

# REMOVAL OF SOLUBLE Cr(VI) IN CEMENTS BY FERROUS SULPHATE MONOHYDRATE, SOLID LIGNIN AND OTHER MATERIALS

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*Various reducing agents such as ferrous sulphate heptahydrate (HH) and monohydrate (MH), solid lignin (SL),  $\text{Na}_2\text{S}_2\text{O}_4$ ,  $\text{NaHSO}_3$ ,  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ ,  $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$  and  $\text{FeS}$  are used to reduce Cr(VI) contents of three types of cements under 2 mg/L, as it is requested by European Parliament Standards. Optimum conversion temperature of HH to MH was found as 130°C, for 20 min., by thermal analysis. Minimum amounts of various agents to be used as additives in cements to reduce Cr(VI) contents under the standard value were determined. Minimum reducing agent amounts of SL, MH and their mixture of 1:3 mole fractions were found as 0.44 %, 0.14 %, 0.24 % by weight, respectively for Portland cement (CEM I 42.5 R), 0.40 %, 0.26 %, 0.24 % for Portland Pozzolan cement (CEM II/A-P 42.5 N) and 0.16 %, 0.05 %, 0.04 % for Pozzolan cement (CEM IV/B (P) 32.5 N). Minimum amounts of other materials to reduce Cr(VI) content of three type cements under the required value, were found as 0.24 %, 0.16 %, 0.09 % ( $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ ), 0.10 %, 0.07 %, 0.04 % ( $\text{Na}_2\text{S}_2\text{O}_4$ ), 0.04 %, 0.025 %, 0.01 % ( $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ ) and 0.28 %, 0.27 %, 0.12 % ( $\text{NaHSO}_3$ ), respectively. It was found that SL, the MH and their mixture of 1:3 mole fractions can be used successfully as additives for reducing Cr(VI) contents of cement. There are two advantages of this usage of MH. It converts Cr(VI) to Cr(III) and extends the shelf-life of cement. On the other hand, SL reduces Cr(VI) and increases durability of cements by lowered water/cement ratio.*

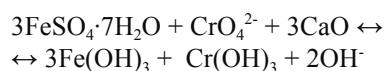
## INTRODUCTION

Cement is a combination of calcium, silicate, aluminium, iron and small amounts of other ingredients, which are mixed homogeneously and ground to a suitable degree of coarseness. Also, cement typically comprises small amounts of Cr(VI) compounds.

Among various forms of chromium, Cr(VI) ions are the most important ions because of its toxicity, solubility and mobility characteristics. Toxicity of chromium depends primarily on its chemical form. Cr<sup>3+</sup> compounds are much less toxic than those of Cr(VI) [1]. In production of cement, chromium is present in raw material, during clinker burning, partially oxidized to toxic hexavalent form. In cement, chromium exists in both Cr(VI) and Cr(III) oxidation states. Chromium-compounds mainly result from raw materials which were used for the production of cement [2]. Cr(VI) is known to be carcinogenic [3], mutagenic [4], and inducer of skin dermatitis [5]. Contact dermatitis is one of the most frequently reported disorders among construction workers who regularly work with cement [6-9].

In order to eliminate the risk of allergic contact dermatitis, it is necessary to reduce the content of Cr(VI) in cement and to prevent the contact of cement with skin. The European Directive 2003/53/EC10 has been implemented on 17 January 2005, introducing restriction on the use of cement and cement products, which contain more than 2 mg kg<sup>-1</sup> of soluble Cr(VI) during hydrating [10]. Cement manufacturers are obliged by the Directive 2003/53/EC10 to add a reducing agent to their products to bring Cr(VI) concentrations down to permitted levels (2 mg/kg) and the producers must provide information on saving shelf life, as only the reducing agent is effective for a limited period. In order to fulfil the legislative requirements and protect against the chromium allergy, it is often necessary to use reducing agents to lower the content of Cr(VI) in cement. The amount of Cr(VI) can be minimized by reducing it to Cr(III). Cr(III) is practically insoluble in water in the cement-water mixture, so it is harmless for the persons working with cement. It is also required that in cement or cement products treated with reducing agents e.g. ferrous sulphates, ammonium ferrous sulphate, manganese (II) sulphate, the expiry date of deliveries should be marked on a package.

Most European cement manufacturers have chosen the addition of ferrous sulphate heptahydrate (HH) in any of its variants, the redox mechanism of which is the following:



with dosage contents comprised between 0.3 % and 0.6 %, depending on the starting proportion of soluble Cr(VI) in cement. Ferrous sulphate (as a HH or monohydrate) is principally used as the reducing agent in the cement industry in order to achieve a Cr(VI) content of less than 2 mg/L. It is known to add dried HH for a dry cement mixture in order to reduce Cr(VI) to Cr(III). The use of dried HH has been problematic as it is dusting and it has a low melting point. If the widely used HH is added during grinding, it undergoes partial dehydration to monohydrate salt, with the consequent loss of reducing activity due to its high water solubility and the high temperatures in the mill[11-14]. Furthermore, it has been demonstrated that the effect of the ferrous sulphate may decrease from the time of manufacture until the cement is used[11,15]. HH is also a corrosive agent and in the long term it can damage the components of both the grinding system and the storage silos. Moreover, its hygroscopicity causes a reduction in the fluidity of the powder at all stages of handling, which is already problematic in terms of workers' health and safety. In addition, if excessive HH is added to cement, the color of the cement becomes green, which is an unacceptable result. Ferrous sulphate monohydrate (MH\*) can be obtained by calcinations of HH in an oven at air but ferrous sulphate is partly converted to ferric sulphate form by oxygen in air and its reactivity is decreased.

