CrVI innovations

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The growth in chromium VI (CrVI)-reducing additives has been particularly strong in Europe because of EC directives, and they have become an integral part of many producers' grinding programmes. Development firstly witnessed the addition of ferrous and tin sulphate powders and has progressed to liquid Cr(VI) additives, before the introduction of the new generation of improved reducers. WR Grace Construction Products has pioneered the use of Cr(VI) reducers through its Synchro range and it sees further opportunities for new types of Cr(VI) reducers.

Low chromium cements are usually obtained by the addition of a Cr(VI)-reducing additive. Powdered iron sulphate is the most frequently used chromium-reducing agent for cement, followed by tin sulphate and several liquid technologies. This article reviews currently used solutions together with a brief description of the latest developments in this field. Particular attention is given to selected patents and commercial applications, emphasising the contribution of Grace Construction Products in this area. Even though a large number of references are discussed, this article is not intended to be an exhaustive literature review of chromium reduction in cement. It is rather a discussion of the technologies which are commercially most interesting, and a note on the authors' opinion on the latest developments and expectations for the future.

Grace focuses only on Cr(VI)-reducing additives in this article. Alternative approaches for lowering Cr(VI) content in cement (ie, raw materials selection, kiln technologies, chromium 'absorbers', contribution of kiln linings and mill media, etc) are not covered here. Additional issues arising from testing methodologies, quality of raw materials, manufacturing processes, etc, are also not discussed here, even though it is recognised that they could play an important role in the performance of chromium-reducing products. Since many Cr(VI)-reducing products are proprietary, the article focuses on publicly available information.

Clockwise from top

Figure 1: iron sulphate heptahydrate powder

Figure 2: tin sulphate powder

Figure 3: Grace's improved Fe-based additive

State-of-the-art

Cement raw materials contain trace quantities of chromium. Resultant cement clinker can contain 100-300ppm chromium. In the oxidising and alkaline burning conditions of the cement kiln, chromium is oxidised to hexavalent chromium (typically 5-20ppm). Cr(VI) is classified as toxic, causing skin irritation on contact and allergic eczema. EU Directive 2003/53/EC [1], effective January 2005, limits the water-soluble chromium content in cement to below 2ppm.

Chromium-reducing additives are usually added in the cement grinding process. The use of $FeSO_4$ (ferrous sulphate) has been known since the early 1970s[2,3]. Ferrous sulphate is the most widely-applied solution. Different types of $FeSO_4$ powders are available on the market, such as hepta- or monohydrate, usually coated, dried and/or mixed with various fillers, at different acidification. The salt may be added at various stages of manufacturing, from the mill entrance to the dispatch unit.

Although widely used due to low cost, iron sulphate is readily oxidised. Therefore, its ability to reduce chromium can be compromised, especially after long periods of cement storage. High dosages of iron sulphate (2-5kg/t cement) are required to reduce Cr(VI) to below 2ppm in cement. Negative consequences of using high dosages of iron sulphate include high cement water demand and brown staining on the surface of finished concrete elements. Recently, comments have been made concerning the potential corrosion of concrete reinforcement [4].

Tin sulphate powder has also been known since the 1990s to be an effective chromium reducer for cement. The first real breakthrough technology came in late 2004, when Grace introduced Synchro™ 100, the first commercially successful liquid chromium reducer [5]. This product was developed to allow cement plants to use their existing delivery systems for liquid additives, without having to incur substantial capital investment for a powder handling system. In addition to the handling advantage, Synchro™ 100 is formulated to allow a liquid delivery of tin sulphate without the early oxidisation experienced with a straight tin sulphate solution.

Research into new iron-based reducers

$FeSO_4$ is widely available at relatively low cost and many researchers have been focusing on solving the main issues related to the use of this powder. Consequently, Grace is observing improvement in the performance of $FeSO_4$-based products, characterised by better flowablity, lower acidity, improved packing behaviour, and longer shelf-life [6-12].

An effort Grace has focused on is a step-change improvement in the stability of $FeSO_4$ against oxidation. The company's laboratory and field data indicates that an improvement in dosage efficiency by factor of 5-10 is possible [13], although the economics do not currently appear favourable for such a technology. A liquid Fe-based product has also been

Figure 4: Synchro™ 200

proposed based on this technical concept. In the authors' knowledge, none of these innovative applications had a significant commercial diffusion to date.

New tin-based reducers

Liquid chromium reducers, based on $SnSO_4$ (tin sulphate) or $SnCl_2$ (tin chloride), and including various stabilisers, oxygen scavengers and/or chelators, have been developed and marketed.

Grace has a continuing research programme for the development of new generations of chromium-reducing technologies under the brand name Synchro™, focusing on minimising efficiency loss to pre-oxidation, with optimised characteristics for product handling. This active research programme has allowed Grace to obtain five patents, with two patents pending [14-16].

