LEACHING BEHAVIOR OF CEMENT-BASED SOLIDIFIED WASTES CONTAINING HEXAVALENT CHROMIUM

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În cadrul lucrării s-a studiat comportarea la levigare a matricilor de ciment cu conținut de crom hexavalent utilizând ca soluție de levigare apa distilată. Pentru determinarea fracției de contaminant eliberat în funcție de timpul de levigare şi raportul apă-ciment au fost efectuate teste de levigare în regim dinamic. Rezultatele obținute au arătat că levigabilitatea cromului scade odată cu creşterea raportului apă-ciment. Indicii de levigabilitate ai cromului hexavalent au fost calculați pe baza unui model de levigare pentru toate condițiile de lucru. Valorile acestora sunt mult mai mari decât valoarea standard arătând mobilitatea redusă a cromului hexavalent în matrici.

Characterization of the leaching behavior of doped cement specimens with hexavalent chromium in distilled water used as leachant was investigated. Dynamic leaching tests on monolithic specimens were carried out to determine the fraction of contaminant release as a function of leaching period and water-to-cement ratio. The results have showed a decreasing of chromium leachability with increasing of water-to-cement ratio. Using a simple leach model, the leachability indexes of hexavalent chromium for all situations were calculated. All the leachability indexes of the cement specimens far exceeded the standard value showing that the hexavalent chromium in the samples has a low mobility.

Keywords: cement specimen, chromium, leachability index, waste

1. Introduction

Cement–based stabilization/solidification (s/s) technologies are widely applied to inorganic hazardous waste containing heavy metals, usually with excellent results for long-term immobilization [1 – 4]. These typically involve the mixing of a waste with a hydraulic binder to reduce the contaminant mobility by

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both physical and chemical mechanisms and to convert the hazardous waste into an environmentally acceptable waste form, which goes to a landfill or is used as building elements [5].

For insuring environmentally safe recycling or disposed of waste form, the potential impact on the environment is typically assessed and predicted by conducting leaching tests [6]. Prediction of long-term leaching behavior of contaminants in the environment can be accomplished by using predictive mathematical models such as mechanistic and empirical leach models. They can help identify leaching mechanism and can provide methods for correlating leach data [7 – 10].

Previous authors addressed a series of aspects concerning the leaching behavior of heavy metals from different type of cement specimens. Based on experimental results of the monolith leach tests conducted by Kosson and coworkers onto a waste consisting of combined municipal waste combustion residues that had treated with Portland cement, Kim and Batchelor used an empirical partitioning leach model, called EPLEM, to simulate the leaching behavior of a series of heavy metals including total chromium. They found a good correlation between the values of leachability indexes for all selected heavy metals calculated from experimental data and the values derived from simulation (experiment LI_{Cr}=12.1; simulation LI_{Cr}=11.9 – precipitation like; simulation LI_{Cr}=12.01 – sorption like). The mechanism assumed to describe immobilization (sorption or precipitation) made little difference in leaching rates simulated by the model [11, 12].

The objective of this paper is to establish based on experimental results, if the water-to-cement ratio used in preparation of cement specimens is one of the factors affecting the leaching behavior of hexavalent chromium from cement specimens. Results of dynamic leaching tests were used to calculate the release flux and leachability indexes of chromium for all experimental conditions.

The Fickian diffusion model is used for the interpretation of the dynamic leaching test results. The assumptions of the model are as follows: the initial concentration of the species of interest is uniformly distributed throughout the homogeneous porous monolith and zero surface concentration of the species of interest at solid-liquid interface (sufficient water renewal; infinite bath assumption). For a one-dimensional geometry, an analytical solution for Fickian diffusion is:

$$M^{t}_{area} = 2 \cdot \rho \cdot C_0 \left(\frac{D_{obs} \cdot t}{\pi} \right)^{1/2} \quad (1)$$

where M^t_{area} is the cumulative mass of the constituent release (surface area bases) at time t, mg/m^2; C_0 is the initial leachable content (available or total elemental content), mg/kg; ρ is the sample density, kg/m^3; t is the time interval, s; D_{obs} is the observed diffusivity of the species of concern, m^2/s.

