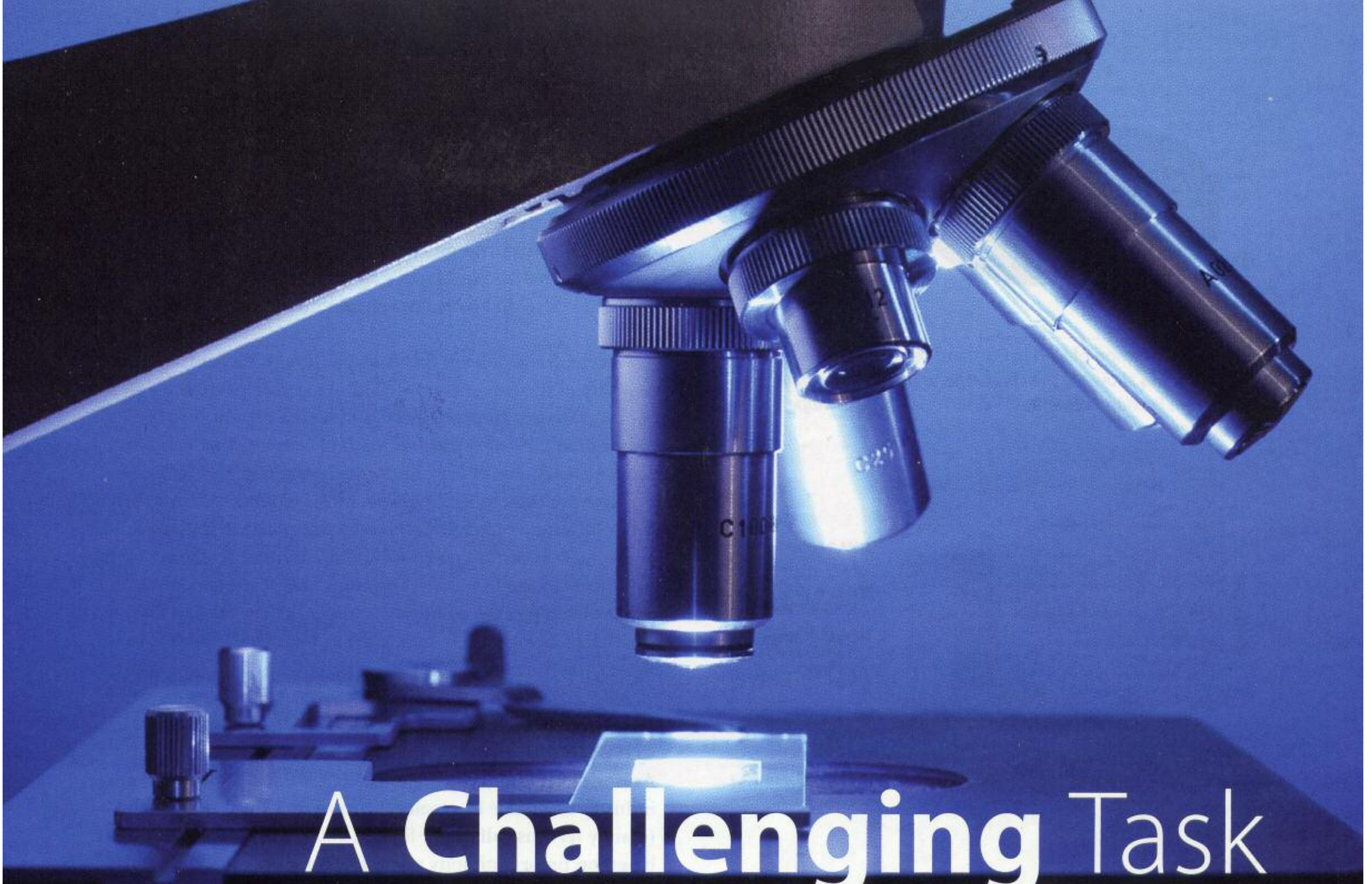


A Challenging Task

Matteo Magistri and Pietro Recchi, Mapei SpA, Italy, tackle the subject of cements with extremely high levels of soluble chromates.

