New Cr(VI) reduction technology

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In the 15th Century, the alchemist Basilius Valentinus wrote a book titled "Currus Triumphalis Antimonii" (The triumphal chariot of antimony)[1], describing the amazing properties of antimony and its use as a medicine. After about six centuries, even though some antimony-based compounds are still used for the treatment of some protozoal diseases (such as leishmaniasis), antimony is no longer used in drugs, but continues to improve lives in different ways (as a component in alloys and other materials, flame retardants, additives for polyester and PET manufacturing)[2]. Recently, a new 'medicine' (not for human beings, but for cement and cementitious materials that need to have treatment for the presence of hexavalent chromium) based on antimony has been launched on the international cement market.

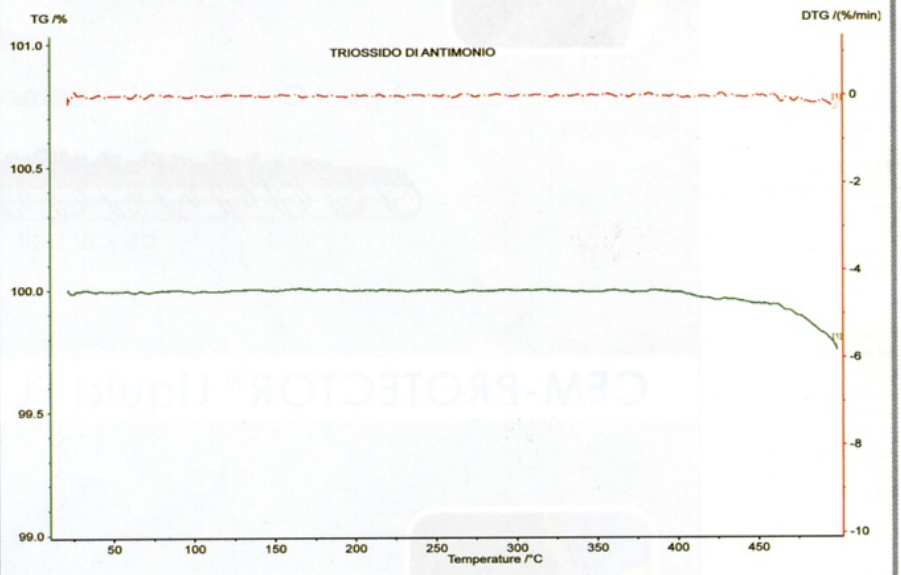
As the most advanced antibiotics are effective where the oldest fail, in comparison to other Cr(VI) reducing agents based on iron or tin this new product achieves better performances. Unlike new drugs, that usually have higher costs, this product offers attractive savings: it can be considered as a treatment not only for cement, but also for cement plant's balance sheets!

MA.P.E./Cr 05 LV: characteristics and advantages

The MA.P.E./Cr 05 LV is based on antimony trioxide, whose characteristics can be summarised as follows[3]:

- **strong reducing Cr(VI)** properties at alkaline pH
- **amphoteric behaviour in water solution:** antimony trioxide is soluble only at very low or very high pH values. This means that, if dispersed on cement during grinding, the reducing agent is not affected by moisture and remains unchanged (maintaining its reducing ability) even after prolonged storage. Therefore, the product stays unaltered inside the cement until the cement is mixed with water and the pH value rises above 12.
- **High thermal stability:** the antimony oxide is stable up to 600°C. In Figure 1 a thermo gravimetric analysis of antimony trioxide is shown: the first alteration can be seen above 600°C. At temperatures commonly found in cement mills no weight increase (oxidation to antimony pentoxide) or weight losses (decomposition) are reported.
- **No reactivity with free lime:** even in the presence of high amounts of free lime, antimony trioxide remains unaltered.

Figure 1: thermogravimetric analysis of antimony trioxide: no weight variation or other alterations up to 600°C (green line)



Thanks to these properties, the advantages of MA.P.E./Cr 05 LV are:

- high efficacy at low dosages
- long-term stability of Cr(VI) reduction, without the need to for over dosages, as with ferrous sulphate
- no loss of reducing agent during grinding, even in the presence of a high amount of cooling water, high grinding temperature and high content of free lime.