In some cement treatment processes, Cr(VI) is eliminated by reduction through the use of certain sulphur compounds (such as metabisulphite  $\text{S}_2\text{O}_5^{2-}$ , sulphite  $\text{SO}_3^{2-}$ , and thiosulphate  $\text{S}_2\text{O}_3^{2-}$ ). The redox potential of these compounds in an alkaline environment in various cases is very low (e.g. the couple  $\text{SO}_4^{2-}/\text{SO}_3^{2-}$ , E: -0.92V), which means that the reduction of the chromate is possible from a thermodynamic point of view under these conditions. While at acidic pH values the constant is very high, at pH: 5 the constant is already reduced to zero: this means that while the reaction is thermodynamically that the ferrous sulphate is in fact effective. Sometimes reducing agent can be used as solution or liquid. However, the water

may cause partly hydration of cements and decrease shelf-life of cements and the strength. This kind of usage can be preferred only for concrete plants and agents can be added during the mixing of cements with water.

A large amount of lignin is wasting out from the paper industries as black liquor. Lignins are amorphous, aromatic biopolymers that make up ~20-30 % of the available polymeric content of hardwood tree stems. In plants, lignin is the second part in natural abundance only to cellulose. Therefore, this material offers a valuable resource that is inexpensive, renewable, and available in abundant quantities. Lignin contains several functional groups such as methoxyl (13-16 % in lignins of softwood, 26-36 % in lignins of hardwood), hydroxyl groups-aliphatic and phenolic (usually 9-11 %), and carbonyl groups[16]. It is hypothesized that these functional groups serve as sites of adsorption of metal ions. Recent studies have shown that lignin and other naturally occurring biomass can serve as effective adsorbents for metal ions from wastewater [17,18].

Superplasticizers are linear polymers containing sulfonic acid groups attached to the polymer backbone at regular intervals. Most of the commercial formulations belong to one of four families: sulfonated melamine-formaldehyde condensates (SMF), sulfonated naphthalene-formaldehyde condensates (SNF), modified ligno-sulfonates (MLS) and polycarboxylate derivatives. The sulfonic acid groups are responsible for neutralizing the surface charges on the cement particles and causing dispersion, thus they release the water tied up in the cement particle agglomerations and then reduce the viscosity of the paste and concrete. Lignins can have the same behaviour because of their similar structure to lignosulphonates which are used for decreasing water/cement ratio and as strength developer in the cement industry[19-21].

## EXPERIMENTAL

### Materials

In this study, three types of cements were used: Portland cement (CEM I 42.5R), Portland Pozzolanic cement (CEM II/A-P 42.5 N), and Pozzolanic cement (CEM IV/B (P) 32.5 N) which contain approximately 17, 11, 4.5 mg kg<sup>-1</sup> Cr<sup>6+</sup>, respectively. Cements were obtained from Denizli Cement Factory. Three types of cements are

Table 1. Chemical analysis results of the cements.

Type of the cement	Component (by wt, %)										
	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	CaO	MgO	SO <sub>3</sub>	Na <sub>2</sub> O	K <sub>2</sub> O	Cl-	Pozzolanic additive	*LOI
CEM I 42.5R	18.89	4.33	4.48	64.49	1.9	3.11	0.24	0.63	0.0005	-	1.34
CEM II/A-P 42.5N	25.40	5.94	4.24	56.85	1.9	1.64	1.26	1.29	0.03	19	1.40
CEM IV/B (P) 32.5N	34.23	9.12	4.30	37.39	2.0	1.45	1.37	2.37	0.05	46	7.51

\*Loss on ignition

usually manufactured in Turkey but Portland cement is the most common type of cement in general use around the world because it is a basic ingredient of concrete, mortar, stucco and most non-specialty grout. The most common use for Portland cement is in the production of concrete. Removal and recovery of chromium were carried out by using low-cost potential adsorbents. For this purpose three types of cement (Portland cement, Portland Pozzolanic cement, and Pozzolanic cement) are produced in Denizli Cement Factory and used in this area. Their chemical analysis and content of Pozzolan were shown at Table 1.

The lignin was obtained as black liquor from SEKA Fabric, Silifke-Mersin-Turkey. Lignin was used as solid (SL) in experiments. It was obtained from black liquor by heating, evaporating in oven, drying and grinding, respectively.

MH is obtained by calcining HH at five different calcination temperatures (110, 120, 130, 140, and 150°C) and different periods (10, 20, 30, 40, and 50 min).

Chemicals were used at chromium reduction at analytical purity (Merck).

#### Characterization of the materials

MH is obtained from HH at different calcinations temperatures and periods under the condition of inert N<sub>2</sub> atmosphere. Crystal water contents of ferrous sulphates were determined by thermal analysis (TG-DTA). TG and DTA curves of ferrous sulphates were obtained simultaneously by using Shimadzu DTG-6OH thermal and thermogravimetric analyzer. The measurements were carried out in flowing nitrogen atmosphere (25 mL min<sup>-1</sup>) within the temperature range of 20-1000°C in alumina crucible. The heating rate was on 10°C min<sup>-1</sup> and the sample masses were in the range of 3-5 mg higher sintered α-Al<sub>2</sub>O<sub>3</sub> was used as the reference material.