Abstract

Some years have passed since the introduction of the obligation to maintain the level of soluble chromates below 2 ppm (Directive 2003/53 of the European Community). The use of suitable reducing agents such as ferrous and stannous salts or antimony compounds has been widely described. Factors influencing the choice of the most suitable product range from economical to technical considerations. In some cases, clinkers present extremely high levels of soluble chromates: the differences in technical performances of reducing agents become the critical point for facing the challenging task of producing a CrVI-free cement.

Introduction

The raw materials for grey Portland cement manufacturing may contain chromium. Due to the highly oxidising and alkaline conditions of the kiln, during clinker production chromium is partially converted to hexavalent chromium and probably fixed as alkaline or calcium chromate (Na_2CrO_4, K_2CrO_4, $CaCrO_4$). As a result, Portland clinkers and cements contain soluble chromates (usually in the range of 5 – 15 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 and also presents a significant challenge from a technical point of view if the concentration of soluble chromates exceeds a certain threshold.

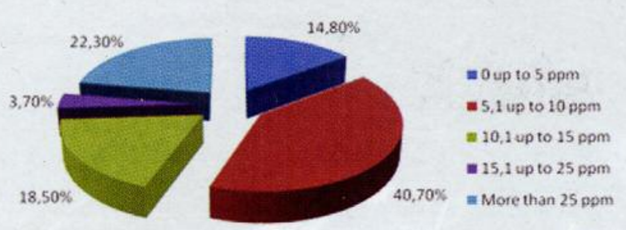


Figure 1. Distribution of CrVI in Portland cements.
The percentages shown in the chart refer to the grand total of 257 different Portland cements analysed since 2002 in Mapei's laboratories.

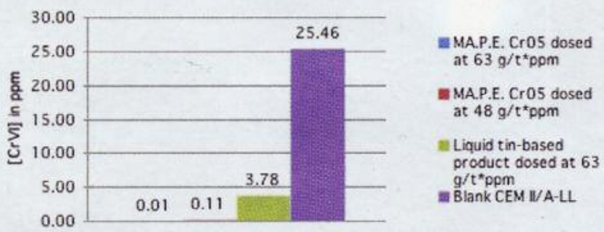


Figure 2. Reduction efficacy - MA.P.E. Cr05 LV vs. tin-based liquid product.

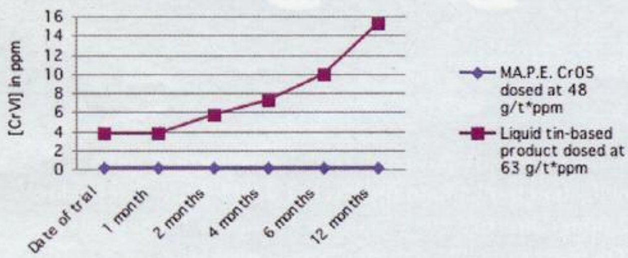


Figure 3. Long term efficacy comparison – MA.P.E. Cr05 LV vs. tin-based liquid product.

High levels of soluble chromates

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: this article specifically deals with the reduction of extremely high concentrations, 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[1]. For example, the use of iron scraps during clinker production (used to adjust the iron content of 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 a straightforward high concentration of chromium.

For reasons that 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 chromate concentrations well above the average. According to information acquired on the field, this could be due to the presence of iron ore in raw materials' extraction points in these regions.

Figure 1 shows a statistical distribution of hexavalent chromium concentration based on the cement samples that have been analysed in Mapei's laboratories since the company started to develop hexavalent chromium reducing agents (2002).

As can be seen from this chart, although the vast majority of the cements produced worldwide present a CrVI concentration <10 ppm, there is indeed a certain number (more than 20% of the grand total) of cements that contain soluble chromates in very high concentrations.

The problem in dealing with such amounts of chromates is not an issue restricted only to cement producers that are located in certain geographical areas: many cement producers located in "low-chromium zones" are buying clinker from foreign countries (China, Turkey, etc.) so that the risk of facing problems related to high CrVI levels is in these cases quite relevant.

