



The effect of flow-through leaching on the diffusivity of heavy metals in stabilized/solidified wastes

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Abstract

The flow-through leaching test is a test method employed to study the leaching behavior of monolithic stabilized/solidified (S/S) hazardous wastes under the condition that the leachate flows through the sample. This method simulates the leaching process of the S/S hazardous waste disposed under a particular landfill condition when the S/S waste is more permeable than its surrounding materials or when the deterioration of the solidified waste form has reached a state that ground water can flow-through the waste via the porosity system of the S/S waste matrix.

This paper describes a study on the long-term performance of the cement-based S/S heavy metal wastes using a flow-through leaching test method. Two series of leaching tests with different synthetic heavy metal waste samples were carried out. The S/S samples were made from five types of heavy metals with two kinds of binders. The metals were Pb^{2+} , Zn^{2+} , Cu^{2+} , Ni^{2+} (positive ions as nitrates), and Cr^{6+} (a negative ion as potassium dichromate), and the binders were type I ordinary portland cement (OPC) and pulverised fuel ash (PFA).

The model developed by Godbee and Joy for simulating the leaching behavior was modified to estimate the diffusivity parameter in this study. The results obtained indicate that since the matrix of the solidified waste in a flow-through leaching tests is always being degraded, the values of diffusivities increase continuously during the leaching period. The diffusivity variation range was from 10^{-13} to 10^{-3} cm^2/s , and were normally higher than those obtained from other test methods such as ANS 16.1 test and other dynamic leaching tests. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Stabilization/solidification; Leaching; Flow-through leaching test; Cement; Heavy metals; Long-term leaching performance

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1. Introduction

1.1. Flow-through leaching test

Leaching occurs when a leachant contacts a waste and carries away contaminants from the waste. A number of leaching mechanisms are generally associated with cement-based solidified waste forms. These mechanisms are dependent on how the leachant comes into contact with the solidified waste. A leachant can contact the waste either by flowing around the waste or by flowing through the waste or a combination of both. In an actual landfill situation, the relative importance of these two ways of contact is dependent on the permeability of the solidified waste and its surrounding materials. When a waste is less permeable than its surrounding materials, such as when it is placed in a sandy soil, the leachant will tend to flow around the waste. When flow around is the major leaching mechanism, the contaminants are carried away from the waste's surface. A concentration gradient then builds up across the waste's cross-section and the contaminants diffuse through the pore system of the waste to the waste leachant interface [2,3]. On the other hand, if a waste is more permeable than its surrounding materials, flow-through will be the dominant mechanism. This occurs, for example, when the waste is deposited in a bed of impervious rock or clay or when the deterioration of the solidified waste form caused by various environmental processes has reached a state where ground water can flow-through the waste via the porosity system of the waste matrix.

Flow-through leaching can be regarded as a dynamic leaching test with a continuous leachant inlet in order to distinguish it from a batchwise dynamic leaching test method such as the American Nuclear Society (ANS) 16.1 test method [4] or a chemical extraction test such as the toxicity characteristic leaching procedure (TCLP) [5]. It has a different leachant flow regime from other dynamic leaching tests used for monolithic solidified wastes [6].

A flow-through leaching test method is designed to simulate the case of the leachate flowing through the waste sample (Fig. 1). When the leachant flows through the waste, it

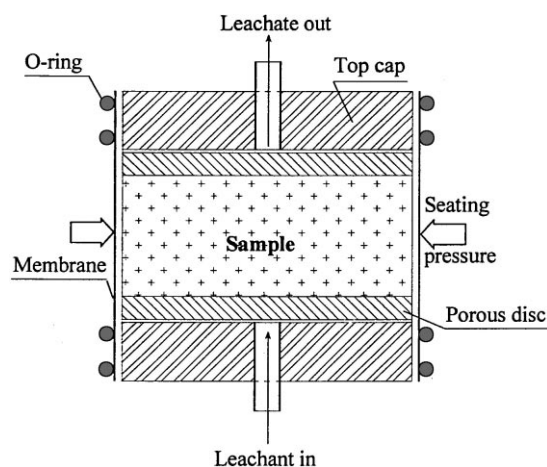


Fig. 1. Equipment setup of the flow-through leaching test.