Under the assumptions of the Fickian diffusion model, an observed diffusivity can be determined for each leaching interval where the slope is 0.5±0.15 [13].

$$D_{obs}^{i} = \pi \left(\frac{M_{area}^{t_i}}{2 \cdot \rho \cdot C_0 \left(\sqrt{t_i} - \sqrt{t_{i-1}} \right)} \right)^2 \quad (2)$$

where D^i_{obs} is the observed diffusivity of the species of concern for leaching interval „i”, m^2/s; M^{ti}_{area} is the mass release (surface area bases) during leaching interval „i”, mg/m^2; t_i is the contact time after leaching interval „i”, s; t_{i-1} is the contact time after leaching interval „i-1”, s.

2. Experimental

Sample preparation

Samples were prepared from CEM I 42.5 R cement, supplied and characterized by CEPROCIM, Bucharest, Romania (institute for research, technological development and consulting in inorganic binders industry), with the chemical composition reported in Table 1. The synthetic waste consisting of solution containing chromium was used in the experiments. Batches of cement were mixed with sodium chromate (Na_2CrO_4) solution with metal concentration of 1 g/L at sodium chromate solution-to-cement ratios of 0.4, 0.7 and 1. In the following description we will refer as water-to-cement ratios (w/c). The samples were mixed until a homogeneous state by hand under laboratory atmosphere, cast in 2.2 cm × 2.2 cm polypropylene cylindrical molds and cured in moist-saturated environment at room temperature for 28 days.

Table 1.

Chemical composition of CEM I 42.5 R cement

Oxide	CaO	SiO_2	Al_2O_3	Fe_2O_3	K_2O	Na_2O	SO_3	MgO	TiO_2	LOI*	IR**
***Mass (%)	62.86	19.45	6.03	3.64	0.85	0.31	2.71	1.36	0.26	2.11	0.17

Blaine surface: 3500 cm^2/g
*Loss on ignition
**Insoluble residue
***Analyses by CEPROCIM, Bucharest, Romania

Leaching experiment

Dynamic leaching tests were carried out on monolithic samples to determine the cumulative release of species of interest as a function of leaching time and water-to-cement ratio. Monolithic cylindrical samples of 2.2 cm × 2.2 cm were immersed in distilled water without agitation. A liquid-to-solid ratio of 2 mL per each square centimeter of exposed surface aria was used in accordance with the infinite bath assumption. The leaching solution was refreshed with an equal volume of distilled water after 1, 2, 4, 8, 16 and 32 cumulated contact days (2^N progression). At the end of each leaching interval the leachates were filtered and analyzed for chromium by UV-Visible Cintra Model 5 spectrometer.

3. Results and Discussion

The cumulative fractions of Cr^{6+} released as a function of leaching time for each water-to-cement ratios used are shown in Fig. 1. The cumulative fraction of metal leached decreases as the water-to-cement ratio increases. The results suggest the presence of a chemical factor like sorption that effects the chromium leaching.

Generally, lower water-to-cement ratios are needed to achieve improved physical immobilization of a species of interest into a cement specimen. This is to be expected, since addition of more water results in a more porous product [14]. If the species of interest does not react in the system then is to be expected an increasing in leaching behavior with increasing of water-to-cement ratio.

The assumption that the chromium does not react is normally not valid. A variety of chemical reactions could result in immobilization of contaminants into a cement specimen by changing their form from a mobile phase to an immobile one. In this case the sorption of chromate ions onto a certain solid phases in cement pastes especially onto calcium-silicate-hydrate (C-S-H), could be the controlling mechanism of immobilization. Increasing w/c ratio increases the hydration rate of cement paste and availability of C-S-H sorption area (the most abundant hydration product). This hypothesis was verified in previous work [15] and is in accordance with the present results.

The logarithm of cumulative fractions of chromium leached were plotted against the logarithm of the leaching time for all water-to-cement ratios in the Figs. 2, 3 and 4 to determine the leaching mechanism of the heavy metal. In all this figures, the solid line represents the cumulative release of chromium based on diffusion leaching model, the solid dots represent the measured cumulative release of chromium and the empty dots represent the calculated cumulative release of chromium.

