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Chromium-Leaching Study of Cements in Various Environments

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Abstract**—**Cement is a basic material used for building construction. Chromium as an indelible non-volatile trace element of raw materials occurs in cement clinker in the trivalent or hexavalent form. Hexavalent form of chromium is harmful and allergenic having very high water solubility and thus can easily come into contact with the human skin. The paper is aimed at analyzing the content of total chromium in Portland cements and leaching rate of hexavalent chromium in various leachants: Deionized water, Britton-Robinson buffer, used to simulate the natural environment, and hydrochloric acid (HCl). The concentration of total chromium in Portland cement samples was in a range from 173.2 to 218.5 mg/kg. The content of dissolved hexavalent chromium ranged 0.23-3.19, 2.0-5.78 and 8.88-16.25 mg/kg in deionized water, Britton-Robinson solution and hydrochloric acid, respectively. The calculated leachable fraction of Cr(VI) from cement samples was observed in the range 0.1--7.58 %.

Keywords**—**Cement, hexavalent chromium, leaching, total chromium.

I. Introduction

CHROMIUM as one of the 25 most common elements in the earth's crust [1] is an indelible trace element occurring in raw materials which are used in the production of cement clinker. It occurs in clays, limestone and iron-based minerals as well as in the linings of cement rotary kiln mainly in the trivalent form as Cr(III) [2]. In cement kilns, however, at high temperatures under an oxidizing atmosphere and alkaline conditions, chromium in oxidation state III can be changed to toxic hexavalent form – Cr(VI) [3]. Hexavalent chromium is generally known to have high solubility in water. Thus, cements containing Cr(VI) compounds with a high solubility such as water-soluble chromates may cause allergic reactions and hypersensitive responses in direct contact with human skin [4]. As reported by [5], an allergic reaction regarding Cr(VI) is observed when cement contains 10 ppm or more of hexavalent chromium. In addition, toxic and carcinogenic influence of hexavalent chromium is also estimated even at lower concentrations during long-term exposition. The concentration of hexavalent chromium in Swedish [6] and Australian cements [7], were measured in the range from 0.2 to 20 ppm. Based on the methods analyzing a dissolution of chromium in acids, it is estimated that the Cr(VI) form represents up to 80% of the total chromium in the cement clinker and 8-26% of the total Cr(VI) is dissolved in water [8], [9]. A similar study [3] was also performed on the Spanish cements, in which the total content of chromium ranged between 20 and 110 mg/kg, and water-soluble hexavalent chromium ranged between 0.9 to 24 mg/kg, which reflected only fraction of the total Cr(VI) in cements. This broad concentration range depends upon several factors [10], in particular on the composition of cements. In accordance with [11], the leaching of heavy metals from fly-ash-based cements increased with the addition of fly ash. Another study reported that leachability of heavy metals was highly dependent upon pH of the medium.

In this study, the concentrations of total chromium and water-soluble hexavalent chromium in Slovak cements were analyzed. In addition, leachability of hexavalent chromium was investigated in two other leachants, Britton-Robinson buffer representing a simulation of the natural environment, and hydrochloric acid (HCl).

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II. Materials and Methods

The content of total and water-soluble hexavalent chromium was determined in four samples of CEM I Portland cement manufactured by four different cement producers in the Slovak republic. CEM I Portland cement contains clinker in 95 wt. %.

A. Chemical Analysis

The basic chemical composition of cements and content of total chromium in tested cements were analyzed by X-ray fluorescence analysis (XRF) using SPECTRO iQ II (Ametek, Germany) with silicon drift detector SDD with resolution of 145 eV at 10 000 pulses. The primary beam was polarized by Bragg crystal and Highly Ordered Pyrolytic Graphite - HOPG target. The samples were measured during 300 s at voltage of 25 kV and 50 kV respectively, at current of 0.5 and 1.0 mA under helium atmosphere by using the standardized method of fundamental parameters for cement pellets. Cement samples were prepared as pressed tablets of diameter 32 mm by mixing 5 g of cement and 1 g of dilution material (M-HWC) and pressed at pressure of 0.1 MPa/m^2.

B. Leaching of Cements

The leachability of Cr(VI) was tested in three leachants: a) deionized water as model leaching environment, b) Britton-Robinson buffer used to simulation of the natural environment, and c) hydrochloric acid (HCl) representing an acidic environment. Cement leachates in deionized water were prepared in accordance with STN EN 196-10 (STN EN, 2007) [12]. The same amount of cement and of ultra-pure deionized water (Rodem 6) with conductivity of 5.72 μS/cm and pH of 6.81 was mixed during 15 minutes at laboratory temperature. The prepared cement paste was separated by vacuum filtration through the glass filter with porosity 4 (Morton). The obtained filtrate was adjusted to final volume of 250 ml. In the filtrate, the content of water-soluble hexavalent chromium was measured.

