Evaluation of leaching behavior and immobilization of zinc in cement-based solidified products

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Abstract

This study has examined the leaching behavior of monolithic stabilized/solidified products contaminated with zinc by performing modified dynamic leaching tests. The effectiveness of cement-based stabilization/solidification treatment was evaluated by determining the cumulative release of Zn and diffusion coefficients, D_e. The experimental results indicated that the cumulative release of Zn decreases as the addition of binder increases. The values of the Zn diffusion coefficients for all samples ranged from 1.2×10^{-8} to 1.16×10^{-12} cm^2 s^{-1}. The samples with higher amounts of binder had lower D_e values. The test results showed that cement-based stabilization/solidification treatment was effective in immobilization of electroplating sludge and waste zeolite. A model developed by de Groot and van der Sloot was used to clarify the controlling mechanisms. The controlling leaching mechanism was found to be diffusion for samples with small amounts of waste material, and dissolution for higher waste contents.

Keywords: stabilization/solidification (S/S); ordinary Portland cement; NEN 7345: 2004; zinc (Zn).

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The content of waste material produced worldwide is rapidly increasing and the great amount of leaching pollutants (heavy metals) has become a severe problem [1].

Metal electroplating industries generate toxic sludge containing heavy metals, *e.g.*, Zn, Pb, Cr, by precipitation of wastewaters with lime. Toxic sludge is not easily implemented on a commercial scale because of the complexity of its chemical composition [2]. It must be stabilized by means of a binder in order to prevent the release of toxic heavy metals to the environment [3]. Natural zeolite is often used to remove heavy metals from wastewaters. After saturation with heavy metals, zeolite becomes possible harmful waste and should be disposed of in a satisfactory manner.

Solidification/stabilization (S/S) processes are very popular in hazardous waste management and have been used for years [4,5]. The objective of S/S technologies is to reduce waste handling or disposal problems by their fixation into a solid matrix as physically or chemically stable as possible [6]. The effectiveness of solidification has been widely studied and discussed in many reports [7–10].

Ordinary Portland cement (OPC) is often used as the binding agent on its own, or in combination with cement replacement materials, which may be hydraulic (cement kiln dust) or pozzolanic (pulverized fuel ash, slag, etc.) in nature [11,12].

The study of leaching behaviors of metals is an important way to obtain valuable information about the chemical speciation of contaminants in the S/S waste matrix and their potential environmental risks [13]. The prediction of leaching behavior in the environment can be accomplished by means of predictive mathematical models such as mechanistic and empirical leach models [14,15]. They can help identify the leaching mechanism and can provide methods for correlating leach information [16,17]. However, the model equations cannot always fully describe the actual leaching behavior and a model is always limited by its assumptions and must be confirmed.

In the present work, the leaching behavior of heavy metals from cement-based solidified plating wastes was assessed using the modified dynamic leaching test.

The monolithic leaching test (EA NEN 7345: 2004) [18] was used to characterize the leaching behavior of waste material and was used as a basis for the UK monolithic Waste Acceptance Criteria (monWAC) [19]. In this monolithic leaching test, a monolith of regular geometry and known surface area is immersed in a definite volume of leachant solution. This test is a rapid and inexpensive way to evaluate the leaching rate of species. The experimental results of the leaching test were used to calculate the release flux of zinc.

Short-term leachability studies of solidified hazardous wastes show diffusion to be the dominant factor [13]. According to the diffusion model, the actual dif-

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fusion coefficients of metals in S/S materials can be calculated using the equation:

$$\left(\frac{a_n}{A_0}\right)\left(\frac{V}{S}\right)\left(\frac{1}{\Delta t_n}\right)=\left(\frac{D_e}{\pi}\right)^{0.5}\left[\frac{1}{(T_n)^{0.5}}\right] \quad (1)$$

where D_e is the effective diffusion coefficient (cm^2 s^{-1}), a_n is the contaminant loss (mg) during the particular leaching period with index n, A_0 is the initial amount of contaminant present in the specimen (mg), Δt_n is the duration of the leaching period (s), V is the volume of specimen (cm^3), S is the surface area of specimen (cm^2) and T_n is the elapsed time to the middle of the leaching period (s) [20].

