

# COMPARATIVE STUDY OF PORTLAND CEMENT-BASED AND ZEOLITE-BASED CONCRETES IN TERMS OF HEXAVALENT CHROMIUM LEACHING

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## Abstract

The paper presents the results of the leaching study of Portland cement-based and zeolite-based concretes regarding water soluble hexavalent chromium. Three leaching water media (distilled water, rain water, and Britton-Robinson buffer) of various pH values were under investigation. The correlation between pH and leached-out concentrations of chromium was not confirmed. The content of hexavalent water-soluble chromium in leachates of zeolite-based concretes was found to be higher than that in leachates of Portland cement-based samples.

**Key words:** leaching, heavy metal, chromium, zeolite, cement composite.

## 1 INTRODUCTION

Puzzolans are materials consisting predominantly of reactive  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  and being able to combine with portlandite ( $\text{Ca}(\text{OH})_2$ ), a by-product of cement hydration, to form further gel products. Therefore, they have been widely used as additives in cement, from which portlandite is a major hydration product. Their widespread use can be explained by their beneficial effect on the properties of concrete leading to technical, economic and ecological advantages [1]. It is widely accepted that puzzolans can increase the durability of concrete composites, reduce the heat of hydration, increase the resistance to sulfate attack and reduce the energy cost per cement unit. One of the most widely used types of puzzolans is a natural zeolite [2].

Natural zeolite is abundantly deposited worldwide and can be easily excavated and processed [3]. The utilization of natural zeolite, when used as a partial replacement for cement, can lead to substantial durability, economic and ecological benefits [4].

Cement-based materials play an important role in the immobilization of heavy metals. They can be used as immobilizing agents, forming a matrix incorporating the heavy metals in a physical or chemical way. Hexavalent chromium is one of the most dangerous forms of heavy metals. Skin diseases including irritant and allergic contact dermatitis are common complaints of cement and concrete workers because of strong alkalinity and a high hexavalent chromium concentration in cement products [5].

## 2 MATERIAL AND METHODS

The leaching of hexavalent chromium from cement/zeolite composites was studied in this experiment. The concrete samples containing 0%, 8%, and 13% of zeolite were prepared as a replacement of Portland cement (Table 1). For this experiment, Portland cement CEM I 42.5 N, (Povazske cementarne, Ladce, Slovakia); natural zeolites (Nizny Hrabovec, Slovakia); and aggregates of fractions 0/4mm, 4/8mm, 8/16mm from local sources (Geca, Slovakia) have been used.

**Tab. 1 Mixtures for 1 m<sup>3</sup> of concrete samples.**

|                            | Unit | Recipe        |               |                |
|----------------------------|------|---------------|---------------|----------------|
|                            |      | 0% of zeolite | 8% of zeolite | 13% of zeolite |
| Sample                     |      | 1, 2, 3       | 4, 5, 6       | 7, 8, 9        |
| CEM I 42.5 N               | kg   | 360           | 331           | 313            |
| Zeolite                    | kg   | 0             | 29            | 47             |
| Water                      | L    | 162           |               |                |
| Aggregates fraction 0/4mm  | kg   | 825           |               |                |
| Aggregates fraction 4/8mm  | kg   | 235           |               |                |
| Aggregates fraction 8/16mm | kg   | 740           |               |                |

The concrete samples prepared by a standard procedure were cured in water during 28 days, then were cut into smaller specimens (with dimensions of 5 cm × 5 cm × 1 cm), dried and weighed to the constant weight. Consequently, the concrete samples were placed into three different leachants for short-term test leaching. The specification of the leachants and the marking of the samples are given in Table 2.

**Tab. 2 Characterisation of the used leachants.**

| Leachant                | Input pH | Input conductivity (μS/cm) | Samples No. |
|-------------------------|----------|----------------------------|-------------|
| Distilled water         | 6.54     | 1.30                       | 1, 4, 7     |
| Rain water              | 6.24     | 11.27                      | 2, 5, 8     |
| Britton-Robinson buffer | 2.01     | 3930                       | 3, 6, 9     |

Leaching is the process by which a liquid dissolves and removes the soluble components of a material. 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. In this study, a basic characterization tank test according to CEN/TR 16142 was used [6]. The concrete samples were placed into tanks filled with liquid media and the specimens were immersed to a depth of at least 2 cm to ensure the permanent contact with the water leachant. The short-term leaching of the tested concrete samples proceeded over a period of 30 days under laboratory temperature of 20 °C. The Britton-Robinson buffer consisting of a mixture of boric acid ( $\text{H}_3\text{BO}_3$ , 0.04 mol/dm<sup>3</sup>), phosphoric acid ( $\text{H}_3\text{PO}_4$ , 0.04 mol/dm<sup>3</sup>), and acetic acid ( $\text{CH}_3\text{COOH}$ , 0.04 mol/dm<sup>3</sup>) was used according to [7] to simulate the natural environment. The original pH of the Britton-Robinson buffer was measured as 2.01.

