

Laboratory trials of liquid chromium reducing agents Tecno Ts (Tecnochem) and Synchro 205 (Grace)

There are certain advantages associated with the use of liquid Cr^{6+} reducing agents. Two liquid Cr reducing agents both based on tin sulphate solutions have been laboratory tested namely Tecno Chrored TS supplied by Tecnochem and Synchro 205 supplied by Grace. Based on the properties of laboratory cements and indicative cost it was observed that the reducing efficiency of Tecno TS is limited and given its high cost it is not recommended for use. Synchro 205 would require a dosage approx. 67 grams/ton of cement/ppm of Cr^{6+} , to reduce Cr^{6+} to the desirable levels. An industrial trial of Synchro 205 is recommended for finally assessing its chromium reducing capacity. Despite, being clearly a more expensive solution at first liquid additives could be beneficial in plants that haven't already invested in FeSO_4 storage and handling equipment and plan to export within EU, or face clogging caused by FeSO_4 inherent stickiness.

Key words: reducing agents, additives, cement

INTRODUCTION

The verification that tin sulphate was found to be stable to oxidation (at least more stable than other metal salts) led to the launching of tin (stannous) sulfate additives for complying with the EC directive for maximum 2 ppm of Cr^{6+} in cement [6]. The principal difficulty for any reducing agent is that oxygen is relatively freely available during grinding and storage of cement [8]. This lowers the availability of the reducing agent for the Cr^{6+} , thus agents have a limited period in which they remain effective and it is necessary to use a large excess of reducing agent to allow for oxidation over time [2, 3]. Indicatively, for ferrous sulphate this means the necessity to use a dosage of between 2000 and 5000 grams/ton of cement, when theoretically it should only require 30 to 73 grams/ton for typical chromium levels. In stannous sulphate there is a similar limitation, however dosages here are lower since stabilization technologies are usually employed that enable extended storage life for treated cement [9].

Tecno Chrored TS (supplier: Tecnochem) is a stannous sulfate solution based on Sn. For manufacturing, tin is electrolyzed in a sulfuric acid to process tin sulfate powder, tin sulfate is dissolved with water and then nitrogen is injected in the solution to assure stability before adding coating agent that aims to protect the SnSO_4 molecule against atmospheric oxygen penetration and prevents loss of reduction

performance. Indicative dosage and cost for Tecno TS were supplied at 50 grams/ton of cement/ppm Cr and 3670 €/t respectively.

Synchro 205 (supplier: Grace) contains a coordination complex of stannous sulfate and involves a stabilization technology that extends the shelf life of cement at a much lower dosage than ferrous sulphate. Indicative dosage and cost for Synchro 205 were supplied at 55-65 grams/ton of cement/ppm Cr^{6+} and 3100 €/ton respectively.

MATERIALS AND METHODS

Concentrations of Cr^{6+} in solutions were estimated by using a colorimetric method with colour-disk comparator [6].

Testing involved;

- the production of laboratory cements with the addition of Tecno TS and Synchro 205 and measurement of Cr^{6+} [7], [9].
- the measurement of Cr^{6+} in the produced cements with Synchro 205 after 55 days (to see the effect of storage life)
- the measurement of Cr^{6+} in selected treated cement after thermal exposure to 100°C (simulating temperature conditions in the mill).
- the determination of Cr^{6+} in OPC-based mortars where Tecno TS and Synchro 205 have been introduced in the added water; this procedure may be used as a quick indication of the additive effectiveness but in no case can be considered more reliable when compared to the respective results on ball mill cements.

Reagents

Reagents used for the mortar preparation and Cr^{6+} determination were of analytical quality.

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Received for Publication: 09. 06. 2013.