For determination of controlling leaching mechanisms of Zn release, the de Groot and van der Sloot's model (Eq. 2) was used. This model was based on the slope of the plot of the logarithm of the cumulative fraction release versus the logarithm of time. If diffusion is the dominant mechanism then theory suggests the equation:

$$\log(B_t)=\frac{1}{2}\log(t)+\log\left(U_{\max}d\sqrt{\frac{D_e}{\pi}}\right) \quad (2)$$

where B_t is cumulative max release of the component (mg m^{-2}), $U_{\max}$ is max leachable quantity (mg kg^{-1}), t is contact time (s), d is the bulk density of the product (kg m^{-3}) and D_e is the effective diffusion coefficient (cm^2 s^{-1}).

According to this model, if the slope of the curve is 0.5, Zn release is slow and diffusion is the controlling mechanism. If the slope is close to 1, the controlling mechanism is dissolution and if the slope is close to 0, the mechanism is wash-off.

EXPERIMENTAL PROTOCOLS

Materials

The binder used for S/S of the sludge from a zinc plating plant was ordinary Portland cement (OPC). OPC (according to EN-197 CEM I) was obtained from CEMEX Croatia cement plant (Kaštel Sućurac, Croatia). Its chemical composition and physical and mechanical properties were determined in laboratory tests and are shown in Tables 1 and 2. Waste zeolite is the natural zeolite from the deposit of Donje Jesenje, Croatia, saturated by zinc ions. Table 1 shows the chemical composition of natural zeolite. The zeolite applied contains clinoptilolite as its major component and impurities like illite, montmorillonite, feldspars, calcite and quartz. After saturation, the zeolite was dried at 60 °C, ground and sieved through the standard 4900 mesh cm^{-2}.

The sludge was produced by precipitation of zinc plating plant wastewater with lime and subsequent filtration of the precipitate. The sludge was approximately 80 wt.% solids and was composed of a hydroxide gel, hydrated oxides and various metal salts resulting from the zinc plating plant operation. The sludge was dried at 105 °C to a constant weight, ground and sieved so that its particle had the same or similar size as the CEM I. The sludge has a pH of 6.58, the percentage of soluble part of the sludge was 17.85%. Loss of ignition at 1000 °C was 1.29%. The ground sludge was digested using concentrated hydrochloric acid and the concentration of elements was analyzed using atomic emission spectrometry. Zn, Fe and Ca were the main elements present in the sludge at concentrations of 157.3, 392.7 and 67.10 mg L^{-1}.

Table 1. Chemical composition, mass%, of CEM I and natural zeolite

Component	CEM I	Natural zeolite
SiO_2	22.85	64.94
Al_2O_3	4.81	13.66
Fe_2O_3	2.79	2.03
CaO	65.23	2.99
MgO	1.61	1.10
K_2O	1.89	1.88
Na_2O	0.18	3.66
Loss of ignition	0.04	9.84

Table 2. Physical and mechanical properties of CEM I

Physical property	Value
Specific surface according to Blaine cm^2 g^{-1}	3300
Standard consistency, %	26
Setting time – start, min	85
Setting time – end, min	150
Average bending strength, Mpa	6.26 (after 3 days) 8.44 (after 28 days)
Average compressive strength, MPa	33.5 (after 3 days) 50.7 (after 28 days)

Methods

Stabilized/solidified samples were prepared by mixing different proportions of sludge and waste zeolite with CEM I and distilled water. The part of mixture (sludge + waste zeolite, (K)) in samples was 5, 10, 20 and 30 wt.% (with 20 wt.% of sludge in the mixture, (M)) relative to the mass of the solid mixture (CEM I + sludge + waste zeolite). For example, if the sample mass is 100 g, mark 5K20M will refer to the addition of 5 g of mixture of zeolite and sludge (with addition of 1 g of sludge in the mixture of sludge and zeolite). Mark 10K20M will refer to the addition of 10 g of mixture with 2 g of sludge in mixture. The water/solid (W/S) ratio of the prepared cement samples was 0.5.

Modified tank leaching test

Monolithic cylindrical samples of 30 mm×34 mm were cured in the thermostat for 28 days at a temperature of 20 °C (isolated contact of samples and water).

