EXTENDED SHELF LIFE OF CR (VI) *Reduction*

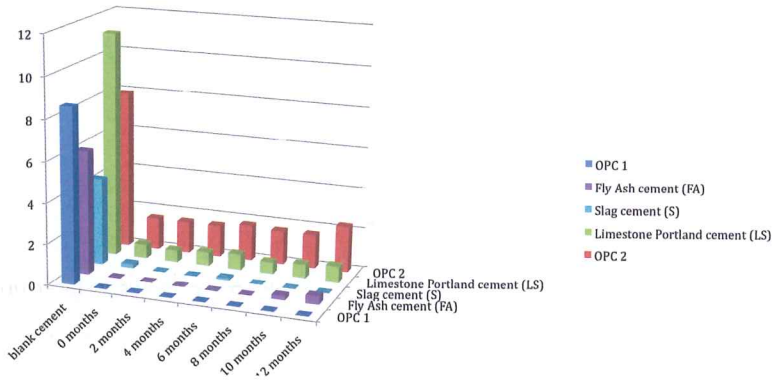
Paolo Forni, Mapei SpA, Italy, presents the results of a study into chromium VI reduction for cements with long shelf lives.

Introduction

Chromium VI reduction in cement is now a mature technology in Europe, with many solutions available on the market. The relevant advantages and disadvantages regarding their use and performance are well-known: for example, the ease-of-use of liquid products is balanced by their higher average price, while most powder reducers have lower dosage efficiency and hence they have to be used at a higher dosage. All manufacturers of reducers and most cement producers have carried out tests to show and check the efficiency of the different products. However, no comprehensive study of the performance of Cr (VI) reducers has been

Table 1. Composition and fineness of the cements tested							
Cement type	**% Clinker**	**% Natural gypsum**	**% Synthetic gypsum**	**% Limestone**	**% Slag**	**% Flyash**	**Blaine SSA m^2/kg**
OPC 1	92	-	5	3	-	-	520
OPC 2	94	6	-	-	-	-	330
Limestone Portland cement (LS)	74	5	-	21	-	-	456
Flyash cement (FA)	68	5	-	6	-	21	442
Slag cement (S)	53	-	5	-	42	-	410

Table 2. Soluble chromium VI measurements on industrially treated cements									
Cement type	**ppm Cr (VI) blank cement**	**ppm MA.P.E./ Cr 05 LV / ppm Cr (VI)**	**ppm Cr (VI) 0 months**	**ppm Cr (VI) 2 months**	**ppm Cr (VI) 4 months**	**ppm Cr (VI) 6 months**	**ppm Cr (VI) 8 months**	**ppm Cr (VI) 10 months**	**ppm Cr (VI) 12 months**
OPC 1	8.6	55	0	0	0	0	0	0	0
OPC 2	7.9	38	1.6	1.6	1.6	1.8	1.7	1.7	2.3
Limestone Portland cement (LS)	11.2	51	0.7	0.6	0.7	0.8	0.6	0.7	0.8
Flyash cement (FA)	6.1	50	0	0	0	0	0	0.2	0.4
Slag cement (S)	4.3	48	0.2	0	0	0.1	0	0	0



Reduction of Cr (VI) remains constant over time.

published for the very long shelf life of treated cements. This article presents a performance report of Mapei product MA.P.E./Cr 05 LV up to one year cement shelf life, for five cements, differing in composition, fineness and initial Cr (VI) content.

Mapei introduced its patented technology based on Antimony in 2007. MA.P.E./Cr 05 LV is a liquid additive, easy to use and hence widely used in many EU countries. The suggested dosage is between 40 and 60 ppm (g/metric t of cement) for each ppm of chromium VI.

Evaluating long-term success

During 2010 and 2011, a series of industrial tests have been run with MA.P.E./Cr 05 LV in several EU plants. The target was of course 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 two months, cements have been sampled from these bags to determine soluble chromium, according to EN 196-10 standard. Table 1 reports the composition and fineness of the cements used for this study.

It was decided that quite different cements would be selected in terms of composition/chemistry (two OPCs, one limestone cement, one pozzolanic/flyash cement and one slag cement), fineness (the two OPCs have very different fineness) and geographical origin (Northern, Central and Southern Europe).

Prior to running field trials, blank samples of each cement were tested for soluble chromium VI levels, to determine the suitable dosage of additive MA.P.E./Cr 05 LV. Targeted dosage was

50 ppm (g/metric t of cement) of reducer for each ppm of Cr (VI) to be reduced: however, in some circumstances the actual dosage differed. The values are reported in Table 2. In the same table, concentrations of soluble chromium in the blank cement are shown, as well as the outcomes of the measurements carried out on the day of the test and every two months after.

As can be seen, MA.P.E./Cr 05 LV is effective in reducing Cr (VI) for all cement compositions and finenesses. When the suggested dosage is used, Cr (VI) is under 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 situation that has been known with other reducers (e.g. ferrous sulfate or stannous sulfate). This is related to the properties specific to Mapei additive, which is activated only when cement is mixed with water and it is not influenced by environmental humidity or by air exposure. On the other hand, the study observed a slightly different behaviour for OPC 2. In this case, the Cr (VI) value stays constant until four months, then it goes up by a few decimals of ppm, remains at 1.7 ppm for an additional four months before gaining 0.6 ppm, marginally surpassing the 2 ppm threshold after one year. This unusual behaviour could indeed be related to the lower dosage of reducing additive (the actual dosage was in fact relatively low at 38 ppm/ppm of Cr (VI)). Additional reasons could be related to the specific characteristics of this cement: this OPC, which originates from central Europe, is quite coarse and has a relatively high amount of sulfates (coming from a natural gypsum source). Further studies would be needed to correlate any of these properties to the increase in soluble Cr (VI) over time and this could definitely be the subject of additional investigation; however, at least up to ten months, it remains on the safe side, i.e. under 2 ppm of Cr (VI).

Conclusion

This study shows that Antimony-based technology, developed by Mapei, can deliver a sound performance in terms of chromium VI reduction. This is true not only within the normally checked two to three months of cement shelf life, but even for prolonged periods, up to one year and beyond. This can result in additional guarantees of safety for the use of bagged cement, even if it is stored for uncommonly long periods of time.