carries away the mobile fraction of the contaminants with it. At the same time the immobile fraction is continuously solubilized to re-establish equilibrium. When a leaching process begins, the leachant permeates through the waste matrix via the porosity system. For the case of flow-around leaching, the contaminants enter the pore water to produce a concentration gradient and the subsequent diffusion is comparatively free and in all directions. However, for flow-through leaching, due to flow of the leachant via the connected porosity, the dispersion action accelerates the transfer process of the contaminants, and transfer is always in the direction of the leachant flow.

It should be noted that the above discussion applies to a solidified waste that is monolithic in nature. Studies of flow-through leaching with non-monolithic wastes using the column test method [7–9] have been well documented and are outside the scope of this study.

Only a few studies concerning flow-through leaching have been published. The previous studies [10,11] explained the advantages of using the flow-through leaching test method to simulate the long-term leaching behavior of heavy metals in monolithic solidified wastes. In these studies, several heavy metals were used and the leachant was either de-ionized water or a TCLP leachant. These studies compared the leaching behavior of different heavy metals under flow-through leaching conditions and analyzed the relationship between the results with the flow rate and applied pressure of the leachant.

In fact, the flow-through leaching process is associated with diffusion, dispersion, chemical reaction and adsorption/desorption actions. Diffusion and dispersion are the primary transfer mechanisms in flow-through leaching and they can be more conveniently analyzed quantitatively and modelled than other factors. Therefore, although chemical reaction and adsorption/desorption factors may not be ignored, due to their complex nature, researchers always inferred these factors in the leaching process by means of experimental results but could not use them to predict leaching behavior.

1.2. Leaching model

A mathematical model of the leaching process is very useful in relating factors influencing the leaching process and the leaching results. The model can also be used to predict the leaching behavior in the future, subject to the constraints of the assumptions and boundary conditions included.

Most leaching models are based on diffusion theories or other mass transport theories to model the system using the data obtained from short to medium term leaching tests [12,13]. Examples of applying these models can be found in the works of Bishop [7,9] and Cote [2]. For a flow-through leaching test, a model can be developed by considering the material balance effected by diffusion, dispersion, adsorption/desorption and chemical reactions. Therefore, the flow-through leaching model is dissimilar to other models for batchwise dynamic leachings [14–16]. A model for flow-through leaching has been proposed by Poon et al. [1], and the material balance equation of flow-through leaching can be written as [1]

$$\frac{\partial C}{\partial t} = D_e \frac{\partial^2 C}{\partial x^2} - u \frac{\partial C}{\partial x} + R \quad (1)$$

where; D is diffusion coefficient (cm^2/s), C concentration of a contaminant in the sample

(mg/l), x distance along the sample (cm), u velocity of the leachant (cm/s), t leaching period (s), R net rate of production of mobile contaminant, caused by chemical reactions and adsorption/desorption (the chemical leaching rate).

To apply Eq. (1) to the flow-through leaching test, the basic conditions are, (a) when $t = 0$, the contaminants are uniformly distributed in the entire specimen and zero concentration at $x = 0$, (b) the leachant flows with a uniform velocity u , and (c) the leachant flow is on the entire cross-section of the sample. Analytical solutions to Eq. (1) with such conditions are complex. Considering only the primary influence factors, (for example diffusion, and both chemical reactions and adsorption/desorption with the form $(\partial KC)/(\partial t)$ are treated as inclusive in the diffusion term) in this preliminary experimental study, the solution of this problem without the advection/dispersive effect is presented by Godbee and Joy [17] as follows:

$$\left(\frac{\sum a_n}{A}\right) \left(\frac{V}{S}\right) = 2 \left(\frac{D'_e}{\pi}\right)^{1/2} t_n^{1/2} \quad (2)$$

