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# The investigation of some properties of cement and removal of water soluble toxic chromium(VI) ion in cement by means of different reducing agents

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## HIGHLIGHTS

- The study for the reduction of Cr(VI) and the investigation of mechanical (strength) and hydration (setting time, volume expansion) properties of cement with reducing reagents.
- The results of this study are important in terms of industrial applicability.
- These amounts in cement on article did not cause any negative effect on concrete properties of cement.

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## ABSTRACT

In this study, solid lignin produced from lignin liquor which is a waste of paper industry, and $Sb_2O_3$, $MnSO_4{\cdot}H_2O$, $K_2(SbO)_2C_8H_4O_{10}{\cdot}3H_2O$ and $FeSO_4{\cdot}H_2O$ were investigated in terms of their reducing effect on Cr(VI) and other effects on cement properties. Test results revealed that $Sb_2O_3$ and $MnSO_4{\cdot}H_2O$ are able to reduce Cr(VI) effectively when they were used at levels of 0,02% and 0,25% by weight of cement respectively and these amounts in cement did not cause any negative effect on concrete properties of cement. Also, they performed stable reducing effects when exposed to high temperature tests and shelf life tests and it is concluded that they can be used conveniently to reduce Cr(VI) in cement industry.



## 1. Introduction

Cement is a hydraulic binder manufactured by grinding clinker with the addition of gypsum and other permitted additives to a very fine powder form. Cement is chemically composed of mainly calcium silicates and calcium aluminates. Also it comprises trace elements such as Pb, Ni, Se and Cr in ppm levels. Chromium in cement is found mainly in the form of Cr(III) and Cr(VI) and also in the form of Cr(IV) and Cr(V) in smaller amounts [1]. Main sources of Cr(VI) in cement are refractory bricks having chromium, raw materials, fuels, oxidising environment in the kiln which causes chromium to oxidise into hexavalent state and chromium alloys used in the grinding mills. Among various forms of chromium, Cr(VI) ion is the most significant ion because of its toxicity, solubility and mobility characteristics. Toxicity of chromium depends primarily on its chemical form. Cr(III) compounds are much less toxic compared with those of Cr(VI) [2]. In fact, Cr(III) form is reported to be very vital for some living functions of the body. For example, it was reported to be responsible for controlling the glucose and lipid metabolisms in mammals [3].

Cr(VI) form is a strong oxidiser and it is highly soluble in water whereas Cr(III) is chemically stable and has low solubility in water. Due to its solubility in water and its oxidising effect, Cr(VI) form can cause severe environmental and health problems. Among the health problems caused by Cr(VI), contact dermatitis is the most prevalent. Contact dermatitis is the reaction of the skin to an irritant or an allergen substance. Contact dermatitis caused by Cr(VI) is prevalent among workers in cement, leather tanning, ceramics and metal industries. Cr(VI) quantity for the contact dermatitis to come out, varies person to person. Some people react to 10 ppm Cr(VI) level, but some sensitive people react only to

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1 ppm Cr(VI) level [4]. Because of the severe negative effects of Cr (VI) ion on human health, many researchers have dealed on these effects of Cr(VI) ion. It was reported that inhalation and retention of Cr(VI)-containing materials can cause perforation of the nasal septum, asthma, bronchitis, pneumonitis, inflammation of the larynx and liver and increased incidence of bronchogenic carcinoma [5]. Additionally, an increase in stomach cancer mortality was reported in an ecological study of villagers exposed to Cr(VI) in drinking water in China [6]. According to the results of such researches, International Agency for Research on Cancer classified Cr(VI) as a Group 1 human carcinogen [7]. In order to minimize the health and environmental risks caused by Cr(VI) ion, the directive 2003/53/EC which restricts marketing as well as use of cement and materials containing cement which has a water soluble Cr(VI) value greater than 2 ppm has been applied by EU member states since January 2005 [8].

By using reducing agents, water soluble Cr(VI) ion is reduced to Cr(III) ion which is insoluble in water. Most common reducing agents used in the cement industry are heptahydrate and monohydrate forms of ferrous sulphate. Required amount for sufficient reduction depends on the initial value of Cr(VI) level of cement and ferrous sulphate is generally used at levels of 0,3–0,7% of the cement. However, there are some disadvantages of using ferrous sulphate as a reducing agent. First of all, ferrous sulphate is oxidised to ferric sulphate by the atmospheric oxygen so that this oxidised inactive portion cannot reduce Cr(VI) anymore [9]. At high dosages, there can be concerns of increased water demand, long setting time, and possible concrete discoloration or mottling [10]. Also, addition of the reducer in the cement mill involves thermal, mechanical and chemical stress, which can accelerate the chemical reaction of the reducers and decrease its effectiveness [11]. Furthermore, there is evidence that ferrous sulphate increases the corrosion of steel reinforcement in concrete [12].

