

Prediction of metal leaching rates from solidified/stabilized wastes using the shrinking unreacted core leaching procedure

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Abstract

The use of cement based stabilization techniques is a common and cost-effective method for stabilization of heavy metals-contaminated sludges and soils. Little is actually known, though, about the mechanisms involved with the release, or leaching, of contaminants from the stabilized waste. Most studies of leaching behavior of cement based systems have assumed that bulk diffusion from the monolith is the main driving force for contaminant release. Recent research has shown that leaching of contaminants is actually a result of the dissolution of the outer shell of the waste form, which results in a solubilization and release of contaminants from the leached shell. The leaching behavior has been successfully modelled as a shrinking unreacted core (SUC). This model incorporates the concept of acid exposure, rather than time, as the master variable in evaluating leaching behavior. The rate of contaminant leaching is controlled by the inward diffusion of acid species into the alkaline depleted leached shell. In this research, the behavior of 'real-world' solidified wastes was studied in order to verify that previously observed behavior in synthesized waste forms applied equally as well to real world wastes. Cored samples of stabilized wastes taken from two sites were used to evaluate a new test procedure designed to model shrinking core behavior. Metals leaching behavior was evaluated as a function of the exposure. © 1997 Elsevier Science B.V.

Keywords: Heavy metal; Leaching; Solidification/stabilization; Shrinking unreacted core

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1. Introduction

Chemical stabilization–solidification (S/S) of hazardous wastes is a widely used technology employed for the treatment and disposal of hazardous wastes. S/S technology is used to immobilize contaminants into a binder–waste mix, rendering them less available for release into the environment. The use of cement based stabilization techniques is a common and cost-effective method for stabilization of heavy metals-contaminated sludges and soils.

Although stabilization of wastes is an ‘approved technology,’ little is actually known about the mechanisms involved with the release, or leaching, of contaminants from the stabilized waste. A better understanding of leaching behavior would enable us to more accurately predict how a waste will behave under ‘real world’ disposal conditions.

Current practice in predicting leaching behavior is generally based upon the concept of bulk diffusion of contaminants from the waste into solution, the driving force being the bulk contaminant concentration in the waste. Although these models cannot accurately predict long-term leaching behavior, they are considered accepted practice in the environmental realm. Attempts have been made to predict long-term behavior by curve fitting experimental results and extrapolating over time. However, bulk diffusion may not always represent the main driving force for contaminant release.

Several studies conducted on cement and cement stabilized waste forms have identified the presence of an inward moving dissolution front in specimens subjected to acidic and alkaline conditions. This behavior has been shown to follow a shrinking core model [1]. The dissolution front is a porous, silica rich shell depleted of calcium and other precipitated contaminants. With evidence of leaching mechanisms other than bulk diffusion at work, it is evident that more information is needed on the controlling leaching mechanisms. A new test method, which can account for the contribution of the inward dissolution front, is needed in order to better understand the role this mechanism plays in contaminant release. The shrinking unreacted core (SUC) leaching model has been proposed to fill this need. The intent of this research was to validate this model using S/S waste specimens from operating facilities.

2. Background

Inorganic contaminants are stabilized in a hydraulic cement–waste system through a variety of physical and chemical mechanisms. The degree and type of stabilization is dependent upon the contaminant type, speciation, concentration, presence of interferents, and the type of binder used, among other factors. Portland cement is the most widely utilized stabilization agent. Other types of cements, such as pozzolanic and slag cements, exhibit the same basic chemistry and hydration reactions, with the basic differences being in the concentrations of the various constituents [2].

Two mechanistic models which have been proposed to describe the release of contaminants, bulk diffusion and the shrinking unreacted core (SUC) model, are described below. There are also empirical models currently used to mathematically

describe observed leach rates, but these models do not yield information on the controlling leach mechanisms [3].

2.1. Bulk diffusion model

The basic premise behind the bulk diffusion model is that contaminant release is a result of the concentration gradient between the leachant (groundwater) and the bulk concentration within the monolith. The rationale behind this model is that in a disposal environment, diffusion through a solid represents a maximum contaminant loss rate when the waste permeability is less than 10^{-3} times that of the surrounding geologic media [4].

The bulk diffusion model, based on Fickian diffusion, was originally developed according to the following equation:

$$\frac{\partial C}{\partial t} = D_c \frac{\partial^2 C}{\partial x^2} \quad (1)$$

where: D_c : effective diffusion coefficient, corrected for porosity and tortuosity ($\text{cm}^2 \text{s}^{-1}$), C : concentration of the contaminant (g cm^{-3}), t : time (s), x : distance (cm).

In applying Eq. (1), a zero surface concentration (and associated zero leachant concentration) is assumed to maintain a dynamic leaching environment. The ANS/ANSI 16.1 test procedure is a commonly used semi-dynamic leach test which incorporates the bulk diffusion model into interpretation of leach test results [5]. Specimens are leached in deionized water with periodic leachant replacement.

Hinsenveld and Bishop [6] presented a bulk-diffusion based theoretical contaminant concentration profile in a specimen as a function of dimensionless time, which can be used to determine leaching rates:

$$c(x, t) = 3c_0 \operatorname{erf} \left[\frac{x}{4D_c t} \right] \quad (2)$$

where c_0 : initial contaminant concentration in the solid, erf: standard error function, x : distance into the solid, t : leaching time.

Unfortunately, the theoretical concentration profile for bulk diffusion does not necessarily agree with various experimental results, including those obtained from leaching in neutral leachants. Because the main driving force in bulk diffusion models is the bulk contaminant concentration, a proportional increase in contaminant concentration would theoretically yield a proportional increase in leaching rates, but this is not often the case [1]. In addition, the bulk diffusion model does not recognize the acidity dependence of contaminant leaching. Under this model, increasing the acidity of the leachant would have no impact on the observed leaching rate, which has been demonstrated to be false [6,7].

2.2. Shrinking unreacted core model

The primary failure of the bulk diffusion models is that the effect of acidity on the leaching process is not addressed. One important component of stabilization is the

degree of chemical interaction between the waste and the cement. For heavy metals, pH dependent precipitation reactions (i.e., hydroxides, carbonates, sulfides) are often an important stabilization mechanism. The subsequent dissolution of these precipitates is likewise dependent upon pH; their availability is generally much greater under acidic conditions. The bulk diffusion model was originally developed to study the leaching behavior of radionuclides from stabilized wastes. The chemistry of these metals, and subsequent stabilization mechanisms, are much different than those for typical priority pollutant metals [8].