where $\sum a_n/A$ is cumulative fraction of the contaminant leached in the sample. In Eq. (2), D'_e represents the effective diffusivity that has only incorporated the diffusion process during flow-through leaching. The term, (V/S) , is the characteristic length (L) of the problem. This equation is widely used for pure diffusion leaching tests. If advective/dispersive effect is included, the pure diffusion problem can be viewed as having a moving coordinate system with speed u . The characteristic length (L) can be transformed to $L' = L - ut$. Thus, D_e is proportional to L (for the same time frame), which is in fact $L(= V/S) = L' + ut$, where L' is the depth of the specimen. To model the long term behavior of a flow-through leaching test, a constant or uniformly varying leachant flow rate is needed. In this study, the leachant flow rate was set to be constant in the leaching tests.

2. Methodology and material

2.1. Waste sample preparation

The synthetic wastes consisting of five kinds of heavy metals elements were used in the experiments. The binder was type I ordinary portland cement (OPC) mixed with and pulverized fuel ash (PFA). Two types of synthetic sludge were used. The first was made from the metals Pb^{2+} , Zn^{2+} , Cu^{2+} and Ni^{2+} added as nitrates and the other was made from Cr^{6+} as a negative ion in potassium dichromate. The sludge was made by adjusting the pH values of the solutions of metal-salts to 9 by adding concentrated NaOH solution. At pH = 9, the solution containing metals of Pb, Zn, Cu and Ni produced precipitates of metal hydroxides. The solution containing Cr^{6+} does not form a metal hydroxide at high pH.

The binder was added to the sludge at OPC–PFA ratio of 40/60 (weight to weight) and then distilled water was added at a water-binder ratio of 0.5. After mixing the binder and the sludge to a homogeneous state by hand, the samples were poured into plastic cylindrical moulds with an internal diameter of 7 cm and a depth of 3 cm. The samples were kept in a moist environment and cured at 20°C constant temperature for 28 days. Tables 1 and 2 show the characteristics and compositions of the prepared samples.

Table 1
Details of prepared samples

Sample I.D.	OPC/PFA (wt/wt, %)	Sample size (mm)	Weight (g)	Dry weight (g)	Dry density (g/cm ³)
1 [#]	40/60	ϕ70 × 30	178.1	140.1	1.21
2 [#]	40/60	ϕ70 × 30	194.5	165.8	1.44

Table 2
Metal contents and dry weight in the samples

Sample I.D.	Metal contents (%)/dry weight (mg)					
	Pb	Cu	Zn	Ni	Cr	Ca
1 [#]	2.926/4099	1.584/2220	1.254/1756	0.896/1255	–	12.494/17504
2 [#]	–	–	–	–	1.351/2240	14.692/24359

2.2. Flow-through leaching tests

Two flow-through leaching tests were carried out using the flexible-wall permeameters (supplied by Trautwein Inc.) shown in Fig. 1. The leachant pressure and the seating (confining) pressure could be controlled accurately and the leachant flow could be maintained in one direction during the leaching period. The flow-through tests were carried out under their respective uniform flow rates (Table 3) except sample 1[#]. For sample 1[#], two stages of flow rates were used. The first stage was under a constant leachant inlet pressure of 50 kPa in order to determine the variation of the flow rate with time. In the second stage a constant leachant flow rate was kept to meet the model assumptions.

The seating pressure of the leaching tests were set to 400 kPa, and the leachant inlet pressure was periodically changed to keep the leachant flow rates uniform. The variation of flow rates was maintained at ±10% of the mean values. Deionized water with a specific resistance of higher than 10 MW/cm was used as the leachant.

2.3. Sampling process and measurement

The inflow of the leachant was kept continuous during the leaching period. All the leachate was analyzed periodically when every 500 ml was collected. The pH values of the leachate were measured using a Philip's PW 9420 pH meter, and the metal measurements were performed with a Perkin Elmer 3030 atomic adsorption spectrophotometer after acidification of the leachate to pH < 2 by concentrated nitric acid.

Table 3
Flow-through leaching conditions

Sample I.D.	Leachant property	Mean flow rate (ml/min.)	Seating pressure (kPa)	Leachate inlet pressure (kPa)
1 [#]	D.I. water	0.0166 ^b	400	50 ^a , 50–240 ^b
2 [#]	D.I. water	0.0302	400	50–155

^a Data in the first leaching stage.