#### Methods

For the determination of total chromium in the cement samples 0.2 g cement sample was treated with 10.0 mL of 0.1 M Na<sub>2</sub>CO<sub>3</sub> solution. After cooling, the sample was completely dissolved in 10.0 mL of a 6 M HNO<sub>3</sub> solution. This procedure was used to determine the total chromium content in cement samples, as an alternative way of total chromium determination via the acid digestion procedure[22]. The final results are given in Table 2.

Determination of the total Cr(VI) content: About 0.2 g of cement (OPC), Portland Pozzolanic cement, and Pozzolanic cement was accurately measured and treated with 10.0 mL of a 0.1 M Na<sub>2</sub>CO<sub>3</sub> solution. The samples were boiled for 10 min, cooled, treated for 2 min in an ultrasonic bath and then filtered. The final volume of the solution was adjusted to 100.0 mL with deionized water. The results are presented in Table 2. The heating period was varied 30 min to test for complete Cr(VI) dissolution.

The method of analysis was used for the determination of Cr(VI) in cement and cement based products, extraction of the soluble chromates by means of the filtration of the water of a cement mortar or paste mix. The quantitative analysis of these chromates (BS EN 196-10) is based on the use of diphenylcarbazide. Chemical methods convert all of the chromium to the hexavalent form for extraction, and then the Cr(VI) is measured by a colorimetric procedure or by atomic absorption[23]. For complexing Cr(VI), 1,5 diphenylcarbazide was the most used agent on cements[24,25], and dust discharge deposit [26], followed by determination of the complex ion by UV-VIS spectrophotometry. The analysis procedure envisages the extraction of the soluble chromates in a 1:1 mixture of water and cement while under agitation (on a magnetic stirrer). The solution obtained from the filtration is analyzed directly without dilutions. 25 g cement samples are treated by 25 mL distilled water and mixed for 15 min and then filtered. After separation samples were analyzed for Cr(VI) content colorimetrically with the use of color reaction of Cr(VI) with diphenylcarbazide, detection of the color complex was performed by spectrophotometer (Shimadzu UV-1601) according to Standard Methods[27]. A purple-violet colored complex was developed in the reaction between Cr(VI) and 1,5- diphenylcarbazide in acidic condition. Absorbance was measured at wavelength 540 nm. The percentage of Cr(VI) removal was calculated as:

$$\% \text{ Cr(VI) removal} = [(C_0 - C_1) / C_0] \times 100$$

where C<sub>0</sub> and C<sub>1</sub> are the initial and equilibrium concentration of Cr(VI) solution (mg/L), respectively. Results are checked by Perkin Elmer A Analyst 700 model Atomic Absorption Spectrometry by max error under 1 %.

The prepared MH is added to cement samples at different amounts (0-0.24%, by weight). Dehydration of HH has been performed using two different methods. In the first method, HH was calcined in an oven at air

Table 2. Summary of the results obtained for total chromium and Cr(VI) (µg g<sup>-1</sup>) determinations with different digestion methods.

Type of the cement	Total Cr (µg g <sup>-1</sup> ) HNO <sub>3</sub> digestion	Total Cr(VI) (µg g <sup>-1</sup> ) Na <sub>2</sub> CO <sub>3</sub> extraction	Cr(VI) (µg g <sup>-1</sup> ) H <sub>2</sub> O extraction
CEM I 42.5R	190.4	144.2	17
CEM II/A-P 42.5N	125.2	93.5	11
CEM IV/B (P) 32.5N	56.3	36.2	4.5

atmosphere (MH\*) whereas in the second method, HH was calcined in an oven where the flow rate is 25 ml/min inert N<sub>2</sub> gas (MH). During the second method, calcined MH was cooled down to room temperature in N<sub>2</sub> atmosphere. This has been done in order to prevent oxidation of ferrous sulphate from ferric sulphate by oxygen in air.

The prepared MH, MH\*, SL and other chemical agents are added to cement samples at different amounts and a minimum amount to reduce Cr(VI) content to less than 2 mg/L for each reducing agent is determined by the explained method.

## RESULTS AND DISCUSSION

Portland cement normally contains soluble and insoluble chromium in the range of 30 to 200 mg/kg. The chromium is originally included in raw materials (limestone: 10.6, clay: 8.0, Fe-slag: 14.1, fire brick: 6.5, silica: 11.1, gypsum: 1.1mg/kg soluble chromium) of cement. These results indicate that the raw materials are not the only source of chromium in cement and that the manufacturing process makes a significant contribution. The contamination is probably due to the refractory bricks that lines the kiln, the grinding media in the final finishing mills and/or the use of chromium containing fuels, such as tannery wastes. The results obtained for the sodium carbonate dissolution method presented in Table 2 indicate that the amount of Cr(VI) in the three type cement samples was very high and mostly above the detection limit. On the other hand, the amount of Cr(VI) in the cements were at measurable levels and significantly higher (ranging from 36.2 to 144.2 µg g<sup>-1</sup>). These results substantiate the observation made with the total chromium determinations, which the presence of Cr(VI) and (III) in cements are mainly due to contamination that occurs during the manufacturing process.

Water-soluble Cr(VI) compounds have a higher penetration rate than the less water-soluble Cr(III) compounds. The chemical behavior of chromium in aqueous solutions is characterized by a change of valence, on the other hand, and by an amphoteric behavior, on the other. Under alkaline conditions (pH>11), chromium as Cr(VI) in the form chromate anion CrO<sub>4</sub><sup>2-</sup> is highly soluble. Sorption capacity of the cement phases Cr(VI) is small. Soluble CrO<sub>4</sub><sup>2-</sup> is therefore reduced technically by the addition reducer salts and precipitated Cr(OH)<sub>3</sub>.

