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Analyzing the leachability of selected heavy metals from cement composites by long-term and cyclic tests

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Abstract

Using of waste materials and secondary products from other industries in building industry to manufacturing building materials is one way to the sustainability. However, application of various waste requires serious monitoring and investigation of the safety of the new composites. Heavy metals presence and their releasing from the building materials can pose a potential risk to the environment and human health. The paper presents the results of a study of concrete composites with blast furnace granulated slag and special hybrid cement based on secondary mineral admixtures in relation to their heavy metals leachability. Selected metals (Cr, Pb, Ba, Ni, As) have been analysed using long-term tank and cyclic testing. The concretes with slag addition and hybrid cement proved more intensive releasing of analysed metals compared to the reference concrete. The aggressiveness of extracting media was strongly affected not only by pH but by the quantity of the ions presented in the liquids before the experiment as well. Although the leached quantities were not extremely high, results confirmed the need to monitor the building products with the incorporated waste.

Key words: concrete, hexavalent chromium, supplementary cementitious materials, waste materials in concrete, heavy metals, human health risk

1 Introduction

The use of secondary raw materials in construction products is stimulated in most EU countries in terms of recycling, conservation of natural resources and energy savings [1]. The main concern is the protection of the environment (air, water and soil quality) and human health, which requires an assessment of the environmental impact of the application of these composite materials based on cementitious matrices [2]. The use of waste in the production of cement composites may on the one hand improve the primary properties of cement composites and immobilize heavy metals [3], but on the other hand may under certain conditions cause increased leachability of some heavy metals [4].

Schmukat et al. [5] focused on the leaching of metals from various construction materials. The authors conclude that specific surface area measurement is an adequate tool to study the release of metals from structural materials. Leaching experiments emphasize the influence of the leachate composition on the leachability of metals from construction materials, as evidenced by the significant influence of ionic strength when water structures are the intended end use. Xiaolu [6] focused on the characterization of the leachability of cement pastes containing solid wastes for the purpose of long-term assessment of the environmental load. He points to the important role of the pH at which leaching takes place. Yu et al. [7] studied the leachability of heavy metals from hardened cement mixtures with the addition of various types of fly ash. The amount of leached heavy metals from cement-stabilized fly ash depended strongly on the type of fly ash used. The highest concentrations were detected for the hexavalent chromium. With the addition of finely ground granulated slag, the content of leached hexavalent chromium decreased. Kayhanian et al. have also studied the leachability of metals from asphalt and concrete surface materials [8]. It was found that the ion concentrations of most metals were below the limit, but the presence of chromium was found in the leachate of the concrete sample. According to the study, the leachability of chromium is influenced by the age of the concrete, permeability, temperature, pH value and contact time with the leachate. Krol [9] paid also special attention to the chromium leaching from the concrete composites and studying its mechanisms. Even though, various leaching tests are used in different countries, e.g. Toxicity Characteristic Leaching Procedure (TCLP) in the USA [10], single-stage batch leaching procedure to waste leaching characterisation in EU [11-14] or Dutch tank test NEN 7375 [15], the main attention is focused only on the leaching of waste itself. There is a lack of systematic knowledge and a valid method for predicting the emissions from cement-based building materials with incorporated waste into the environment. The European standard [16] dealing with a study of the characteristic leaching behaviour of hardened concrete for use in the natural environment partially suits for the purposes of assessing the potential risk of concrete materials. The test procedure must be developed as a characteristic test designed to determine the leachability of new building products.

The paper focuses on examination the leachability of selected heavy metals from cement composites with incorporated waste materials by long-term and cyclic tests. The relationships between conductivity, pH and heavy metal concentration in leachates are studied and the leachability of heavy metals and the resistance of analysed cement composites exposed to several media are compared.

