Technical Notebook

HEXAVALENT CHROMIUM REDUCING AGENTS FOR PORTLAND CEMENTS AND CEMENT-BASED MATERIALS
1. MAPEI GROUP

Mapei was founded in Milan in 1937 and today its 80 years of experience have made it the world’s leading manufacturer of adhesives and ancillary products for the installation of all types of floor and wall coverings. The company also specialises in other chemical products for the building industry, from waterproofing products and special mortars and admixtures for concrete and cement, to products for the renovation of historic buildings. With its 79 subsidiaries, 7 of which are non operational companies and 67 plants in 32 different countries, today Mapei is to be considered the world’s leading supplier of the most innovative products for the building industry.

ECO-SUSTAINABILITY

Mapei liquid cement additives form a system of innovative solutions for cement works; they allow a reduction of clinker while offering the same mechanical performance of cement, thus guaranteeing a reduction of 5-10% in CO₂ emissions and a saving in non-renewable raw materials.

CEMENT ADDITIVES DIVISION

Founded in 2000, C-ADD (Cement Additives Division) has grown every year in terms of turnover and volume, thanks to innovative and high-quality products combined with technical support and dedicated Research and Development. Today, supported by the group’s structure and expertise, C-ADD is supplying all major cement groups worldwide, offering new technologies and local technical assistance. By combining high quality raw materials, fully computer-based production facilities and specific expertise in terms of product chemistry, industrial employment and grinding plant technology, C-ADD is able to guarantee high levels of customer assistance and product quality.
RESEARCH & DEVELOPMENT

By investing over 5% of its turnover and 12% of its Human Resources in Research and Development, the Mapei Group has become market leader in terms of innovation. The dedicated C-ADD scientists at Mapei’s Research Centres not only develop new raw materials and grinding aid components, but are also active in customer support. In fact, Mapei’s state of the art laboratories allow C-ADD to perform specific and in-depth clinker and cement analysis in order to optimise the use of cement additives and to offer customized solutions for cement performance enhancement and production improvement.

TAG TEAM (TECHNICAL ASSISTANCE GROUP)

A team of experienced process engineers from the cement industry joined C-ADD in order to provide specific technical assistance to C-ADD customers. By performing complete plant audits and by analysing the grinding circuit’s performance, they are able to assist C-ADD customers with the implementation of cement additives and to optimise the grinding process in all its aspects.
2. HEXAVALENT CHROMIUM IN PORTLAND CEMENTS - INTRODUCTION

The raw materials for grey Portland cement manufacturing may contain chromium. Due to the highly oxidizing and alkaline conditions of the kiln, during clinker production chromium is partially converted to hexavalent chromium and is probably fixed as alkaline or calcium chromate (Na₂CrO₄, K₂CrO₄, CaCrO₄). As a result, Portland clinkers and cements contain soluble chromates (usually in the range of 5 – 20 ppm or mg/kg, while the total chromium may reach 200 ppm) which are reported to cause skin irritation (allergic contact dermatitis). This is the reason why the European Community introduced the obligation (Directive 2003/53/EC) to maintain the level of soluble chromates below 2 ppm; this has a significant economical impact on the cement industry.

3. HEXAVALENT CHROMIUM REDUCTION - CHEMICAL BACKGROUND

While Cr (VI) is a strong oxidising agent in acid solution, in an alkaline media (such as the cement gauge water) the situation is different and it is impossible to reduce the Cr (VI) using most of the reducing agents which usually work at pH lower than 7. The reason lies in the fact that the red-ox potential of the couple Cr (VI) / Cr (III) changes with pH. Using the Nernst equation it is possible to calculate the value of red-ox potential at different pH and estimate which red-ox couple can reduce Cr (VI) to Cr (III).

3.1 REDUCTION OF SOLUBLE CHROMATES: IRON (II) AND TIN (II) SALTS

The reduction of soluble chromates is usually obtained with the addition of ferrous or stannous salts (in powder or liquid form) during cement grinding. Both ferrous and stannous salts present advantages and disadvantages. Ferrous sulphate is very cheap, but presents serious problems related to the durability of the reducing properties: it is very
sensitive to moisture and temperature and tends to lose efficacy after grinding and during cement storage. This requires the use of very high dosages of ferrous sulphate, causing costs to be higher than expected as well as triggering unfavourable side-effects (formation of red spots on the concrete surfaces, due to the characteristic colour of Fe$^{3+}$ compounds, is very frequent). The poor durability of iron (II) reducing agents can be explained considering the acid character of iron and the presence of crystallisation water. We can suppose that ferrous sulphate may react during cement grinding (or storage) with very alkaline free lime, being partially converted to ferrous hydroxide.