The behavior of cement in acidic leachants has been well documented [9–12]. These studies found a calcium depletion zone, with a sharp interface, on the exterior layer of samples leached in acid solutions. There was also a depletion of acid-soluble species in this zone. An unreacted zone was noted in the interior of the leached specimens. Cheng [7] reported the following leached specimen characteristics for stabilized wastes leached under acidic conditions:

- The leached layer was essentially depleted of calcium and soluble contaminants.
- The leached layer consisted of an amorphous silica-rich gel with a much higher porosity than the unleached specimens.
- A thin zone of calcium-rich remineralization (100 μm) was noted at the leach front.
- The specimen beyond the leach front was essentially unchanged.
- A small pH gradient in the leached shell was noted, followed by a large pH change over the very narrow leaching zone. Beyond the leaching zone, there was a constant high pH in the unreacted core.

Batchelor [13] applied a numerical leaching model to specimens leached under conditions typical of a TCLP leach test. This model recognized that acid diffusion into the specimen was the controlling mechanism. The model predicted the interior pH distribution noted by Cheng, along with a reprecipitation of lead hydroxide in the specimen interior.

The shrinking unreacted core (SUC) model was developed by Hinsenveld and Bishop [6] to describe leaching mechanisms from solidified/stabilized specimens. In the bulk diffusion model, contaminant leaching is considered a result of diffusion from the monolith, into the leachant. Under the SUC model, contaminant leaching results from acidic species diffusing into the solid matrix. As acid penetrates into the monolith, a leached 'shell', depleted of free calcium and contaminants, is formed. Solubilized species are subsequently released into the leachant, or diffuse inward, where they are reprecipitated at the higher pH conditions of the unreacted matrix. The leached shell is clearly delineated by this region of remineralization. The inner 'core' of the monolith is assumed to remain unaltered. This model is summarized below; for the complete mathematical model derivation, see Hinsenveld [1]. Fig. 1 presents a schematic illustration of the SUC model.

In Hinsenveld's model development, three possible limitations in the kinetics were evaluated:

- Diffusion through the concentration boundary layer
- Diffusion through the leached shell
- Chemical reactions at the leached shell–core interface.

Cheng [7] originally postulated that the limiting leaching mechanism is the diffusion-

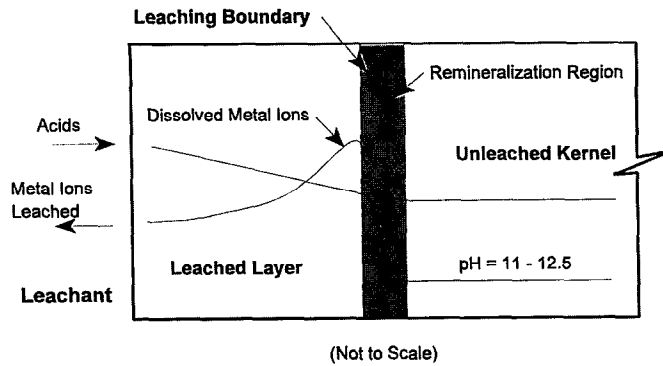


Fig. 1. Principles of the shrinking unreacted core (SUC) model.

controlled fast reaction of the acid species into the leached shell. Further evaluation of this data by Hinsenveld [1] more clearly defined hydrogen ion diffusion into the leached shell as the limiting mechanism. For this reason, the shell diffusion limitation will be the only limitation discussed here. Hinsenveld [1] developed the following concepts associated with the derivation of the SUC model:

2.2.1. Conversion

The conversion, ζ , is a term relating the amount of leached shell to the original amount of material. With flat specimens, this is simply the acid penetration depth (APD) of the leached shell. With specimens of cylindrical or spherical geometry, the conversion is a dimensionless number relating the original specimen radius to the core radius.

2.2.2. Exposure

The amount of acid a specimen is exposed to under acidic conditions is defined as the acid exposure, which is equivalent to the acid concentration multiplied by the leaching time ($c \times t$), measured in units of acid equivalents \times time/volume (mol min l^{-1}). During leach testing, the acid concentration is a function of leaching time; the pH increases as the alkalinity of the solid is consumed. In order to compensate for the change in acid concentration over time, the exposure integral, $I(t)$, is presented:

$$I(t) = \int_0^t \bar{c}_T \partial t \quad (3)$$

where \bar{c}_T is the average acid concentration [6].

2.2.3. Solid acid neutralization capacity

The solid acid neutralization capacity, β_c , is defined as the quantitative capacity of cement to react with a strong acid to a pre-determined pH. For the purposes of this work, the ANC is the buffering capacity in the cement, expressed as a solids concentration, eq cm^{-3} .

Under the leached shell diffusion limitation, the conversion, as measured by acid penetration depth (cm), follows the following relationship for strong acids:

$$\zeta = \sqrt{\frac{2D_{e,s}(c_{H,i} - c_{H,c})}{\beta_c} t} \quad (4)$$

where $D_{e,s}$: effective diffusion coefficient (for acid species) ($\text{cm}_2 \text{s}^{-1}$), $c_{H,i}$: hydrogen ion concentration at the liquid interface (kmol m^{-3}), $c_{H,c}$: hydrogen ion concentration at the core boundary (kmol m^{-3}), β_c : acid neutralization capacity (kmol eq m^{-3}).

Of particular note with this limitation is the square root of time relationship, similar to that in the bulk diffusion model.

The driving force is provided by the bulk hydrogen ion concentration in the leachant. By assuming the H^+ concentration at the leaching front is much less than that in the bulk liquid, the exposure integral (Eq. (3)) can be substituted into Eq. (4) to give:

$$\zeta = \frac{2D_{e,s}I(t)}{\beta_c} \quad (5)$$

The previous relationship can be applied to predicting the conversion under a certain set of leaching conditions. Because the conversion is related to the exposure integral, $I(t)$, and not to acid concentration or time alone, a theoretical basis for an acceleration of the leaching process can be developed. For example, a specimen leached at an average pH of 4.0 for 10 days would theoretically yield the same conversion as an identical specimen leached at an average pH of 3.0 for one day or at an average pH of 7.0 for 1000 days, assuming that the difference in pH does not significantly affect metals speciation.

Hinsenveld [1] broke the preceding equation into three basic components. The left hand side of the equation is a function of the conversion, and can be defined as the leaching function, L . The right hand side of the equation can be broken down into a leaching constant, K , and the acid exposure, $I(t)$, yielding the following relationship:

$$L_2 = K_2 I(t) \quad (6)$$

where L_2 : leaching function for leached shell diffusion limitation.

One basic premise of the SUC model is that contaminant release is directly related to the conversion, or acid penetration depth:

$$M''(t) = l_s C_m f_{mo} \quad (7)$$

where $M''(t)$: contaminant release per unit surface (mol cm^{-2}), C_m : solid contaminant concentration (mol cm^{-3}), f_{mo} : leachable fraction (dimensionless), l_s : thickness of the leached shell (cm).