2 Material and Methods

2.1 Concrete materials

The following materials were used to prepare samples of cement composites for the experimental study of heavy metal leachability: Portland cement CEM I 42.5N (Považská cementáreň, a.s., Ladce); hybrid cement based on by-products and waste, (Považská cementáreň, a.s., Ladce); an admixture based on finely ground granulated blast furnace slag (Považská cementáreň, a.s., Ladce) serving as a substitute for a part of Portland cement. A total of 6 formulations were proposed for the experimental study of the leachability of heavy metals from cement composites, of which reference formulation without the addition of additives. The concrete samples with blast furnace granulated slag were marked B1 (65 wt.% of slag); B2 (75 wt.% of slag); B3 (85 wt.% of slag); and B4 (95 wt.% of slag). The reference sample B0 did not contain any slag substitution and the H sample represented concrete with 100% of hybrid cement based on the various mineral waste. The manufactured concrete samples were cut to smaller dimensions of 40 × 40 × 20 mm and these samples were subsequently used for the testing of their leaching performance. Two samples of each formula were tested in the leaching experiments.

2.2 Leaching procedures

Two types of leaching tests, based on the [16], were configured: long-term tank tests under static conditions, and cyclic immersion tests. Different environments were chosen for individual types of tests (long-term and cyclic experiments), since according to literary it was proven that the deterioration of concrete samples is accelerated by alternating between wetting and drying within the cyclic tests. So the aim of the work was not to compare the resistance of samples tested according to the individual type of tests, but the resistance of concrete samples with waste and secondary materials to the particular medium and each other. Prior to the experiment itself, all concrete samples were dried in a laboratory oven at 105 ° C to constant weight.

2.2.1 Long-term tank tests

Long-term tests were performed for a period of 500 days. Based on the sample weights, the leachate volume was calculated to maintain a sample-to-leachate ratio of 1:10. The samples were immersed into liquid media to glass containers with a volume of 720 mL. A pre-calculated volume of the extracting liquid medium was poured into these vessels and then a sample was placed in them. The glass containers were covered with aluminium foil throughout the experiment to prevent evaporation and also the ingress of impurities. The extracting media were not renewed during the experiment, thus the experimental procedure represented static conditions and a steady state of concrete materials.

Three different extracting media were modelled in the study: distilled water (DW) with pH = 7.08 and conductivity of 2.71 $\mu S.cm^{-1}$; natural rainwater (RW) of pH = 6.54 (conductivity C = 99.3 $\mu S.cm^{-1}$); and Britton-Robison solution (BRS) with concentration 0.04M H_3BO_3 + 0.04M CH_3COOH + 0.04M H_3PO_4 (pH = 2.16; C = 2850 $\mu S.cm^{-1}$).

At the indicated intervals (30, 240, 300, and 500 days), the pH and also the conductivity have been measured by Mettler Toledo equipment. At the end of the experiment, liquid media were analysed to determine the concentrations of selected heavy metals by absorption atomic spectrometry (AAS) using equipment SpectrAA-30 (Varian).

2.2.2 Cyclic tests

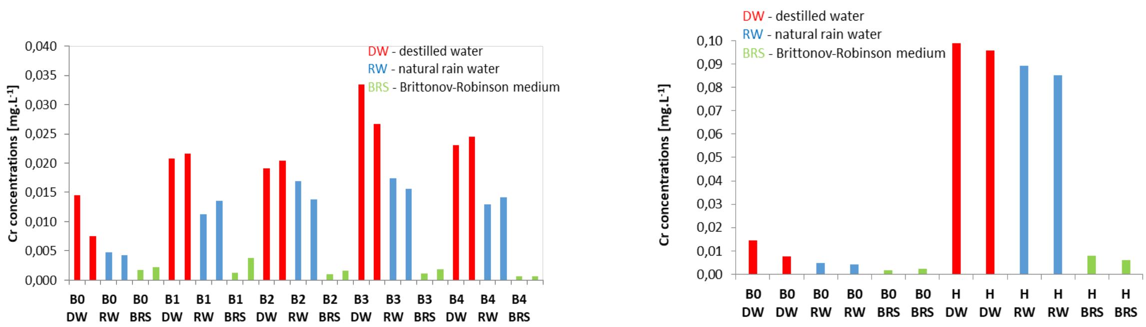
The concrete samples of the same composition as in the long-term experiments were subjected to a 7-day experimental cycle: they were first immersed in a solution simulating acid rain (H_2SO_4 + HNO_3 solution, pH = 3.5, C = 97.0 μS.cm^{-1}) for five days and then naturally dried at room temperature for two days. The samples were tested in this way for five consecutive cycles. The experiments were performed at room temperature (approximately 24 ± 1 °C). The constant pH of 3.5 was kept in the liquid media during the experiment. At the beginning of each experiment, the pH of the extracts was monitored once an hour and adjusted to the initial values every day with a 6 M solution of HNO_3 using a pH meter (Toledo Mettler). The conductivity of solutions and the concentrations of selected heavy metals was analysed by spectrometric analysis on DR 2800 (Hach Lange, Germany).

