

The Rate of Chromium Leaching from Slag-based Cement Composites in Different Leachants

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Abstract—In this experiment, the reference concrete samples containing Portland cement as binder, and the concrete samples with the addition of ground blast furnace slag (65% and 95%, respectively as replacement of Portland cement) were analysed regarding the leachability of chromium. The prepared concrete samples were subjected to long-term leaching test for 500 days in three different leachants (distilled water, rainwater and Britton-Robinson solution). Subsequently, the concentration of chromium in the various leachates was measured by AAS method. The leaching parameters as values of the pH and the conductivity were also studied.

Measured values of dissolved hexavalent chromium clearly indicate that the higher amount of slag was incorporated into the concrete samples the more of chromium was leached-out. Distilled water was found as the most aggressive leachant for chromium when compared to the other leachants used. This experiment clearly shows the need for the regulation and control of the waste addition to the construction materials and the need for long-term study in relation to the leaching of heavy metals into the environment.

Keywords—concrete composites, heavy metal, hexavalent chromium, leaching

I. INTRODUCTION

THE problem of heavy metal immobilization becomes more and more actual, with the increasing contamination of the environment. New technologies will be developed only when heavy-metal-containing by-products can be sufficiently and safely removed. In many research centers studies are being carried out to solve this problem. One of possibilities is to incorporate these by-products to construction materials. Although stabilization of wastes is a confirmed technology, little is still known about the mechanisms involved with the leaching of contaminants from the stabilized waste [1].

It is necessary to study whether the incorporation of alternative materials in the production of the cement is liable to increase the quantity of heavy metals [2]. The term heavy

metal has been used as a general term for those metals and semimetals with potential human or environmental toxicity. One of the most harmful forms of heavy metals is hexavalent chromium. Groundwater is the most threatened by leaching of hexavalent chromium into the environment [3]. Skin diseases including irritant and allergic contact dermatitis are common complains in cement and concrete workers because of strong alkalinity of and high hexavalent chromium concentration in cement products [4]. Authors [5] investigated the leaching of harmful trace metals from eight Portland cement concretes. Results for the de-ionized water test showed partial leaching of Cr, Hg, and Ni. Authors [6] undertook various leaching tests on cement mortars. A better understanding of leaching behavior would enable us to more accurately predict how a waste will behave under 'real world' disposal conditions [1]. The objective of this paper was to study the leachability of hexavalent chromium from concrete samples containing waste materials.

II. MATERIAL AND METHODS

The concrete samples containing 65% and 95% of a slag additive as a replacement of Portland cement and samples without this special additive were prepared for the leaching experiments. The compositions of 1 m³ of fresh concrete mixtures for are given in Table I. In this experiment, Portland cement CEM I 42.5 N, (Povazska cementaren, Ladce, Slovakia); blast-furnace slag additive (Povazska cementaren, Ladce, Slovakia) and natural aggregates of local source (Vychodoslovenske stavebne hmoty, Geca, Slovakia) have been used.

Table I Composition of concrete mixtures

Mixture components	0 % of slag	65% of slag	95% of slag
Cement (kg/m ³)	360	126	18
Slag additive (kg/m ³)	0	234	342
Water (L/m ³)	162	162	162
Aggregates, fraction 0/4mm (kg/m ³)	825	825	825
Aggregates, fraction 4/8mm (kg/m ³)	235	235	235
Aggregates, fraction 8/16mm (kg/m ³)	740	740	740

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Samples marked as 1, 2, 3, 4, 5, and 6 contain 0% of slag addition, samples 7, 8, 9, 10, 11, and 12 contain 65% of slag addition, and samples 13, 14, 15, 16, 17, and 18 contain 95% of slag addition,

The concrete samples prepared by standard procedure were cured in water during 28 days, then were cut into smaller specimens with dimensions of 50×50×15 mm, dried and weighted to the constant weight. Constant weight has been achieved when less than 0.1 % of the test sample wet mass is lost during an additional exposure to the drying process.

Consequently, concrete samples were placed into various leachants as follows: concrete samples 1, 2, 7, 8, 13 and 14 to distilled water (DW) with a pH of 7.08; concrete samples 3, 4, 9, 10, 15 and 16 to rain water (RW) with a pH of 6.54; and concrete samples 5, 6, 11, 12, 17 and 18 to Britton-Robinson buffer (BRB) with a pH of 2.16 to tank test leaching. According to a basic characterization tank test reported in CEN/TR 16142, the concrete samples were placed into tanks filled by particular leachant: distilled water, rain water and Britton-Robinson buffer, respectively so that the specimens were immersed at least 2 cm to ensure the permanent contact with liquid leachant. Leaching of the tested concrete samples proceeded over a period 500 days under laboratory temperature of 20 °C.

Conductivity and pH of leachant were measured at the beginning and after 500 days of the experiment by using Multimeter X-matePro MX300 (Mettler Toledo) and pH meter FG2 – FiveGo™ (Mettler Toledo).