Under acid concentration (pH<3) chromium exists as soluble CrOH<sup>2+</sup> with a changed valence. The stability field of the hardly soluble Cr<sub>2</sub>O<sub>3</sub> or Cr(OH)<sub>3</sub> is located in the range in-between or under slightly reducing conditions also highly alkaline media (pH<13.5). The concern that at high pH values (pH above 12) some of the Cr(III) compound can be dissolved as negatively charged Cr(OH)<sup>4-</sup> complex ions seems to be reasonable according to Coedo et al. [28]. Special investigations by Rai et al. [29], showed that the actual solubility of Cr(OH)<sub>3</sub> at high pH values remains constant and that the possibility of Cr(OH)<sup>4-</sup> formation was overestimated.

### DTA and TG analysis of HH and MH

Figures 1 and 2 shows DTA and TG curves and for uncalcined HH and MH at 130°C, for 20 min and calcined ferrous sulphate (anhydrite) at 290°C, for 20 min, at inert atmosphere. Optimum calcining conditions were found by calcining of HH at different temperatures and periods as 130°C, for 20 min.

The first peak in the DTA heating curve occurs during the removal of the first three water molecules. This dehydration from HH to FeSO<sub>4</sub>·4H<sub>2</sub>O takes place at a temperature below 100°C. The water, which is at atmospheric pressure, is not completely vaporized during this first step of the dehydration process. The second step

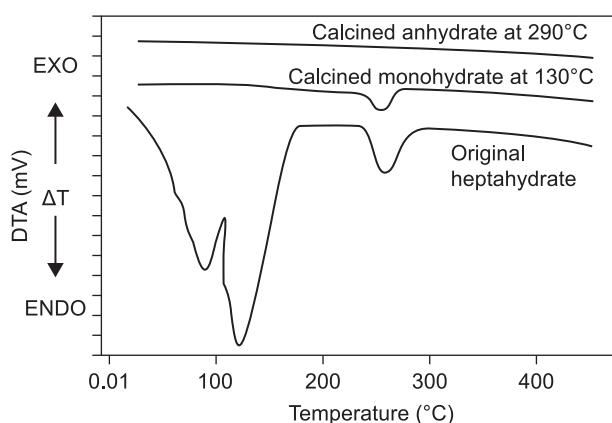


Figure 1. DTA thermograms for the original and the calcined ferrous sulphates under different conditions.

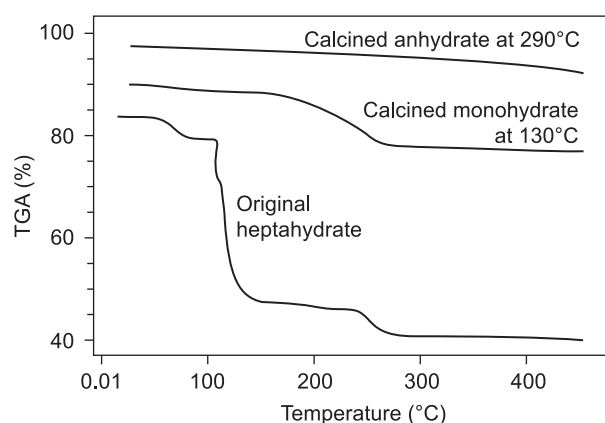


Figure 2. TG curves for the original and the calcined ferrous sulphates under different conditions.

of dehydration from  $\text{FeSO}_4 \cdot 4\text{H}_2\text{O}$  to MH takes place over a temperature range from 100 to 149°C. Water generated by this dehydration step is vaporized. Simultaneously, water from the first dehydration step is vaporized as the temperature rises to 100°C or greater. The second peak in the DTA heating curve represents the removal of the three water molecules and the vaporization. On DTA curves, endothermic pic at 250°C attributed to 1 mole crystal water of MH. The endothermic pic 70°C is due to removing of three water molecules and adsorbed moisture. The mass loss values obtained from TG thermograms between 70-128°C for 6 moles water is approximately 35 %, about 250°C for 1 mole water is approximately 10 % as expected at theoretically.

#### Removal of Cr(VI) with HH, MH, MH\* and SL

Figure 3 shows the results for used HH, MH, MH\* and SL to reduce Cr(VI) contents by adding them to different cements at various ratios.

For CEM I 42.5R as shown at Figure 3a; the best result is obtained as 0.14 % by using MH. The worse results are belong to MH\* (0.23 %) although its decreased water content are due to the lack of  $\text{Fe}^{2+}$  ions because of the oxidation of divalent iron to trivalent by  $\text{O}_2$  in atmosphere during the calcination. To reduce Cr(VI) to less than 2 mg/L; 0.16 %, 0.08 % and 0.04 % HH must be used for CEM I 42.5R, CEM II/A-P 42.5N and CEM IV/B (P) 32.5N, respectively. For CEM I 42.5R, the necessity of more amounts of HH to reduce Cr(VI) in cement is attributed to its content of high water comparatively the MH. For CEM II/A-P 42.5N and CEM IV/B (P) 32.5N; Cr(VI) content of the cements are increased because of the pozzolanic additive and HH brought better results than MH. This can be explained by the adsorption of some MH by the pozzolanic additive. It is because of the pacification of  $\text{Fe}^{2+}$  ions that are settled down in the pores and remained there after hydration.