3 Results and discussion

3.1 Long-term tests

3.1.1 Concentrations of heavy metals due to long-term exposition

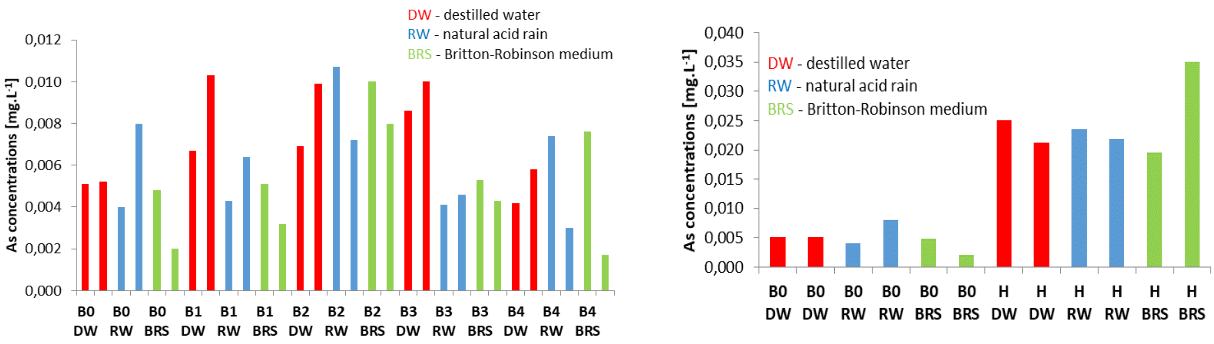
The concentrations of the measured extracted heavy metals in the individual extraction media after the 500-day leaching interval are presented in Figures 1-5.



a) b)

Figure 1: Leached-out amounts of chromium per individual concrete samples a) with granulated slag; b) with hybrid cement