The chemical composition of the concrete samples before the experiments was measured using X-ray fluorescence (XRF) methods by SPECTRO iQ II, (Spectro-Ametek, Kleve, Germany) with silicon drift detector having a resolution of 145 eV at 10 000 pulses. The primary beam was polarized by a Bragg crystal and highly ordered pyrolytic graphite target.

Measurements were performed for 300 and 180 s at voltages of 25 kV and 50 kV and currents of 0.5 and 1.0 mA in the presence of helium.

For determination of chemical composition, cement composites were powdered (MSK-SFM-1 Desk-Top planetary ball mill, MTI Corporation, Richmond, USA), 5 g was mixed with 1 g of a dilution material (Hoechst wax C micropowder, Merck Millipore, Darmstadt, Germany), and subsequently pressed into a pellet at a pressure of 0.1 MPa.m², and analyzed by XRF. The concentrations of chromium in leachates were measured by Atomic Absorption Spectroscopy (AAS) using SpectrAA-30 (Varian).

III. RESULTS AND DISCUSSION

The measured parameters: pH, conductivity and Cr concentrations in leachates after 500 days of the leaching experiment are illustrated in Table II.

As can be observed in Table II, pH values of all leachates have been moved to the alkali region up to value of 9.20. The highest increase in pH was measured for concrete samples with 0% of slag whereas the lowest increase was measured for the samples with 95% of slag. The increasing of pH during the experiment was caused by leaching the alkali compounds from the cement matrix. No significant difference in final pH was found for the individual leachants even though the input pH values vary markedly.

Conductivity of distilled water (DW) and rain water (RW) increased 400 fold and 10 fold, respectively when compared the input and final values. On the contrary, the conductivity of Britton-Robinson buffer (BRB) decreased from 2850 to 987 µS/cm as seen in Table II.

Table II Measured parameters in concrete leachates

Sample	Leachant	Leached-out mass of Cr(VI) (µg/L)	Conductivity (µS/cm)		pH		
			Input	Final	Input	Final	
0% of slag	1	DW	14.5	2.71	979	7.08	9.05
	2	DW	7.5		936		9.19
	3	RW	4.8	99.30	1023	6.54	9.20
	4	RW	4.3		869		9.16
	5	BRB	1.7	2850	987	2.16	9.03
	6	BRB	2.2		891		8.98
65% of slag	7	DW	20.8	2.71	766	7.08	9.01
	8	DW	21.6		768		8.99
	9	RW	11.2	99.30	696	6.54	8.97
	10	RW	13.5		664		8.98
	11	BRB	1.3	2850	763	2.16	8.85
	12	BRB	3.8		889		8.97
95% of slag	13	DW	23.1	2.71	665	7.08	8.64
	14	DW	24.5		757		8.59
	15	RW	12.9	99.30	561	6.54	8.65
	16	RW	14.2		554		8.56
	17	BRB	0.6	2850	610	2.16	8.64
	18	BRB	0.7		725		8.76

This points to the different leaching of concrete composites in distilled and rain water compared with Britton-Robinson buffer. The highest leached-out masses of hexavalent chromium were measured in distilled water followed by rain water and Britton-Robinson buffer. To evaluate the leachability of the concrete samples with various portions of slag addition, the Cr (VI) leached-out masses were calculated per 1 kg of binder. The comparison of the dissolved concentrations of hexavalent chromium in ppm (mg/kg) is illustrated in Fig. 1.

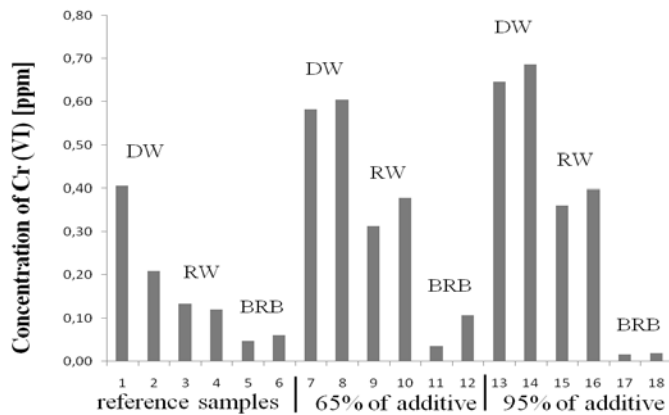


Fig. 1 Comparison of Cr (VI) leaching from concrete samples

As seen in Fig. 1, the more intensive leaching was found for the concrete samples with 95% of slag addition in both distilled and rain waters.

The total leaching rate V_d was calculated for all samples by dividing the measured dissolved mass of chromium in a particular water leachant by the corresponding time of exposure (12000 hours) and total surface of the sample, as shown in equation (1) according to [7]:

$$V_d = \frac{X_d}{(T \times S)} \quad (1)$$

where

V_d = Cr (VI) leaching rate per unit area ($\mu\text{g}/\text{h}\cdot\text{m}^2$);

X_d = maximum amount of hexavalent chromium ions leached out during the experiment (μg);

T = period of test [= 24 x days of leaching (hours)];

S = area of exposure surface (m^2).