Accepted for Publication: 15. 08. 2013

- Concentrated hydrochloric acid.
- CEN standard sand, in accordance with EN 196-1.
- Chromate kit (Cr-1A powder , Cr-2A liquid)
- Distilled or deionised water

Apparatus

- Balances. Analytical balance, capable of weighing to an accuracy of $\pm 0,0005$ g, and a laboratory balance, capable of weighing to an accuracy of ± 1 g.
- Laboratory ball mill. A laboratory ball mill was employed for the grinding of different samples of laboratory cements with specified Blaine fineness. The simple and robust construction of the mill allows slow horizontal rotational speed. The fineness of the cement samples was controlled through the optimization of the grinding time [2,3,5].
- Paste Mixer. A "ToniMIX" mixer automatically programmable from "Toni Technik" was employed for the preparation of binder pastes with automatic mixing procedure including water feeding in accordance with EN 196-1 [4].
- Filtration equipment consisting of a Buchner funnel, (e.g. diameter 205 mm, fitted onto a 2 litre filter flask), partially full of sand, inside which is a low form beaker to collect the filtrate, placed on top of the bed of sand. The apparatus is connected to a vacuum pump.
- Filter media, of pore size 7 μm or less, composed of fibre, free from organic binders, or equivalent fritted glass filter.
- Volumetric glasswares (low form beaker 15ml, 25 ml) 5,0 ml pipettes.
- Chromate Kit for colourimetric analysis.
- Timer, capable of measuring to an accuracy of ± 1 s.

Extraction procedure

Principle

Cement is made into a mortar using CEN standard sand and distilled or deionised water [1]. The mortar is mixed for a specified time and then filtered. From the filtrate and by using the chromate kit we determine colourimetrically the chromium concentration in ppm.

Preparation of mortar

The proportions by mass shall be one part of cement, three parts of CEN standard sand and one half part of water (i.e. water/cement ratio 0,50). The water to be used is analytical grade. Each batch shall consist of (450 ± 2) g of cement, (1350 ± 5) g of sand and (225 ± 1) g of water [4].

Mixing of mortar

Weigh the cement by means of the laboratory balance. When water is added automatically by volume and is dispensed with an accuracy of ± 1 ml. Mix each batch of mortar mechanically using the

automatic mixer. The timing of the various mixing stages refers to the times at which mixer power is switched on/off and shall be maintained within ± 2 s.

The mixing procedure shall be as follows:

- place the cement into the bowl, taking care to avoid loss of cement.
- immediately the water and cement are brought into contact when we start the mixer at the low speed whilst starting the timing of the mixing stages. After 30 s of mixing, the sand is added also automatically during the next 30 s. The mixer is switched to the high speed and continue the mixing for an additional 30 s.
- stop the mixer for 90 s. During the first 30 s, remove by means of a rubber or plastics scraper the mortar adhering to the wall and bottom part of the bowl and place in the middle of the bowl.
- continue the mixing at the high speed for 60 s.

NOTE: Normally these mixing operations are carried out automatically. Manual control of these operations and timings may be used.

Filtration

Ensure that the filtration equipment (filter flask, filter crucible or Buchner funnel and filter medium and low form beaker) is dry before each use. Fit the filter crucible or Buchner funnel and filter medium. Do not pre-wet the filter medium. Apply the vacuum and place the mortar into the filtration equipment.

Filter for a maximum of 10 min to obtain a volume of 10 ml to 15 ml of filtrate. If 10 ml is not obtained in this time, continue filtering to obtain sufficient quantity to carry out the determination(s). The filtrate may be stored for up to 8 h before determination of the Cr^{6+} content but if the storage period exceeds 30 min it shall be kept in a sealed airtight container to prevent evaporation.

Determination of Cr^{6+}

After we take the filtrate as described above we follow the procedure below in order to determine the Cr^{6+} concentration.

First we take 6 ml from the filtrate and put it in one small bottle of the chromate kit and after we add one small spoon of Cr-1A powder then 6 drops of Cr-2A and 2-3 drops of concentrated hydrochloric acid and shake the bottle for good mixing and leave it to rest for 5 min to take the right colour. After 5 min we put it in the Colourimetric kit and compare the filtrate colour with the standard colour and by this comparison we take the Cr^{6+} concentration from the numbers below the standard colour. These numbers give us the Cr^{6+} concentration in ppm. Every standard colour of the Chromate kit has below the Cr^{6+} concentration in ppm. In the same way we proceed for all the samples.

RESULTS AND DISCUSSION

Tecno TS (Tecnochem).

Results on ball mill prepared cements are provided below:

Table 1 - Laboratory ball mill produced cement in the presence of Tecno TS.