The concentrations of hexavalent chromium in the leachates were measured by using a colorimetric analyzer DR 2800 (Hach Lange, Germany). The 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 conductivity and pH of the leachant were measured at the beginning and after 30 days of the experiment. In this experiment, the laboratory equipment for conductivity measurement Multimeter X-matePro MX300 (METTLER TOLEDO) and a FG2 FiveGo™ pH meter (METTLER TOLEDO) were used.

### 3 RESULTS AND DISCUSSION

The measured hexavalent chromium concentrations in the leachates after 30 days of the experiment as well as the final pH and final conductivity are given in Table 3.

**Tab. 3 Concentration of hexavalent chromium, pH, and conductivity of leachants after concrete's short-term leaching.**

| Sample | Medium                  | Input pH | Final pH | Input conductivity [μS/cm] | Final conductivity [μS/cm] | Cr(VI) concentrations after 30 days [mg/L] |
|--------|-------------------------|----------|----------|----------------------------|----------------------------|--|
| 1      | Distilled water         | 6.54     | 9.38     | 1.3                        | 210                        | 0.019                                      |
| 4      |                         |          | 9.35     |                            | 172                        | 0.022                                      |
| 7      |                         |          | 9.37     |                            | 183                        | 0.030                                      |
| 2      | Rain water              | 6.24     | 9.12     | 11.3                       | 235                        | 0.018                                      |
| 5      |                         |          | 9.93     |                            | 198                        | 0.022                                      |
| 8      |                         |          | 9.08     |                            | 203                        | 0.030                                      |
| 3      | Britton-Robinson buffer | 2.01     | 5.44     | 3930                       | 1361                       | 0.008                                      |
| 6      |                         |          | 4.62     |                            | 1108                       | 0.010                                      |
| 9      |                         |          | 4.97     |                            | 1272                       | 0.012                                      |

An increase in conductivity values of two leachants – distilled and rain water has been observed after the experiment. This was caused by the dissolving and dissociation of the cement matrix components in the water environment. Comparable values of conductivities have been measured for particular concrete composites in distilled and rain water after the 30-day leaching as seen in Table 3. On the contrary, a decrease in conductivity

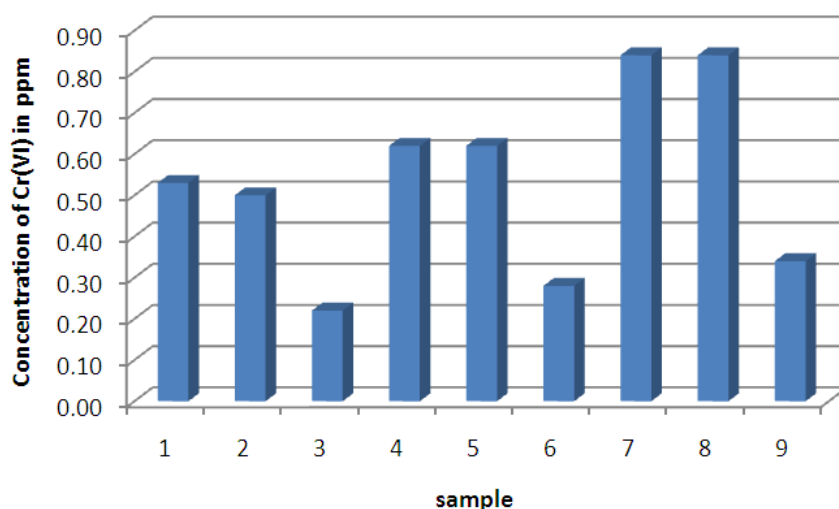
was measured for the Britton-Robinson buffer, which was likely linked to the neutralisation reaction of acids in the solution with the alkali compounds from the cement matrix. In spite of this fact, the final conductivity values measured in the Britton-Robinson buffer after the short-term leaching were still higher than those measured in water. The decreased but still high final values of conductivity in the Britton-Robinson buffer were caused by very high input conductivities. The high input conductivity of the Britton-Robinson solution originated from the very high amount of dissociated ions since the Britton-Robinson buffer was prepared by mixing three acids: phosphoric, acetic, and boric. These acids are known as weak electrolytes, however, are slightly dissociated into hydrogen cations and anions in a water solution. The dissociation of acids was confirmed by the high concentration of hydrogen cations  $\text{cH}_3\text{O}^+ = 0.02 \text{ mol/L}$  measured through pH. As already mentioned, the original pH of the Britton-Robinson solution was measured as 2.01.