Dynamic leaching tests were carried out on monolithic samples to determine the cumulative release of zinc as a function of leaching time and content of waste materials in samples. After solidification, samples were immersed in distilled water (liquid/solid ratio = 10:1). Leaching occurred in the sealed glasses for defined periods of 18, 24, 72 and 168 h. After leaching, the zinc concentration in eluates was determined by means of energy dispersive X-ray fluorescence (EDXRF).

RESULTS AND DISCUSSION

The cumulative fraction of zinc released was plotted against the leaching time for different additions of waste material in Figure 1. The results are shown in this way rather than using linear graphs, because this is the best way to clearly show zinc leachability. In treated samples, an increase in the amount of binder led to decrease in the amount of zinc leached. More accurately, as shown in Figure 1, when the binder content increased from 70 to 95%, zinc leachability decreased significantly (from 90 to 5% of the total). The results so far clearly show that the Portland cement treatment tested was effective in immobilizing Zn.

There was early interest in investigating the reaction of zinc with cement [21,22]. It is known that zinc interact with the cement minerals during hydration and retard setting. Lieber *et al.* demonstrated, using X-ray diffraction, the intermediate formation of the crystalline calcium zincate during the retardation time. Later, Poon *et al*. investigated the zinc release from a cementitious matrix by leaching tests and they concluded that $Ca(OH)_2$ was the major phase involved in the fixation mechanism [23]. Cocke *et al*. confirmed the presence of calcium zincate with X-ray photoelectron spectroscopy, ion scattering spectroscopy, SEM and Fourier transformed infrared spectroscopy [24]. They proposed the preferential deposition of zinc on the surface of the cement grains.

The controlling leaching mechanisms were evaluated by means of a diffusion model (Eq. (2)). The slope and R^2 values generated from the diffusion model for all samples are presented in Figures 2 and 3 and Table 3. For 10K20M, 20K20M and 30K20M samples, the slope values ranged from 0.998 to 1.204. This indicates that dissolution was the controlling leaching mechanism. In this case, dissolution of material from the surface proceeds faster than diffusion through the pore space [20]. However, for the 5K20M sample, the slope value was 0.442 and diffusion was the controlling mechanism.

Diffusion coefficients, D_e, were calculated and are listed in Table 4. According to previous studies, diffusion coefficients generally range from 10^{-5} cm^2 s^{-1} (very mobile) to 10^{-15} cm^2 s^{-1} (immobile) [20].

The values of Zn diffusion coefficients for all samples ranged from 1.2×10^{-8} to 1.16×10^{-12} cm^2 s^{-1}. The samples with higher amount of binder had the lower D_e values. More specifically, the 5K20M sample showed a decrease in D_e of three and four orders of magnitude compared to the 30K20M sample, respectively. Moreover, it can be concluded that zinc mobility was significantly reduced with this treatment.

The leachant pHs was also determined in this study. Table 5 shows the pH values for different additions of