	Dosage (grams/ton/ppm Cr ⁶⁺)	Dosage (in % b.w. of cem)	Cost, € per ton of cem	(Cr ⁶⁺) (ppm)	(Cr ⁶⁺), under thermal (20min.-100°C)
Suggested dosage	55-65 grams/ton/ppmCr⁶⁺ reduced				
Test 0	0	0	0	15,80	
Test 1	50	0,07	2,7	8,8	8,1
Test 2	60	0,09	3,3	7,5	
Test 3	76	0,11	4,2	7,2	
Test 4	97	0,14	5,3	5,2	
Test 5	122	0,180	6,61	4,34	

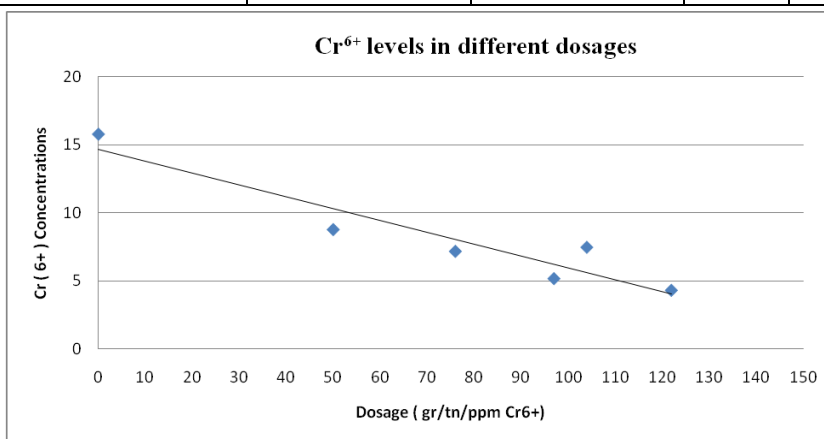


Figure 1 - Cr⁶⁺ Levels of lab ball mill produced cement in different dosages of Tecno TS

- Using Tecno TS at its suggested dosage decreased Cr⁶⁺ levels to about half but remained much higher than our target (i.e. < 1 ppm).
- Increased addition of Tecno TS decreased Cr⁶⁺ in cement almost linearly but even by doubling the suggested dosage the results were far from complying with the < 1 ppm target.
- Thermal treatment of cement at conditions simulating those of the mill (i.e. 20 min retention on 100 °C in a furnace), increased the efficiency of the Tecno TS, but at almost negligible levels. It seems that the absence of mill temperature conditions is not the reason for the low Tecno TS activity.

Table 2 - OPC-based cement with Tecno TS added in water

Cement	TS dosage (grams/ton/ Cr ⁶⁺ reduced)	TS dosage (b.w. of cement)	Cr ⁶⁺ (ppm)
OPC-REF	0	0,00	11,7
OPC	50	0,05	8,7
OPC	104	0,11	0,4

In the quick testing that Tecno TS was added in the mortar water results testified that the suggested dosage cannot fulfill the target, however when doubled the Tecno TS dosage the results were satisfactory.

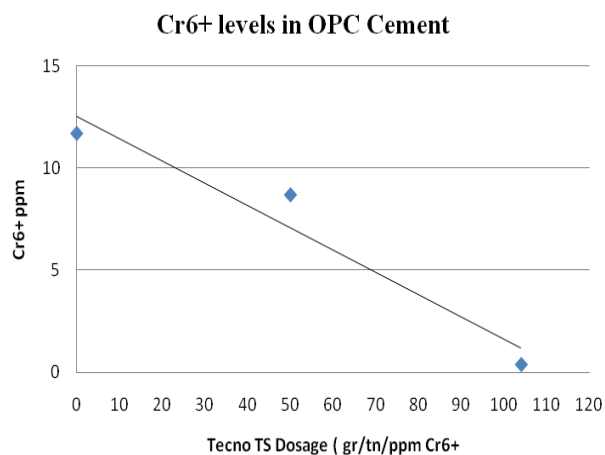


Figure 2 - Cr⁶⁺ levels in OPC Cement with Tecno TS added in water

Synchro 205 (Grace).