^b Data in the second leaching stage.

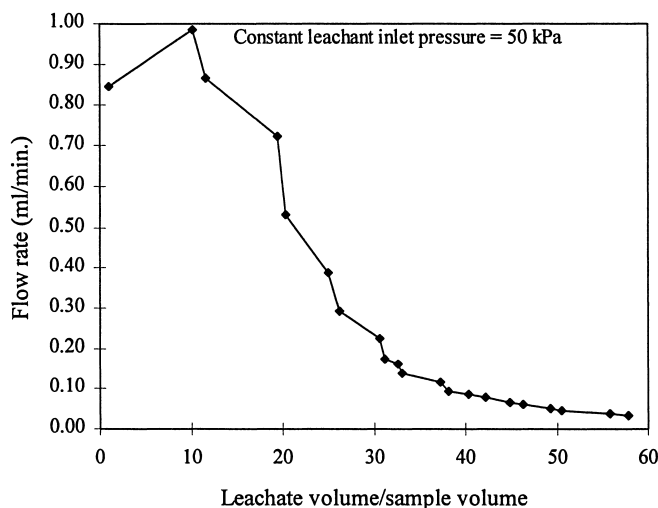


Fig. 2. Sample 1[#], the variation of leachate flow rate under 50 kPa leachate inlet pressure.

3. Results and discussion

3.1. Variations of the leachant flow rate

In the first test stage of sample 1[#], the leachant inlet pressure was set to 50 kPa, and the flow rate decreased from 1.0 to 0.03 ml/minute continuously (Fig. 2). It is believed that this was due to hydration of the cementitious matrix continued when the leachant (de-ionized water) entered the samples and the porosity of the samples reduced as a result.

When the leachant inlet pressure was kept at a constant value, the variation of the leachant flow rate was not in a regular pattern which could be modelled by using mathematical equations. Similar results were obtained in a previous study [10]. Therefore, due to the importance of having a constant flow rate in modelling the flow-through leaching process, the flow-rate had to be set to a constant value in the later part of the experiment.

Different characteristics of the metal sludge led to different permeabilities of the samples. For similar leachant inlet pressure, the flow rate of the leachant in sample 2[#] was higher than that in sample 1[#] (Fig. 3a and b), indicating the hydraulic resistance of the matrix of sample 2[#] was lower than that of sample 1[#]. This might be the result of the metal salts forming insoluble precipitates in sample 1[#] producing a higher hydraulic resistance while Cr in sample 2[#] was only kept in the pore water of the matrix.

3.2. Variations of pH values and Ca concentrations

Generally, the rise of pH is a result of the dissolution of $\text{Ca}(\text{OH})_2$ and calcium silicate hydrates which are the primary products of cement and PFA hydration. In sample 1[#], the variation of pH values followed the trend of Ca concentration in the leachate (Fig. 4a and b).