MA.P.E./Cr 05 LV is a suspension of solid particles of antimony trioxide in water. Therefore, it has a neutral (or alkaline) pH, while other liquid additives based on tin have strong acid pH value (corrosive). The viscosity of the product (that decreases as the shear stress increases, as happens with non-Newtonian fluids: see Figure 2) and the small dimensions of the antimony trioxide particles allow very easy pumping and dosing.

Industrial use

In laboratory test the dosage of MA.P.E./Cr 05 LV is about 50g/t for each ppm of Cr(VI) to be reduced. During industrial

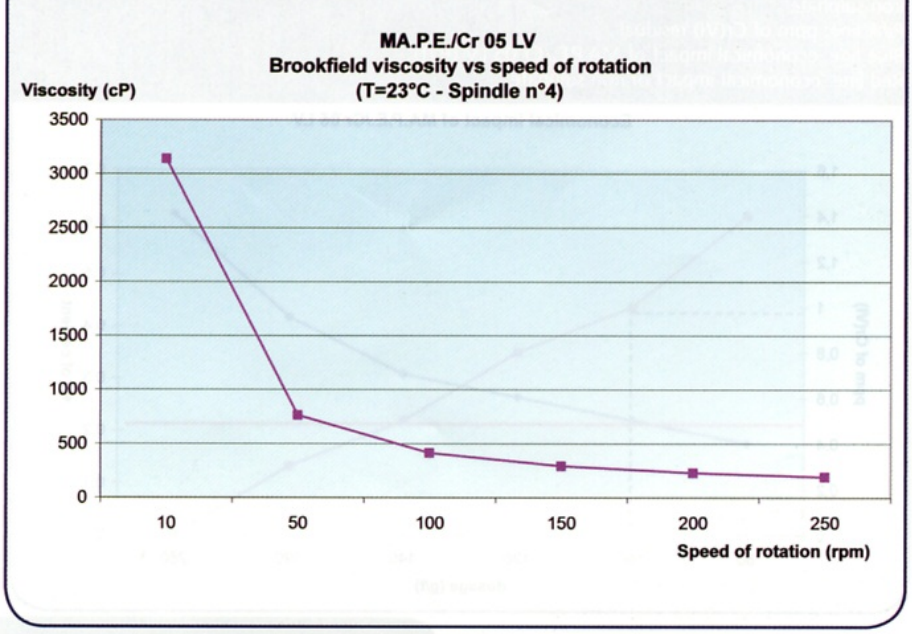
trials dosages are sometimes lower, in the range of 40-45g/t for each ppm of Cr(VI). This difference is probably related to a better dispersion of the product in cement, allowed by industrial milling.

MA.P.E./Cr 05 LV should be dosed directly onto the clinker/feed conveyor belt using a peristaltic or a piston pump, with a dedicated pipeline. MA.P.E./Cr 05 LV should be stored avoiding contamination with different products (eg, grinding aids, reducing agent based on tin).

MA.P.E./Cr 05 LV is a very stable suspension, so it doesn't need additional mixing to avoid solid particle sedimentation.

Figure 3 shows a typical industrial application.