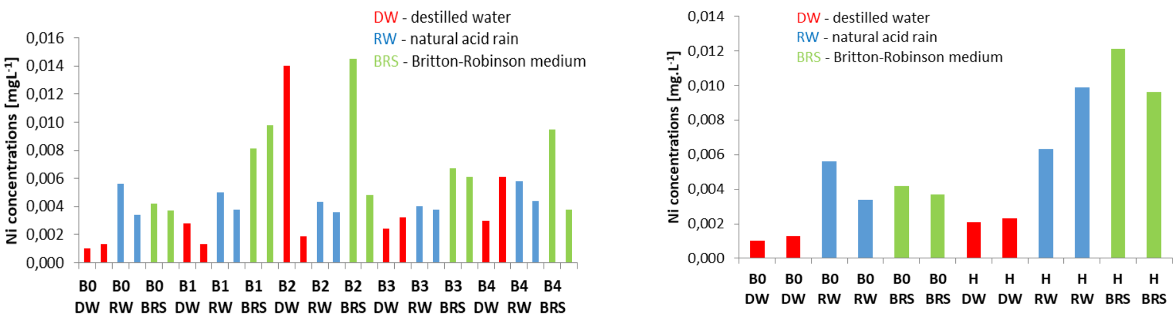
As can be seen in Figure 1, the concentrations of chromium ions extracted from slag-based and hybrid cement-based concrete samples immersed in distilled water are up to 8.8-fold higher than for reference samples in the same leachate; in rainwater 17.4 times higher than the reference samples in the same leachate; in Britton-Robinson solution 3.5-fold higher than the reference samples in the same leachate. From the point of view of the aggressiveness of the leachate, distilled water appears to be the strongest leachate, rainwater to be the weaker leachate and the Britton-Robinson solution to appear to be the weakest leachate. This seems surprising at first sight, as distilled water had the highest pH and several authors report a significant effect of pH on metal leaching [6]. This is true, but primarily when comparing solutions of the same composition but with different acidity [17]. In our case the more important role likely played the quantity of the already presented ions in extraction media and stated equilibrium in ion concentrations. When comparing the conductivity of the extraction media, the values increased in order DW < RW < BRS. This could partially explain the worse leachability of solid chromium-based compounds from the concretes in the more acidic media. Another reason for the lower concentrations of chromium in the more acidic solutions could be based on the observation, that chromium was initially leached from the samples into Britton-Robinson solution was subsequently incorporated into the precipitates formed on the surface of the samples. The highest chromium leached-out quantities have been observed for the H samples followed by B3 samples.



a) b)

Figure 2: Leached-out amounts of arsenic per individual concrete samples a) with granulated slag; b) with hybrid cement

As can be seen in Figure 2, a larger amount of arsenic ions was leached from the concrete samples with ground slag as a substitute for the Portland cement than from the reference samples. The leachability of arsenic ions from samples with hybrid cement was approximately five times higher than from reference samples.

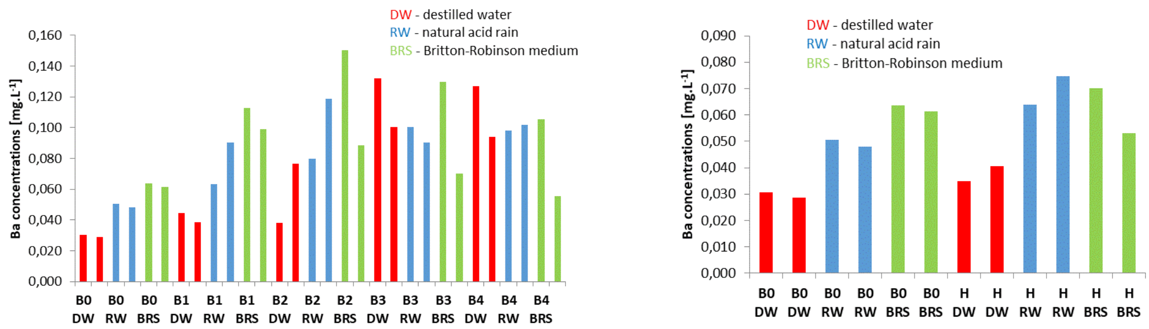


a) b)

Figure 3: Leached-out amounts of nickel per individual concrete samples a) with granulated

slag; b) with hybrid cement

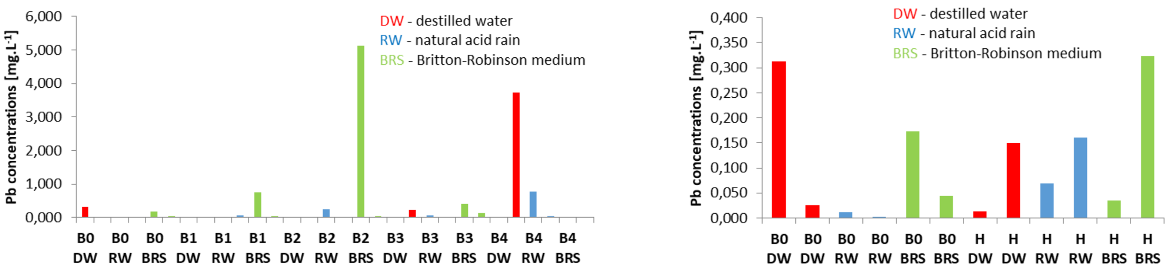
The lowest leachability of nickel ions was observed in the reference samples (Figure 3), the largest in B2 samples with 75% slag addition. When comparing the leachability of nickel ions from slag-based samples and hybrid cement-samples (Figure 3) separately in individual environments, it is clear that from the samples with hybrid cement, a larger amount of nickel ions was leached in each case.