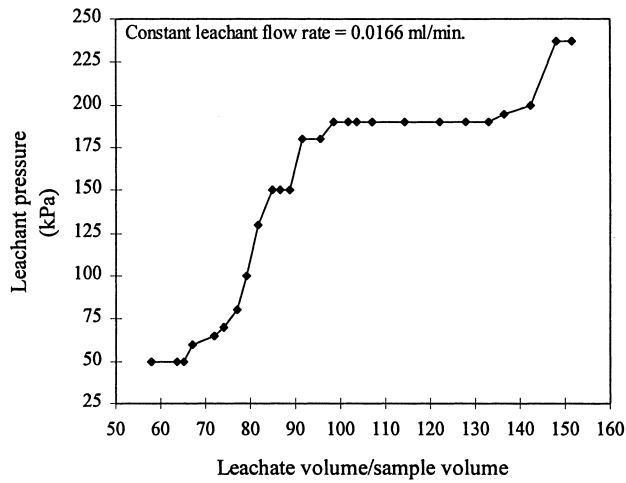
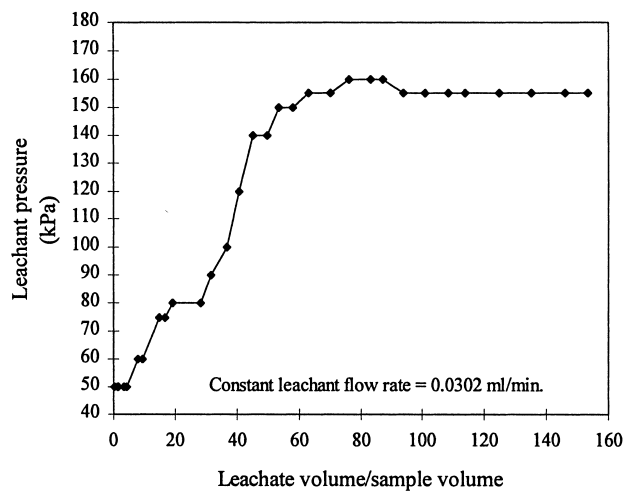
(a) Sample 1[#](b) Sample 2[#]

Fig. 3. Variation of the inlet pressure to keep the constant leachant flow rate.

In sample 2[#] (Fig. 4c), the pH value decreased during the leaching period. Much less Ca was leached from sample 2[#] and the Ca concentration in the leachate varied irregularly. This is probably because Cr does not exist in the waste matrix as a precipitate and could be leached easily. When the leachant (D.I. water) entered the sample, the contaminant became a weak alkaline potassium dichromate solution and would decrease the dissolution of $\text{Ca}(\text{OH})_2$ and calcium silicate hydrates due to the high pH. The results may also be due

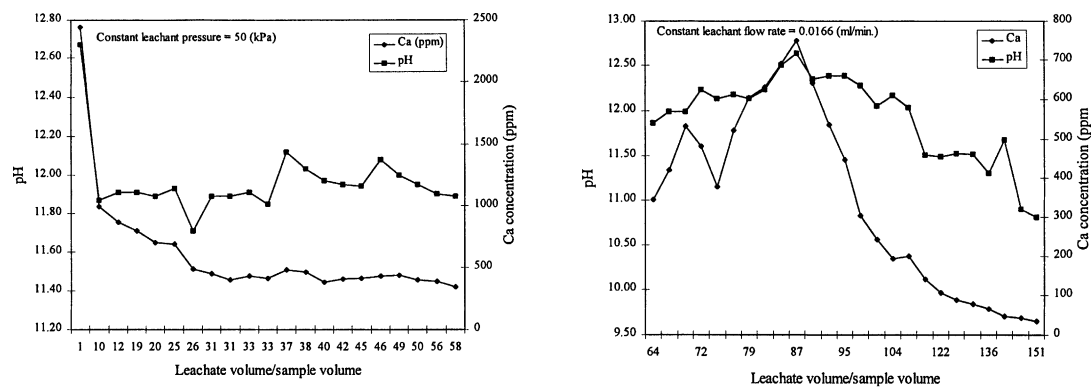
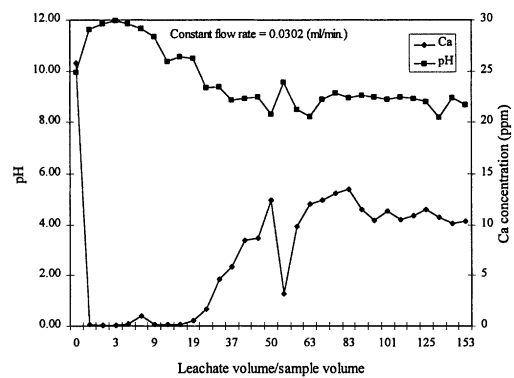
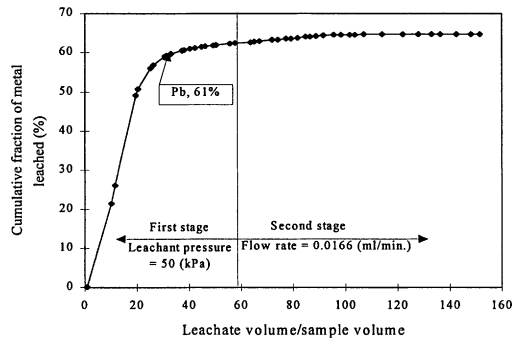
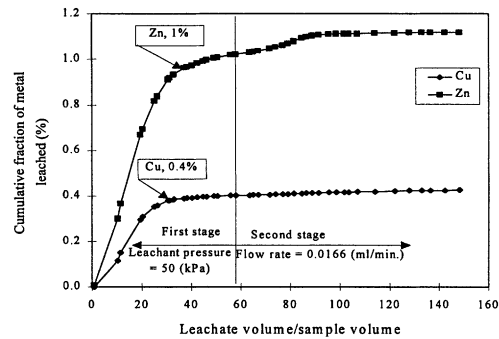
(a) Sample 1[#], in the first stage(b) Sample 1[#], in the second stage(c) Sample 2[#]