Figure 3 shows that SL is being added much more than ferrous sulphates. Although this seems a disadvantage, it is advantageous for CEM IV/B (P) 32.5N type cements because of its strength increasing effect. The worse results of SL in, CEM II/A-P 42.5N type cement can be explained by the adsorption of SL by the pozzolanic additive. High porous pozzolanic additive has adsorption ability because of its high surface area. SL reduces Cr(VI) in cement less than 2 mg  $\text{kg}^{-1}$  when added 0.44 %, 0.40 % and 0.16 % (by weight), to CEM I 42.5R, CEM II/A-P 42.5N and CEM IV/B (P) 32.5N, respectively. A clear statement cannot be said about whether an adsorption or reduction or combination of both for the removal mechanism of Cr(VI) from cement by lignin. Adsorption process is dominantly effective, as a general opinion. An evidence of possible strong

adsorption may be the absence of Cr(VI) in the extraction solution which contains excess lignin and Cr(VI). Lignin contains hydroxyl groups-aliphatic and phenolic [30]. During the treatments, undesirable structural changes may occur such as oxidation of some functional groups of lignin (i.e. phenolic moieties converted into carboxylic groups). It is hypothesized that aliphatic primary alcohols

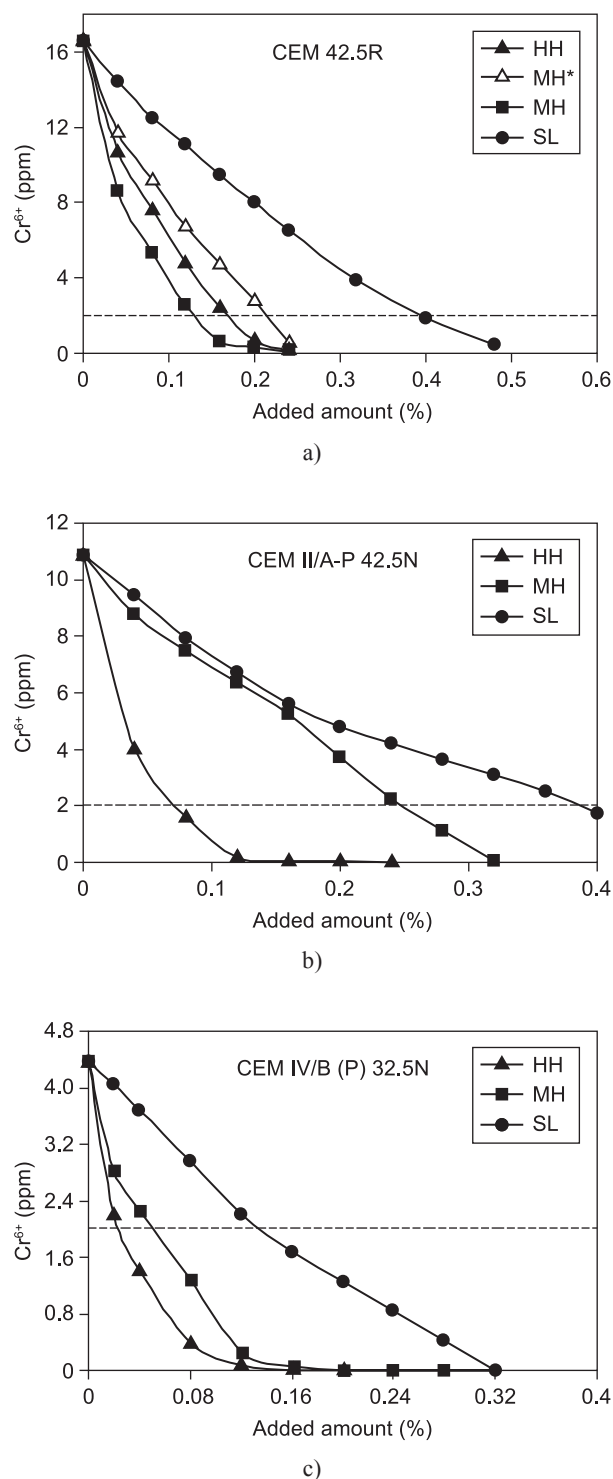


Figure 3. Plot of Cr(VI) amounts in cements against added HH, MH, MH\* and SL.