a) b)

Figure 4: Leached-out amounts of barium per individual concrete samples a) with granulated slag; b) with hybrid cement

From the point of view of leachability of barium, the reference sample was again the most resistant and, conversely, the samples with the slag were the least resistant (Figure 4). It should be noted that the barium ions dissolved in the leachate react very rapidly even with a minimal amount of sulphate ions leached from the cement matrix, forming a precipitate of almost insoluble barium sulphate. The concentrations of barium ions in the extracts from the hybrid cement samples are only slightly higher compared to the concentrations of the reference samples (Figure 4).



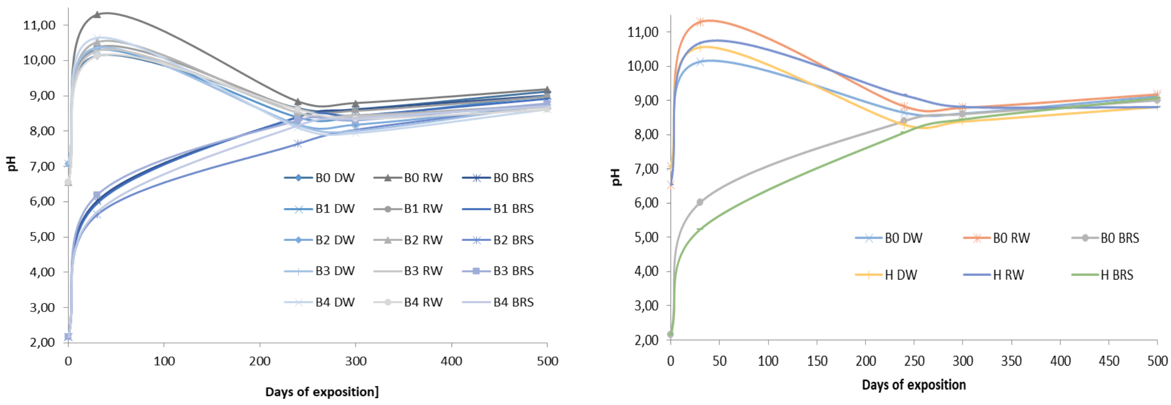
a) b)

Figure 5: Leached-out amounts of lead per individual concrete samples a) with granulated slag; b) with hybrid cement

When evaluating the results of measuring the concentrations of lead ions in extracts from reference samples, samples with slag and hybrid cement (Figure 5), no dependence on the composition of the samples or the environment was observed. In the case of sample B2 in Britton-Robinson solution, a value of 5.118 $mg.L^{-1}$ was measured, while according to the American method "EPA Test Method 1311 - TCLP, Toxicity Characteristic Leaching Procedure" the limit value for lead content is 5 $mg.L^{-1}$ and exceeding this value is considered waste as hazardous.

3.1.2 pH changes in liquid media

At the beginning of the experiment, the pH of distilled water (7.08) was measured before immersing the samples in various leachers; rainwater (6.54) and Britton-Robinson solution (2.16). The most significant increase in pH values was recorded within 30 days from the beginning of the experiment, which was caused by the leaching of hydroxide ions from the matrix into the leachate (Figure 6). After 240 days, the dispersion of pH values narrowed from 7.65 for sample B2 in Britton-Robinson solution to 8.83 for sample B0 in rainwater. After 300 days, the dispersion of the pH values narrowed even further, from 7.95 for sample B4 in distilled water to 8.79 for sample B0 in rainwater. The narrowest variance of pH values was recorded after 500 days, ranging from 8.61 for sample B4 in rainwater to 9.18 for sample B0 in the same medium.



