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Hexavalent chromium reduction by ferrous sulphate heptahydrate addition into the Portland clinker

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Abstract

Nowadays, hexavalent chromium and its content in Portland cement is very actual and often discussed topic. The goal of this study was to observe the influence of different ways of addition of ferrous sulphate heptahydrate on the reduction of hexavalent chromium at the hydration of Portland clinker. Ferrous sulphate heptahydrate was added as crystalline powder and also in an aqueous solution. Obtained experimental results clearly showed higher reduction ability of a liquid form compared to the solid substance. The influence of the grain size on the reduction of hexavalent chromium was investigated immediately after mixing clinker with water and also during the first days of hydration process. New oxidation layer containing Fe^{3+} species forms around the non-oxidation part of sulphate species. That is why larger grain size showed lower reduction ability of chromium. In this case the additional chromium reduction effect was observed during the first days of hydration. The results were acquired by UV/VIS method according to STN EN 196-10.

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1. Introduction

The presence of water-soluble hexavalent chromium in the Portland cement causes a lot of problems in the manufacturing process. The studies show that hexavalent chromium can cause an allergic reaction. Workers exposed to cement with high chromium (VI) concentrations show a higher prevalence of cement eczema. In vitro and in vivo

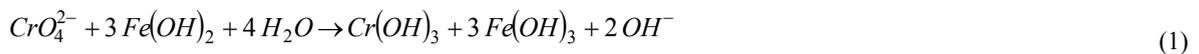
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studies clearly indicate that chromium (VI) in contrast to chromium (III) is relatively well absorbed. In human skin in vitro uptake of chromium (VI) into the epidermis was more than ten times higher than that of chromium (III) even when chromium (III) was applied at twofold higher concentrations [1].

Chromium usually occurs in the compounds in the form of chromium (VI) or chromium (III), which are the most stable and common oxidation states of chromium. The compounds containing chromium have different solubilities and toxicities [2]. The leaching of trivalent chromium and its other species is much weaker than the leaching of hexavalent chromium. That is why the leachate is composed of hexavalent chromium with the content of 80–90 % [3]. During the clinkerization of Portland clinker at high temperatures, Cr^{3+} can be oxidized to Cr^{4+} , $\text{Cr}^{4.6+}$, Cr^{5+} , and Cr^{6+} . Among these species, Cr^{6+} is the most toxic [4]. The use of materials to reduce the level of Cr (VI) formation is especially prevalent in the European cement industry due to the Directive 2003/5C/EC which prohibits sale of cement containing more than 2 ppm of soluble Cr (VI) when hydrated. The reduction of hexavalent chromium and its content has been solved for many years [5,6].

The amount of soluble hexavalent chromium depends on the fineness of Portland cement, on type and amount of gypsum and on the presence of other additives. β -hemihydrate shows faster solubility kinetics than gypsum and anhydrite. With increasing amount of calcium sulphate in the solution, less chromium is immobilized in the hydration products. The reason is, that when cement is mixed with water the dissolution of phases immediately starts. But in the presence of chromate (coming from the clinker itself) chromium-bearing ettringite-like structure phase is formed first. It converts to usual (and more stable) sulphate ettringite as the amount of sulphate in the solution increases due the dissolution of gypsum, which allows the release of chromate. This could be the explanation of the reversibility of immobilization of chromates in Portland clinker compared to Portland cement [7,8]. This is the reason why the reduction of hexavalent chromium is needed. Ferrous sulphate is the most used reduction substance. The reaction of reduction is as follows:



The mechanism of reaction of ferrous salts can be considered as follows [9]:

- as soon as cement (ground together with reducing agent) is mixed with water, chromates and ferrous salts are released into the solution, while the pH quickly increases due to the hydration of cement;
- Fe^{2+} ions form insoluble hydroxides, their redox potential drops (in particular as the pH increases, their redox potential drops faster than the redox potential of Cr^{6+}) and $\text{Fe}(\text{OH})_2$ becomes a strong reducing agent;
- soluble chromates are reduced to $\text{Cr}(\text{OH})_3$.

2. Materials and methods

2.1. Materials

Portland clinker from Slovakia cement plant was used in all experiments. The particle size of used clinker was $d_{45} = 5.41 \mu\text{m}$, $d_{50} = 6.77 \mu\text{m}$, $d_{90} = 36.31 \mu\text{m}$, $d_{99} = 69.36 \mu\text{m}$ (the numbers mean the percent (45%, 50%, 90% and 99 %) of particles smaller than this value). The mineralogical composition of Portland clinker was determined by XRD analysis (see Table 1.). The method used was RIR (reference intensity ratio) – semiquantitative analysis based on the comparison with reference standards (e.g. $\alpha\text{-Al}_2\text{O}_3$).

Ferrous sulfate was used in heptahydrate form ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) from Penta s.r.o. with p.a. purity. The maximum content of chloride is 0.01 %, ferric ions 0.2 % and insoluble salt 0.01 %. Calcium sulphate dihydrate pure was used in precipitated form from Lachema s.r.o.

Table 1. Portland clinker composition (XRD).