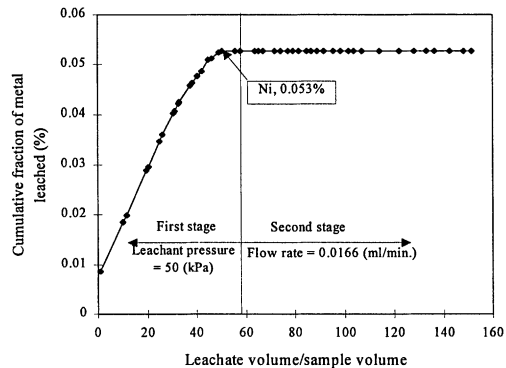
Fig. 4. Variations of pH values and Ca concentrations in the leachate.



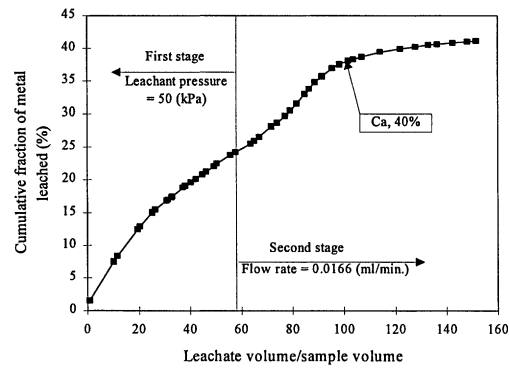
(a) Pb



(b) Cu and Zn



(c) Ni



(d) Ca

Fig. 5. Sample 1[#], cumulative fraction of metal leached.

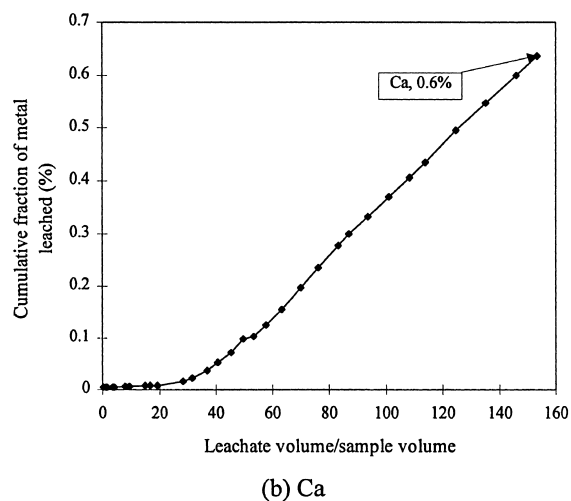
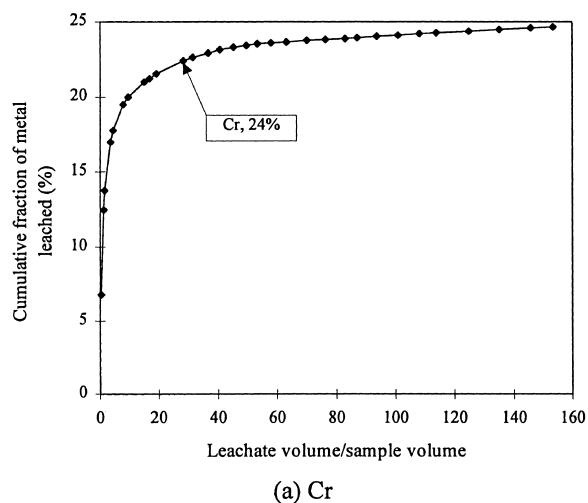