The contaminant release per unit surface is determined to be:

$$M''(t) = \sqrt{\frac{2D_{e,s} f_{mo}^2 C_m^2 I(t)}{\beta_c}} \quad (8)$$

As can be seen from Eq. (8), for a given exposure integral, the predicted contaminant release per unit surface is a function of a few basic parameters: the bulk contaminant concentration (C_m) and availability (f_{mo}) in the S/S specimen, the porosity and tortuosity of the leached shell and their effect on the diffusivity of the acid species ($D_{e,s}$), and the solid ANC of the S/S specimen (β_c).

The potential release factor (PRF) was introduced as a means of ranking the S/S specimens according to their leach resistance [1]:

$$\text{PRF} = \frac{\sqrt{2D_{e,s} f_{mo}^2 C_m^2}}{\beta_c} \quad (9)$$

Lower PRF values are desirable, in that they yield a lower potential for leaching. The PRF should be independent of the conditions under which leaching occurs, provided diffusion of acid into the leached shell is the limiting mechanism and f_{mo} does not change. Because the PRF values obtained are low, Hinsenveld [1] introduced an additional term, the stabilization quality index, which is simply the negative logarithm of the PRF:

$$\text{SQI} = -\log(\text{PRF}) = -\frac{1}{2} \log \left[\frac{2D_{e,s} f_{mo}^2 C_m^2}{\beta_c} \right] \quad (10)$$

The SQI is analogous to the leachability index (LX) values obtained in the ANS 16.1 test procedure; the LX values obtained in the ANS 16.1 procedure are actually SQI values which have not been corrected for the acidity dependence. A theoretical SQI can be determined for various waste forms, but by conducting leach tests which incorporate the acid exposure, this value can be better estimated. A good correlation between the theoretical and experimental SQI values would indicate that acid penetration is the controlling mechanism. Based upon a leached shell diffusion, the experimental SQI is calculated as follows:

$$\text{SQI} = -\log \left(\frac{M''(t)}{I(t)^{0.5}} \right) \quad (11)$$

3. Experimental

3.1. Sample sources

Two sets of samples were used in this study. The first set of samples (Site 1) was collected as part of a study conducted by the University of Cincinnati for an evaluation of the durability of solidified/stabilized wastes exposed to environmental conditions at various sites. The second set of samples (Site 2) consisted of representative samples from a USEPA SITE demonstration project.

Site 1 is a former metal plating facility. Primary metal contaminants found in the contaminated soil were chromium, zinc, nickel, and cadmium. The less contaminated materials were solidified with cement, on-site. Core samples from the monolith were

collected from the resulting monolith core, the monolith edge (outer 30 mm of the core), adjacent soil, and 'background soil'. Site 2 is a former electric service shop. The primary contaminants of concern at this site were PCBs, but four priority pollutant metals were present in detectable quantities: lead, chromium, copper, and zinc. The contaminated soils were solidified/stabilized in-situ.

3.2. Sample preparation

The samples used in this research were of two basic forms. Samples from Site 1 consisted of 2 in. (5.1 cm) diameter cores collected in-situ. Samples from Site 2 consisted of 6 in. (15.2 cm) diameter cylinders.

For this research, it was necessary to isolate one sample surface for leach testing. The Site 1 samples were saw-cut using an automatic feed circular rock saw in order to obtain one smooth, circular surface. The surfaces of the sample, except that to be exposed to the leachant, were sealed with an epoxy sealant. The resin was allowed to harden for 48 h. The Site 2 samples were initially saw-cut into widths of approximately 2 in. (5.1 cm), resulting in a 6 in. (15.2 cm) diameter disk. Each disk was sectioned into four squares, approximately 2 in. \times 2 in. (5.1 cm \times 5.1 cm). Unexposed surfaces were then sealed in the same manner as above, with one surface left unsealed. The samples were rinsed with ASTM Type II water before initiation of the leach test.

3.3. SUC leach test

The SUC model test is not much more complex than currently used standard sequential leach tests, such as the ANS 16.1 Leach Test. The basic rationale behind this test is that the rate of contaminant release from the stabilized/solidified specimen is due to the inward penetration of acid species, and not the outward diffusion of contaminants. Because of this basic assumption, the kinetics of contaminant release are evaluated as a function of acid exposure, rather than of time.

The basic procedures followed are described below. Table 1 contains a summary of the specific conditions for each sample tested, which includes sample ID (samples designated with S1 indicate Site 1 samples, those designated with S2 indicate Site 2 samples; A and B indicate different cores), initial liquid to solid (L/S) ratio, leachant composition, overall bulk liquid pH, and leaching duration. The complete standard procedure can be found in Baker [14].

Each experimental run consisted of leaching a group of between four and six samples. The samples were suspended via nylon monofilament in the approximate center of the leachant. A teflon magnetic stir bar was placed in each container, and the leachant was mixed throughout the experiment using a magnetic stirrer. The leachant pH was controlled through addition of acid to the leachant to maintain the pre-determined pH after each measurement was taken. The acid used for pH control was of the same ratio of $H_2SO_4:HNO_3$ as the initial leachant. The initial pH, volume of acid added, and ending pH were recorded each time the pH was measured.

Samples were collected at regular intervals throughout the leaching experiment. The sampling frequency should be dictated by the acid exposure, and not strictly by time. In

Table 1
Leaching experiments summary

Sample ID	Bulk liquid pH	H ₂ SO ₄ :HNO ₃ ratio (wt%:wt%)	Leach time (d)	Leachant volume: surface area (cm ³ cm ⁻²)
S1A-1	3.3	30:40	7	20
S1A-3	4.0	30:40	7	40
S1A-5	4.0	30:40	7	40
S1A-6	3.3	30:40	7	20
S1A-7	3.0	30:40	8	20
S1A-8	2.7	30:40	8	20
S1A-9	2.1	30:40	8	20
S1A-10	2.3	30:40	8	20
S1B-1	3.6	0:100	14	20
S1B-2	3.6	0:100	14	20
S1B-3	3.9	0:100	14	20
S1B-5	3.9	0:100	14	20
S1B-8	3.3	0:100	14	20
S2-4-1	3.0	60:40	14	20
S2-4-2	3.0	60:40	14	20
S2-4-3	3.3	60:40	14	20
S2-4-4	3.3	60:40	14	20
S2-2-1	4.0	30:40	14	20
S2-2-2	4.0	40:40	14	20
S2-3-1	2.3	30:40	14	20
S2-3-2	2.6	30:40	21	20
S2-3-3	2.3	30:40	14	20
S2-3-4	2.6	30:40	21	20
S2-2-4	N/A	DI H ₂ O	51	20
S1B-6	N/A	DI H ₂ O	51	20

general, samples were collected at a daily frequency for the first four days of the test, and every other day thereafter. In addition to the regular leaching samples, a method blank, consisting of a container with the same leachant volume and the equivalent volume and concentration of acidic leachant, was run during the experiment. Two samples, one from each site, were leached in deionized water as controls.