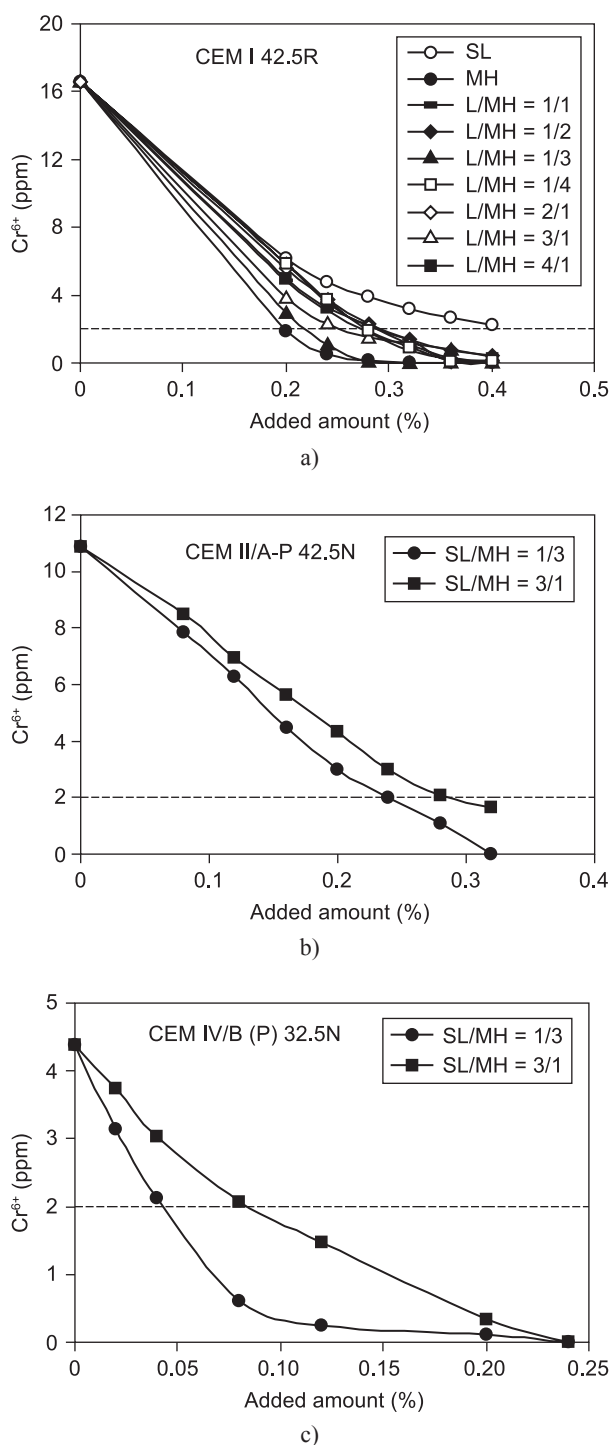


Figure 4. The plot of Cr(VI) amounts in cements against added mixtures of MH-SL at different mole fractions.

Table 3. Optimum amounts of the added HH, MH, MH\*, SL, 1:3 and 3:1 SL/MH mixtures for reducing Cr<sup>6+</sup> content of cements less than 2 mg/L.

Type of the cement	Optimum amount of the added material (by wt, %)					
	HH	MH*	MH	SL	SL/MH = 1/3 mixture	SL/MH = 3/1 mixture
CEM I 42.5R	0.16	0.23	0.14	0.44	0.24	0.27
CEM II/A-P 42.5N	0.08	-	0.26	0.40	0.24	0.28
CEM IV/B (P) 32.5N	0.04	-	0.05	0.16	0.04	0.05

groups in lignin structure may be oxidized to aldehyde or organic acid in alkali media and Cr(VI) is reduced to Cr(III) ions in cement[30,31].

SL firstly adsorbs/reduces Cr(VI) by active site on functional groups. Cr(III) surface complexes have an octahedral coordination[32]. SL is preferred instead of black liquor because of the negative effects of water of it on hydration and storing time of cements.

Figure 4 shows the results for added mixtures of MH and SL to CEM I 42.5R at different mole fractions comparatively. The best result was obtained from the ratio of 1:3 SL/MH mixtures. Also the ratio of 3:1 SL/MH mixtures is better from the others. The reason of unexpected results is the adsorbed Fe<sup>2+</sup> ions by lignin [30]. Especially the bad results for 1:2 SL/MH mixtures show that a part of Fe<sup>2+</sup> is adsorbed by SL and the adsorption capacity of lignin decreases. The good result of 3:1 and 1:3 mixtures indicates that more added components' properties become dominant in the mixture. For all of the cements, 1:3 SL/MH mixtures give better results than 3:1 mixtures. Optimum amounts of the added HH, MH, SL, 1:3 and 3:1 SL/MH mixtures for reducing Cr(VI) content of cements under 2 mg/L; are given at Table 3 collectively.

#### Removal of Cr(VI) with other reducing agents

We used different materials such as NaHSO<sub>3</sub>, Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub> etc. to reduce Cr(VI) content in the cements to a level of below 2 mg L<sup>-1</sup> as you see at Figure 5. Minimum amounts of other materials to reduce Cr(VI) content of CEM I 42.5R less than 2 mg kg<sup>-1</sup>, were found as 0.24% (for N<sub>2</sub>H<sub>4</sub>·H<sub>2</sub>O), 0.10% (for Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub>), 0.04% (for SnCl<sub>2</sub>·2H<sub>2</sub>O) and 0.28% (for NaHSO<sub>3</sub>).

Experiments with other pozzolanic cements show similar results with CEM I 42.5R cement. Optimum amounts of added materials to cement for reducing Cr(VI) amount under 2 mg/L are given at Table 4, collectively. The use of stannous salts allows obtaining better performances: the dosages are close to stoichiometric and the reducing effect is higher and longer-lasting in comparison to Fe<sup>2+</sup>. The oxidation products of Sn<sup>2+</sup> do not cause spots on concrete surface. The reducing properties of Sn<sup>2+</sup> in alkaline conditions are based on the formation of stannous hydroxide Sn(OH)<sub>2</sub> that has a redox potential E = -0.96V at pH = 13. [33] Stannous salts have acid properties and in presence of traces of