Fig. 6. Sample 2[#], cumulative fraction of metal leached.

to leachant flowing directly through the sample and not causing much deterioration to the cementitious matrix. This is also reflected in the changes of pH values. The pH values of the leachant in sample 1[#] varied from 13 to 11, which was higher than that in sample 2[#] (from pH 12 to 8).

3.3. Leachabilities of the heavy metals

In sample 1[#] (Fig. 5), leaching began to slow down and reached a plateau (steady point) when 61% of Pb had been leached. Zn and Cu showed a similar leaching pattern. Ni and

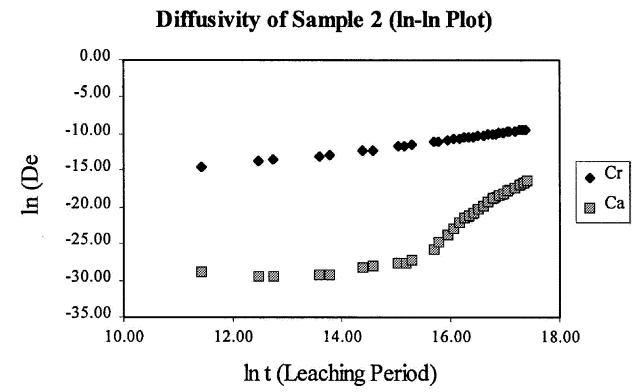
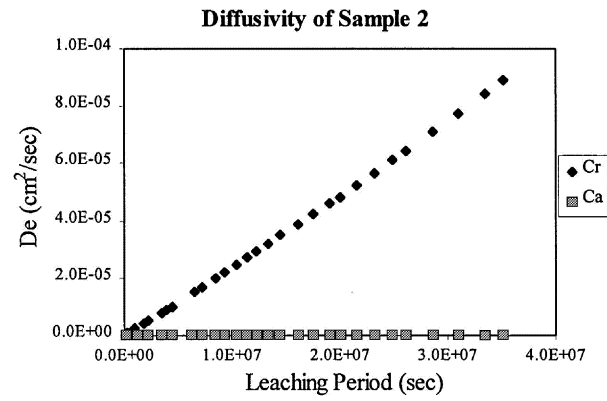
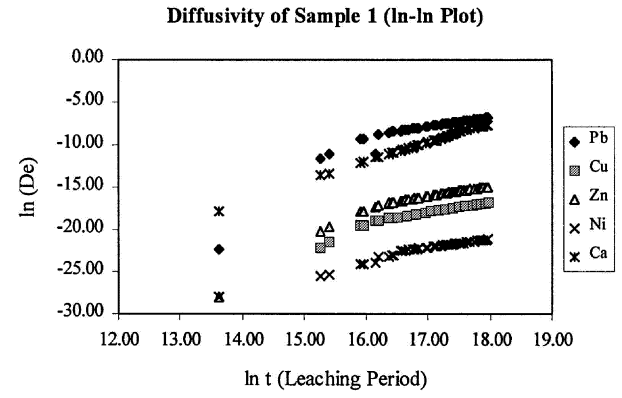
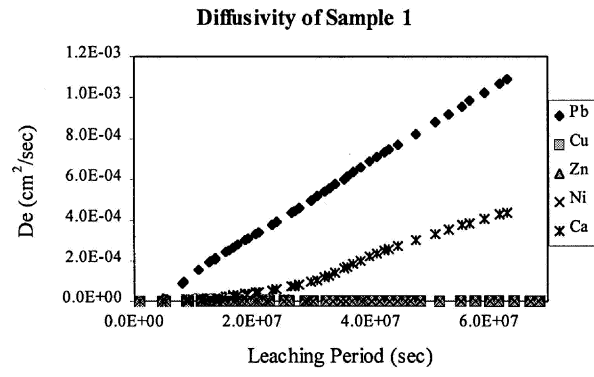


Fig. 7. Plots of diffusivities of heavy metal against time.

