6.79
CEM II/A-LL 42.5 R	Hydrosulphite	S ₂ O ₄ ²⁻	0.3 %	0.02	7.15
CEM II/B-M (LL-V) 32.5 R	-	-	-	4.35	4.64
CEM II/B-M (LL-V) 32.5 R	Thiosulphate	S ₂ O ₃ ²⁻	0.3 %	0.02	3.95
CEM II/B-M (LL-V) 32.5 R	Hydrosulphite	S ₂ O ₄ ²⁻	0.3 %	0.02	4.37
CEM II/B-P 32.5 R	-	-	-	6.33	5.98
CEM II/B-P 32.5 R	Thiosulphate	S ₂ O ₃ ²⁻	0.3 %	0.01	5.48
CEM II/B-P 32.5 R	Hydrosulphite	S ₂ O ₄ ²⁻	0.3 %	0.02	5.66
CEM I 52.5 R	-	-	-	13.81	13.53
CEM I 52.5 R	Metabisulphite	S ₂ O ₅ ²⁻	0.1 %	0.02	13.62
CEM I 52.5 R	Metabisulphite	S ₂ O ₅ ²⁻	0.2 %	0.00	13.55
CEM I 52.5 R	Metabisulphite	S ₂ O ₅ ²⁻	0.3 %	0.00	13.40
CEM I 52.5 R	Metabisulphite	S ₂ O ₅ ²⁻	0.5 %	0.00	13.40
CEM I 52.5 R	-	-	-	9.70	9.83
CEM I 52.5 R	Ferrous sulphate	FeSO ₄ 7H ₂ O	0.3 %	0.00	0.00
CEM I 52.5 R	Ferrous sulphate	FeSO ₄ 7H ₂ O	0.1 %	0.00	0.00
CEM I 52.5 R	Ferrous sulphate	FeSO ₄ 7H ₂ O	0.03 %	5.14	5.07
CEM I 52.5 R	Stannous sulphate	SnSO ₄	0.03 %	0.00	0.00
CEM I 52.5 R	Stannous sulphate	SnSO ₄	0.02 %	0.00	0.00
CEM I 52.5 R	Stannous sulphate	SnSO ₄	0.01 %	1.15	1.21
CEM I 52.5 R	Stannous chloride	SnCl ₂ 2H ₂ O	0.03 %	0.00	0.00
CEM I 52.5 R	Stannous chloride	SnCl ₂ 2H ₂ O	0.02 %	0.00	0.00
CEM I 52.5 R	Stannous chloride	SnCl ₂ 2H ₂ O	0.01 %	1.33	1.28

Table 3: Ineffective reducing agents

Residual Cr(VI) ppm	
EN-196-10 (diphenylcarbazide)	Mapei/Unichim (Ion Chromatography)
0.15	9.13
5.31	9.15
0	9.05
0.02	8.52
0.01	7.79
0.02	6.79
0.02	7.15
0.02	3.95
0.02	4.37
0.01	5.48
0.02	5.66
0.02	13.62
0	13.55
0	13.4
0	13.4
r Column 1	Column 2 0.0310

oxidise some of the Cr(III) to Cr(VI). In the same way the peroxodisulphate has a standard potential $E^\circ = 2$ V, superior to that of Cr(VI). In theory some of the Cr(III) in solution could be oxidised to Cr(VI).

It is possible to verify this in the following manner: a solution containing 50ppm of Cr(III) was prepared by dissolving in water some basic chrome sulphate and then brought to a pH = 14 using sodium hydroxide. Chromium hydroxide precipitates and under agitation dissolves slowly forming hydroxochromate $[\text{Cr}(\text{OH})_4]^-$ giving a blue-green coloured solution.

A small sample of this solution, analysed according to the standard procedure, does not show any presence of Cr(VI). Repeating the analysis, following the treatment for the elimination of the reduction agents with peroxodisulphate in one case and with bromine in the other, one obtains very different results (see Table 1).

Ion Chromatography

A method of analysis which does not present these inconveniences is that of ion chromatography.

Table 4: effective reducing agents

Residual Cr(VI) ppm	
EN-196-10 (diphenylcarbazide)	Mapei/Unichim (Ion Chromatography)
0	0
0	0
5.14	5.07
0	0
0	0
1.15	1.21
0	0
0	0
1.33	1.28
r Column 1	Column 2 0.9999

At the Mapei R&D laboratories a decision was made to use ion chromatography for the determination of soluble chromates in cements and cement-based materials. This is an analytical technique which allows different ions to be separated and identified making use of the differences in their charge/radius ratio.

The analysis procedure envisages the extraction of the soluble chromates in a 1:1 mixture of water and cement while under agitation (on a magnetic stirrer). The solution obtained from the filtration is analysed directly without dilutions or the addition of reactants.

