

Research Study: Stannous Sulfate

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Matteo Magistri
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D'Arcangelo,
Mapei SpA,
Italy, present
a study
investigating
factors that
influence
the stability
of stannous
sulfate.

Introduction

It is well known that the European community has recently introduced the obligation (Directive 2003/53/EC) to maintain the level of soluble chromates below 2 ppm¹. Up to now, ferrous sulfate and stannous sulfate have been the most common products used to reduce Cr(VI) to Cr(III) in any type of cement. It is widely acknowledged that FeSO₄ has a low intrinsic stability and its reduction effects are limited over time, while SnSO₄ is considered the best technical solution. This article presents a study performed by Mapei SpA at its laboratory, on the efficiency of stannous sulfate in clinkers with different amounts of free lime. It should be noted that in the presence of humidity and with clinkers with a high free lime content, a higher than usual SnSO₄ dosage could be needed.

Experimental work

For this purpose, the company studied stannous sulfate powder behaviour on three clinkers with different free lime content. Afterwards, the product's shelf life was checked over time.

Each clinker was ground in a laboratory ball mill, together with 5% of gypsum and 1.5% of water. At the same time, SnSO₄ was added into the mill at the dosage of 15 g/t for each ppm of Cr(VI) to be reduced. Table 1 shows the characteristics of each clinker.

After 10 minutes from the end of the grinding, the Cr(VI) content (according to EN 196-10 standard test method) of ground cements was checked. The shelf life of the stannous sulfate was evaluated by checking hexavalent chromium at six different ages: 1, 2, 7 and 14 days and 1 and 2 months. Table 2 and Figure 1 show the complete laboratory results.

The conclusions seem to be the following:

- Stannous sulfate works very well and ensures long shelf life when added to a cement produced from a clinker with low content of free lime, even in the presence of humidity (cement 1).
- In the presence of humidity, as the free lime content increases (cement 2 and cement 3), stannous sulfate (at the dosage of 15 g/t-ppm) tends to become less efficient.

Cr(VI) Reduction

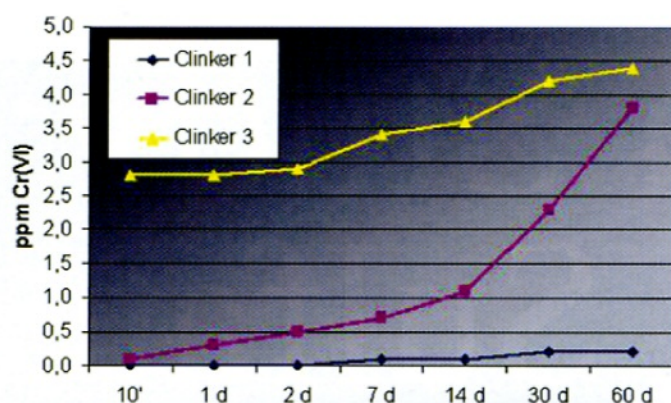


Figure 1. SnSO₄ performance over time at different free CaO content.

Table 1. Clinker characteristics

	Clinker 1	Clinker 2	Clinker 3
Free CaO	0.33%	1.25%	1.78%
Cr(VI) content	8.8 ppm	15.2 ppm	10.0 ppm
SnSO ₄ dosage	15 g/t ppm	15 g/t ppm	15 g/t ppm

Table 2. SnSO₄ performances and shelf life

	ppm Cr(VI) after grinding		
Time after grinding	Cement 1	Cement 2	Cement 3
10 min	0.0	0.1	2.8
1 day	0.0	0.3	2.8
2 days	0.0	0.5	2.9
7 days	0.1	0.7	3.4
14 days	0.1	1.1	3.6
1 month	0.2	2.3	4.2
2 months	0.2	3.8	4.4

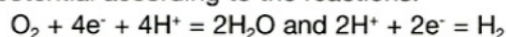
- Both shelf life and instantaneous performance are affected. In particular, with clinker 3 only about 70% of the initial Cr(VI) has been reduced.

Discussion

It is possible to explain these results by considering the red-ox properties of stannous sulfate and its acid-base properties.

In order to understand the electrochemical behaviour of a chemical element in function of pH, it is useful to refer to the Pourbaix diagram, a graph that reports the red-ox potential E (the basic parameter for evaluating the reducing power, measured in volts) as a function of pH. As described², E can be strongly modified by the formation of precipitates and by increasing pH.