Products for the reduction of hexavalent chromium

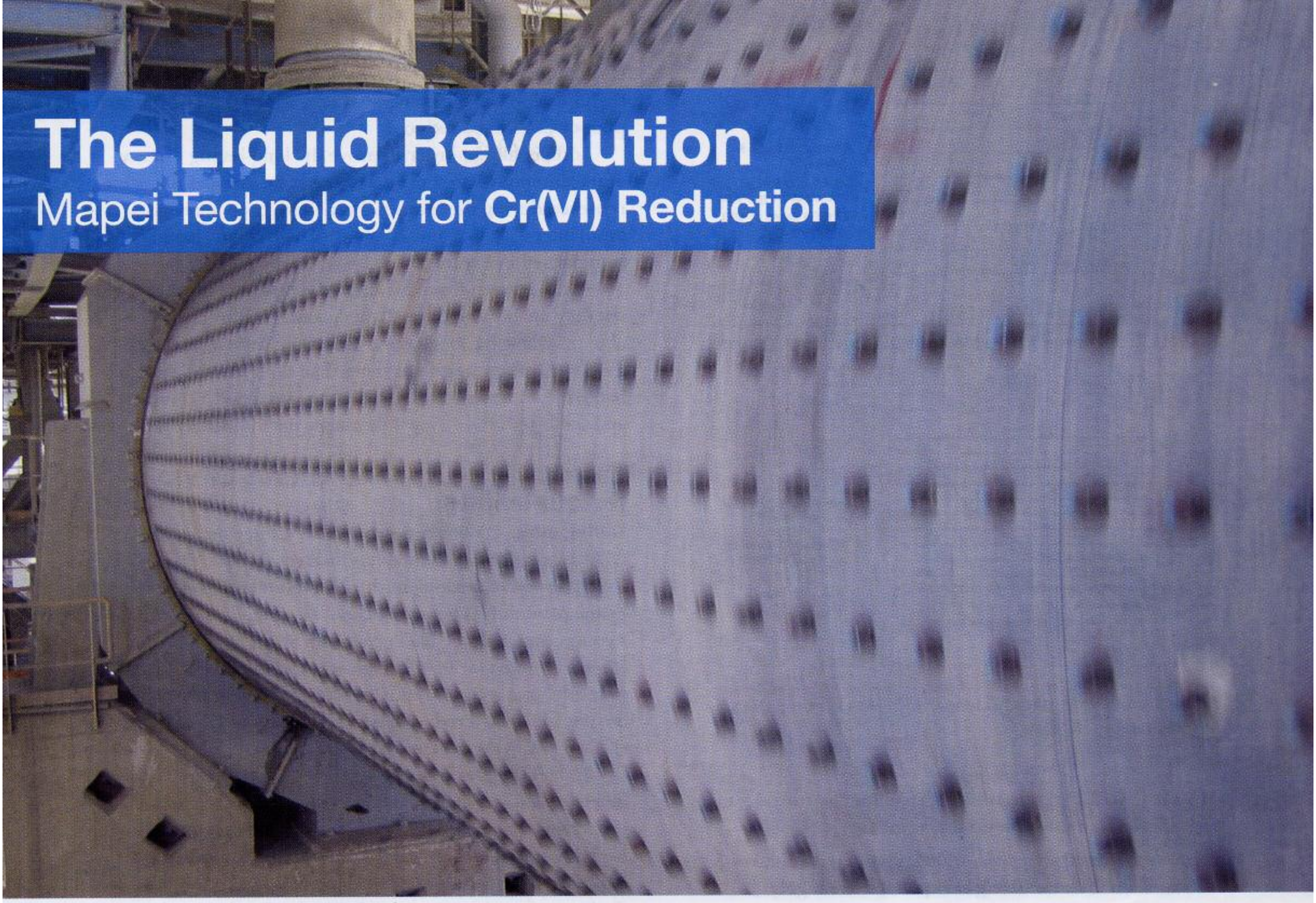
As is widely known, the products that are used in the cement industry to reduce hexavalent chromium can be either solid (mainly ferrous sulfate) or liquid (solutions/suspensions based on tin or antimony salts). Due to its low price, ferrous sulfate remains to this date the most widely utilised solution. Nevertheless, ferrous sulfate's effectiveness is strongly influenced by factors such as humidity and temperature, which determine its over-dosage, substantially above the stoichiometric one: ferrous sulfate is usually dosed at about 400 - 500 g/t for each ppm of hexavalent chromium to be reduced. While with low amounts of soluble chromates this value translates to a few kg/t, with high amounts this dosage becomes enormous: for example, with 30 ppm CrVI the cement plant should add about 15 kg/t of ferrous sulfate, with negative repercussions on the quality of the final products, for example in the form of red spots once the finished product becomes utilised in concrete. In addition, high amounts of $FeSO_4$ could increase the total amount of soluble sulfates, thus giving weaker performances in terms of setting time and workability. On the other hand, liquid reducers based on tin salts (mainly stannous sulfate) that have been present on the market for many years have been proven to lose part of their reduction efficacy with CrVI levels greater than 15 – 20 ppm, with the need of very high dosages and therefore costs.