The pH value of the leachates of all samples has been increased while for the samples in distilled and rain water has been moved to the alkali region up to the values of 9.93. The final pH of the leachates of samples in the Britton-Robinson buffer varied from 4.62 to 5.44. Regarding the pH and conductivity values, distilled water and rain water are leachants with very similar properties.

When comparing the leached-out concentrations of hexavalent chromium from the cement composites as given in Table 3, we can conclude that the concrete composites without zeolite addition leach less chromium than the composite with zeolite. Moreover, the higher mass of leached-out hexavalent chromium was observed with an increasing content of zeolite in the samples. This trend was found out in each leachant: distilled water, rain water, and Britton-Robinson buffer, respectively.

According to [8], the lower the original pH of medium is, the higher the hexavalent chromium concentration should be detected. Despite the low pH value of the Britton-Robinson buffer (2.01), a low level of leached hexavalent chromium was observed; even lower than that in water solutions. This phenomenon was probably caused due to the high concentration of dissociated ions in the Britton-Robinson buffer, which inhibited the possibility of heavy metal leaching [9, 10]. Thus the correlation between pH and leached-out concentrations was not confirmed.

The concentrations of leached-out hexavalent chromium ions calculated to 1 kg of binder (ppm) are illustrated and compared for the particular concrete samples in Figure 1.



**Fig. 1 Comparison of dissolved masses of hexavalent chromium from analysed concrete samples expressed per 1 kg of binder.**

As seen in Figure 1, the highest leached-out masses have been measured for the concrete composites containing 13 % of zeolite following by the composites with 8 % of zeolite.

#### 4 CONCLUSION

In this experiment, the reference concrete sample and two concrete samples with zeolite as replacements of part of Portland cement were analysed. The content of hexavalent chromium ions in the leachates of the samples with zeolite was higher than that in the leachates of the reference samples without zeolite. In fact, the higher leachability of hexavalent chromium was caused by the porous structure of zeolite incorporated in the concrete. Lower concentrations of hexavalent chromium ions were observed in Britton-Robinson buffer leachates (despite a low value of pH) due to a high value of conductivity. Distilled water and rain water were more aggressive than the Britton-Robinson buffer.

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## REFERENCES

- [1] KARAKURT C., TOPÇU İ. B. Effect of blended cements with natural zeolite and industrial by-products on rebar corrosion and high temperature resistance of concrete. *Construction and Building Materials*. 2012, **35**, 906-911.
- [2] NAJIMI M., SOBHANI J., AHMADI B., SHEKARCHI M. An experimental study on durability properties of concrete containing zeolite as a highly reactive natural pozzolan. *Construction and Building Material*. 2012, **35**, 1023-1033.
- [3] HASANBEIGI A., PRICE L., LIN E. Emerging energy-efficiency and CO<sub>2</sub> emission-reduction technologies for cement and concrete production: A technical review. *Renewable and Sustainable Energy Reviews*. 2012, **16**(8), 6220-6238.
- [4] AHMADI B., SHEKARCHI M. Use of natural zeolite as a supplementary cementitious material. *Cement and Concrete Composite*. 2010, **32**(2), 134-141.
- [5] CHEN C.-J., et al. The total body burden of chromium associated with skin disease and smoking among cement workers. *Science of the Total Environment*. 2008, **391**(1), 76-81.
- [6] EUR 17869 EN. Development of a leaching method for the determination of the environmental quality of concrete. Luxembourg, 1997.
- [7] BRITTON H.T., ROBINSON R.A. Universal buffer solutions and the dissociation constant of veronal. *Journal of Chemical Societ*. 1936, 1456-1462.
- [8] KOMONWEERAKET K., CETIN B., AYDILEK A.H., BENSON C.H., EDIL T.B. (2015). Effects of pH on the leaching mechanisms of elements from fly ash mixed soils. *Fuel*, **140**, 788-802.
- [9] GWENZI W., MUPATSI N.M. Evaluation of heavy metal leaching from coal ash-versus conventional concrete monoliths and debris. *Waste Management*. 2016, **49**, 114-123.
- [10] TIWARI M.K., BAJPAI S., DEWANGAN U.K., TAMRAKAR R.K. Suitability of leaching test methods for fly ash and slag: A review. *Journal of Radiation Research and Applied Sciences*. 2015, **8**(4), 523-537.