Stannous sulphate has a superior reduction capacity (thus allowing lower dosages) and has no undesired side-effects, but is very expensive. Nonetheless it has been reported that, in presence of high amounts of free lime and moisture, stannous compounds partially lose their reduction ability. This is particularly evident with liquid additives based on tin (II) compounds (stannous chloride/sulphate). The reason may lie in the fact that tin (II) has strong acid properties, and during cement grinding it can react with free lime and water being partially converted to stannous hydroxide, similarly to the case of ferrous sulphate.

3.2 A BRAND NEW TECHNOLOGY: ANTIMONY (III) COMPOUNDS

A very promising and innovative class of reducing agents has been studied, developed and patented by Mapei SpA. The efficacy and the superior performances of products is based on the red-ox properties of antimony (III). The couple Sb (V) / Sb (III), has a red-ox potential in alkaline solution of $E=-0.59$ volt. From a thermodynamic point of view, this means that Sb (III) is a strong reducing agent at high pH and can reduce Cr (VI) present in the cement mixing water, according to the following equation:

$$2\text{CrO}_4^{2-} + 3\text{H}_2\text{SbO}_3 + 2\text{H}_2\text{O} = 2\text{Cr(OH)}_3 + 3\text{SbO}_3^{2-} + 4\text{OH}^{-}$$
The Pourbaix diagrams reported in Figure 3.1 show that the Sb (III) is stable at alkaline pH. In comparison to ferrous and stannous salts, Sb (III) compounds have weaker acid properties. This is an interesting advantage, because the reaction with free lime does not proceed, avoiding any efficacy loss during cement grinding or storage, even in case of high free lime content and high level of humidity.

As a result, the reduction performance of antimony (III) is unaffected by moisture and high grinding/storing temperatures. Several tests performed in our Central R&D facilities have demonstrated how the reducing properties of antimony (III) remain unchanged even after more than one year.

![Pourbaix diagrams](image)

Fig. 3.1a and 3.1b – Pourbaix diagrams of antimony (left) and tin (right).

The variation of red-ox potentials of oxygen and hydrogen have been pointed out.

4. MA.P.E./Cr 05 - MAPEI’S REVOLUTIONARY PRODUCT FOR HEXAVALENT CHROMIUM REDUCTION

The formulation of a liquid additive based on antimony (III) for the reduction of hexavalent chromium requires the selection of the most appropriate Sb (III) compound.

It should possess the following characteristics:
• be easy to incorporate in a water-based formulation
• have an economical impact inferior to tin-based liquid additives
• have no effect on the properties and quality of the cement

Most of all, in order to guarantee its reduction ability for as long as possible, the reducing agent should remain unaltered during the storage of both the additive and the cement. If it could be possible to activate the reducing agent only when cement is mixed with water, we could obtain an excellent improvement of shelf life and durability after a prolonged storage.

We have found that it is possible to reach all the targets using a liquid additive based on antimony trioxide. This compound is amphoteric: it is soluble only at very low or very high pH and is completely insoluble at medium pH. A liquid additive with a high load of insoluble particles of antimony trioxide can be prepared by using the well-known technology of solid liquid dispersion. Thanks to its insolubility and low acidity, antimony trioxide is not modified by water or free lime and it remains unaltered until cement is mixed with water: at pH higher than 12 the antimony trioxide is dissolved in water and is fully available to reduce the Cr (VI) released in water. The result of this research is the revolutionary product MA.P.E./Cr 05, the world’s best-selling and most innovative liquid additive for Cr (VI) reduction. MA.P.E./Cr 05 is available in two different versions: LV (low-viscosity) and AF (anti-freeze).