The calculated leaching rates of chromium for all analyzed samples are given in Table III and illustrated in Fig. 2.

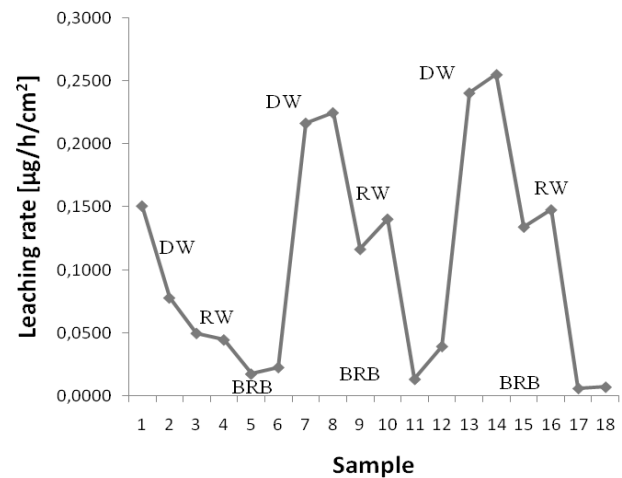


Fig. 2 Leaching rates of Cr (VI)

The calculated average leaching rates ranged from 0.0068 to 0.2479 $\mu\text{g}/\text{h}\cdot\text{m}^2$ (Table III). When compared the leachants, the highest leaching rates were found in distilled water for all concrete samples. Therefore, distilled water was found to be the most aggressive leachant for chromium when compared to the other leachants used. Contrariwise, the lowest leaching rates were calculated in Britton-Robinson buffer. The difference in leaching rates was most significantly observed for the concrete samples with 95% of slag addition. This founding points to the fact that conductivity of the leachant can be more important than pH value regarding the chromium leaching.

Comparing the concrete samples with/without slag addition, the highest leaching rates were found for the concrete samples with 95% of slag addition in all leachants: distilled water, rain water and Britton-Robinson buffer. Measured values of dissolved hexavalent chromium clearly indicate that the higher amount of slag was incorporated into the concrete samples the more of chromium was leached-out.

In addition, the Table III shows a percentage of leached-out hexavalent chromium. The percentage of leached-out hexavalent chromium was calculated by comparing the total chromium contents in concrete samples with the leached-out masses. The concentrations of total chromium in samples prepared to the experiment were 178.67 ppm (per 1 kg of binder), 201.89 ppm and 168.35 ppm in samples with 0%-of-slag, 65%-of-slag and 95%-of-slag, respectively.

The highest percentage of leached-out chromium was found in case of samples with 95% of slag additive immersed in distilled water. In leachates of Britton-Robinson buffer there was very low concentration of leached-out chromium. This phenomenon was caused due to high level of dissolved ions (high conductivity) in Britton-Robinson buffer.

Samples with higher content of slag additive immersed in the same medium leached higher amount of chromium than samples containing lower content of slag additive and reference samples, respectively. This was observed in distilled water and rain water. In Britton-Robinson buffer there were

concentrations of chromium in leachates near the detection limit.

Table III Leaching rates and percentage of leached-out hexavalent chromium

	Sample	Leachant	$V_d(\text{Cr})$ ($\mu\text{g}/\text{h}/\text{m}^2$)	Average $V_d(\text{Cr})$ ($\mu\text{g}/\text{h}/\text{m}^2$)	Percentage of leached- out Cr (%)
0% of slag	1	DW	0.1510	0.1146	0.18
	2	DW	0.0781		
	3	RW	0.0500		
	4	RW	0.0448		
	5	BRB	0.0177		
	6	BRB	0.0229		
65% of slag	7	DW	0.2167	0.2208	0.30
	8	DW	0.2250		
	9	RW	0.1167		
	10	RW	0.1406		
	11	BRB	0.0135		
	12	BRB	0.0396		
95% of slag	13	DW	0.2406	0.2479	0.40
	14	DW	0.2552		
	15	RW	0.1344		
	16	RW	0.1479		
	17	BRB	0.0063		
	18	BRB	0.0073		

IV. CONCLUSION

The incorporation of secondary raw materials and waste into building materials brings economic benefits, but on the other hand, there is a substantial risk of harmful emissions into the environment. In this experiment, higher leaching of hexavalent chromium from samples with the addition of slag compared to the reference sample without slag it was demonstrated. Distilled water was found as the most aggressive leachant for chromium when compared to the other leachants used which can be likely linked with a very small amount of dissolved ions. The least aggressive leachant was Britton-Robinson buffer, even when there was very low pH value, but it contains large amounts of dissolved ions. It follows the need for extra care when incorporating waste into building materials.

Measured values of dissolved hexavalent chromium confirm the assumption that the higher amount of slag was incorporated into the concrete samples the more of chromium was leached-out.

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