The well-known Synchro™ 200, 201 and 205 have shown both superior performance and an appreciable ease of use [17]. In one example, a plant producing a cement with around 15ppm Cr(VI) had previously evaluated iron sulphate, but found that dosage was required to be as high as 5000g/t, causing issues with iron staining, setting time, and material handling. In addition, flowability problems with the iron sulphate were experienced in the winter. Synchro™ 205 was able to meet its objectives for 2ppm Cr(VI) in cement with a dosage of 650g/t. The use of this liquid product eliminated material handling problems and allowed for predictable dosing.

In a second plant there was a need to reduce only 2-3ppm Cr(VI) to ship cement to Europe. Using Synchro™ 205 allowed the plant to invest in a small liquid dosing system costing less than €10,000 rather than investing in a larger powder handling system which would have cost up to €500,000. The use of Synchro™ 205 also solved a logistics problem allowing the transport of small volumes of liquid material from Europe rather than a larger bulk volume of iron sulphate, which would have been readily oxidised on the ocean transport in the hot, humid Mediterranean summer.

Table 1 summarises the developments from Grace under the Synchro™ brand name. Noteworthy is the upcoming Synchro™ 300 line, a formulated product range optimised for strongly oxidising conditions frequently seen in industrial ball mills. Figure 4 shows the clear and homogeneous appearance of Synchro™ 200.

Blended $SnSO_4$ powdered additives, based on similar technologies to those in use for the $FeSO_4$, have been developed and introduced in the market. Co-additives have also been used to improve the performance of $SnSO_4$, in powder or liquid form. However, a significant drawback for tin-based additives has been the increasing cost

Figure 5: reference market price of tin over the last five years

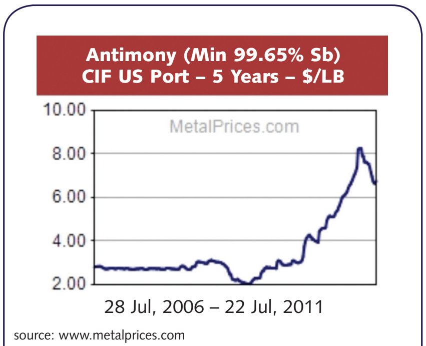

Figure 6: reference market price of antimony over the last five years

Table 1: Grace Synchro™ developments

Synchro™ 100	*Synchro™ 200/201/205/206*	*Synchro™ 300*
2005	2007	2012
Sn(II)-based pumpable liquid	Sn(II)-based colloidal suspension	Based on multiple Cr(VI) reducers
Technology to limit oxidation of Sn(II) to Sn(IV)	Formulated additive – further stabilises Sn(II) for long periods of cement storage	High-efficiency in harsh oxidising conditions; long cement storage stability
	Temperature stability	Non-corrosive

of the tin metal, which has limited the application of tin sulphate and other tin-based products (see Figure 5).

Antimony-based reducers

Antimony was first introduced for this application as antimony potassium tartrate (Tartox [18]). This was followed by an additive based on antimony trioxide (Sb_2O_3) in a liquid form [19,20]. Both technologies have good efficiency for Cr(VI) reduction, but there are concerns about the safety of antimony compounds. For example, Sb_2O_3 is classified by IARC "2B, Possibly Carcinogenic to Humans" [21] and leaching of antimony-based chemicals is possible from hardened concrete, which was well studied by Magistri and co-workers [22].

The antimony metal, which is mainly mined in China, has also faced a dramatic increase in cost recently, similarly to that of tin, as shown in Figure 6.

Other reducers

Scientists from the cement industry, chemical companies and academic institutions have struggled for more than 20 years to find and propose alternative options to iron and tin metal salts for chromium reduction in cement.

Proposed technologies without commercial success include: manganese compounds [23], lignosulphonates [24], aldehyde derivatives [25], barium chloride [26], and slag powders [27].

Since the implementation of the 2003/53/EC Directive [1] the search for alternative solutions has undergone a rapid acceleration. Proposed technical solutions by different sources include: hydroxylamine/hydrazine derivatives [28], disulphides and polysulphides [29], colloidal suspensions of hydroxides of tin, iron, or manganese [30], dithionite [31], protection of metal reducers by means of organic solutions or emulsions [32], transition metal carbonyls [33] and zinc sulphate and/or sodium nitrite [34].

The factors limiting commercial application of these technologies include poor technical performance, or more commonly, the unfavourable costs when compared to existing technologies.

Expectations for the future

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The costs associated with the development of new chemicals under REACH norm is also likely to play a role in limiting the number of chemicals that could be developed for this purpose.

Finally, a better fundamental understanding of the mechanisms behind Cr(VI) reduction, from academic and industrial research institutions, is likely to allow the development of novel systems for reduction of Cr(VI).

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