The main advantages of MA.P.E./Cr 05 are the following:

• neutral (or alkaline) pH, while other liquid additives based on tin have strong acid pH and are highly corrosive
• no recrystallisation of partially solubilised salts (the active component is completely insoluble) and consequently no formation of precipitate and difficulties in pumping

• no reducing agent lost, in any mill conditions (high amount of cooling water, high temperature). This allows the cement plant to avoid any extra dosage, as usually happens with ferrous sulphate and sometimes with tin-based liquid reducing agents

• no reducing agent lost during storage: this allows to maintain the Cr (VI) content constant for a very long time (six months long guaranteed reduction)

4.1 MA.P.E./Cr 05 VS. FERROUS SULPHATE AND STANNOUS SULPHATE - LABORATORY TRIALS

The performances of ferrous sulphate, stannous sulphate and MA.P.E./Cr 05 LV have been compared by means of several laboratory trials. One particularly representative example is described in the following paragraphs.

A cement has been reproduced in a laboratory mill by grinding clinker and gypsum. A clinker with a very high level of free lime has been chosen (free CaO = 1.78%). The amount of soluble Cr (VI) released in water (without reducing agent) is 10 ppm. The same cement has been reproduced by grinding with the reducing agents reported in the following table.

<table>
<thead>
<tr>
<th>REDUCING AGENT</th>
<th>DOSAGE (WEIGHT % OVER CEMENT WEIGHT)</th>
<th>DOSAGE (g/t) FOR EACH PPM OF Cr (VI)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ferrous sulphate</td>
<td>0.200 %</td>
<td>200 g/t•ppm</td>
</tr>
<tr>
<td>Stannous sulphate</td>
<td>0.020 %</td>
<td>20 g/t•ppm</td>
</tr>
<tr>
<td>MA.P.E./Cr 05 LV</td>
<td>0.045 %</td>
<td>45 g/t•ppm</td>
</tr>
</tbody>
</table>

The samples of cement have been stored in the same conditions and the soluble Cr (VI) content has been evaluated for a period of six months. The results are summarized in Figure 4.1.
It can be clearly seen that with this cement (characterised by a high content of free lime) the stannous sulphate is effective only for a limited period of time: after two months the soluble Cr (VI) content already exceeds the limit of 2 ppm. The ferrous sulphate at a dosage commonly used (0.2%) is not even able to reduce Cr (VI) below the 2 ppm threshold. The performances of antimony trioxide (MA.P.E./Cr 05 LV) are clearly superior: the Cr (VI) level is close to zero even after several months. Since 2008 (introduction of MA.P.E./Cr 05 in the market), these results have been confirmed off-field by means of more than fifty different industrial trials.

Figure 4.1: Performance of different Cr (VI) reducing agents in the 1 day – 6 months time span

4.2 LONG-LASTING REDUCING EFFECT OF MA.P.E./Cr 05 - INDUSTRIAL CASE STUDIES

During 2010 and 2011, a series of special industrial tests have been run with MA.P.E./Cr 05 LV in several EU plants. The target was in the first place to bring Cr (VI) values under the 2 ppm limit set by the regulations, but at the same time to collect treated cement samples to be stored for a long time. Samples were collected in regular, closed cement bags and kept in a storage room without any particular conditioning, in order to simulate actual storage conditions in a warehouse. Every 2 months, cements have been sampled from these bags to determine soluble chromium, according to EN 196-10 standard. Table 2 reports the composition and fineness of the cements used for this study.
We decided to select quite different cements in terms of composition/chemistry (2 OPCs, one limestone cement, one pozzolanic/fly ash cement, and one slag cement), fineness (the 2 OPCs have very different finenesses), as well as geographical origin (Northern, Central and Southern Europe). Prior to running field trials, blank samples of each cement were tested for soluble Cr (VI) levels, in order to determine the suitable dosage of MA.P.E./Cr 05 LV. Targeted dosage was 50 ppm (grams per metric ton of cement) of reducer for each ppm of Cr (VI) to be reduced; Figure 4.2 shows the concentrations of soluble chromium in the blank cement, as well as the outcomes of the measurements carried out on the day of the test and every 2 months after.

