

# Environmental Impact Assessment of the Concrete Composites in Terms of the Selected Toxic Metals Leaching

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The concrete materials have to fulfill a lot of technical criteria before being built and used in the building structures depending on their application. In general, concrete is considered to be very stable and harmless material. However, due to various atmospheric influences on concrete materials, such as acid rain, as well as due to massive utilization of wastes in concrete production in various forms, concrete materials testing for the toxic metals leaching is of great importance at present.

The paper presents the results of the various concrete composites leaching analyses in various liquid media (distilled water, rain water and Britton-Robinson buffer). The exposition to the model liquid environment proceeded over a period of 30 to 240 days. The leachability and toxicity of heavy metals depends on a number of factors even some elements may have very different toxic profiles depending on their chemical form. Hexavalent chromium and barium have been selected to be analysed representing the most leachable metals in cements. The Cr (VI) and Ba ions concentrations leached have been measured using colorimetric analysis. The additional parameters such as pH and conductivity have been also investigated.

## 1. Introduction

Building industry is one of the most polluting industries. Therefore, the minimization of energy requirements of buildings, as well as the reduction of emissions produced within the buildings life cycle has become a point of interest of many researchers (Porhinčák and Eštoková, 2012). Every process in construction sector requires large amounts of energy, which mostly originate from fossil fuels, emits substantial amounts of CO<sub>2</sub> or SO<sub>2</sub> and produces waste or pollution (Eštoková et al., 2011).

Use of secondary raw materials in construction products is stimulated in most EC countries for recycling, conserving natural resources and saving energy. Steel slag is one of the by-products of steel producing process. Enormous quantities of these wastes are generated and they are considered problematic and hazardous for the environment (Marion et al., 2005). Concrete with application of slag aggregates with different percentages of slag in substitution of cement and sand have been found to have better mechanical properties than conventional concrete specimens (Akinmusuru, 1991). Thus the utilization of slag in cement production is useful not only in order to removing of waste material but in improving of the cement composites properties as well.

On the other hand, the waste utilization in concrete composites requires an assessment of the environmental impact of the application of these composite materials based on cement matrix (CEN/TR 16142, 2011). The main concern is to protect the environment and human health. With the increasing contamination of the natural environment, the problem of heavy metal mobilization becomes more and more significant (Deja J., 2002). Although cementitious materials play an important role in the immobilization of heavy metals, there is a need to study whether the incorporation of huge amount of the alternative materials in the production of cement is not liable to increase the quantity of heavy metals in the environment (Qasrawi H., 2014).

This paper is aimed at the study of slag-based composites in terms of the hexavalent chromium and barium leachability.

## 2. Materials and methods

### 2.1 Characteristics of input materials

Portland cement CEM I 42.5 N, (Ladce, Slovakia), aggregates of fractions 0/4mm, 4/8mm and 8/16mm of local source (East Slovakia) and special additive based on blast furnace slag have been used to produce testing samples. The chemical analysis of the Portland cement and the special additive are given in Tables 1 and 2.

*Table 1: Chemical composition of Portland cement*

Component	Weight %
CaO	57.15
SiO <sub>2</sub>	18.11
Al <sub>2</sub> O <sub>3</sub>	4.02
Fe <sub>2</sub> O <sub>3</sub>	2.69
SO <sub>3</sub>	1.49
MgO	1.37
K <sub>2</sub> O	1.12
P <sub>2</sub> O <sub>5</sub>	0.33
TiO <sub>2</sub>	0.18
Na <sub>2</sub> O	<0.11
Residuum	13.43

*Table 2: Chemical composition of slag-based special additive*

Component	Weight %
CaO	39.55
SiO <sub>2</sub>	38.95
MgO	10.11
Al <sub>2</sub> O <sub>3</sub>	8.33
MnO	0.74
SO <sub>3</sub>	0.57
Fe <sub>2</sub> O <sub>3</sub>	0.54
K <sub>2</sub> O	0.48
TiO <sub>2</sub>	0.37
Na <sub>2</sub> O	<0.11
Residuum	0.25

### 2.2 Concrete samples

To study the leachability of heavy metals from cement composites, the concrete samples containing 75 % and 95 % of a special additive based on slag as a replacement of Portland cement as well as samples without this special additive were prepared (see Table 3).