Figure 2: viscosity of MA.P.E./Cr 05 LV

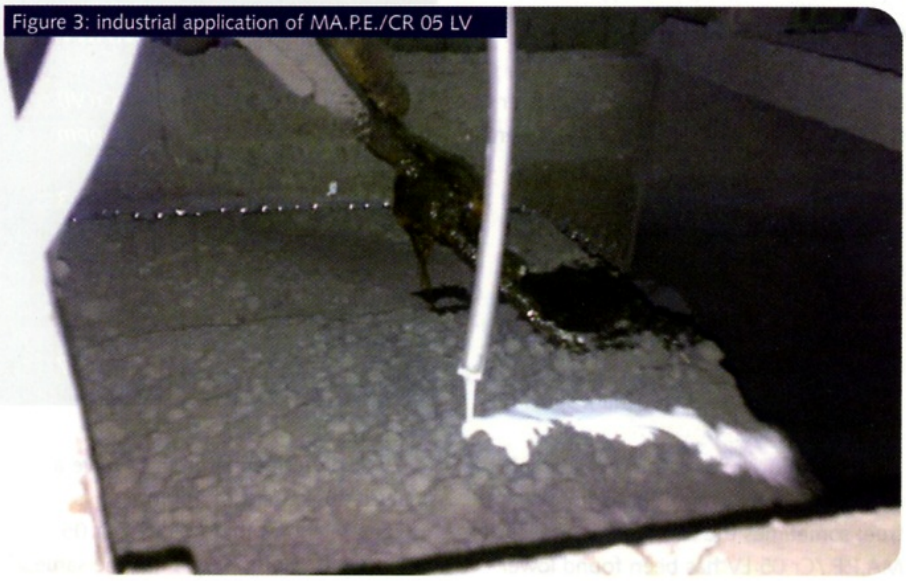


How to use MA.P.E./Cr 05 LV

It is important to point out that, thanks to the long-term stability, it is not necessary to reduce completely the hexavalent chromium present in cement. MA.P.E./Cr 05 LV can be dosed in order to reach a Cr(VI) level of about 1ppm. This value will usually be maintained even after several months, which allows excellent cost savings.

MA.P.E./Cr 05 LV has a great Cr(VI) reducing effect on any type of cement, as shown in Table 2.

Figure 3: industrial application of MA.P.E./CR 05 LV



Comparison with stannous sulphate

Stannous sulphate is a commonly used Cr(VI) reducing agent, available in both powder and liquid form. Usually, the powder is more difficult to handle and to dose accurately than the liquid product. The average dosage of stannous sulphate is 15g/t for each ppm of Cr(VI) and guarantees a Cr(VI) reduction for several months. Stannous sulphate prices have increased very much in the last few months. At the moment we can consider a price of around €8-9/kg.

Industrial case study N°1

A CEM I 52.5 R is produced with 5000cm^2/g Blaine fineness, with a mill productivity of 48tph. The hexavalent chromium content of this cement is about 13ppm. The reducing agent used is stannous sulphate (powder form) at a dosage of 15g/t*ppm. MA.P.E./Cr 05 LV was tested in comparison to stannous sulphate. As summarised in Table 3, it has been possible to dose MA.P.E./Cr 05 LV at 48g/t*ppm, allowing a 17 per cent cost saving.

Compared to stannous sulphate MA.P.E./Cr 05 LV presents the following advantages:

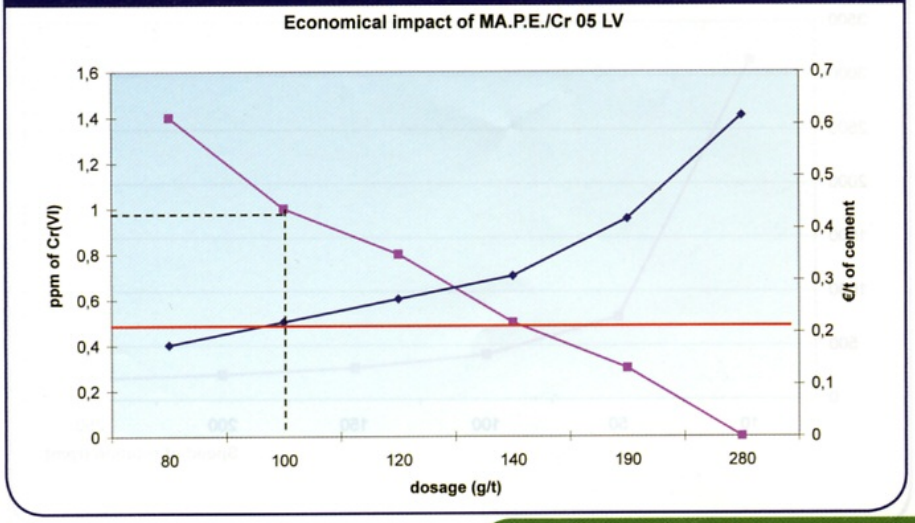
- **Technical advantages:** easy dosing and pumping
- **Economical advantage:** cost savings in the cement production process (-17.3 per cent).