Similar results with the use of Synchro 205 in the ball mill prepared cements are as follows:

Table 3 - Lab ball mill produced cement in the presence of Synchro 205

	Dosage (grams/ton/ppm Cr ⁶⁺)	Dosage (in % b.w. of cem)	Cost, € per ton of cem	(Cr ⁶⁺)ppm	Storage time (days)	(Cr ⁶⁺) ppm
Suggested dosage:	55-65 grams/ton/ppm Cr⁶⁺ reduced					
Test 0	0	0	0	15,8	0	
Test 1	50	0,07	2,3	4,9	55	5,5
Test 2	61	0,09	2,8	2,6	55	3,0
Test 3	67	0,10	3,1	0,2		

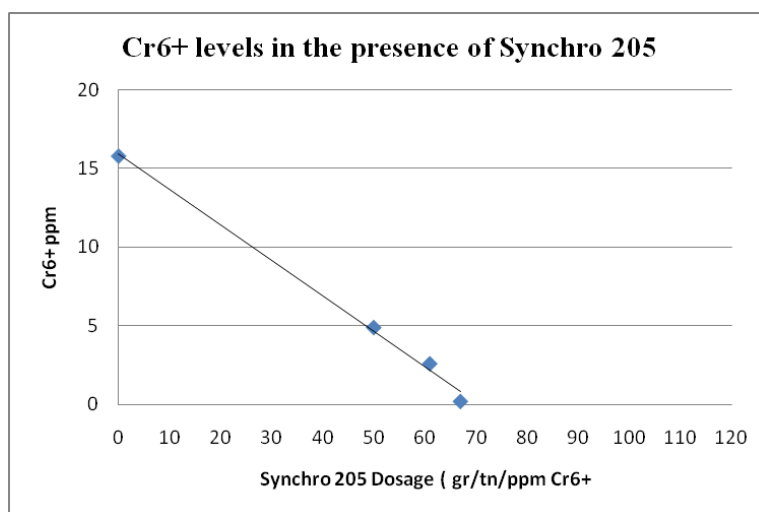


Figure 3 - Cr⁶⁺ Levels of lab ball mill produced cement in different dosages of Synchro 205

Using Synchro 205 at the lowest recommended dosage (55 grams/ton/ppm Cr⁶⁺) had a good reducing effect but in order to achieve the < 1 ppm target, the maximum recommended dosage (65-67 grams) should be applied. Synchro 205 treated cements exhibited a good Cr⁶⁺ re-oxidation profile for a shelf life of 55 days.

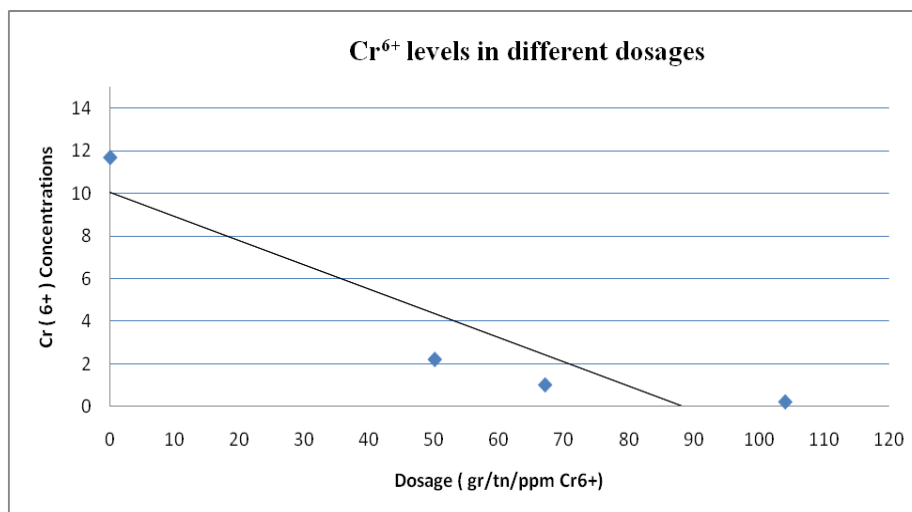


Figure 4 - Cr⁶⁺ levels in OPC Cement with Synchro 205 added in water

Good results of Synchro 205 were verified with the mortar test as well as shown in Table 4.