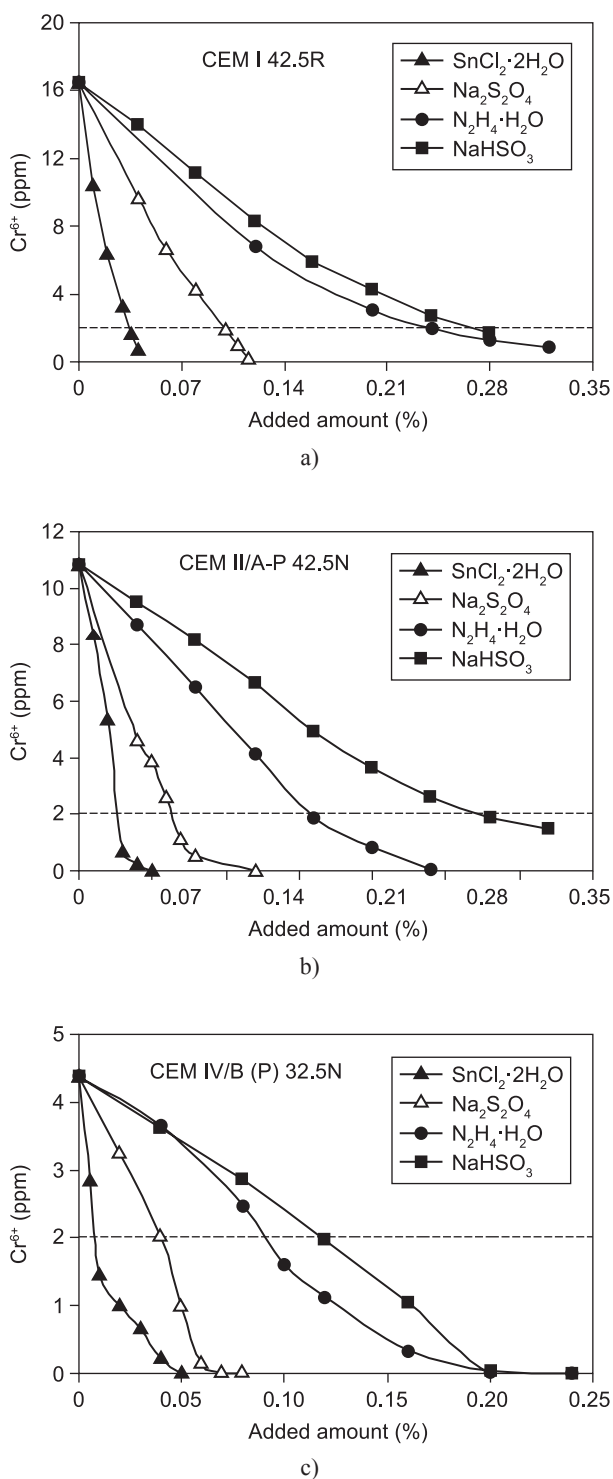
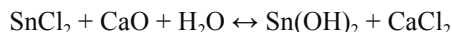


Figure 5. Plot of Cr(VI) amounts in cements against some added reducing agents.

water they can react with the very alkaline lime giving stannous hydroxide, according to the following reaction:



This is the reason why the stannous salts are not profitable when they are used in grinding of clinker with high amount of free lime: stannous hydroxide can be formed and quickly oxidized to Sn<sup>4+</sup> and the amount of Sn<sup>2+</sup> must be increased in order to obtain the elimination of soluble chromates.

The results Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub> and NaHSO<sub>3</sub> are favourable; however, sodium is not more available because of alkali-silica reactions and distorted effects on cements[34]. On the other hand, the compounds containing sulphide were not preferred because of their bad smell. N<sub>2</sub>H<sub>4</sub>·H<sub>2</sub>O is in liquid phase and containing water, it causes negative effects on cement hydration and storing period. Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub> and NaHSO<sub>3</sub> may be used for reducing Cr(VI) content of cement, which contains lower sodium. But the risk of oxidation by O<sub>2</sub> in atmosphere must be remembered. Sodium dithionite, which achieves a complete reduction by adding 0.1 % by mass, is not storable in humid surroundings. It was observed that despite of added high amounts of FeS to cement, Cr(VI) content of cements couldn't be decreased. This result can be explained by the low solubility of FeS in strong basic media in cement.

Figure 6 shows the different experiments that were made by 0.44 g SL or 0.20 g MH added CEM I 42.5R type cement. After adding the additive; the plaster is mixed for 10 min and then is kept being waiting for different periods. It was observed that 10 min is effectual as reducing time of Cr(VI) and while the plaster is waiting,

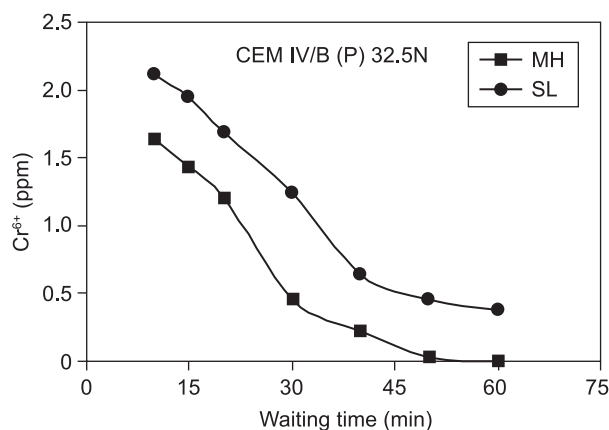


Figure 6. Plot of Cr(VI) amounts in CEM I 42.5R type cement against waiting time.

Table 4. Optimum amounts of the added other materials that are used for reducing Cr(VI) content of cements less than 2 mg/L.