Following completion of each experiment, samples leached at higher exposures (e.g., lower pH, longer durations) were manually fractured to determine the presence of a leaching boundary and the pH profile in the leached shell, per procedures outlined by Cheng [7]. However, it was typically found that an insufficient leached shell thickness was generated to ascertain any variations in pH via pH indicators. The maximum leached shell thickness obtained was approximately 1 mm. If a sufficient leached shell was present, the thickness was measured using a dial-type caliper.

3.4. Generalized acid neutralization capacity test

Determination of the acid neutralization capacity (ANC) for each of the sample sets was accomplished using a modification of the general acid neutralization capacity

(GANC) Test, developed by Isenburg and Moore [15] as a batch titration procedure to determine the neutralizing capacity of solidified/stabilized samples.

Samples from each site were crushed, passed through a 3/8 in. (0.95 cm) sieve, and dried in an oven for 48 h at 10°C. The sample was then ground and passed through an ASTM #40 sieve. 1.000 ± 0.005 g samples were weighed out and placed into a 125-ml HDPE bottle. 21 samples, labelled 0 through 20, were weighed out per sample set, with triplicate samples run for each leach interval. A total of 20 ml of leachant was added to each bottle, with the equivalents of acidity per each sample increasing incrementally for each sample by diluting the stock leachant to 20 ml with ASTM Type II water.

The original procedure proposed by Isenburg and Moore [15] called for the use of acetic acid as the leachant, primarily because this was the leachant used in the TCLP test. For this procedure however, the composition ($\text{H}_2\text{SO}_4:\text{HNO}_3$) of the acidic leachant was chosen to mirror the same composition as that used in the leach tests.

The samples were tumbled for 48 h in a rotary mixer. Samples were then removed, and allowed to sit for 15 min. The pH of the decanted water was then measured and recorded, and the ANC computed. The pH meter was recalibrated after every 10 pH measurements.

3.5. Physical and chemical measurements

The water content and bulk density of solid samples were measured using the procedures described in Ref. [14]. Leachate acidity, alkalinity and pH measurement procedures are also described there.

Solid samples for metals analysis were digested using the procedure presented by Cheng [7], with the exception that hydrochloric acid (HCl) was used following the initial nitric acid digestion. The procedure consisted of adding 50 ml of ASTM Type II water and 10 ml of redistilled nitric acid to the beaker, and evaporating on a hot plate, with a ribbed watch glass, to a volume of 10 to 20 ml. The sample was cooled, 10 ml of trace metal-grade hydrochloric acid was added, and the digestate was evaporated to 5 to 20 ml. The final volume of digested sample was adjusted to a volume of 100 ml with ASTM Type II water and stored in a 125 ml polyethylene bottle for metals analyses. All metal elements determined (Ca, Zn, Cd, and Pb) were analyzed with flame atomic absorption spectrophotometry (AAS) using a Perkin Elmer Spectrophotometer, Model 3030. Inductively coupled plasma (ICP) spectrometry was used for the analysis of cadmium for one sample set (Site 1, Core B).

4. Results and discussion

4.1. Physical and chemical characterization

Physical and chemical characterization studies were carried out on the specimens used in this research. The results of these analyses are summarized in Table 2.

There have been several methods proposed for determination of the ANC. Isenburg and Moore [15] stated that the ANC is equivalent to the amount of acidity added to a

Table 2
Waste characterization

Sample	Bulk density (kg m ⁻³)	Water content (%)	ANC (meq cm ⁻³)	Ca (mg cm ⁻³)	Zn (mg cm ⁻³)	Cd (mg cm ⁻³)	Pb (mg cm ⁻³)
Site 1, Core A	1.78	6.6	20.6	415.2 ± 21.7	2.92 ± 0.15	0.76 ± 0.01	ND
Site 1, Core B	1.64	6.5	17.1	385.8 ± 54.7	2.49 ± 0.02	0.67 ± 0.01	ND
Site 2	1.54	10.4	20.5	364.7 ± 1.8	0.13 ± 0.01	ND	1.54 ± 0.04

ND: Not Detected

predetermined pH of 8.5, the inflection point when acetic acid is used. Cheng [7] found that a trial and error method served best in determining the ANC, based upon the correlation between acid penetration (conversion) and solid ANC consumed by the leachant. Hinsenveld [1] refined this concept and determined the ANC to be equivalent to the best fit slope of the conversion vs. ANC leached curve; this method recognizes the linearity between the conversion and the ANC leached. In this work, accurate correlations between acid penetration depth and ANC leached could not, in most cases, be established due to the very shallow acid penetration depths resulting from the leaching procedure used. Cote [16] utilized Gran functions in interpreting binder–acid leachant titration data, similar to the data collected in the GANC test. The advantage in using Gran functions is that direct interpretation of inflection points can be very difficult due to the gradual slope of the resulting curves. Gran functions were therefore used to calculate the solid ANC in this work.

4.2. Exposure calculation

Leachant pH was controlled during the leach tests through addition of mineral acids into the leachant as solid alkaline species were consumed. The mineral acids used in this work, nitric acid (HNO₃) and sulfuric acid (H₂SO₄), can be assumed to be fully ionized in dilute solutions. The acid concentration in the leachant was calculated based upon an assumed leached shell diffusion limitation, in which both dissociated and partially dissociated acid species are incorporated. The acid concentration then becomes the sum of hydrogen ion and bisulfate ion, neglecting the minimal amounts of undissociated nitric and sulfuric acid:

$$c_T = [H^+] + [HSO_4^-] \quad (12)$$

where c_T : total acid concentration contributing to leached shell diffusion.

In developing the exposure integral, Hinsenveld [1] defined the average acid concentration over a leaching interval, for a weak acid, as follows:

$$\bar{c}_{T,ave} = \frac{\bar{c}_{T,initial} + \bar{c}_{T,final}}{2} \quad (13)$$

The leach tests originally evaluated by Hinsenveld [1] were conducted using acetic acid as the leachant (0.1 to 0.5 M), with the pH change over a leach interval generally within one pH unit. The linear change in acid concentration was therefore justified as an

acceptable approximation for the average acid concentration. With strong, fully ionized acids, however, the rate of change in pH could be greater, due to the lack of buffering capacity in the leachant. An alternative method of estimating the average acid concentration, therefore, needed to be developed. Two possible methods of estimating the exposure integral were evaluated. The first method assumed simple first order kinetics; the rate of consumption of acid was related to the total acid concentration at that time. The second method incorporated the assumptions made under the SUC model. Under this method, the consumption of ANC is assumed to be limited by leached shell diffusion, with the rate of change of acid species following a square root of time relationship. Both methods for exposure estimation generally resulted in a fairly linear relationship between exposure and time. The latter method was selected for estimation of the exposure integral, because it better approximated the kinetics associated with the SUC model.