*Table 3: Composition of the test samples*

	The weight ratio kg : kg		
	Sample 1	Sample 2	Sample 3
CEM I 42.5 N : Special additive based on slag	360 : 0	90 : 270	18 : 342
CEM I 42.5 N : Water	360 : 162	90 : 162	18 : 162
Aggregates fraction 0/4mm:4/8mm:8/16mm	825 : 235 : 740	825 : 235 : 740	825 : 235 : 740

The prepared standardized concrete specimens with dimensions of 100 x 100 x 400 mm were cured for 28 days in water and afterwards cut into small prisms with dimensions of 50 x 50 x 10 mm.

## 2.3 Leaching

Leaching is the process by which a liquid dissolves and removes the soluble components of a material. With respect to cement materials, leaching can be discussed two ways: potential leaching from products made with cement, and the use of cement to control the leaching of waste materials, such as fly ash and slag. Leaching tests are used to simulate the real conditions and specifically affecting variables. Different test procedures are available for the characterization of materials depending on their leaching. "Basic characterization" tank test, collecting information on the short and long-term leaching characteristics of a material, according to CEN/TR 16142 was used in our study.

Concrete samples were placed in vessels (tanks) filled by liquid media (distilled water, rain water and Britton-Robinson buffer) so that the specimens were immersed at least 2 cm to ensure the permanent contact with the leachant. Leaching of the tested concrete samples proceeded during 30 and 240 days, respectively under laboratory temperature of 20 °C.

As mentioned above, three leaching media were used in the experiment. Distilled water was chosen as a reference medium in accordance with the CEN standard procedure. The pH of distilled water was 7.08; conductivity was measured of 2.71  $\mu\text{S}/\text{cm}$ . Rain water (pH 6.54; conductivity 96.6  $\mu\text{S}/\text{cm}$ ) was chosen to analyse the leachability of metals from the cement composites in real natural local conditions and Britton-Robinson buffer (pH 2.16; conductivity 2.85  $\text{mS}/\text{cm}$ ) was used to simulate the strongly acidic conditions.

## 2.4 Analytical methods

Conductivity and pH of leachants were measured after 30 and 240 days of the experiment. The laboratory equipment for conductivity measurement Multimeter X-matePro MX300 (METTLER TOLEDO) and pH meter FG2 – FiveGo™ (METTLER TOLEDO) were used in this experiment.

The concentration of hexavalent chromium and barium in leachates were measured by using colorimetric analyzer DR 2800 (Hach Lange, Germany). Chromium (VI) content was analysed spectrophotometrically, as a red-violet complex of chromium formed with benzocarbazine ( $\lambda_{\text{max}} = 545 \text{ nm}$  at 10 mL cell). The Barium Reagent Powder combines with barium in leachates to form a barium sulfate precipitate, which is held in suspension by a protective colloid ( $\lambda_{\text{max}} = 450 \text{ nm}$  at 10 mL cell). The amount of turbidity present caused by the fine white dispersion of particles is directly proportional to the amount of barium present.

The chemical composition of the input materials has been measured by X-ray fluorescence analysis (XRF). SPECTRO iQ II (Ametek, Germany) with SDD silicon drift detector with resolution of 145 eV at 10,000 pulses was used for the analysis. 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 at current of 0.5 and 1.0 mA under helium atmosphere by using the standardized method of fundamental parameters.

## 3. Results and discussion

### 3.1 Conductivity and pH

The results of conductivity and pH of cement composites samples leachates are listed in Table 4. Value  $\text{pH}_0$  means pH measured at the beginning of the experiment,  $\text{pH}_{30}$  means pH measured after a period of 30 days and  $\text{pH}_{240}$  after the period of 240 days. The same way of indexing was used for conductivity parameter ( $C_0$ ,  $C_{30}$  and  $C_{240}$ ). Distilled water used as a reference leachant is labeled as "a"; rain water as "c" and Britton-Robinson buffer as "e".