The principal advantages of this technique are as follows:

- It is a direct measurement. The Cr(VI) is directly measured and not a product of its reaction with a reagent.
- The analysis is performed directly on the filtered solution, without any pH correction (instead an alkaline eluent is used, based on carbonate/bicarbonate). In this way one completely avoids the possibility of obtaining false results due to the presence of other reducing agents.
- In general limp solutions are obtained in contrast to that which happens when adding the diphenylcarbazide to cement-based formulations containing organic substances etc. In some cases these inconveniences make it impossible to read by photometric methods the content of chromium in solution. The disadvantage of this method is

Table 5: cement without reducing agents

Residual Cr(VI) ppm	
EN-196-10 (diphenylcarbazide)	Mapei/Unichim (Ion Chromatography)
9.21	9.15
9.73	8.93
9.29	8.67
4.35	4.64
6.33	5.98
13.81	13.53
9.7	9.83
r Column 1	Column 2 0.9918

the high cost of the instrumentation required and the need to have specialised operators.

Table 2 shows data from both methods are confronted, carried out on different types of cements with and without reducing agents. The cements come from various European cement plants; the chromate reducing additives were added into the mix water before acidification (as per EN 196-10). The data shown represent the average of two determinations for each sample.

It is clear that while in the cements without any additives the agreement between the methods of analysis is good, on the other hand with the addition of reducing agents the results obtained can be quite different: This is due to the variation of the redox property of many compounds in relation to a variation in pH (see Table 2).

In order to better analyse the results of Table 2, the data was grouped (Tables 3, 4 and 5) according to the type of chromate reducing additive used, where for 'non efficient' one means nitrite, formaldehyde, thiosulphate, hydrosulphite, metabisulphite, for 'efficient' one means ferrous sulphate and stannous sulphate and finally in the third column the results are expressed for the cements when no chromate-reducing additives were used.

On measuring the correlation index between the two columns of results one can observe an excellent positive linear correlation ($r > 0.99$) between the two methods for the determination of Cr(VI) in the case efficient reducing agents (iron or

tin salts) are utilised or chromate reducing agents are not employed. On the other hand one may note the absence of a linear correlation ($r = 0.0310$) between the results obtained from the two methods analysing cements treated with 'non efficient' chromate reducing agents. The methods measure values of the same size (amount of Cr(VI)) on the same shared samples, but in the case where 'non efficient' Cr(VI) reducing agents were used the method pr EN 196-10 seems to be not reliable, producing false results.

Atomic Spectroscopy

The aqueous solution containing the chromates may also be analysed by means of atomic spectroscopy. This method is based on the fact that each chemical element when stimulated by a source of high energy (eg a high temperature flame) absorbs and emits electromagnetic radiation at characteristic wavelengths. Atomic spectroscopy may be employed to evaluate the total Cr content in a cement: it does not however allow to distinguish between the various states of oxidation of the chromium. The utilisation of the method in the cement sector is based on the consideration that Cr(III) (in alkaline conditions) does not form water soluble compounds. In reality it is well known that at high pH values chromium hydroxide $\text{Cr}(\text{OH})_3$ dissolves forming hydroxochromate $[\text{Cr}(\text{OH})_4]^-$. We therefore consider this method not to be of significant interest, especially to determine the efficiency of reducing agents whose effect should be evaluated in each particular case.

On the other hand, in Figure 5 we present data from the comparison of the two methods of ion chromatography (IC) and atomic spectroscopy (ICP-AES) carried out on two 'pure' Portland CEM I 52.5 R cements having very different Cr(VI) contents and without any addition of chromium reduction agents. In this case on completely analysing the data, the results obtained with the ICP-EAS method indicate an average value systematically lower than that obtained with the IC, even though in general it has a lower standard deviation, confirming the good level of accuracy of the measurements.

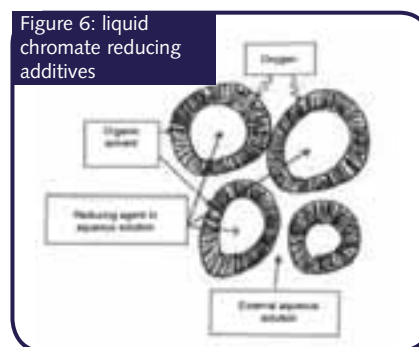
Chromate reducing additives in liquid form

