HEXAVALENT CHROMIUM LEACHING FROM CEMENTS AND CEMENT COMPOSITES

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ABSTRACT

Chromium is one of the 25 most widespread elements in the Earth’s crust and occurs as an indelible non-volatile trace element in raw materials used in cement clinker production (clay, limestone and iron additives in particular). Chromium in raw materials mentioned above is mainly in form of trivalent chromium. Naturally occurring chromium (III) is not initially harmful, since it is chemically stable. Only at high temperatures found in cement rotary kilns, inert trivalent chromium oxidizes to form more dangerous hexavalent chromium.

The paper presents the results of the experimental investigation of the hexavalent chromium releasing from cement samples and cement composites to the water environment under various conditions. The samples of Portland cement as well as the cement composites with different composition were used for the experiments. The chemical composition of cement samples and cement composites were determined by using X-ray fluorescence analysis (XRF); the soluble hexavalent chromium concentrations in cement leachates and cement composites leachates were analysed by colorimetric analysis. The determination of chromium (VI) by spectrometry was based on the reaction of hexavalent chromium with diphenylcarbazide by forming the purple coloured compound.

The content of water soluble chromium was measured to be lower in cement composites leachates than in cement leachates. The soluble hexavalent chromium concentrations in cement composites were measured from 0.13 to 0.22 mg/kg and 0.07 to 0.15 mg/kg, when studied powdered and compact cement composites leachates, respectively. The concentration of Cr (VI) in cement leachates reached the average value of 2.85 mg/kg.

Keywords: chromium, leaching, cement, building materials

1. INTRODUCTION

Cement significantly affects the environment not only during its production, but also in the process of its consumption causing a negative impact on both the environment and human health (Winter, 2009). Heavy metals belong to the most significant hazardous elements presented in cement and cement compounds. These toxic elements originate mainly from the raw materials, but also from refractory bricks lining the kiln, mineral admixtures or the grinding media (normally high-chromium white cast iron) in the final finishing mills (Reference Document on Best Available Techniques in the Cement, Lime and Magnesium Oxide Manufacturing Industries, 2010).

Chromium is an indelible trace element of raw materials used in cement clinker production. It occurs in natural materials (clay, limestone and iron additives in particular) in the form of chromium (III) (Frias, 2002). Trivalent chromium is modified to hexavalent chromium at high temperature in an oxidizing atmosphere and alkaline conditions in cement kilns. This form of chromium in cement is harmful and allergenic and it has very
high water solubility and thus can easily come into contact with the skin masons (Potgieter, 2003). The paper is aimed at the study of hexavalent chromium releasing from cements as well as cement composites into the water environment.

2. MATERIAL AND METHODS

The content of water soluble hexavalent chromium was measured in most often used cement type CEM I (Portland cement) containing only clinker and no other single constituents as well as in 3 types of cement composites made from this cement.

2.1. Samples preparation and characterisation

The CEM I 42.5N Portland cement samples were used for the experiment without any modification. Three types of cement composites (1 – 3) were prepared in accordance to the Slovak standard STN EN 206-1 – C35/45. The recipes for 1 m³ of cement composites prepared are presented in Table 1.

<table>
<thead>
<tr>
<th>Cement composite</th>
<th>Materials</th>
<th>Aggregate (kg)</th>
<th>Plasticizer (l)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CEM (kg)</td>
<td>water (l)</td>
<td>0/4 mm</td>
</tr>
<tr>
<td>1</td>
<td>360</td>
<td>170</td>
<td>–</td>
</tr>
<tr>
<td>2</td>
<td>360</td>
<td>197</td>
<td>20</td>
</tr>
<tr>
<td>3</td>
<td>360</td>
<td>198</td>
<td>–</td>
</tr>
</tbody>
</table>

The cement composites samples prepared were treated during 28 days in water environment. After hardening, the part of cement composites was crushed and powdered by using MSK-SFM-1 Desk-Top planetary ball miller (MTI Corporation, USA) and investigated in terms of the chemical composition using X-ray fluorescence spectrometry. The cement composites samples for XRF analysis were prepared as pressed tablets (pellets) of diameter 32 mm by mixing of 5 g of sample and 1 g of dilution material (M-HWC) and pressed by pressure of 0.1 MPa/m². The cement samples for XRF analysis have been prepared the same way.