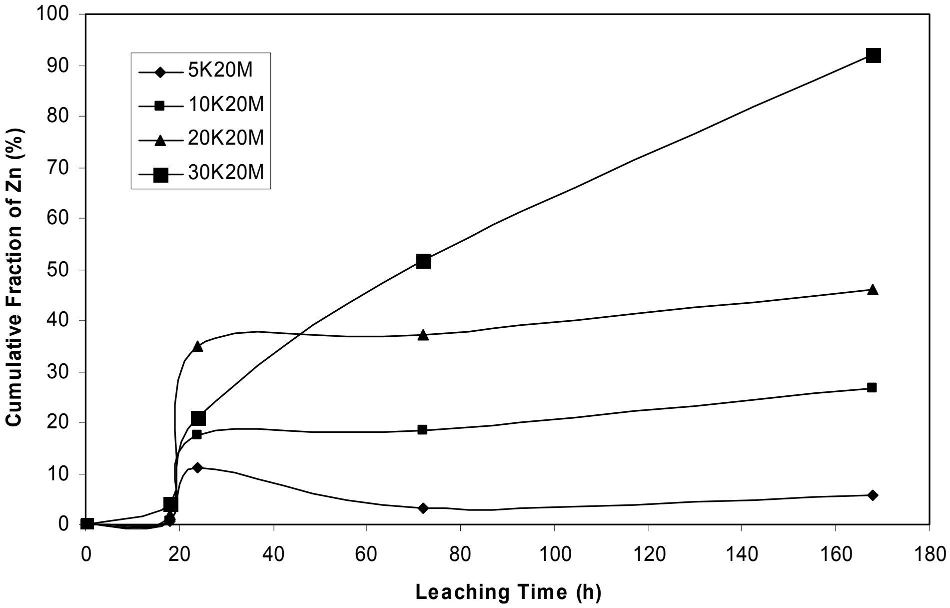

Figure 1. Cumulative release of Zn during leaching time.

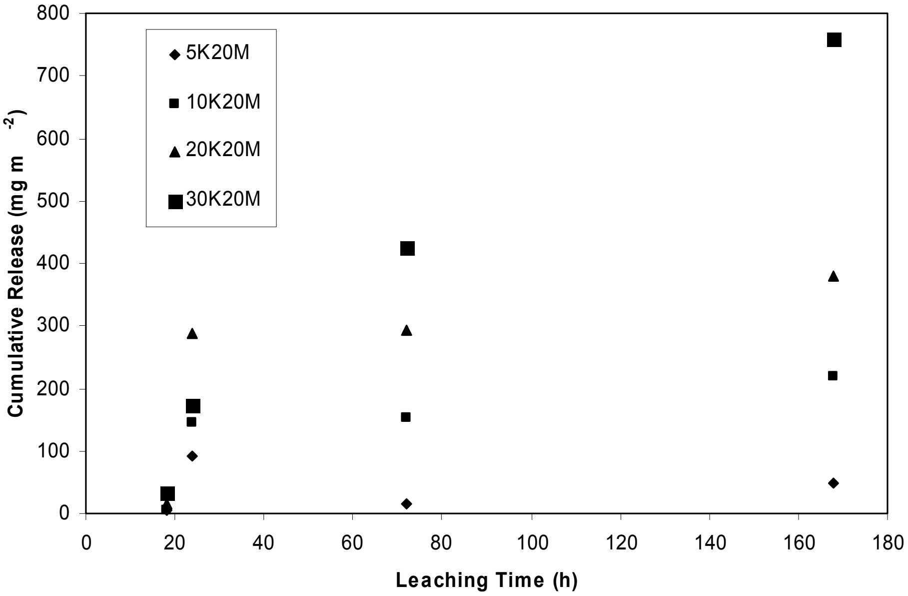

Figure 2. Cumulative release of Zn versus leaching time.

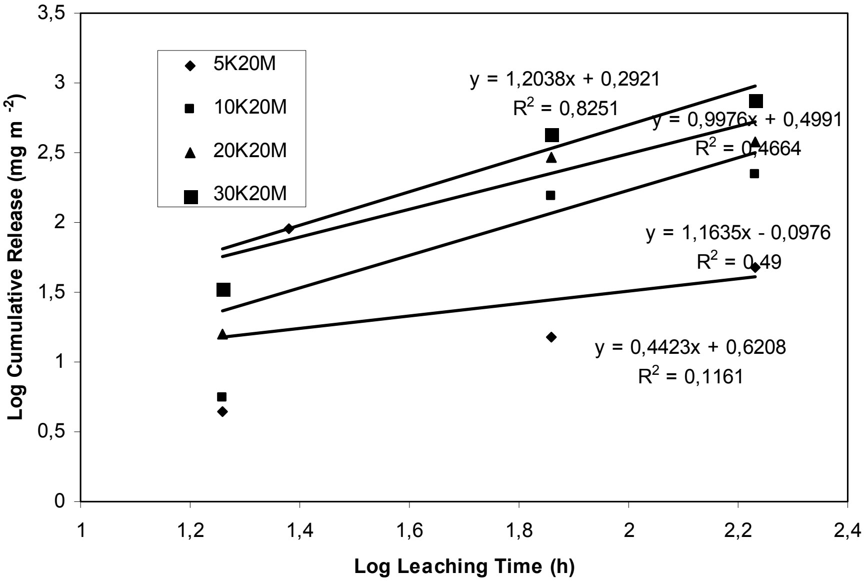

Figure 3. Logarithm of the cumulative release of the Zn versus the logarithm of leaching time.