The measured cumulative release always includes the measured leaching of previous period. This means that any deviations in a period affect the following periods that can make interpretation difficult. The calculated cumulative release determines only the cumulative leaching up to and including period „i” on the basis of the measured leaching in period „i”. These values can be used to assess whether the leaching is determined by diffusion. After plotting the logarithm of the calculated cumulative release against the logarithm of the leaching time, the slope of the relation over the complete interval and/or smaller intervals can be determined. The mechanism of leaching during each interval can be derived from the slope of the data from the respective interval. Under the assumption of the Fickian diffusion model, an observed diffusivity can be determined for each leaching interval where the slope is 0.5±0.15.

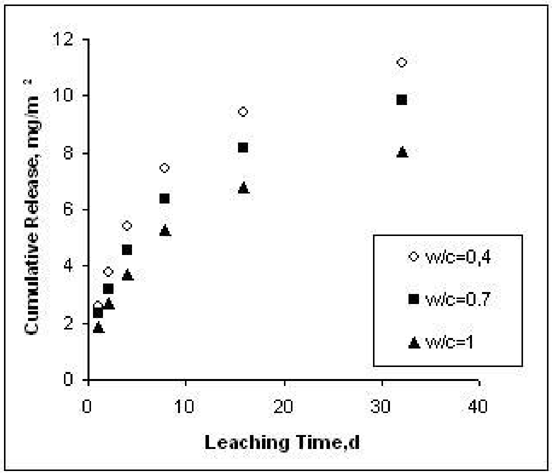

Fig. 1. The cumulative release of Cr^{6+} against of cumulative leaching time

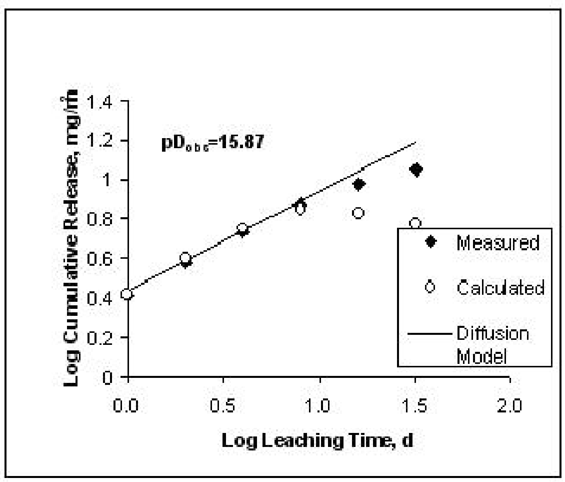

Fig. 2. Log-log plot of cumulative release of Cr^{6+} against cumulative leaching time for w/c = 0.4

As it is shown in Figs. 2, 3 and 4, only the first four data have a linear trend with the slope approximately 0.5. The final two dots are not in linear trend and the slope is negative. This trend indicates that depletion of chromium may have occurred at higher leaching time. Thus, the observed diffusivity was calculated only for the first four intervals. The overall observed diffusivity is then determined by taking the average of the interval observed diffusivities.

It can be seen that there is a small but steady decrease in observed diffusivity respective a steady increase in negative logarithm of the observed diffusivity (Leachability Index – LI) as the water-to-cement ratio increases suggesting that the leaching behavior of chromium could be determined by a specific type of immobilization mechanism. As it showed in previous work [15], the immobilization mechanism could be the super-equivalent adsorption of chromate anions onto availability of C-S-H sorption aria.

The experimental value of LI brings certain information concerning the mobility of species of interest in cement specimen. A high value of leachability index represents a lower release of the contaminant from monolithic sample. Generally, if $LI < 11$ the component has a high mobility, if $11 < LI < 12.5$ the component has an average mobility and finally, if $LI > 12.5$ the component has a low mobility [16]. The experimental values of LI greater then 12.5 show a low mobility of component in cement specimen. These results reflect the non-hazardous characteristics of resulted product.