Britton-Robinson buffer is a universal solution, which is used as mentioned above, to simulate the conditions of the natural environment. It was prepared by mixing 0.04 M H_3BO_3 (boric acid), 0.04 M H_3PO_4 (orthophosphoric acid) and 0.04 M CH_3COOH (acetic acid) in the same proportions. Mixing these acids, a solution with a pH of 6.95 was prepared according to the study [13]. 10 g of cements were mixed with 100 ml of Britton-Robinson buffer with pH 6.95 for 15 minutes. Consequently, the sample was filtered through a Buchner filtration system and then the filtrate´s pH was adjusted to 7 by 0.5 M NaOH. The filtrate thus obtained was evaluated for hexavalent chromium concentration.

Cement samples for leaching in hydrochloric acid were prepared by mixing 10 g of cements with 100 ml of 10 % HCl for 15 minutes. After this period, the pH of leachate was adjusted to value 7 by 0.5 M NaOH. The precipitate of $Fe(OH)_3$, which was formed during cement´ dissolution in HCl, was removed from the leachate by filtration through a Buchner filtration system [9]. The residual filtrate was analyzed with regard to the amount of the dissolved hexavalent chromium.

C. Cement Leachates´ Analysis

The measuring of hexavalent chromium concentrations was based on the reaction of dissolved Cr(VI) with diphenyl carbazide by forming the purple colored compound. The concentration of dissolved hexavalent chromium was proportional to the intensity of purple-colored complex. The concentrations of Cr(VI) in liquid samples were measured by spectrophotometer DR 2800 (Hach Lange, Germany) at wavelength of 540 nm.

III. Results

The percentage of the basic components of tested Portland cement samples as well as the content of total chromium measured by XRF spectroscopy are given in Table I. The chemical composition of analyzed cement samples was in accordance with the standard chemical composition of Portland cement [14].

The concentrations of total chromium in Portland cement samples ranged 173.2 to 218.5 mg/kg and these values correlated with the concentrations of total chromium in Portland cements in Czech Republic, which were measured in the range 87 to 283 mg/kg [15]. The highest concentration of total chromium was detected in the sample 3 and the lowest content in sample 1. The concentration of total chromium in cements depends on raw materials of cements. According to the work [8] cement clinker contains significantly more total and hexavalent chromium as limestone. Chromium content in the raw meal according to the reference document on best available techniques in the cement industry [16] is in the range 10-40 mg/kg while the content of chromium in limestone and in clay materials ranged 1.2-21 mg/kg and 20-109 mg/kg, respectively. Chromium in natural limestone occurs dominantly in the form of Cr(III) and it is expected that the majority of Cr(VI) present in the cement clinker originates from the production process [8]. Consequently, the cement samples were tested for the content of hexavalent chromium by leaching in deionized water, Britton-Robinson solution and HCl. The results of water-soluble hexavalent chromium measured by spectrophotometer are illustrated in Fig. 1.

TABLE I
CHEMICAL COMPOSITION OF TESTED PORTLAND CEMENTS (%)

Component	Sample1	Sample 2	Sample 3	Sample 4
MgO	1.54	2.14	2.03	3.82
Al_2O_3	4.06	3.91	4.17	4.39
SiO_2	17.83	19.76	19.24	19.65
SO_3	3.25	3.13	3.17	3.17
Cl	0.019	0.025	0.039	0.012
K_2O	1.151	0.492	0.660	0.583
CaO	54.23	63.60	63.93	58.15
TiO_2	0.209	0.227	0.234	0.212
MnO	0.330	0.330	0.330	0.352
Fe_2O_3	2.63	2.73	2.38	3.25
Other	14.2	3.53	3.24	6.28
Total Cr	0.0173	0.0210	0.0219	0.0179

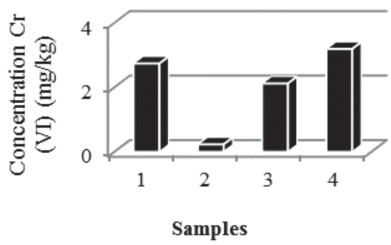

Fig. 1 Dissolved Cr(VI) from Portland cement samples in deionized water

The hexavalent chromium concentrations dissolved in deionized water varied from 0.23 to 3.19 mg/kg. The highest mass of Cr(VI) was leached out from the sample 4 and the least one from the sample 2. The significant difference in water-soluble chromium Cr(VI) in case of analyzed Portland cements is likely due to both raw materials composition of cements and different production strategies of producers.

Taking into account the maximum value for packed cements 2.0 mg per kg of cement (2.0 ppm = 0.0002 %) stated by Slovak legislative [17], samples 1 and 4 did not meet this requirement by exceeding the permissible content of Cr(VI). That means these cements may be distributed only in the fully automated operation without any possibility to cement contact with the workers' skin. The content of water-soluble chromium Cr(VI) in the other evaluated cement samples (samples 2 and 3) was under permissible limit.

The concentrations of hexavalent chromium dissolved in Britton-Robinson solution ranged from 2.0 to 5.78 mg/kg. The measured Cr(VI) concentrations for particular cement samples are illustrated in Fig. 2.