Table 3. Mathematical analyses for Zn release

Sample	Slope	R^2
5K20M	0.442	0.116
10K20M	1.164	0.490
20K20M	0.998	0.466
30K20M	1.204	0.825

Table 4. Diffusion coefficients (D_e / cm^2 s^{-1}) for Zn

Leaching time, h	5K20M	10K20M	20K20M	30K20M
18	1.16×10^{-12}	2.06×10^{-12}	1.56×10^{-11}	7.43×10^{-11}
24	3.96×10^{-10}	1.00×10^{-9}	4.00×10^{-9}	1.20×10^{-8}
72	1.16×10^{-12}	1.63×10^{-11}	1.77×10^{-11}	3.00×10^{-9}
168	1.66×10^{-11}	3.31×10^{-10}	1.00×10^{-9}	4.00×10^{-9}

Table 5. pH data for treated samples

Time, h	5K20M	10K20M	20K20M	30K20M
18	11.98	11.83	11.87	11.77
24	12.01	11.85	11.90	11.81
72	12.28	12.08	12.17	12.04
168	12.20	11.98	12.08	11.78

wastes. Experimental results have shown that the alkaline nature of the solidified products significantly change the initial pH of distilled water as a leachant from 6.0 to approximately 12.0 by the end of the test. All samples exhibited pH values ranging between 11.77 and 12.28.

The leachant pH was lower for samples with higher content of waste in cement matrix. When the leachate pH was higher than 12, Zn leachability was significantly decreased. With longer leaching time, pH slightly increased.

Zinc is expected to form hydroxides in the high pH values (> 8) of cement system [25]. The hydroxy complexes $Zn(OH)_4^{2-}$ and $Zn(OH)_5^{3-}$ can be present in a strong alkaline solution. Their anionic properties preclude their adsorption onto the negative surface of the C–S–H, but they may form the calcium zinc complex hydrated compound calcium zincate [26].

CONCLUSIONS

The dynamic leaching test was performed to evaluate zinc leachability in cement-based samples. The leaching mechanisms were identified with the mechanisms responsible for Zn immobilization. Moreover, it may be concluded that zinc mobility was significantly reduced with this treatment.

Cement-based treatment was effective in reducing Zn leachability and the leaching of zinc was controlled by diffusion for small amounts of waste material in cement systems and by dissolution for higher content of wastes.

According to Environment Canada, the resulting cement-based material could be used for specific utilization such as road-based material, quarry rehabilitation, lagoon closure, etc.

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IZVOD

ISPITIVANJE IZLUŽIVANJA CINKA IZ STABILIZIRANIH/SOLIDIFICIRANIH MONOLITNIH PRODUKATA NA BAZI CEMENTA

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(Naučni rad)

Ovaj rad istražuje izluživanje iz stabiliziranih/solidificiranih monolitnih produkata kontaminiranih cinkom pomoću modificiranog dinamičkog testa za izluživanje. Uspješnost stabilizacije i solidifikacije otpada cementom ispitivana je određivanjem kumulativnog otpuštanja cinka i difuzijskih koeficijenata, D_e. Eksperimentalni podaci pokazuju da vrijednosti kumulativnog otpuštanja cinka opadaju povećavanjem količine veziva. Vrijednosti difuzijskih koeficijenata cinka za sve uzorke se kreću u granicama od $1,2\times10^{-8}$ do $1,16\times10^{-12}$ cm^2 s^{-1}. Uzorci s većim količinama veziva imaju niže vrijednosti D_e. Iz dobivenih rezultata se može zaključiti da je stabilizacija i solidifikacija otpada cementom efikasna u imobilizaciji otpadnog zeolita i mulja iz pogona završne obrade metala. Za određivanje kontrolirajućeg mehanizma korišten je model koji su razvili de Groot i van der Sloot. Za uzorke s malim količinama otpadnog materijala mehanizam koji kontrolira izluživanje je difuzija, dok je otapanje kontrolirajući mehanizam za uzorke s većim količinama.

Ključne reči: Stabilizacija/solidifikacija (S/S)• Portland cement bez dodataka • NEN 7345: 2004 • Cink (Zn)