The relation between water-to-cement ratio and chromium release decreasing is reflected in Fig. 5, which shoes the logarithm release flux of chromium as a function of total experimental logarithm leaching time. It can be seen a small but steady decrease in release flux of chromium with water-to-cement ratio. This is in accordance with the above results.

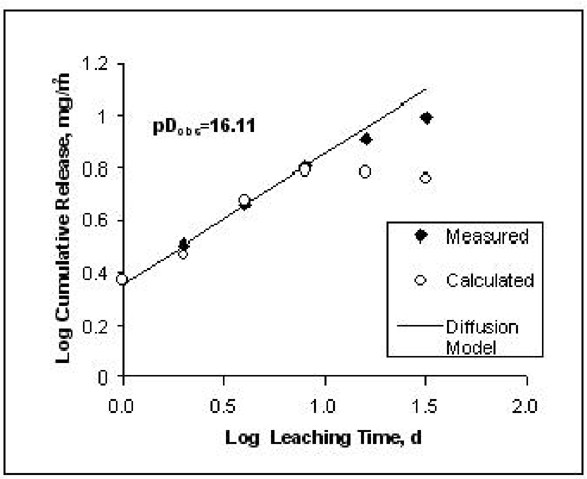

Fig. 3. Log-log plot of cumulative release of Cr^{6+} against cumulative leaching time for w/c = 0.7

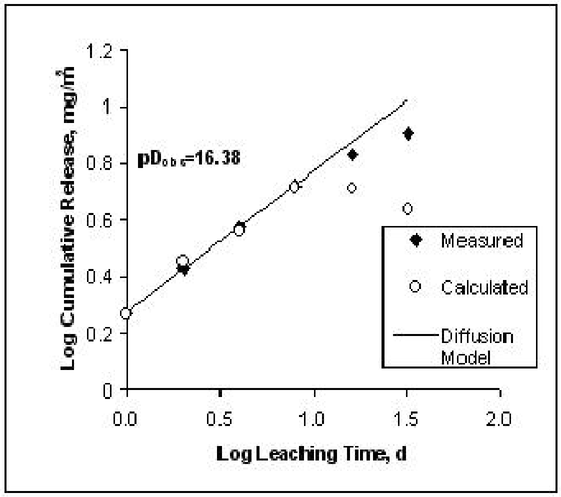

Fig. 4. Log-log plot of cumulative release of Cr^{6+} against cumulative leaching time for w/c = 1

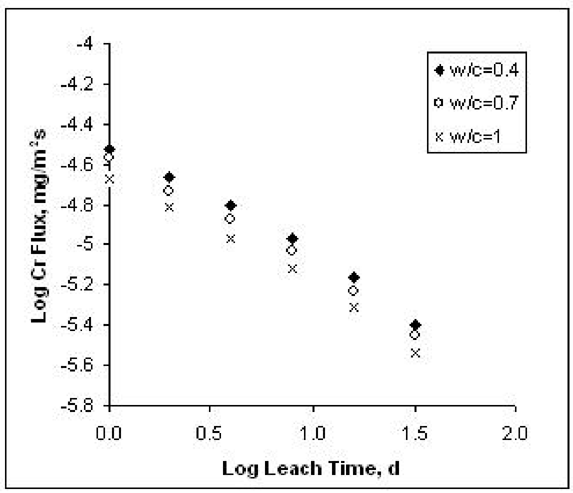

Fig. 5. Release flux of Cr^{6+} against cumulative leaching time

4. Conclusions

The water-to-cement ratio was found to determine the leaching behavior of chromium in cement specimen. An unusual behavior leaching of chromium with the water-to-cement ratio of cement specimens consisting in decreasing of the leachability with increasing of water-to-cement ratio, suggests a chemical immobilization of Cr^{6+} in cement specimen.

The mechanism of chromium release was investigated under diffusion-controlled scenario. A diffusion-controlled release was identified for all cases only for first four leaching periods (i.e. 1, 2, 4, 8 days). For the next two (16, 32 days) leaching periods the depletion of released chromium was occurred.

Using a simple leach model, the leachability indexes of chromium for all situations have been calculated. The values of those show a low mobility of component in cement specimen.

R E F E R E N C E S

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