4.3. ANC release

Hinsenveld [1] illustrated the linearity between the release of calcium and solid ANC. Contaminants are mobilized and leached out of the specimen as ANC is released; if all contaminants are in a mobile phase, there should be a resultant linear relationship between ANC and contaminant release. Thus, the release of ANC can provide the basis for determining the potential leachability.

The acid neutralization capacity (ANC) leached versus exposure and time was determined by summing the total equivalents of acid added to the leachant at each interval and subtracting the difference between the total equivalents of acidity in the leachant at the start and end of each interval.

$$\begin{aligned} & \text{meq ANC consumed} \\ & = \text{meq acidity added} - (\text{meq residual acidity} - \text{meq initial acidity}) \end{aligned} \quad (14)$$

As a check on Eq. (14), the ANC leached was also estimated by incorporating the pH change and estimated build-up and change in bisulfate ion (HSO_4^-). This was accomplished by summing up the change in residual acidity, measured as hydrogen ion, and bisulfate ion concentration multiplied by the leachant volume, over each time interval. This method resulted in good correlations with the direct measurement of ANC leached. In general, incorporation of the bisulfate ion resulted in a slight overestimate of the ANC leached, which could be attributed to the reaction of sulfate with the cement matrix. When bisulfate ion was not incorporated (change in H^+ only), a slight underestimate of the ANC leached was obtained.

The three curves shown in Fig. 2 represent: (1) the calculated ANC released based upon Eq. (14), (2) the estimated ANC leached based upon pH change only, and (3) the estimated ANC leached based upon change in pH and taking into account undissociated HSO_4^- . Directly measuring the ANC leached, although the most accurate method, was also the most labor intensive. Alternative methods, such as incorporation of the pH change, or measurement of an effective tracer of ANC, such as calcium, would be easier to obtain with little loss in accuracy. The use of calcium as an alternative to measurements of ANC leached will be discussed later.

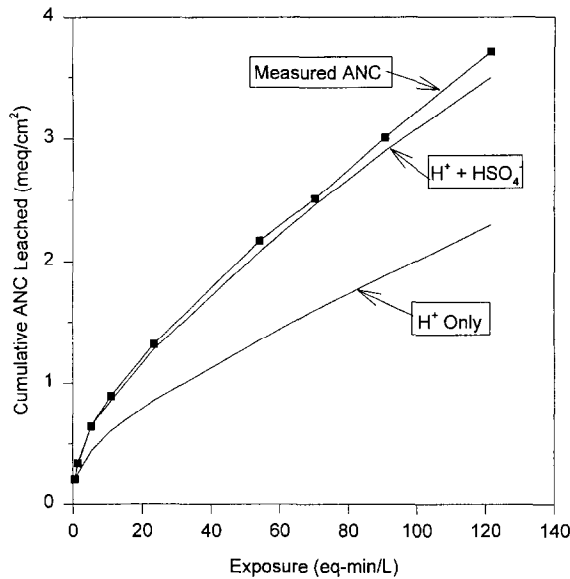


Fig. 2. Example of ANC leached vs. exposure.

According to the SUC model, contaminant leaching from cement-stabilized wastes results from the inward penetration of acid species, followed by dissolution and release of solid ANC from the specimen. The ANC provides buffering capacity and the high pH environment under which chemical precipitation occurs, primarily as hydroxides. The dissolution reaction for alkalinity can be represented by:



When the shell diffusion leaching function, L_2 , is plotted against exposure, a linear fit indicates leached shell diffusion is controlling. An example of this plot for Sites 1 and 2 samples is shown in Fig. 3. The linearity of the L_2 leaching function vs. exposure plots suggest that leached shell diffusion is most probably the dominant leaching mechanism for these specimens.

The governing equation for contaminant release, assuming shell diffusion limitation, is:

$$M(t) = \sqrt{2D_{e,s}\beta_c I(t)} \tag{16}$$

The parameters needed to evaluate this equation are solid ANC (meq cm^{-3}), and the effective diffusion coefficient ($\text{cm}^2 \text{s}^{-1}$). The effective diffusion coefficient was calculated based upon the diffusivity of free hydrogen ion ($9.33 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ at 25°C), which is the dominant acid species, and retardation values in agreement with those reported in the literature. The retardation factor is calculated as follows:

$$\text{Retardation} = \frac{\epsilon}{\tau} \tag{17}$$

where ϵ : leached shell porosity and τ : leached shell tortuosity.

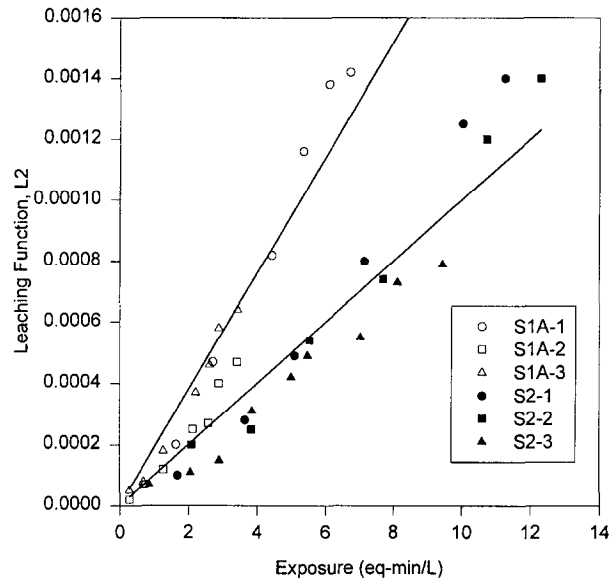


Fig. 3. The effect of exposure on the leaching function L_2 for Site 1, Core A, and Site 2 samples.

Leached shell porosity for laboratory synthesized portland cement specimens leached in acetic acid was reported as 0.8 [7]. For Site 1 samples, a retardation factor of 0.5 was selected. For Site 2 samples, a retardation factor of 0.4 was selected. These values were

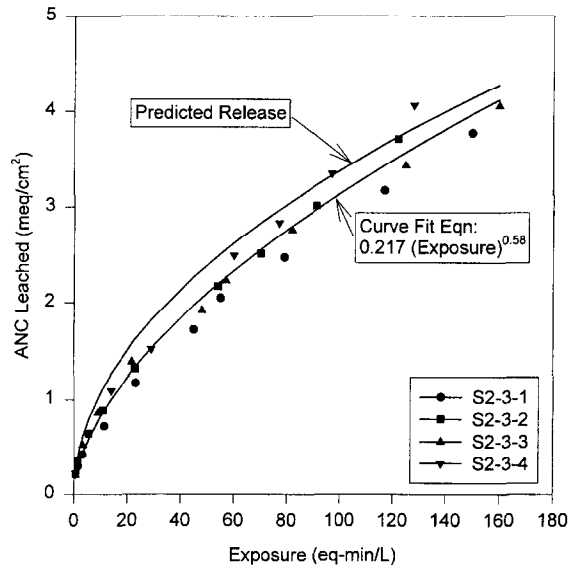


Fig. 4. The effect of exposure on ANC leached from Site 2 samples using leachants with pH less than 3.0.