The Pourbaix diagram of tin³ (Figure 2) shows the stability range of several tin compounds in function of pH and red-ox potential is showed. The red dotted lines represent the variation with pH of oxygen and hydrogen red-ox potential according to the reactions:



It is possible to observe the following:

- Sn²⁺ and Sn⁴⁺ ions in water solution at very low pH form respectively stannous and stannic hydroxide Sn(OH)₂ and Sn(OH)₄.
- The red-ox potential of Tin(IV)/Tin(II) (line between Sn(OH)₄ and Sn(OH)₂ areas) decreases as the pH increases, so the Tin(II) is a better reducing agent in alkaline solution and it is oxidised to Tin(IV) by a wide range of oxidising agents (such as chromate).
- The stability area of stannous hydroxide is reduced as the pH rises, this means that in the pH range of Portland cement mixing water (between 12 and 13, orange area in the diagram) Tin(II) compounds are thermodynamically unstable and can decompose themselves in Tin(0) and Tin(IV) compounds, according to a reaction usually known as disproportionation⁴.
- Tin(II) compounds at high pH are readily oxidised even by water, as reported in Figure 2, where the red-ox potential of H⁺ (red dotted line) always lies above the red-ox potential of Tin(II).

As soon as cement is mixed with water, the following processes take place:

- The pH immediately rises, following the hydration of the more reactive phases of the clinker.
- The soluble chromates are released.
- The stannous sulfate dissolves in water, leading to the presence in solution of Sn²⁺ and SO₄²⁻ ions. The solubilisation kinetics of stannous sulfate and of chromates are probably very quick, so they are released in the solution at the same time.

The Sn²⁺ ion, in the very alkaline media, is converted to stannous hydroxide Sn(OH)₂ leading to a strong lowering of the red-ox potential. The chromates, already present in solution, are immediately reduced to chromium(III)². The effectiveness of SnSO₄ as a reducing agent is based on the fact that the reaction with Cr(VI) is faster than the deactivation caused by water.

Stannous sulfate (and in general tin salts) is very acidic⁵, and it can react quickly with a strong base such as calcium oxide, according to the following reaction:



During grinding of Portland cement, moisture is often present, coming from the cooling water of the cement mill or from humidity of raw material (slag, limestone, pozzolan). It can be supposed that at high levels of free lime the reaction (as shown in equation 1) can take place and lead to a partial conversion of SnSO₄ to Sn(OH)₂ directly in the mill, when chromates are not yet released. The reducing agent could be deactivated and lose efficacy and, as a consequence, a higher amount is needed to assure a long lasting reduction. This hypothesis agrees well with the laboratory data reported, where the increase in free lime leads to worse efficacy of stannous sulfate.

When looking at liquid products for the reduction of hexavalent chromium, it has been reported that stannous chloride water solutions display better performances in comparison to stannous sulfate solution⁶. The hypothesis of the reaction with free lime during grinding can also

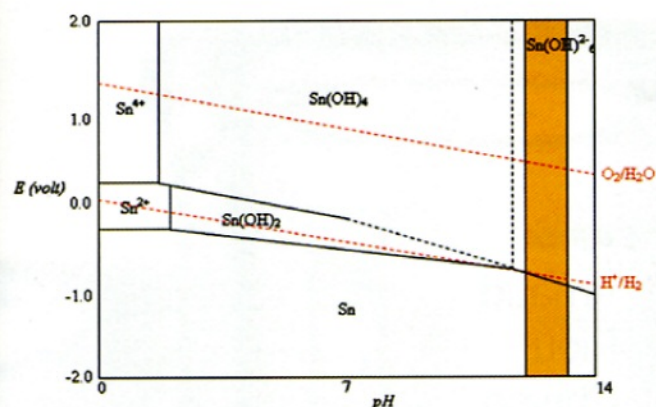


Figure 2. Tin Pourbaix diagram.

explain this fact. In the following reaction:



calcium chloride is produced, while in equation 1, the product is calcium sulfate. The latter has a very low solubility⁵ and this can shift the reaction (equation 1), leading to a more complete conversion of stannous sulfate to stannous hydroxide.

The whole process can be summarised in the following steps:

- During grinding of cement, stannous sulfate can be partially solubilised in the water that may be present in the mill (coming from cooling water or from raw material moisture).
- As the fineness of clinker increases, free lime is exposed and can come into contact with water and stannous sulfate.
- An acid-base reaction between stannous sulfate and lime can take place. The result is the formation of stannous hydroxide.
- The Tin(II) converted to hydroxide is deactivated and it is not available for chromates reduction.

Conclusion

Stannous sulfate is the best available solution for reducing hexavalent chromium in cement based materials. This study has found that in some cases (e.g., in the presence of humidity and when looking at clinkers with high levels of free lime) the efficacy of stannous sulfate can be reduced. The reason lies in the fact that Tin(II) can react with free lime during grinding giving stannous hydroxide that is unstable. •

References

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