Ca reached their steady points in succession behind the other three metals. Ni had the lowest leaching rate. Except Ca, all metals had obvious steady points in the leaching period. Although the leaching of Ca began to slow down after about 40% of it had been leached, the steady point was relatively indistinctive.

The leachabilities of the different metals in sample 1[#] varied greatly due to the different nature of the metal cations and their interactions with the cementitious matrix. The orders of leachabilities of the heavy metals were $\text{Pb} > \text{Zn} > \text{Cu} > \text{Ni}$.

For sample 2[#], the leaching process of Cr reached the steady point very quickly (at 10 sample volume of leachant, see Fig. 6a). This might be due to the inability of $\text{Cr}_2\text{O}_7^{2-}$ anion to form an insoluble precipitate in the cementitious matrix. Before the leaching of Cr reached the steady point, the leaching rate was high. The leaching rate of Ca was low (Fig. 6b) although the steady point had not been reached. The results indicate that the leaching of Cr was independent from the degradation of the solidified waste matrix.

3.4. Diffusivity estimation

In the present leaching tests, the advective/dispersive effect cannot be neglected. If $D \sim 10^{-10} \text{ cm}^2/\text{s}$ and $u \sim 10^{-5} \text{ cm/s}$, the characteristic time (D/u^2) is indeed on the order of seconds. For preliminary estimation of the effective diffusion coefficients, Eq. (2) is modified to incorporate the advective/dispersive effect on the coefficients. The characteristic length of Eq. (2) is replaced by the characteristic length of the moving coordinate system as mentioned earlier.

The computed diffusivities (D_e') of the heavy metals in every leaching interval are shown in Fig. 7. From the diagrams of D_e' versus t and $\ln(D_e')$ versus $\ln(t)$, it is clear that the diffusivities of all the contaminants and Ca increased with time. This situation means that under constant flow conditions the matrices of solidified waste samples were always degrading. The values of diffusivities are in the range of 10^{-13} to $10^{-3} \text{ cm}^2/\text{s}$, which correspond to the case of liquid phase diffusion [18] and are normally higher than those obtained from other test methods such as the ANS 16.1 test or the dynamic leaching test [2,19,20]. But it should be made clear that the high values of diffusivities obtained are the results of the combined effect of diffusion and dispersion.

4. Conclusions

The results of the experiments indicate that, in flow-through leaching tests with D.I. water as the leachant, the leaching process of the heavy metals can be generally divided into two stages. The first stage is a rapid leaching stage in which the leachabilities increase, the leaching rates of all heavy metal contaminants are high and reach their respective steady points after different periods of time. The leaching process then reach the second stage in which the leachabilities increase very slowly. In the second stage the increase in leachability of Ca is larger than other heavy metals, and this will lead to the matrices of solidified wastes degrading before other heavy metals are leached out. Also the leaching rates of different metals are significantly different from each other depending on their interactions with the binders.

The different matrix conditions will lead to the different leaching behaviors of calcium and hence the degradation of the cementitious matrices. When the sludge is prepared with Cr^{6+} , the leaching rate of calcium in a solidified waste will be lower than that prepared with other metals that form insoluble precipitates in the matrix. But the leaching rate of Cr is much higher than other heavy metals.

The computed results based on the flow-through leaching model indicate that the diffusivities always increase during the leaching period under the experimental conditions. It indicates that under constant flow conditions, the matrices of the samples in the flow-through leaching test are always being degraded. This conclusion also indicates that the porosity of the solidified waste increases during the leaching period. The values of diffusivities obtained due to the combined effect of diffusion and dispersion are in the range of 10^{-8} to $10^{-3} \text{ cm}^2/\text{s}$ and are normally higher than those obtained from other test methods such as ANS 16.1 test and other dynamic leaching tests.

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