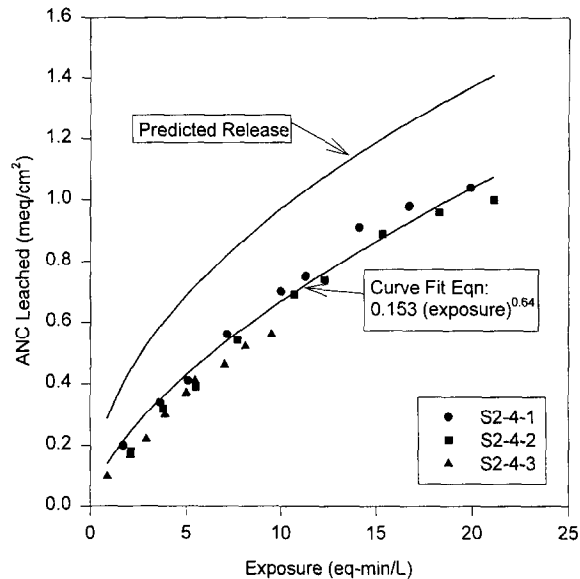


Fig. 5. The effect of exposure on ANC leached from Site 2 samples using leachants with pH greater than 3.0.

higher than those selected by Cheng [7], 0.2, and Hinsenveld [1], 0.27, for laboratory synthesized specimens. The higher values used in this research, as compared to past work, are justified given the quality of the specimens used in this work.

Fig. 4 and Fig. 5 illustrate the ANC leached versus exposure for the Site 2 samples leached under acidic conditions. The four samples shown in Fig. 4 were leached under very aggressive leaching conditions (pH range of 2.3–2.6). The samples shown in Fig. 5 were leached under somewhat less aggressive conditions (pH range of 3.0–4.0). The overall best curve fit line, along with predicted results using the equations given above, are also shown in the figures.

The power coefficients of the best fit lines for these samples show that the curve fit power coefficients were generally slightly greater than the expected 0.5. Two possible leaching limitations are reaction (linear relationship with exposure) and shell diffusion (square root of exposure) limitations. In the work conducted by Cheng [7], shell diffusion was found to be the limiting mechanism. Hinsenveld [1] postulated that reaction limitations may become controlling at lower exposures or under higher acid concentrations. It is also possible that another mechanism, such as bulk diffusion, is contributing in a minor way to the ANC release from Site 2 samples. At a lower pH, the SUC leaching mechanism appears to become more controlling.

4.4. Calcium leaching

Hinsenveld [1] demonstrated that ANC and calcium release are strongly correlated, because solid ANC is primarily found in portland cement-based systems as calcium hydroxide. The anticipated molar ratio of calcium to ANC leached is 1:2; expressed on a

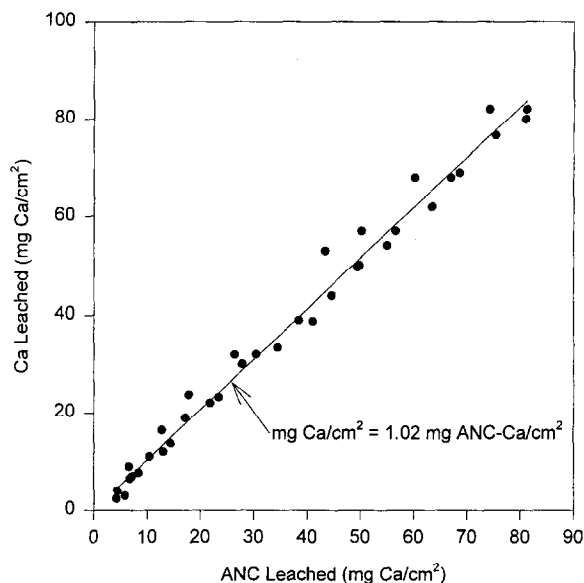


Fig. 6. The relationship between the amount of ANC leached and leaching of calcium.

weight basis, it becomes 1 mg Ca:1 mg ANC (as Ca). The ratios of calcium to ANC leached were calculated for each sample. Fig. 6 presents the calcium vs. ANC leached plots for Site 2; Site 1 reacted in a similar way, although there was slightly more scatter. Samples from Site 2 had very close to a 1:1 ratio (mg mg^{-1}). Because of the direct relationship between leaching of calcium and ANC, calcium concentrations, which are much easier to determine than ANC, can be used in data analyses when evaluating contaminant leaching mechanisms.

Evaluation of the resultant calcium release curve fit equations was compared to a predicted release equation, similar to that used for the ANC leached data, assuming leached shell diffusion as the limiting mechanism. The predicted release equation is:

$$M''(t) = ae^{0.5} \quad (18)$$

where $M(t)$: calcium leached (mg cm^{-2}), and $a = \sqrt{\frac{2D_{e,s}(f_{m,o}C_{m,o})^2}{\beta_c}}$.

Fig. 7 shows the calcium leached vs. exposure curves for the Site 1, Core A samples. Core B results were similar, although there was slightly more scatter due to the heterogeneity of the sample. As can be seen, the prediction equation fit the data very well, with a power coefficient of 0.5 as expected.

Fig. 8 shows the calcium leached vs. exposure for samples from Site 2 subjected to aggressive leaching (leachant pH < 3.0). Again, the predicted and best curve fit equations are very close, with a power function of 0.55 for the curve fit equation. For samples leached with less aggressive leachant (leachant pH > 3.0), the amount leached was slightly less than predicted (Fig. 9). Examination of the curve fit equations shows

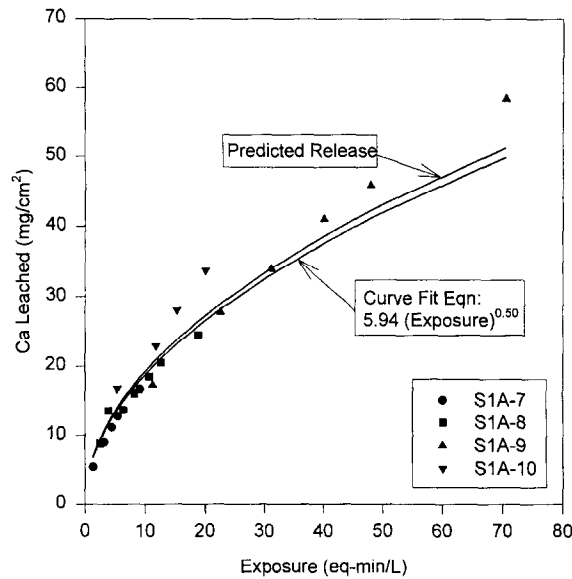


Fig. 7. The effect of exposure on leaching of calcium from Site 1, Core A samples.