Type of the cement	Optimum amount of the added material (by wt, %)			
	Na <sub>2</sub> S <sub>2</sub> O <sub>4</sub>	SnCl <sub>2</sub> ·2H <sub>2</sub> O	NaHSO <sub>3</sub>	N <sub>2</sub> H <sub>4</sub> ·H <sub>2</sub> O
CEM I 42.5R	0.10	0.036	0.28	0.24
CEM II/A-P 42.5N	0.07	0.025	0.27	0.16
CEM IV/B (P) 32.5N	0.04	0.01	0.12	0.09

the reducing continues. Because of this, the additives for reducing Cr(VI), even at low amounts, will be efficient.

These are organic and inorganic reducing agents that can reduce the chromates in the different steps of the cement production process, i.e. before, during or after the grinding of the clinker with calcium sulphate. The reducing agents, solids, in solution or in suspension, may be applied either at a various steps of the cement processing or by simple additivation when the cement is finished in the storage, transport or dispatch step by means of suitable studied dosing systems. The use in the clinker grinding step can be optimum. By using percentages that can vary from 0.01 to 4 % of organic and inorganic reducers, according to the reducing capacity thereof and the practical possibility of reacting on the basis of the conditions of use, it is possible to obtain a reduction in the amount of Cr(VI) up to 2 ppm maximum. The other principle involves making the hexavalent chromium insoluble by reducing it to trivalent chromium using different reagents with strong reducing effects. Naturally, the alkalinity of the cement itself will lead, according to the formation of hydroxides, hydrated oxides, all compounds which are insoluble in water.

#### Compressive Strength

The effect of chromium-reducing agents on the compressive strength of 1:3 cement-sand mortars has been determined at 2, 7, 28 and 90 days. The results are given in Table 5. As can be seen from the attached tables of contributions have not had a significant effect on cement strength. Especially MH, MH\* and MH/SL mixture obtained from the results is slightly higher than the control mixture. Alone and in combination with intensive SL extent of the compressive strength was slightly lower exit, but this difference is not important. In a mixture containing excess SL and SL in the solution phase because of the intense precipitation of hydration products and other factors have influenced the speed of expected strength of cement did not increase substantially. SL containing more water than cement is added to the normal consistency of the strength of cement was found to fall quite seriously. This is for all the cement water/cement ratio is a case of the expected increases in cement, but this effect with SL is much more extreme. Hydration products be blocked by molecules in solution intensive lignin and calcium silicate hydrate gel is due unable to grow enough channel.

#### CONCLUSIONS

For reducing Cr(VI) in cements; MH is more advantageous than HH because of using smaller amounts and increasing shelf-life longer of storing time of the cement. MH\* is not suitable for reducing Cr(VI) because of oxidation of a part of the  $Fe^{2+}$  to  $Fe^{3+}$ . But it can be successfully used for cements, which contain lower Cr(VI).

Advantageously, in the present invention, the mixing of the crude precipitated MH, neutralizing agent and water are conducted in one mixing apparatus. This means that mixing, neutralization, drying and granulation all occur in one mixing apparatus and partially concurrently. The whole process takes typically a few minutes to perform, i.e. the end product with good physical properties, such as flow properties, is obtained in a few minutes from starting the mixing of the untreated raw materials.

SL can be used for reducing Cr(VI) in cements. But the disadvantage of this usage is the necessity of high amounts of SL, compared to with ferrous (II) sulphates. It can be successfully used for cements with low content of Cr(VI). Additionally, SL will increase the strength of cements by lowering cement/water ratio. Industrial using of SL, which is a waste material that causes serious environmental problems, will be beneficial.

The amount of SL/MH mixture of 1:3 mole fractions for reducing Cr(VI) in cements to less than 2 mg/L is not very high although the added amount is more when only MH is added. For eliminating the hazardous effects of Cr(VI), obtaining cements of high strength and durability, making the storing time of cement longer and evaluating of lignin which is a waste material; the usage of the SL/MH mixtures in cement is beneficial.

Especially good results are obtained by  $SnCl_2 \cdot 2H_2O$ ,  $Na_2S_2O_4$  and  $NaHSO_3$ . Unfortunately, there are disadvantages like the excess of  $Na^+$  ions and bad smells caused by sulphide. At cement mills, temperature rises above  $100^\circ C$ . At these temperatures sodium dithionite and sodium bisulphide may be decomposed and because of that, using these additives are not favourable. The disadvantages can be overcome when they are added at the package stage. The principal disadvantage of thin salts, which limit their use in the field of cement, is the high cost of these materials and reduced availability in certain markets. We have also rejected  $SnCl_2$  due to its hazardousness, its bad solubility and high prices, in addition to the fact that it incorporates chlorides to

Table 5. The Effects of some additives on compressive strengths of CEM I 42.5 R.

Days	Compressive Strength MPa (N/m <sup>2</sup> )							
	CEM I 42.5R	MH*	MH	SL	HH	MH/SL:1/3	MH/SL:3/1	MH/SL:1
2	21.8	21.6	21.7	23.1	23.4	28.5	25.7	22.3
7	34.2	36.7	37.5	33.8	33.8	38.8	37.5	35.2
28	44.6	49.1	48.9	45	48.5	47.4	47.6	44.5
90	50.1	54	54.5	50.4	53.8	54.8	55.7	50.7



cement, which is always hazardous for the final use thereof it is given that they are included among the worst enemies of reinforced concrete. Hydrazine is not an available material because of its liquid phase. It causes negative effects on cement hydration and storing period because of its water content. Iron (II) sulphide does not give any positive results so it is not a proper additive to cement.

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