Another common reducing agent utilized in cement industry for reduction of Cr(VI) is stannous sulphate. It is very effective in reduction of Cr(VI) in small amounts, but it is very expensive [13]. Also, a disadvantage of stannous sulphate was reported that in presence of high amounts of free lime and moisture, stannous compounds partially lose their reduction ability [14]. Other sulphur containing compounds such as sodium dithionite ($Na_2S_2O_4$), sodium metabisulphite ($Na_2S_2O_5$) and sodium thiosulphate ($Na_2S_2O_3$) are also used as alternative reducing agents by some cement manufacturers. In a previous study, it was reported that $Na_2S_2O_4$ was found to be the most effective one among these sulphur containing reducing agents [15]. Lignin liquor which is a waste product of paper industry is composed of inorganic chemicals like $Na_2S$, NaOH and organic chemicals; namely, dissolved lignin and carbohydrates. Previously, our study group remarked that solid lignin derived from lignin liquor decreased the Cr(VI) level of Portland cement when used at 0.44% of the cement by weight [9]. In another study, it was reported that $MnSO_4$ was able to reduce Cr(VI) in the cement. It was found that by adding $MnSO_4$ at an amount of 0.75% of the cement by weight which was produced by using clinker having 19.70 ppm of Cr(VI), cement's Cr(VI) level was reduced completely [16].

## 2. Experimental

In this study, Portland cement which has a 17,19 ppm Cr(VI) content was used. It was obtained from Denizli Cement Factory. Chemical and mineralogical analysis of the cement is given in Table 1.

EN 197-1 CEM I 42,5R type Portland cement was selected as the control cement because it has the highest clinker amount compared to other types of cements and thus having more Cr(VI) content. Also EN 197-1 CEM I 42,5R type Portland cement is the most common cement type in Turkey and all around the world, which is generally used for concrete which requires high strength. Lignin liquor was obtained from OYKA Paper Packing Factory, Çaycuma-Zonguldak-Turkey. Solid form of lignin used here was obtained from liquid liquor by evaporation of its water at 100 °C. After grinding, solid lignin was stored in a closed vessel to prevent from oxidation with air. FeSO4·H2O was obtained from a local supplier at a purity of 98%. Monohydrate form was selected instead of heptahydrate form because bounded water of ferrous sulphate heptahydrate can lead to partial hydration of cement thus decreasing the quality of cement. Other chemicals, $MnSO_4{\cdot}H_2O$, $Sb_2O_3$ and $K_2(SbO)_2C_8H_4O_{10}{\cdot}3H_2O$ were provided from Merck at analytical purity.

For the determination of Cr(VI), diphenylcarbazide method was used. The analysis procedure utilizes 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 analysed without dilutions. 25 g cement samples are treated by 25 mL distilled water and mixed for 15 min and then filtered. After filtration, samples were analysed for Cr(VI) content colorimetrically at wavelength of 540 nm with the use of color reaction of Cr(VI) with diphenylcarbazide. Detection of the colored complex was performed by Thermo UV–vis spectrophotometer on the basis of DS 1020 Dannish Standard. A purple–violet colored complex was developed in the reaction between Cr(VI) and 1,5-diphenylcarbazide in acidic condition [17].

For the experiments, first of all, required amount of each reducing agent for reducing Cr(VI) level below 2 ppm was determined by using Thermo UV-Spectrofotometer according to standard DS 1020 and then by adding these amounts into cements, shelf life tests, temperature resistance tests and mechanical tests were performed. While preparing the cement samples containing reducing agents, reducing agents were added to cement samples in plastic bags and stirred with a spatula. After closing the bags, samples were shaken vigorously for further homogenization.

For shelf life tests, cement samples having required amount of different reducing agents were stored for different periods and then they were analysed for their Cr(VI) quantities.

For temperature resistance tests, cement samples having required amount of different reducing agents were kept in an oven at 105 °C for 2 h, then they were analysed for their Cr(VI) contents.

And finally for mechanical tests, cement samples having required amount of different reducing agents were analysed for their compressive strength by using Atom Technic compressive strength test machine according to standard method EN 196-1

**Table 1**
Chemical and mineralogical analysis of the Portland cement.

| | Component (by wt,%) | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Cement type | $SiO_2$ | $Al_2O_3$ | $Fe_2O_3$ | CaO | MgO | $SO_3$ | $Na_2O$ | $K_2O$ | $C_3S$ | $C_2S$ | $C_3A$ | $C_4AF$ | *LOI |
| CEM I 42.5R | 18.97 | 4,78 | 3,26 | 63,04 | 1,85 | 3,12 | 0,08 | 0,74 | 61,94 | 8,63 | 7,15 | 9,92 | 4,16 |

* Loss on ignition.