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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

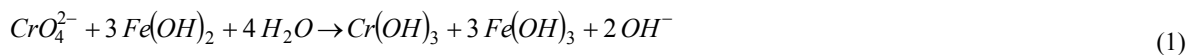
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studies clearly indicate that chromium (VI) in contrast to chromium (III) is relatively well absorbed. In human skin in vitro uptake of chromium (VI) into the epidermis was more than ten times higher than that of chromium (III) even when chromium (III)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

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