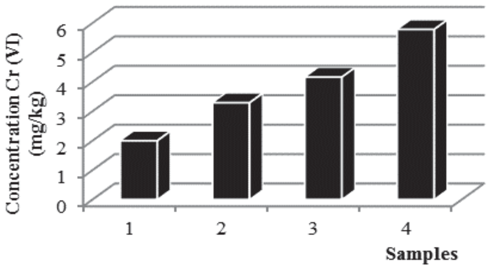

Fig. 2 Dissolved Cr(VI) from Portland cement samples in Britton-Robinson solution

Similar to the one in deionized water, the highest Cr(VI) leachability was measured for the sample 4. The lowest mass of leached Cr(VI) was measured for the sample 1. Comparing the leachability of Cr(VI) in Britton-Robinson solution and in deionized water, the mass of Cr(VI) leached out from cement samples in Britton-Robinson solution have been measured to be higher than in deionized water excepting the cement sample 1.

Fig. 3 presents the concentrations of hexavalent chromium leached out from cement samples in an acidic environment.

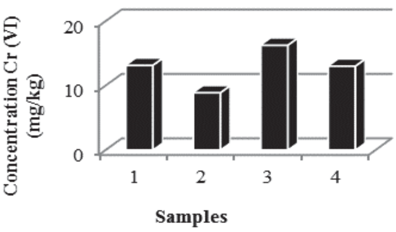

Fig. 3 Dissolved Cr(VI) from Portland cement samples in HCl

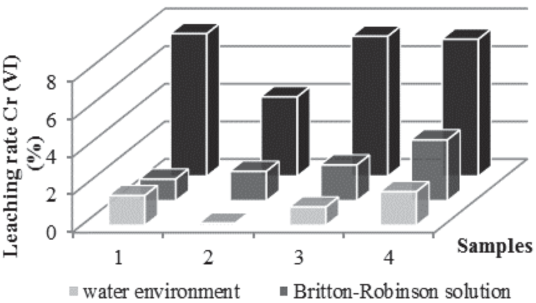

Fig. 4 Leachable fraction of Cr(VI) from cements regarding total Cr content for the leaching media

The Cr(VI) mass dissolved in HCl was in the range 8.875-16.25 mg/kg. The least Cr(VI) leachability in acidic environment was detected for the sample 2 and the highest one for the sample 3. For all studied samples, the leached out masses of Cr(VI) due to hydrochloric acid have been measured to be higher than Cr(VI) masses leached out in both deionized water and Britton-Robinson solution, as assumed.

The leachability of Cr(VI) from cements in deionized water reached 2-25% of Cr(VI) leachability in Britton-Robinson solution. Dissolved Cr(VI) mass in Britton-Robinson solution represents 15-45% of the Cr(VI) mass measured in HCl.

At last, the leachable fraction of Cr(VI) from cement samples regarding the total concentrations of chromium in cements were calculated for particular medium and the results are illustrated in Fig. 4.

The leached-out portion of Cr(VI) in deionized water ranged from 0.1 to 1.8% of the total chromium mass in cements; whereas in Britton-Robinson solution it was in the range from 1.15 to 3.24%. The highest percentage of leached-out Cr(VI) from cements was observed after dissolution the cement samples in HCl (from 4.22 to 7.58%). However, the measured concentrations of Cr(VI) dissolved in the hydrochloric acid cannot be considered as the total concentration of Cr(VI) in cements, since the addition of HCl may result in a partial reaction in which the chromium in oxidation state VI is reduced to chromium in the oxidation state III. Based on this fact, it is assumed that the overall Cr(VI) content in cements is significantly higher than that has been found by Cr(VI) leaching from cements in water or not even by dissolution in HCl. According to the studies [8], [9], Cr(VI) form represents 30-80% of the total chromium in the cement.

IV. Conclusion

The contents of hexavalent and total chromium were studied in four samples of Portland cement (type CEM I). The experimental results showed that the concentration of total chromium in Portland cement samples was in the range from 173.2 to 218.5 mg/kg. The dissolved content of hexavalent chromium ranged 0.23-3.19 mg/kg in deionized water, 2.0-5.78 mg/kg in Britton-Robinson solution, and 8.875-16.25 mg/kg in hydrochloric acid.

Mass of leached Cr(VI) measured in the Britton-Robinson solution was in 75% of samples higher than mass of leached Cr(VI) measured in deionized water. This fact points to the possibility of increased migration of Cr(VI) in the real environmental conditions in comparison with the results of standard tests when using deionized water.

The mass of chromium dissolved in HCl was measured by 75-97% higher than chromium mass found in cement leachates in water and by 55-85% higher than that found in the Britton-Robinson solution.

Experimental results showed that only a small part of Cr(VI) was extracted from the total chromium content in the cement samples: 0.1-1.8% into deionized water, 1.15-3.24% into Britton-Robinson solution, and 4.22-7.58% into hydrochloric acid. Low proportions of leached-out Cr(VI) into the analyzed media in comparison with the total concentration of chromium in cements could be also linked to the presence of chromium not only in the oxidation state VI but in oxidation state III as well.

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