Additionally, ferrous sulfate is not usually able to provide a reduction that lasts over time, while there are still some concerns about the efficacy of tin-based products in this regard[2]. This issue becomes particularly important in the case of cement plants located outside the European Community that export cement into the EC (e.g. Turkey): these cement plants have to reduce the hexavalent chromium after the 2003/53 directive, but also assure a long-lasting reduction, since in the case of exported cement the time gap between production and effective use of the product can be quite long.

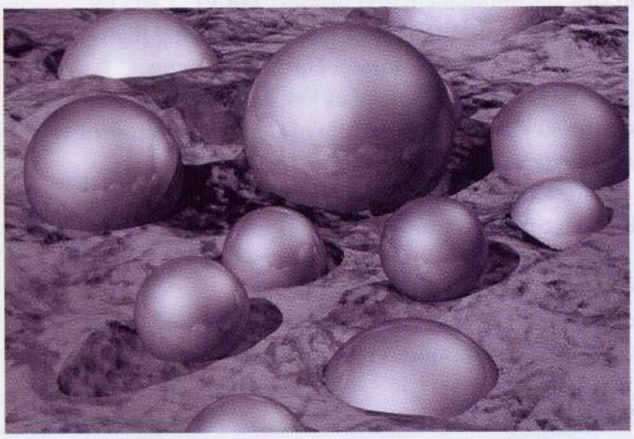
In the authors' experience, the only hexavalent chromium that has proven itself to be always effective, even in case of extremely high concentration of CrVI, is the

The Liquid Revolution

Mapei Technology for **Cr(VI) Reduction**



MA.P.E./Cr 05 is a new, patent pending technology for the reduction of Cr(VI) in your cement. In fact, this new technology allows you to improve the efficiency of Cr(VI) reduction in terms of technical performance, practical application and economic impact.



- Liquid product
- Simple and cheap dosage systems
- Lower operational and specific costs
- Low dosages < 50 g/t* ppm Cr(VI)
- Long lasting Cr(VI) reduction > 6 months
- Neutral pH (no ADR)
- Patented technology, result of MAPEI Research & Development

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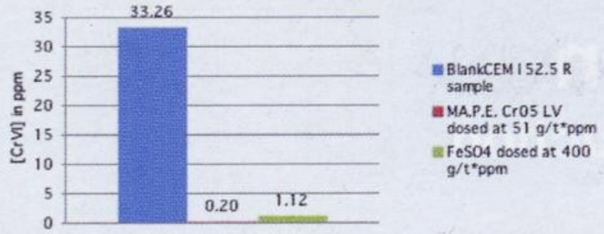

Figure 4. Reduction efficacy - MA.P.E. Cr05 LV vs. ferrous sulfate.