Table 4 - OPC-based cement with Synchro 205 added in water

Cement	Synchro 205 dosage (grams/ton/Cr ⁶⁺ reduced)	TS dosage (b.w. of cement)	Cr ⁶⁺ (ppm)
OPC-	0	0.00	11,7
OPC	50	0.05	2.2
OPC	67	0.07	1
OPC	104	0.11	0.5

CONCLUSIONS

Considering the results on Cr⁶⁺ reduction, the agents indicative prices and the cost per ton of cement with Cr⁶⁺ <1 ppm (analyzed in the Table 5 below) it is derived that;

Table 5 - Indicative prices of Cr⁶⁺ reducing agents

	€/tn	Dosage required per tn of cement, in kgs	Cost (€) per ton of cement
Ferrous sulfate	202	3,0	0,6
Tecno Chrored TS	3670	>1.8	>6.6
Synchro 205	3100	1.0	3.1

Tecno Chrored TS cannot be recommended for use. Approximately 67 grams/ton of cement/ppm of Cr⁶⁺ of Synchro 205 are required to reduce Cr⁶⁺ to the desirable levels. This means an extra cost of almost 2.5 € per ton of cement compared to the ferrous sulphate (for the same reduction) considering only the purchase cost. An industrial trial of Synchro

205 is recommended for finally assessing its chromium reducing capacity. In addition, its reducing capacity with respect to cement shelf life must be determined before suggesting its use.

Despite, being clearly a more expensive solution at first, liquid additives based on tin sulphate could be beneficial in plants that haven't already invested in FeSO₄ storage and handling equipment and plan to export within EU, or face significant maintenance costs due to clogging caused by FeSO₄ inherent stickiness.

REFERENCES

- [1] EN 197-1, June 2000 Cement – Part 1: Composition, Specifications and Conformity Criteria for Common Cements. pp. 9-16
- [2] Pecani, A., 2010: Çimento, Tiranë 2010, pp.25-53.
- [3] Pecani A., Çimento dhe teknologjia e prodhimit te saj, Qershor 1990, pp. 28-37
- [4] EN 196.01 Methods of testing cement- Part 1: Determination of Strength pp 6-15.
- [5] EN 196.06 Methods of testing cement: Determination of fineness pp 11 - 19.
- [6] EN-196-10 Methods of Testing Cement – Part 10: Determination of water soluble chromium (VI) content of cement pp 8-14.
- [7] Walter H. Duda, (2009) Cement Data Book, Volume 1: International Process Engineering in the Cement Industry, pp 186-206.
- [8] Philip A. Alsop PhD; Hung Chen PhD; Herman Tseng Pe- Cement Plant Operations Handbook - Fifth Edition October 2007 pp 92-103.
- [9] H.F.W TAYLOR 1997: Cement Chemistry Academic Press, London, 2nd Edition pp 182-204.

IZVOD

LABORATORIJSKA ISPITIVANJA TEČNOG HROMA REDUKCIJOM AGENASA TECNO TS (TECNOCHEM) I SINCHRO 205 (GRACE)

Postoje određene prednosti povezane sa korišćenjem tečnih Cr⁶⁺ redukcionih sredstava. Dva tečna Cr redukciona sredstva, na bazi sulfatnih rastvora, su laboratorijski testirana pod nazivom Tecno Chrored TS a isporučena su kao Tecnochem i Sinchro 205 (Grace). Na osnovu svojstava laboratorijskih cementa i indikativnih troškova uočeno je smanjenje efikasnost i ograničenost Tecno TS i ima svoju visoku cenu, pa se ne preporučuje za upotrebu. Sincro 205 bi zahtevao doziranje od oko 67 grama / tona cementa / ppm Cr⁶⁺, da se smanji Cr⁶⁺ do željenog nivoa. Industrijska ispitivanja Sinchro 205 se preporučuju za konačno ocenjivanje njegove hrom kapacitivnosti. Uprkos tome, što je očigledno skuplje rešenje, prvi tečni aditivi mogu biti od koristi u biljkama koje nisu već investirale FeSO₄.

Ključne reči: redukciona sredstva, aditivi, cement

Originalni naučni rad

Primljeno za publikovanje: 09. 06. 2013.

Prihvaćeno za publikovanje: 15. 08. 2013.