Table 4: The pH and conductivity of samples leachates

Sample	$\text{pH}_0$	$\text{pH}_{30}$	$\text{pH}_{240}$	$C_0$ [ $\mu\text{S}/\text{cm}$ ]	$C_{30}$ [ $\mu\text{S}/\text{cm}$ ]	$C_{240}$ [ $\mu\text{S}/\text{cm}$ ]
1a	7.08	11.19	8.57	2.71	793	711
1c	6.54	11.29	8.84	96.6	884	811
1e	2.16	6.15	8.34	2.85	1,310	1,240
2a	7.08	10.14	8.48	2.71	291	480
2c	6.54	10.39	8.53	96.6	352	488
2e	2.16	5.54	7.51	2.85	1,479	680
3a	7.08	10.57	8.15	2.71	382	508
3c	6.54	10.13	8.44	96.6	302	458
3e	2.16	5.54	7.97	2.85	1,442	777

After 30 days of leaching pH of the sample 1a increased from the value of 7.08 to 11.19, pH of the sample 1c increased from the value of 6.54 to 11.29 and pH of the sample 1e increased from the value of 2.16 to 6.15. The increasing of pH value was due to the leaching of alkali compounds to distilled water, resulting in an increase in the conductivity of the sample 1a leachate value of 2.71  $\mu\text{S}/\text{cm}$  to 793  $\mu\text{S}/\text{cm}$ , as well as the sample 1c the increase of the value of conductivity 96.6  $\mu\text{S}/\text{cm}$  to 884  $\mu\text{S}/\text{cm}$  and a decrease in the conductivity of the sample 1e leachate value of 2.85  $\text{mS}/\text{cm}$  to 1.31  $\text{mS}/\text{cm}$ . Similar trend was observed for sample 2 and sample 3 leachates.

The decrease in the pH of the leachate of sample 1a after 240 days from the value of 11.19 to 8.57, decrease in the pH of the sample 1c from the value of 11.29 to 8.84 and increase in the pH of the sample 1e from the value of 6.15 to 8.34 was probably caused by mutual neutralization reactions of ions in solution and simultaneously absorbing  $\text{CO}_2$  from air and the solution was acidified. Similar trend is observed in sample 2 and sample 3 leachates. Values of pH after 240 days balance from 7.51 to 8.84, which is variance near the value of 7, neutral value.

Comparing the cement composites in relation to their composition, pH of the leachates of the cement samples with the replacement of the cement by slag have reached lower values after 240-day leaching experiment than reference sample leachate (Table 4). This could indicate the higher resistance of the slag-based cement composites against dissolving the alkali compounds during the experiment.

### 3.2 Chromium and barium leaching

Measured barium and hexavalent chromium ions concentration after 30 and 240 days are given in Tables 5 and 6, respectively. The concentrations are expressed in [mg/L] as measured in leachates.

*Table 5: Concentration of barium and hexavalent chromium ions after 30 days*

Sample	Barium [mg/L]	Chromium [mg/L]
1a	6	0.012
1c	1	0.011
1e	1	0.005
2a	15	0.018
2c	3	0.012
2e	2	0.008
3a	20	0.010
3c	16	0.009
3e	9	0.008

Concentration of barium ions in leachate of the sample 1a after 30 days was measured of 6 mg/L, in leachate of the sample 2a after 30 days of 15 mg/L and in leachate of the sample 3a after 30 days of 20 mg/L. Higher concentration of barium ions in sample 2 and sample 3 leachates is probably due to higher content of barium in special additive based on the slag. Concentration of hexavalent chromium ions in leachates of the samples 1, 2 and 3 after 30 days was the highest in distilled water (leachates 1a, 2a and 3a), and the lowest in Britton-Robinson buffer (leachates 1e, 2e and 3e).

*Table 6: Concentration of barium and hexavalent chromium ions after 240 days*

Sample	Barium [mg/L]	Chromium [mg/L]
1a	6	0.015
1c	1	0.018
1e	5	0.005
2a	2	0.024
2c	2	0.021
2e	5	0.006
3a	2	0.026
3c	5	0.023
3e	2	0.006

Concentration of hexavalent chromium ions in leachates of the samples in distilled water after 240 days ranged from 0.005 mg/L to 0.026 mg/L; in rain water from 0.018 mg/L to 0.023 mg/L and in Britton-Robinson

buffer from 0.05 to 0.06 mg/L. The rain water used in the experiment seems to be the most aggressive leachant in terms of the chromium ions dissolving. Barium ions concentrations have been measured 2 to 6 mg/L, 1 to 5 mg/L and 2 to 5 mg/L for distilled water, rain water and Britton-Robinson buffer, respectively. The dissolved amounts of metals in relation to 1 kg of cement composite are illustrated in [ppm] in Figures 1 and 2.