Considering the use of stannous sulphate-based liquid additives, it is clearly possible to overcome the difficulties in handling a powder, but the economical impact for cement producers using this additive is obviously higher, sometimes even 40–50 per cent higher than using MA.P.E./Cr 05 LV.

Table 1: physic-chemical characteristic of MA.P.E./Cr 05 LV

Reducing agent	Sb_2O_3
Colour	White
Active phase	21 %
pH	9
Density	1.22kg/l
Dosage	45-50g/t.ppm of Cr (VI)

Figure 4: industrial case study – economical impact of MA.P.E./Cr 05 LV in comparison to iron sulphate
Pink line: ppm of Cr(VI) residual
Blue line: economical impact of MA.P.E./Cr 05 LV (€/t)
Red line: economical impact of iron sulphate



Conclusions

1. MA.P.E./Cr 05 LV is a new liquid additive for Cr(VI) reduction in cement and cement based materials.

2. Thanks to the properties of its active ingredient (antimony trioxide), MA.P.E./Cr 05 LV shows superior performances in comparison to iron and tin based products.

3. In most cases, the use of MA.P.E./Cr 05 LV has lower economical impact (in terms of euros for each tonne of cement produced), with technical performances comparable (or superior) to other reducing agents.

Comparison with iron sulphate

Iron sulphate is available only in powder form. It is commonly employed in cement plants in spite of the following technical problems:

- **Unstable product:** over dosage is necessary to guarantee Cr(VI) reduction for at least three months
- **Dosing system:** difficult and expensive handling
- **Side effects:** possible red/dark spots on concrete surface.

The very low price is the only advantage of iron sulphate, even if this is not always true: sometimes the economical impact of MA.P.E./Cr 05 LV has been found lower than (or comparable to) iron sulphate. The following example describes one of Mapei's practical experiences.

Industrial case study N°2

An Italian cement plant produces a CEM II/A-LL 42.5 R (80 per cent clinker, 15 per cent limestone, five per cent gypsum) with Cr(VI) content of 5ppm. To reduce and maintain a constant level of Cr(VI) for three months, iron sulphate is used at a dosage of 1.5kg/t (0.15 per cent) of cement produced. The price of iron sulphate is €0.14/kg (including delivery costs) so its economical impact is €0.21/t of cement.

Several dosages of MA.P.E./Cr 05 LV were tested in order to clarify the economical impact. Considering that no overdosing is needed, it is not necessary to reduce Cr(VI) completely: the industrial trial was performed in order to have a final Cr(VI) content of 1ppm.

Figure 4 shows that MA.P.E./Cr 05 LV dosed at about 100g/t has the same economical impact as iron sulphate. Any dosage below this value means lower economical impact and enables the level of Cr(VI) to be maintained below 2ppm even for several months.

Table 2: efficacy of MA.P.E/Cr 05 on different cements

Cement type	*Cr(VI) ppm*	*Dosage kg/t*	*Cr(VI)Cr(VI) after six months*	
CEM I 52.5R	22.3	1.02	1.1	1.1
CEM II/A-LL 42.5R	10.3	0.45	1.0	1.0
CEM II/B-S 32.5R	7.6	1.29	0.9	0.9
CEM II/B-M (LL-P) 32.5R	6.0	1.23	0.8	0.8
CEM III/A 32.5N	4.4	0.17	1.0	1.0
CEM IV/B-P 32.5R	5.7	0.22	1.2	1.2

Table 3: industrial case – comparison with stannous sulphate

Cement type	*Stannous sulphate*	*MA.P.E./Cr 05 LV*
Price (€/kg)	8.5	2.2
Dosage (g/t*ppm of Cr(VI)	15	48
Dosage (g/t)	195	624
Economic impact (€/t)	1.66	1.37
Differences (%)	–	-17.3%

References

1. http://en.wikipedia.org/wiki/Basilius_Valentinus
2. Ullman's Encyclopedia of Industrial Chemistry, 5th Edition
3. M.Magistri, P.D'Arcangelo: "New chromium reducing agent for cement" – ZKG International, 3-2008.