![Figure 4.2: Cr (VI) in blank samples and samples ground with MA.P.E./Cr 05 LV](image)

Table 2: Composition and fineness of the tested cements

<table>
<thead>
<tr>
<th>CEMENT TYPE</th>
<th>% CLinker</th>
<th>% NATURAL GYPSUM</th>
<th>% SYNTHETIC GYPSUM</th>
<th>% LIMESTONE</th>
<th>% SLAG</th>
<th>% FLY ASH</th>
<th>BLAINE SSA m²/kg</th>
</tr>
</thead>
<tbody>
<tr>
<td>OPC 1</td>
<td>92</td>
<td>5</td>
<td></td>
<td>3</td>
<td></td>
<td></td>
<td>520</td>
</tr>
<tr>
<td>OPC 2</td>
<td>94</td>
<td>6</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>330</td>
</tr>
<tr>
<td>Limestone Portland cement (LS)</td>
<td>74</td>
<td>5</td>
<td></td>
<td>21</td>
<td></td>
<td></td>
<td>456</td>
</tr>
<tr>
<td>Fly Ash cement (FA)</td>
<td>68</td>
<td>5</td>
<td></td>
<td>6</td>
<td>21</td>
<td>442</td>
<td></td>
</tr>
<tr>
<td>SLAG CEMENT (S)</td>
<td>53</td>
<td>5</td>
<td></td>
<td>42</td>
<td></td>
<td></td>
<td>410</td>
</tr>
</tbody>
</table>

Table 2: Composition and fineness of the tested cements
As can be seen, MA.P.E./Cr 05 LV is very effective in reducing Cr (VI) for all cement compositions and finenesses. When the suggested dosage is used, Cr (VI) is reduced below the limits of detection (i.e. 0 ppm), and the level remains zero (or very close to zero) up to one year of age of the sample. Even when zero is not reached (i.e. LS cement), the initial value is kept without increases over time, contrary to the well-known situation normally happening with other reducers (e.g. ferrous sulfate or stannous sulfate). This is related to the specific properties of Mapei’s additive, which is activated only when cement is mixed with water and it is not influenced by environmental humidity or air exposure.

4.3 EFFECTIVE REDUCTION OF CEMENTS WITH EXTRAORDINARILY HIGH LEVELS OF Cr (VI)

Usually, the concentration of soluble chromates in Portland clinkers - and therefore cements - ranges from 5 up to 15 ppm. Nevertheless, it is not unusual to deal with clinkers that present higher concentrations: in the following paragraphs we will describe how cement manufacturers may deal with the reduction of extremely high concentrations of Cr (VI), i.e. concentrations of soluble chromates ranging from 20 up to 50 ppm.

The factors that determine such extremely high concentrations are various and still not completely understood. For example, the use of iron scraps during clinker production (used to adjust the iron amount in the clinker) can favour the formation of significant amounts of hexavalent chromium in the finished product, as well as certain kiln conditions and/or the use of raw materials that present straightforward an high concentration of chromium. For reasons which are still not completely clear, there seems to be quite a constant correlation between the geographical origin of the clinker and the corresponding amount of chromates: for example, clinker produced in certain regions (e.g. Turkey, some countries of Eastern Europe) present in most cases chromates concentrations well above the average. According to information acquired on the field, this could be due to the presence, in these regions, of iron ore in raw materials’ extraction points. Figure 4.3 shows a statistical distribution of hexavalent chromium.

Figure 4.3
As can be seen from this chart, although the vast majority of the cements produced worldwide presents a Cr (VI) concentration <10 ppm, there is indeed a certain number of cements that contain soluble chromates in very high concentrations. Dealing with such amounts of chromates is an issue that is not restricted to cement producers located in certain geographical areas: as is widely known, due to economic and environmental aspects, many cement producers located in “low-chromium zones” purchase clinker from other countries (for instance China or Turkey), so that the risk of facing problems related to high Cr (VI) levels may become quite relevant. The efficacy of MA.P.E./Cr 05 products in reducing extremely high levels of Cr (VI) is demonstrated by means of the industrial case studies described in the following paragraphs.

4.3.1 INDUSTRIAL CASE STUDY NO.1
A cement plant located in Italy started in 2007 to import a clinker with an average concentration of Cr (VI) ranging between 28-34 ppm, thus
determining a concentration in the final product (a type II/A-LL limestone cement) of about 23 – 28 ppm. Using a commercially available tin-based liquid product, the cement plant was not been able to reduce the hexavalent chromium under the threshold of 2 ppm. Trials with higher dosages of this product with respect to the producer’s recommended ones have proven themselves to be unsuccessful and way too expensive. As can be seen from the chart below (Figure 4.4), MA.P.E./Cr 05 LV has been able to reduce Cr (VI) all the way down to zero even while adopting a dosage slightly below the recommended one (which is 50 g/t for each ppm of Cr (VI) that has to be reduced).