that the power functions for both were nearly the same; the equations differ mainly in the first term in the equation, which is a function of basic physical–chemical parameters: solid calcium concentration, availability, tortuosity, porosity, and solid ANC. The

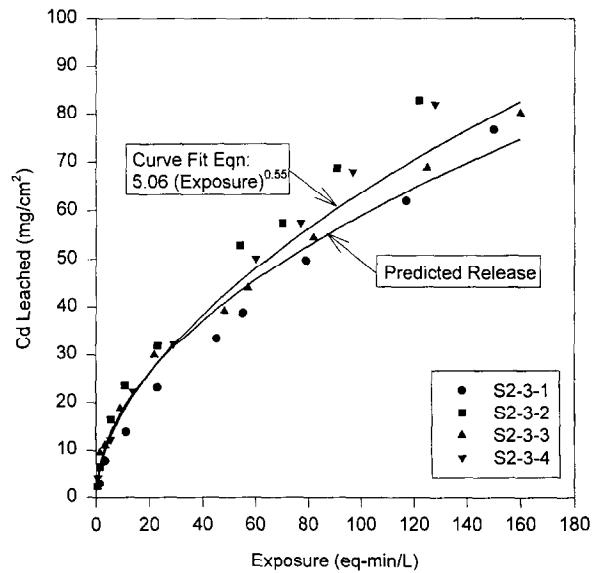


Fig. 8. The effect of exposure on leaching of calcium from Site 2 samples using leachants with pH less than 3.0.

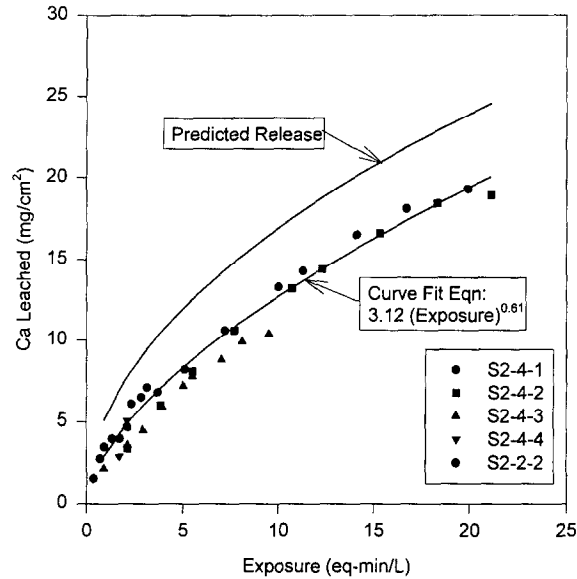


Fig. 9. The effect of exposure on leaching of calcium from Site 2 samples using leachants with pH greater than 3.0.

increased leaching potential of the samples exposed to more aggressive conditions can be attributed to one or more of the following potential factors:

- An increased porosity–reduced tortuosity of the leached shell resulting from increased dissolution of the leached shell, when exposed to higher acid strengths.
- The more aggressive leaching conditions resulted in a greater availability of calcium species to leaching.
- The difference in leaching was simply due to sample heterogeneity.

4.5. Trace metals release

The leaching behavior of trace metals was evaluated to determine the applicability of the SUC model for metals leaching. The trace metals which were evaluated included: cadmium (Site 1), lead (Site 2), and zinc (Sites 1 and 2).

In order to better establish the release mechanisms for contaminant releases, Hinsenfeld [1] plotted the fraction of contaminant released as a function of exposure. The fraction of contaminant released is defined as the actual contaminant released divided by the theoretical contaminant release. According to the SUC model, the contaminant is speciated so that it is either available (i.e., precipitated as a hydroxide or other easily soluble form in the primary matrix of the cement) or unavailable for leaching (i.e., chemically incorporated into the secondary matrix). Under the simplest form of this model, the fraction of contaminant leached is a function of specimen conversion only. The resultant plot of theoretical fraction leached versus exposure would consist of a straight line, parallel to the x -axis (exposure). Additional contributing mechanisms

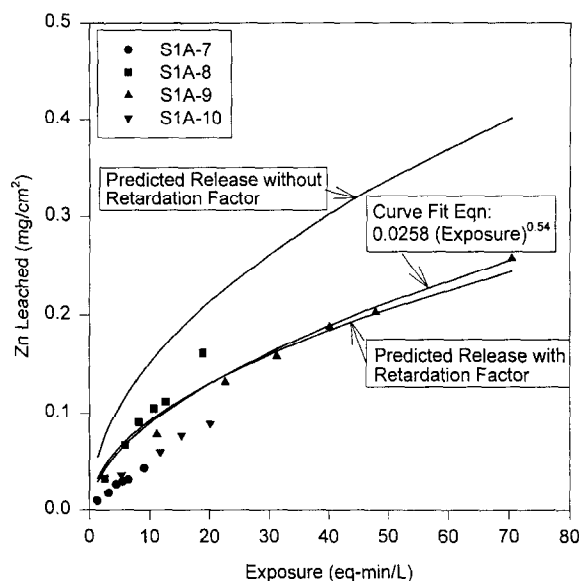


Fig. 10. The effect of exposure on leaching of zinc from Site 1, Core A samples, including predicted release rates (with and without a retardation factor).

which were identified by Hinsenveld would result in a deviation from this parallel line. Adsorption of the contaminants onto the surface of the leached shell would result in a slight decrease from this line, indicating that as the depth of the leached shell increases, the number of adsorption spaces increases, reducing the amount of contaminant released. Bishop [17] postulated that adsorption of contaminants onto the leached shell may play a significant role as a secondary stabilization mechanism. Another mechanism contributing to a deviation from a parallel line is a slower, kinetically controlled release of contaminants from the secondary matrix [1]. This may occur as a result of incongruent dissolution of the secondary matrix, which may be important at lower pH values. The resultant plot of fraction released vs. exposure would result in a line with a slightly positive slope.