The chemical composition of samples was determined by using XRF 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 25 and 50 kV, at current of 0.5 and 1.0 mA, respectively. The standardised pellet method of fundamental parameters was used for measurements.

2.2. Leaching experiments

The cement composites as well as used cement as a reference material were investigated in terms of water soluble chromium releasing. The Portland cement samples testing proceeded for 500 days during various time of cement ageing. To monitor the content of Cr (VI) during various times the cement material was stored in optimal conditions (constant temperature between 20 - 22 °C, average relative moisture 38 %).

The leachates of Portland cement samples were prepared with accordance to STN EN 196-10 Methods of cement testing (Appendix C). 25 g of sample was mixing with 25 ml of distilled water (Rodem 6) with conductivity of 5.72 μS/cm and pH of 6.81 during 15
minutes at the laboratory temperature. The prepared 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. The trace concentration of soluble hexavalent chromium was measured in leachates by the spectrophotometry. The determination of chromium (VI) was based on the reaction of hexavalent chromium with diphenylcarbazide by forming the purple coloured complex. The concentration of soluble chromium was measured by using the DR 2800 spectrophotometer (Hach Lange, Germany) at 540 nm. The leaching of cement composites was studied in both powdered and compact composite form. The leaching of powdered cement composites was investigated in the same way as the Portland cement samples mentioned above. The leaching experiments of compact cement composites proceeded during 70 day-period. The compact cement composites were deposited into water environment and the concentration of hexavalent chromium in leachates was measured in periodical intervals. The chromium concentrations were stated by using DR 2800 spectrophotometer.

3. RESULTS

The chemical composition of cement used and cement composites samples studied measured by XRF spectroscopy is summarised in Table 2 as percentage of principal oxides.

<table>
<thead>
<tr>
<th>Samples</th>
<th>MgO</th>
<th>Al₂O₃</th>
<th>SiO₂</th>
<th>P₂O₅</th>
<th>SO₃</th>
<th>Cl</th>
<th>K₂O</th>
<th>CaO</th>
<th>TiO₂</th>
<th>MnO</th>
<th>Fe₂O₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>CEM</td>
<td>3.82</td>
<td>4.39</td>
<td>19.6</td>
<td>0.093</td>
<td>3.17</td>
<td>0.012</td>
<td>0.58</td>
<td>58.2</td>
<td>0.21</td>
<td>0.35</td>
<td>3.25</td>
</tr>
<tr>
<td>1</td>
<td>3.04</td>
<td>5.21</td>
<td>30.2</td>
<td>0.096</td>
<td>2.89</td>
<td>0.016</td>
<td>0.77</td>
<td>31.3</td>
<td>0.27</td>
<td>0.38</td>
<td>4.04</td>
</tr>
<tr>
<td>2</td>
<td>2.73</td>
<td>5.39</td>
<td>45.6</td>
<td>0.094</td>
<td>2.72</td>
<td>0.019</td>
<td>0.79</td>
<td>26.2</td>
<td>0.25</td>
<td>0.36</td>
<td>3.75</td>
</tr>
<tr>
<td>3</td>
<td>2.87</td>
<td>4.53</td>
<td>25.9</td>
<td>0.089</td>
<td>2.95</td>
<td>0.016</td>
<td>0.79</td>
<td>31.6</td>
<td>0.26</td>
<td>0.38</td>
<td>3.78</td>
</tr>
</tbody>
</table>

The chemical composition of studied cement composites was similarly to the chemical composition of the assessed Portland cement except for calcium and silicon content. The content of SiO₂ in cement was measured 19.6 %, in cement composites ranged from 25.9 to 45.6 %. The content of SiO₂ in the composites increased as supposed due to the aggregate and silica fume (sample 2) addition. The content of CaO in cement was 58.2 %, in cement composites was in the range 26.2 – 31.6 %. Differences in composition also depend on the structure of the composites as well as on the processes that take place in composite materials during hardening.