It is known that the use of reducing

Figure 5: comparison of the two methods of ion chromatography

CEMENT TYPE	ION CHROMATOPHY					ICP-AES			
	1 st test	2 nd test	3 rd test	Average value	Standard Dev.	1 st test	2 nd test	Average value	Standard Dev.
CEM I 52.5 R Hungary	35,951	36,248	36,602	36,27	0,326	30,168	30,338	30,25	0,120
CEM I 52.5 R Hungary	28,846	30,91	31,832	30,529	1,529	31,594	31,082	31,34	0,362
CEM I 52.5 R Hungary	35,227	35,764	36,648	35,880	0,718	33,002	32,752	32,88	0,177
CEM I 52.5 R Hungary	34,518	29,578	30,855	31,850	2,564	31,660	32,188	31,92	0,373
CEM I 52.5 R Hungary	34,646	34,598	34,451	34,564	0,101	32,866	32,822	32,84	0,031
	Average					Average			
	33,778					31,847			
	Standard dev. of average					Standard dev. of average			
	2,565					1,102			
	Average standard dev					Average standard dev			
	1,048					0,213			
	1 st test	2 nd test	3 rd test	Average value	Standard Dev.	1 st test	2 nd test	Average value	Standard Dev.
CEM I 52.5 R Italy	9,887	10,418	10,512	10,272	0,337	8,517	8,473	8,495	0,031
CEM I 52.5 R Italy	9,863	9,875	9,973	9,904	0,060	7,785	7,855	7,82	0,049
CEM I 52.5 R Italy	10,158	10,496	10,26	10,305	0,173	8,023	7,992	8,008	0,022
CEM I 52.5 R Italy	10,373	10,072	10,266	10,237	0,153	7,943	8,173	8,058	0,163
CEM I 52.5 R Italy	9,848	9,914	9,729	9,830	0,094	8,123	8,075	8,099	0,034
	Average					Average			
	10,110					8,096			
	Standard dev. of average					Standard dev. of average			
	0,224					0,247			
	Average standard dev					Average standard dev			
	0,163					0,060			

agents in powder form creates many practical problems, principally due to the difficulty of handling the material and the precision of the dosage. In the case of ferrous sulphate it is also possible to have some problems related to the formation of spots or marks on the surfaces of the manufactured unit, especially if added after grinding. The use of liquid chromate



reducing additives during grinding can eliminate these problems and provide the following advantages:

- ease of dosage
- perfect mixing of the reducing agent in the cement
- absence of spots or marks in the cement
- possibility to use a single grinding aid/ Cr(VI) reducing additive

The principal factor which has limited the utilisation of liquid chromate reducing additives is the high cost with respect to ferrous sulphate in powder form.

In any case we are sure that research and innovation in this field will continue, producing solutions which will be more competitive with the powder products.

Mapei R&D laboratories have recently developed a new family of liquid chromate reducing products (MA.P.E./Cr) with various innovative characteristics for specific applications and these may be divided as follows:

- liquid chromate reducing additives
- liquid chromate reducing and grinding aid additives

As an example of the first group we may present the MA.P.E./Cr 01 additive, characterised by an original method of protection of the reducing agent from the oxidising action of the ambient air; as an example of the second group we have the MA.P.E./Cr 02 product, Cr(VI) reducing agent and excellent grinding aid additive.

MA.P.E./Cr 01

The use of iron and tin salts in liquid formulations entails many problems, due to their poor stability in aqueous solutions and their tendency to precipitate, in particular at neutral/alkaline pH. Divalent salts of iron and tin are easily oxidised by atmospheric oxygen or even by water at high alkaline pH. Even at strongly acidic pH, where these salts are much less susceptible to oxidation, their duration over time is limited if they are not suitably protected from atmospheric oxygen.

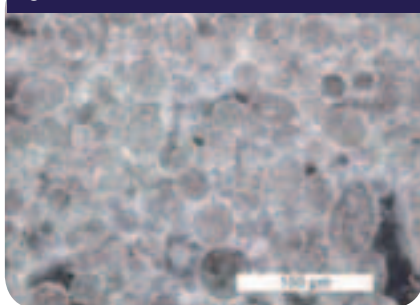
To make full advantageous use of these reducing agents in liquid formulations it is imperative to limit the contact between the metallic cation in solution and atmospheric oxygen. In Mapei this objective has been achieved developing a liquid emulsion additive.

The chromate reducing additive MA.P.E./Cr 01 is a triple emulsion: The aqueous reducing agent solution is protected in an emulsion surrounded by a layer of an organic solvent (specifically selected so that the diffusion of atmospheric oxygen is impeded), all of which is dispersed in a second aqueous solution. The organic solvent functions as a barrier which impedes contact between the reducing agent and atmospheric oxygen, thus avoiding the loss in performance.

In the Figure 7 (obtained with an optical microscope) the Mapei MA.P.E./Cr 01 additive is shown in an intermediate state of preparation: it is possible to observe directly what has previously been illustrated schematically.