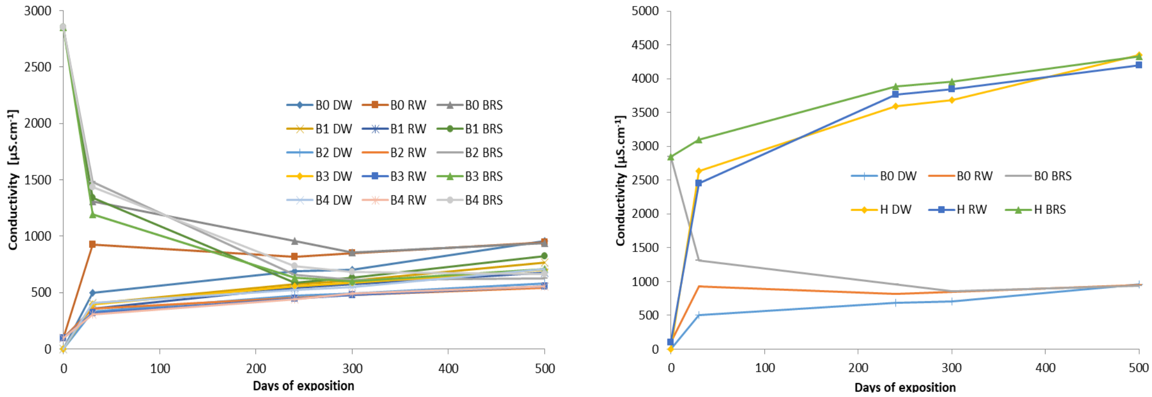
a) b)

Figure 6: Trends in pH in solutions of concrete samples a) with granulated slag; b) with hybrid cement

3.1.3 Changes in conductivity of liquid media

When monitoring the changes in the conductivity of the extracts from the hybrid cement samples compared to the conductivity of the extracts from the reference sample, an enormous difference in the conductivity values was found (Figure 7). The conductivity value of the extract of the H samples in distilled water after 500 days was 4.54 times higher than that of the reference sample in the same medium; the H samples in rainwater 4.43 times higher than the reference sample in the same medium and the H samples in Britton-Robinson solution

4.61 times higher than the reference sample in the same medium.



a) b)

Figure 7: Trends in conductivity of solutions of concrete samples a) with granulated slag; b) with hybrid cement

3.2 Cyclic tests

Chromium leaching was chosen as indicative testing for the analysed concrete samples using the cyclic tests. In the environment simulating acid rain, a significant part of hexavalent chromium Cr(VI) was leached already in the first days of the experiment, as can be seen in Figure 8.

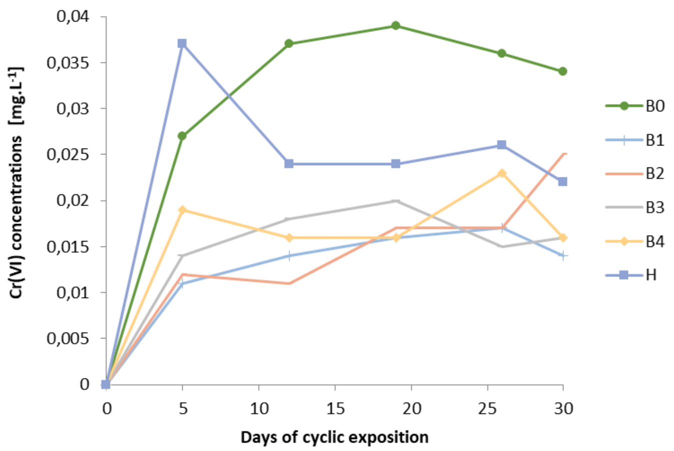


Figure 8: Leached amounts of hexavalent chromium in the cyclic experiment from concrete samples with granulated slag (B1-B4) and with hybrid cement (H)