Phase	Content (%)
C ₄ AF	11.9
C ₂ S	8.5
C ₃ S	76.6
C ₃ A	3.0

2.2. Sample preparation

The experimental slurry consisted of 25 g of Portland clinker and 25 ml of distilled water (sample of pure Portland clinker). The slurry was carefully homogenized for 15 min and then filtered through 0.45 µm filter paper. The amount of hexavalent chromium was detected in the solution prepared by mixing 5 ml of filtrate, 20 ml distilled water and 5 ml 1,5-diphenylcarbazine. The pH was adjusted to 2.1–2.5 with chloric acid. The solution prepared this way was transferred to 50 ml volumetric flask and topped up. This process is described in the STN EN 196-10 standard - Methods of testing cement - Part 10: Determination of the water-soluble chromium (VI) content of cement [10]. This process was repeated with different addition of calcium sulphate dihydrate and ferrous sulphate heptahydrate.

The reducing agent (ferrous sulphate heptahydrate) was tested in the form of crystal powder and also of aqueous solution. In the first case, calculated amount of crystalline substance was added to the Portland clinker. The mixture was perfectly homogenized and then it was mixed with water. In the case of determination of hexavalent chromium amount during the hydration, a water to cement ratio was 0.4. In aqueous addition, the calculated amount of ferrous sulphate was dissolved in distilled water. The solution was added to the Portland clinker.

2.3. UV/VIS method

The principle of determination of hexavalent chromium is the chemical reaction of 1,5-diphenylcarbazine with chromate or dichromate in acid water medium. The result of this reaction is red-violet colored complex. The dependence of absorbance of colored solution on the hexavalent chromium concentration is linear. The absorbance was measured with the wavelength of 540 nm by HACH LANGE DR spectrophotometer.

3. Results and discussion

3.1. The chromium reduction by the reduction substance in liquid form

Pure Portland clinker contained 0.27 ppm of leachable hexavalent chromium. In the presence of gypsum, the value increased above permissible 2 ppm limit (see Table 2). According to many authors, the chromate analogue of ettringite is formed during the hydration of Portland cement. This analogue is unstable in the presence of sulphate anions. It could be the reason why the concentration of chromate anions increased with the addition of gypsum. The same effect was observed in the literature [8].

Table 2. The amount of hexavalent chromium in the mixture of Portland clinker with gypsum.

SO ₃ (%)	CaSO ₄ ·2H ₂ O (%)	αA	Øc Cr ^{VI} (ppm)
0	0	0.022 5	0.27
1.18	2.0	0.320 5	12.44
1.77	3.0	0.295 0	11.46
2.36	4.0	0.325 5	12.64

The aim of this section was to clearly define whether or not hexavalent chromium is released into the solution in

the case of complete replacement of gypsum by ferrous sulphate heptahydrate. The assumption was that the function of sulphate ions would be the same as in Portland cement (formation of AFt or AFm phase). Chromate ions should be released into the solution where they should be immediately reduced by present ferrous ions.

The reduction ability of present ferrous salts was observed (see Table 3). All received values are below the amount of hexavalent chromium in pure Portland clinker. The reduction of chromium as well as iron oxidation is accompanied by a rust-color of cement.

Table 3. The amount of hexavalent chromium in the mixture of Portland clinker with ferrous sulphate.

SO ₃ (%)	FeSO ₄ ·7H ₂ O (%)	αA	Øc Cr ^{VI} (ppm)
0	0	0.022 5	0.27
0.10	0.34	0.010 0	0.06
0.20	0.69	0.009 0	0.05
0.30	1.03	0.009 0	0.05
0.40	1.38	0.010 0	0.06
0.50	1.72	0.009 5	0.06

3.2. The influence of grain size of reducing substance on leaching of hexavalent chromium

The amount of reducing agent was the same for all mixtures (0,5 wt. %) in this experiment. Ferrous sulphate heptahydrate was milled and subsequently sieved for required fractions.

The results showed the correlation between the particle size of reducing agent and the amount of released hexavalent chromium (see Table 4).

Table 4. The influence of grain size of reducing substance on leaching of hexavalent chromium.

Particle size (µm)	αA	Øc Cr ^{VI} (ppm)
63–100	0.010 0	0.06
100–250	0.034 0	0.46
250–400	0.036 0	0.49
400–500	0.038 0	0.53

The bigger size of a reducing agent, the worse reduction of hexavalent chromium was achieved. It could be caused by the formation of oxidized Fe³⁺ layer around the center of reducing agent. The water access to non-oxidized part of grain is blocked. This statement is based on Fig. 1, which shows the fracture area of tested specimen. The rusty color around the particle of reducing substance can be observed by careful monitoring. The center of particle is whitish color which means that non oxidized ferrous part is still present. These color changes explain the changes in oxidation numbers of iron.