The advantages of this technology are

Figure 7: MA.P.E./Cr01 additive



numerous:

- the reduction agent is protected from contact with atmospheric oxygen and is stable for a long time;
- in this same formulation it is possible to insert other 'active components' (grinding aids, strength enhancers, workability improvers) in order to obtain an additive which, other than reducing the Cr(VI), is able to improve further characteristics of the cement;
- the structure of the emulsion may be regulated during production allowing the viscosity and general rheology of the additive to be controlled.
- the presence of an organic phase limits the problems of corrosion and dangerousness related with aqueous solutions at high levels of acidity (usually associated with products based on divalent salts of iron and tin).

MA.P.E./Cr 02

The MA.P.E./Cr 02 is a dual function additive used as chromate reduction agent and grinding aid at the same time. This product allows the two functions to be combined in one product, thus eliminating (or significantly reducing) the use of traditional grinding aids.

The product is a transparent aqueous solution in which the reduction agent is specially stabilised and protected from oxidation and is perfectly integrated with the grinding aid fraction. The rheological characteristics of the additive (the product has a viscosity similar to that of water) allow for a precise dosage to be achieved using normal pumps already in use in cement plants for the cement grinding additives; in this way normal waste or left over traces, typical of high viscosity products are avoided (additive resting on storage container walls, difficulty of dosing very low dosages precisely, etc).

MA.P.E./Cr 02 also has the advantage of being stable even under difficult ambient conditions (from -15°C up to +40°C) and can be stocked for long

periods of time. This product is suitable for use in fully automatic dosage plants.

Examples of industrial trials with additives of the MA.P.E./Cr family

In Figure 8, the average results from a period of industrial use of the chromate reducing additives MA.P.E./Cr 01 and MA.P.E./Cr 02 in a cement plant are shown. The plant produces various types of cement: a pure Portland cement, a limestone cement and three fly ash cements.

The chromate reducing additives were dosed on to the clinker conveyor belt by means of a piston dosage pump. The clinker temperature entering the mill varied between 60° to 80°C. The mill, 3.4m x 12.0m, was cooled with water in the first chamber. The addition occurs automatically when the temperature of the cement exiting from the mill exceeds 90°C.

As regards the MA.P.E./Cr 01 the dosage used was 60g/t ppm of Cr(VI) in the cement. The traditional grinding aid additive was employed as usual on all cements again dosed on to the clinker conveyor belt.

In the case of the MA.P.E./Cr 02 the dosage was 45g/t ppm of Cr(VI) in the cement. In this case the traditional grinding aid additive was reduced by 60 per cent maintaining unchanged the productivity of the mill.

Conclusion

In this article various problems related to the determination and the reduction of soluble hexavalent chromium compounds in cement-based materials have been examined. We may summarise the principal conclusions as follows.

Many of the more well known reducing agents for hexavalent chromium are found to be ineffective as a result of the general characteristics of cement and in particular due to the high pH values resulting from the mixing of cement with water. A detailed explanation from a chemical point of view was given of the thermodynamic and kinetic factors which determine why the pH has such an influential role.

In consideration of the importance of pH in relation to the effectiveness of reducing agents, the principal analytical methods currently available to the cement industry were described and it was underlined how ion chromatography guarantees the highest levels of precision and simplicity.

The characteristics of the Mapei liquid additives for the reduction of hexavalent chromium were illustrated. Examples of

Figure 8: examples of industrial trials with additives of the MA.P.E./Cr family

Industrial results with MA.P.E./Cr 01					
Cement type	Mill type	Normal grinding aid	Initial Cr(VI) ppm	Final Cr(VI) ppm	MA.P.E./Cr 01 dosage
CEM I 52,5 R	3,4x12,0	Yes	6,10	0,03	370 g/t
CEM III/A-LL 42,5 R	3,4x12,0	Yes	4,72	0,01	285 g/t
CEM III/B-M (LL-V) 32,5 R	4,0x14,2	Yes	3,20	0,02	195 g/t
CEM IV/A (V) 32,5 R	4,0x14,2	Yes	3,00	0,02	180 g/t
CEM IV/A (V) 42,5 R	4,0x14,2	yes	4,56	0,03	275 g/t

Industrial results with MA.P.E./Cr 02					
Cement type	Mill type	Normal Grinding Aid reduction	MA.P.E./Cr 02 dosage	Initial Cr(VI) ppm	Final Cr(VI) ppm
CEM I 52,5 R	3,4x12,0	60 %	330	7,31	0,01
CEM III/A-LL 42,5 R	3,4x12,0	65 %	200	4,45	0,02
CEM III/B-M (LL-V) 32,5 R	4,0x14,2	60 %	185	3,93	0,01

industrial trials have shown the validity of these liquid additives as alternatives to powder ferrous sulphate, especially in cases where the utilisation of ferrous sulphate may not be technically possible.

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