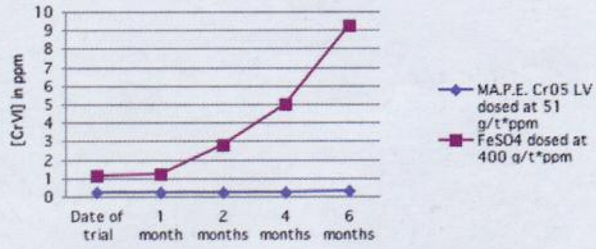

Figure 5. Long term efficacy comparison – MA.P.E. Cr05 LV vs. ferrous sulfate

MA.P.E. Cr05 LV[3]. Entirely based on antimony trioxide, the characteristics of this product are as follows:

- Neutral (or alkaline) pH, while other liquid additives based on tin have strong acid pH and are highly corrosive.
- 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 sulfate and sometimes with tin-based liquid reducing agents. Due to this unique characteristic, MA.P.E. Cr05 LV represents the best technical solution in case of high levels of hexavalent chromium.
- No reducing agent lost during storage: this enables the Cr(VI) content to remain constant for a very long time, without requiring an over dosage.

All the aforementioned advantages connected to the use of MA.P.E. Cr05 LV are demonstrated in the two following case studies.

Case study no.1 – MA.P.E. Cr05 LV vs. tin-based liquid product

A cement plant located in Italy began to import clinker from Turkey in 2007. This clinker had an average concentration of Cr ranging between 28 – 34 ppm, thus determining a concentration in the final product (a type II/A-LL limestone cement with 80 – 82% of clinker) of about 23 – 28 ppm. Using a commercially available liquid product, the cement plant has 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 too expensive.

As can be seen from Figure 2, the antimony-based product Cr05 LV has been able to reduce the hexavalent chromium all the way to zero even while adopting a dosage slightly below the recommended one, which is 50 g/t for each ppm of CrVI to be reduced.

Additionally, in order to prove the long-lasting efficacy of the antimony-based products, the same samples that were retrieved during the industrial trial have been analysed again after 1, 2, 4, 6 and 12 months. The results have been summarised in Figure 3.

As can be seen from this chart, the tin-based product is not only unable to reduce all the hexavalent chromium: it is also unsuitable for long-lasting reduction, since after 6 months the CrVI concentration has more than doubled. On the other hand, the antimony-based product has provided a complete and stable reduction even 1 year after the industrial trial.

Case study no.2 – MA.P.E. Cr05 LV vs. ferrous sulfate

During spring 2009, a cement plant in Turkey began to export CEM I type Portland cement towards countries in the EU. The concentration of hexavalent chromium in 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. Cr05 LV, the cement plant tried ferrous sulfate as a reducing agent, dosing it at 13 – 14 kg/t (1.3 to 1.4% in the cement recipe).

Besides the practical problems of dosing high amounts of ferrous sulfate, such quantities had a negative impact on the cement's characteristics in that it lowered the compressive strengths and red spots formed once used in concrete. Even in this case, the MA.P.E. Cr05 LV has managed 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 CrVI. Additionally, the company has 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 is practically unvaried, the samples produced in presence of ferrous sulfate presented values well above the limits defined by the European directive.

Conclusion

Given all the information collected during laboratory tests, as well as the experience acquired during industrial trials, it is apparent that the antimony-based product MA.P.E. Cr05 LV represents a technically efficient solution for reducing high amounts of hexavalent chromium in Portland cements.

This occurs not only because of its low dosage, which remains set at 50 - 55 g/t for each ppm of CrVI even in case of high concentrations, but also because its effectiveness remains unchanged for long periods of time, which is especially desirable when cement is produced mainly for export.

Acknowledgement

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References

1. HILLS, L. and JOHANSEN, V.C., 'Hexavalent chromium in cement manufacturing: literature review', *PCA R&D* Serial n° 2983.
2. WASSING, W., 'Experience with the production of chromate reduced cements and cement-containing preparations', *6th International VDZ Congress*, 2009.
3. MAGISTRI, M. and D'ARCANGELO, P., 'New chromium reducing agent for cement', *ZKG International*, 3-2008.