Trace metal contaminants evaluated from the Site 1 samples were cadmium and zinc. As expected, zinc concentrations were generally higher in the leachant. Many of the measured cadmium concentrations for samples leached under 'less' aggressive conditions (Core A, Group 2, and Core B) were below practicable detection limits. This was attributed both to the lower solids concentrations and speciation leading to a higher leach resistance Fig. 10 and Fig. 11 are examples of the use of the SUC model to describe metal leaching from S/S wastes. These show zinc and cadmium, respectively, vs. exposure from Site 1, Core A. Site 2 samples responded in a similar fashion. As can be seen, although the resultant curve fit equations for both cadmium and zinc fit closely to the power of 0.5, indicating a possible leached shell diffusion limitation, actual metals leaching was generally less than predicted by the SUC model. The model parameters used assumed 100 percent availability of metals for leaching. Apparently, this was an

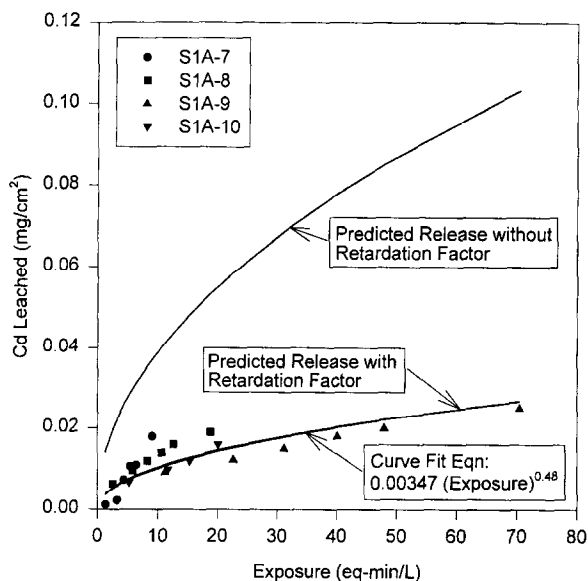


Fig. 11. The effect of exposure on leaching of cadmium from Site 1, Core A samples, including predicted release rates (with and without a retardation factor).

erroneous assumption; some portion of the metals was probably incorporated into the paste matrix and unavailable for leaching.

Site 2 samples were also tested for leaching of lead (Fig. 12). Again, leachate

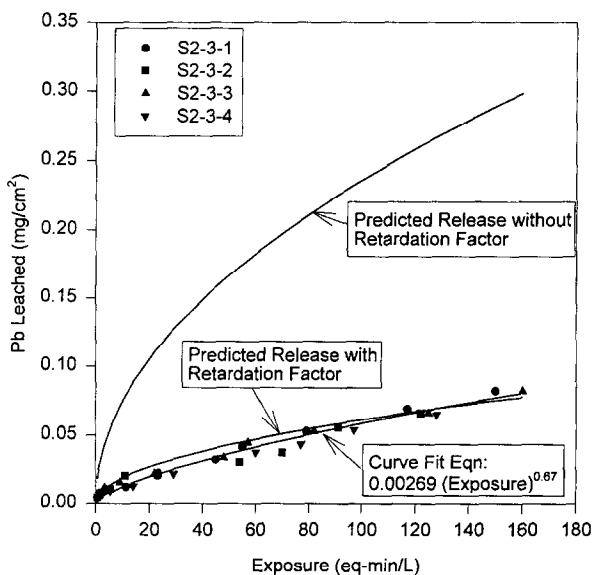


Fig. 12. The effect of exposure on leaching of lead from Site 1, Core A samples, including predicted release rates (with and without a retardation factor).

Table 3
Retardation factors for sample groups

Sample ID	Zn	Cd	Pb
Site 1, Core A—all samples	0.61	—	—
Site 1, Core A—Leachant pH < 3.0	0.58	0.26	—
Site 1, Core A—Leachant pH > 3.0	0.72	—	—
Site 1, Core B—all samples	0.34	0.13	—
Site 2—all samples	1.09	—	0.26

concentrations were much less than predicted using the SUC model and assuming 100 percent lead availability.

The retardation factor of a contaminant (incorporating the effects of the availability factor and adsorption) can be determined through evaluation of the fraction released plots. In the development of the predicted release equations, the retardation factor was assumed equal to 1, with the contaminant being completely available for leaching. This assumption was shown, in most cases, to result in an overestimate of the contaminant release. Table 3 presents the calculated retardation factors for the sample groups. When the retardation factors shown were applied to the model, the curve fits matched the leaching data almost exactly (see Figs. 10–12).

Evaluation of the retardation factors shows that cadmium and lead, the two priority pollutant metals, have low retardation factors, indicating they were successfully stabilized. For Site 1 samples, zinc was less successfully bound. Zinc can be assumed to be 100% available for the Site 2 samples, with an average retardation factor of approximately 1.

4.6. Evaluation of SQI

The stabilization quality index (SQI) was calculated for each sample set. Table 4 presents a summary of the calculated SQI values for the samples studied in this research.

Table 4
SQI values for leached samples

Sample ID	SQI values		
	Ca	Zn	Cd
Site 1, Core A—Predicted	3.66	6.02	6.84
Site 1, Core A—Leachant pH < 3.0	4.72	7.35	8.39
Site 1, Core A—all samples	4.73	7.29	8.48
Site 1, Core B—predicted	3.65	6.05	6.86
Site 1, Core B—all samples	4.71	7.71	8.89
Site 2—Predicted	3.76	7.42	6.85
Site 2—Leachant pH < 3.0	4.71	8.30	8.48
Site 2—Leachant pH > 3.0	4.93	—	—
Site 2—all samples	4.81	8.33	—

Blank values in the table indicate those samples whose measured concentrations were below the analytical detection limit for that metal. The predicted value shown for these samples was calculated using an assumed availability factor, f_{mo} , of 1. As can be seen in the table (and as shown previously) use of an availability factor of 1 for contaminants generally results in an underestimate of the SQI, or a conservative (over) estimate of contaminant leaching rates.

5. Conclusions

The behavior of "real-world" solidified wastes was studied in order to verify that previously observed shrinking unreacted core (SUC) leaching behavior in synthesized waste forms applied equally as well to real world wastes. Cored samples of solidified/stabilized wastes taken from two sites were used to evaluate a new test procedure designed to model shrinking core behavior. Metals leaching behavior was evaluated as a function of the exposure.

The use of the exposure integral was successful in modelling leaching from solidified/stabilized wastes. The exposure integral can easily be estimated from periodic pH measurements during leaching, and a knowledge of the kinetics associated with the rate of consumption of solid ANC. The specimens used in this research fit the SUC model well. This included ANC leaching, calcium leaching and leaching of heavy metals (if a retardation factor incorporating the effects of availability factor and adsorption of the metal were used).

Measurements of ANC leaching can be adequately estimated using pH measurements, eliminating the need for labor intensive direct measurement of ANC. Measurement of calcium release could also be used to describe the leaching of ANC.

These results show that leaching of S/S wastes under acidic conditions can be modelled well as a shrinking unreacted core. The results, coupled with the concept of the exposure integral can be used to estimate the long-term effects of acid leachants on these wastes. The use of this leaching test is a vast improvement over the commonly used bulk diffusion model. It can be combined with a knowledge of the disposal conditions to describe long-term leaching under natural conditions.

Additional work is still needed to assess whether this model is accurate when the leachant is neutral or alkaline where bulk diffusion may play a greater role.

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