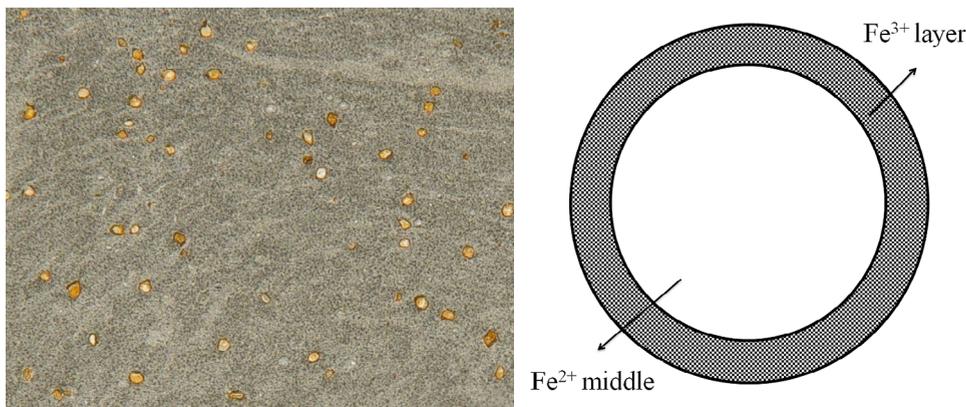


Fig. 1. The fracture area of tested specimen (Portland clinker with ferrous sulphate 400–500µm).

The smallest particles were completely dissolved so all ferrous ions were available for the reduction. The amount of reduced hexavalent chromium by reducing agent consisting of the smallest particles (63–100 µm) is the same as the amount of hexavalent chromium reduced by aqueous solution.

3.3. The influence of hydration on leaching of hexavalent chromium

Another problem to be solved is the influence of age of hydration on leaching of hexavalent chromium. Current literature contains only minimum information about it. The mechanism of repeated chromium leaching into the solution is not explained.

The samples were prepared in the same way as the previous ones (0.5 wt. % ferrous sulphate). The necessary quantities of samples were collected in certain days, the samples were milled, sieved (63 µm) and analyzed.

The addition of reducing agent (ferrous sulphate) with the smallest particle size caused higher values of concentration of hexavalent chromium after 4, 7 and 14 days compared to the value obtained immediately after mixing with water. The additions of reducing agent with larger particle sizes showed sharp fall in the measured values after 4 days. The concentration grew slightly after 7 and 14 days (see Table 5), but it was still lower than the value obtained immediately after mixing Portland clinker with solid reducing agent and water (see Table 4).

The reason for dramatic fall of concentration after 4 days is the Fe^{3+} layer around the Fe^{2+} part of particle. Due to the milling ferrous ions are reactivated and enabled to reduce of hexavalent chromium. The increasing concentration after 7 and 14 days is caused by slow oxidation of non-oxidized particle (see Fig. 2).

Table 5. The influence of grain size of reducing substance on leaching of hexavalent chromium.

Particle size (μm)	ϕA	$\text{O}_c \text{Cr}^{\text{VI}}$ (ppm)
4 th day		
63–100	0.026 0	0.31
100–250	0.023 5	0.29
250–400	0.027 0	0.34
400–500	0.028 0	0.35
7 th day		
63–100	0.019 2	0.22
100–250	0.027 0	0.34
250–400	0.029 0	0.38
400–500	0.032 5	0.43
14 th day		
63–100	0.026 5	0.34
100–250	0.031 5	0.42
250–400	0.029 3	0.38
400–500	0.036 0	0.50

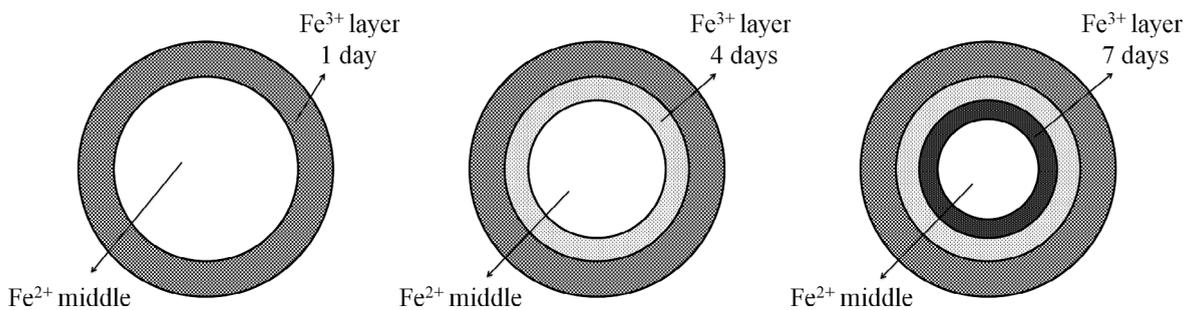


Fig. 2. The oxidation of ferrous part of reducing agent.

4. Conclusions

From the results of analyses it is clear that the form of reduction substance has an important influence on leaching of hexavalent chromium. The easiest way for the reduction of hexavalent chromium is the use of an aqueous solution of ferrous sulphate. It could be a problem for many companies delivering cement in a dry form.

The amount of hexavalent chromium is released during the hydration. The best results were achieved with reducing agent having the smallest particle size and in this case the leaching of hexavalent chromium was also the lowest during the hydration.

The next study will be focused on investigation of the influence of ferrous sulphate on the hydration of Portland clinker and its hydration products.

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