Figure 4.4: Comparison between the industrial performance of MA.P.E./Cr 05 and a tin-based liquid product

4.3.2 INDUSTRIAL CASE STUDY NO.2

During spring 2009, a cement plant in Turkey started to export CEM I type Portland cement to EU countries. The concentration of hexavalent chromium of the clinker produced by the plant ranges between 32 and 36 ppm, thus determining a concentration in the final product of about 30 to 34 ppm (clinker counted for 95% of the cement’s recipe). Prior to the industrial trial with MA.P.E./Cr 05 LV, the cement plant tried ferrous sulphate as reducing agent, dosing it at 13-14 kg/t (1.3 to 1.4% in the cement recipe). Besides the practical problems of dosing very high amounts of ferrous
sulphate, such quantities had a negative impact on the cement’s characteristics in form of compressive strengths decreases and the formation of red spots once used in concrete. Even in this case, the \textbf{MA.P.E./Cr 05 LV} has permitted to reduce the hexavalent chromium well below the threshold of 2 ppm while using the recommended dosage of 50 g/t for each ppm of Cr (VI). Additionally, we performed long-term analyses on the cement samples recovered during this particular trial and while after 6 months the reducing effect of the antimony based product was basically unvaried, the samples produced with ferrous sulphate presented values well above the limits defined by the European directive.

Results of both analyses are reported in \textit{Figures 4.5 and 4.6}. 

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure4.5.png}
\caption{Comparison between the industrial performance of MA.P.E./Cr 05 LV and ferrous sulphate}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure4.6.png}
\caption{Long-term Cr (VI) analyses of cement ground with MA.P.E./Cr 05 LV and ferrous sulphate}
\end{figure}
5. MA.P.E./Cr07
MICRO ENCAPSULATED, CONTROLLED RELEASE HEXAVALENT CHROMIUM REDUCTION TECHNOLOGY

Antimony trioxide - on which the MA.P.E./Cr 05 series is based - is certainly the best for hexavalent chromium reduction in cements. Its use in powder form (for example during cement bagging, or in ready mix mortar and - generally speaking - in cement based products blending operations) presents the risk of inhaling antimony trioxide dusts, which are potentially hazardous. This is why, until now, the development of powder products based on antimony trioxide has been severely limited.

Mapei efforts in R&D and the constant cooperation with main producers of antimony trioxide recently succeeded in overcoming this limit by developing the controlled release technology, which consists in the encapsulation of antimony trioxide in a special polymer: this allows the complete elimination of antimony trioxide dust and allows the use of this reducing agent in a completely safe way. The polymer is chosen in order to be quickly soluble in alkaline media (such as cement-based materials’ gauge water) and, as soon as cement is mixed with water, antimony trioxide is released and expresses its full reducing power.

The use of this so-called “encapsulation/controlled release” technology (widely used in pharmaceutical industry) presents several advantages:

- Antimony trioxide is completely embedded in the polymer matrix, thus avoiding any possibility of dust release.

- Particle size distribution can be careful controlled, with total elimination of the finest fraction, as antimony trioxide is usually very fine (100% particle size distribution below 20 µm). The presence of free antimony trioxide is completely eliminated.
• Possibility of tailor made products in terms of particle size distribution. Depending on the addition point to cement (in the grinding mill, at separator level, in powder blenders, during cement bagging or elsewhere), different particle size distributions may be required, ranging from finer (20-200 µm) to coarser (100-500 µm) ones.

Figure 5.3 and 5.4: Masterbatch technology - complete elimination of free antimony trioxide. Details of particle size distribution (obtained with laser powder diffraction) showing free antimony trioxide (on the top, particles completely below 10 µm) and antimony trioxide based masterbatch (on the bottom, 40-600 µm PSD).

Figure 5.5 and 5.6: Encapsulation technology permits the production of antimony trioxide-based reducing agents with complete control on the powder’s particle size distribution.
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