The results of monitoring the water soluble hexavalent chromium content in Portland cement in dependence on time of materials aging are presented in Figure 1 as average chromium concentrations.
The water soluble hexavalent chromium concentrations in Portland cement samples ranged from 2.34 to 3.19 mg/kg with average value of 2.85 mg/kg during 500 day-monitoring. Authors in (Yamaguchi, 2006 and Potgieter, 2003) referred that between 30 and 90 % of the total chromium in cement clinkers are Cr (VI) compounds and 8 – 26 % of the total amount of Cr (VI) species is water soluble. In spite of the fact, the highest chromium concentrations were measured for fresh Portland cement from the production, no significant effect of time dependence on the content of Cr (VI) in cements has been demonstrated by the experimental study. The concentrations of hexavalent chromium measured in powder samples of cement composites compared to the average concentration measured in Portland cements samples are illustrated in Figure 2.

Figure 1. The chromium (VI) content in cement depending on time of materials aging.

Figure 2. Comparison of the measured water-soluble content of chromium (VI) in the cement and cement composites.

The content of water soluble chromium was measured to be lower in cement composites leachates than in cement leachates. The concentration of Cr (VI) in cement reached the average value of 2.85 mg/kg. The concentrations in cement composites samples were in
the range 0.13 – 0.22 mg/kg, what representing 4.5 – 7.5 % of water soluble chromium content when comparing to the cement samples. 

The concentrations of soluble hexavalent chromium released into water environment from compact cement composites immersed in water environment were measured in range 0.06 – 0.07, 0.12 – 0.16 and 0.13 – 0.17 mg/kg for samples 1, 2 and 3, respectively. The comparison of Cr (VI) concentrations is shown in Figure 3.

![Figure 3](image1.png)

**Figure 3.** The chromium (VI) content in cement composites depending on time of immersion in water environment.

The lowest concentrations of hexavalent water soluble chromium were measured in leachates of cement composite sample 1, the concentrations of chromium in leachates of samples 2 and 3 reached very similar values.

The average concentrations of chromium leached from cement composites immersed in water environment in compact state were compared with the average concentrations of chromium from cement composites in powder form (Figure 4).

![Figure 4](image2.png)

**Figure 4.** Comparison of chromium (VI) content in cement composites in compact state and powder form.
The average chromium concentrations in leachates from cement composites immersed in water environment in compact state varied from 0.07 to 0.15 mg/kg; the average chromium concentrations in leachates from cement composites in powder form ranged from 0.13 to 0.22 mg/kg. The content of chromium was measured to be lower in compact cement composites leachates than in powdered cement composites leachates as assumed.

4. CONCLUSIONS

The concentration of water soluble hexavalent chromium was measured in cement type CEM I – Portland cement and in 3 types of cement composites made from this cement.

- The content of water soluble chromium was measured to be lower in cement composites leachates than in cement leachates.
- Measured concentrations of water soluble chromium for powdered cement composites represented 4.5– 7.5 % of water soluble chromium content comparing to the cements. The chromium concentrations for compact cement composites reached 2.46 to 5.26 % in comparison to the cement samples.
- The releasing of the soluble chromium was found to be higher in case of powdered cement composites than in case of the compact state cement composites.
- Experimental evaluation of the content of Cr (VI) in cement in relation to the time has not showed a significant effect of storage time of the cement on the content of Cr (VI).

ACKNOWLEDGEMENTS

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REFERENCES