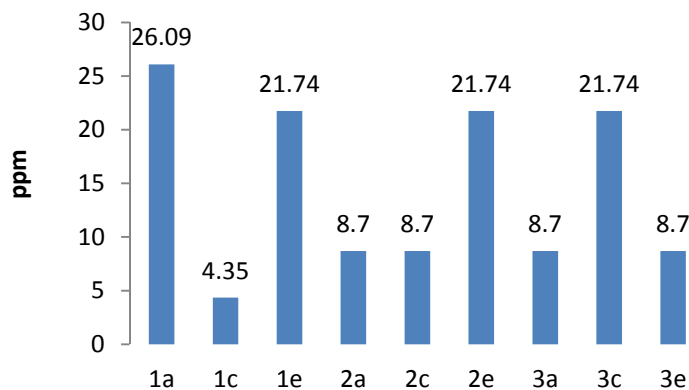


Figure 1: Dissolved barium concentration after 240-day experiment

Comparing the leached concentrations of barium in various leachant, there cannot be stated clear and definite relation between the percentage of slag replacement in cement composites and dissolving of barium. The analysis of the chemical composition of the concrete samples before and after the experiment is still in progress.

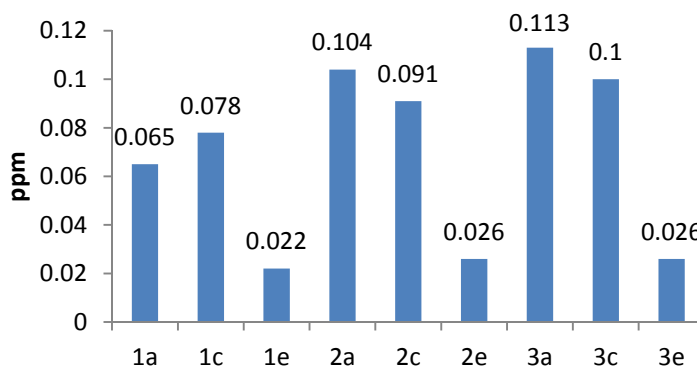


Figure 2: Dissolved hexavalent chromium concentration after 240-day experiment

Leaching study showed that the concentrations of dissolved Ba and Cr in the studied concrete were much lower than the Toxicity Characteristic Leaching Procedure (TCLP) criterion concentrations (100 and 5 mg/L, respectively) stated for the individual waste materials evaluation. Standard CEN/TR 16142 states Cr concentration of the concrete's leachate after 7 days of 0.15 mg/kg and the concentration of 0.5 mg/kg after 64 days of leaching. The value of 0.5 mg/kg has been not exceeded even after longer period of leaching (240 days). Limit values of Ba concentrations are not indicated in the standard. The results in this paper indicate that the elements in the studied concrete materials are very tightly bound and dissolved relatively in the low rate from the matrix.

Although, wastes incorporation into the cement based materials can reduce the quantity of leached heavy metals from waste, the concentrations of the dissolved metals from the concrete with slag addition have been measured to be higher than from the samples without waste. As mentioned, it was confirmed that the leaching of heavy metals from cement materials increases with waste material addition e.g. the fly ash or slag (Yu et al. 2005). Similarly, Shen and Forssberg (2003) reported the amounts of added fly ash increased the concentration of dissolved heavy metals from the concrete samples. In spite of the fact, the dissolved metals

concentrations measured in this study were low; there is still a need to test the leachability of the waste based concrete materials in order to ensure the environmental safety of these materials.

#### 4. Conclusions

Three various cement composites based on the slag application were studied in this paper in terms of the barium and hexavalent chromium dissolving in three environments: distilled water, rain water and acidic buffer. Concluding the results:

- The rain water used in the experiment seems to be the most aggressive leachant in terms of the chromium ions dissolving calculated to 1 kg of cement composite.
- Surprisingly, the lowest concentrations of dissolved hexavalent chromium have been observed in acidic buffer.
- The value of 0.5 mg/kg stated in Standard CEN/TR 16142 for Cr concentration in leachate after 64 days of leaching has been not exceeded even after longer period of leaching (240 days).
- Comparing the dissolved concentrations of barium in various leachants, there cannot be stated clear and definite relation even between the percentage of slag replacement in cement composites and dissolving of barium even the conclusion about the aggressiveness of the leachant.

As assumed, the increase in studied metals mobility from the waste-cement composites into the environment was not observed. The results presented will be confirmed by other results, e.g. chemical analysis of the concrete samples before and after the experiment, which is still in progress.

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