The least resistant sample for Cr(VI) leaching was the B0 sample. The course of the curve of the sample with hybrid cement was different in comparison with the course of the other curves, while after five days the concentration of Cr(VI) reached the highest value among all samples. The lowest values of Cr(VI) concentrations were reached by the extract from the B1 sample with the lowest slag content. The leachability coefficients LC [μg.h^{-1}.m^{-2}] in simulated acid rain was calculated per each analysed concrete sample and the comparison of the values of the coefficients is given in Figure 9.

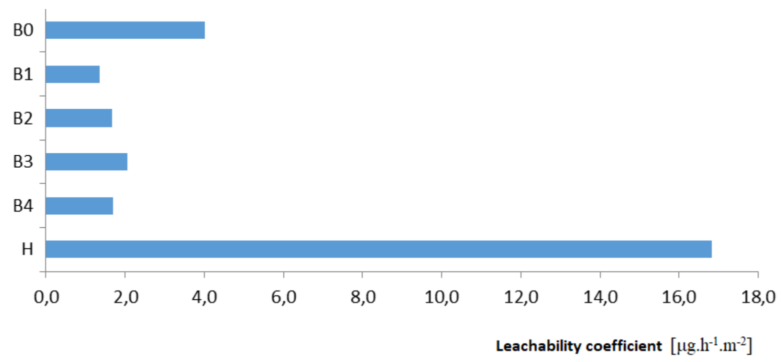


Figure 9: Comparison of the LC per the individual samples

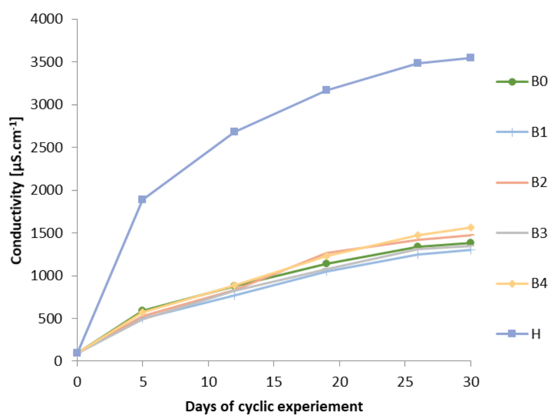


Figure 10: Trends in conductivity of the concrete samples with granulated slag (B1-B4) and hybrid cement (H) in the cyclic experiment

The conductivity of all extracts increased over time. The extracts from the samples with the admixture of blast furnace ground slag had very similar conductivity values and the course of the curves of the conductivity of the extracts from time was also very similar. Significantly different conductivity values were recorded for the hybrid cement sample. This means that more intensive leaching was proven in case of the hybrid cement concrete, probably not connected only to heavy metals leaching but also to the deterioration processes of cement matrix as reported in [18,19].

4 Conclusion

From an experimental study of the leachability of heavy metals from cement composites in various environments, it appears to be the most aggressive environment simulating acid rain, whose e.g. leachability of hexavalent chromium was several times higher than the coefficients

for other environments. Distilled water and natural acid rain appeared to be less aggressive environments. The least aggressive environment appears to be Britton-Robinson's solution, although in fact metals were leached-out in this medium, but precipitated back from the solution in the form of precipitates on the samples´ surfaces.
The concretes with the addition of ground slag were found to be more resistant than the concretes with hybrid cement. However, much more heavy metals were leached in the individual environments from all concretes containing waste and secondary materials than from concretes without waste. Although the concentrations of heavy metals in leachates were often low, it should be borne in mind that the negative impact of heavy metals on human health and the environment is marked even at very low concentrations.

Acknowledgment

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