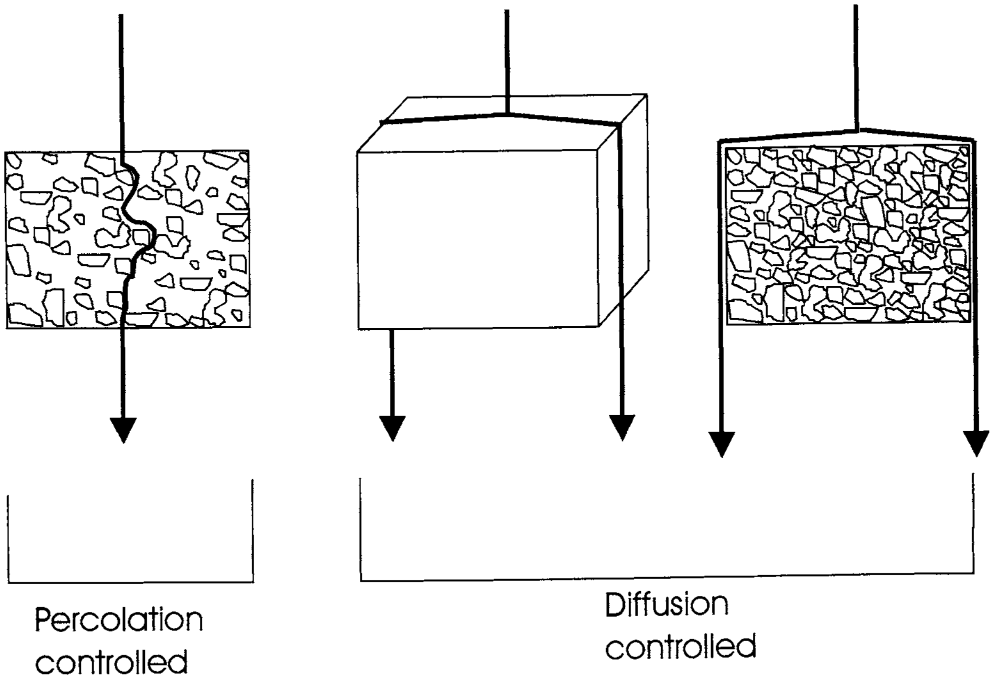
CHAPTER 20 - LEACHING OF PRODUCTS

20.1 INTRODUCTION

MSW incinerator residues are widely being considered as an aggregate substitute in a variety of construction applications. These construction applications result in the incorporation of incinerator residues in products such as asphalt pavement and cement structures, or direct use as a compacted granular aggregate after varying degrees of treatment or component separation. The evaluation of potential environmental impacts from the use of these products focuses on release of contaminants via leaching.

As previously described in Chapter 12-15, there are different mechanisms which dominate leaching behaviour of granular versus monolithic materials (Figure 20.1). This chapter focuses primarily on the mechanisms of dissolution, surface wash off and diffusion through the product to the surface where the water-product interface exists. The information presented in this Chapter will serve as the framework for utilisation criteria discussed in Chapter 21.

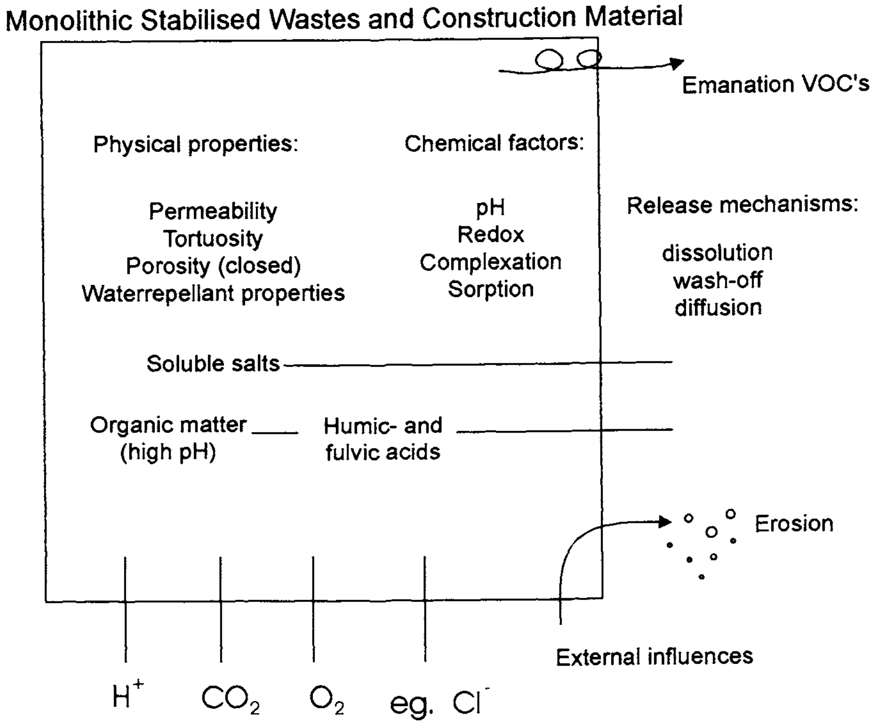
Figure 20.1 Comparison of Percolation and Diffusion Controlled Leaching



20.2 PHYSICAL AND CHEMICAL FACTORS WHICH EFFECT CONSTITUENT RELEASE

The physical and chemical properties of a product and the interactions with the surrounding environment define the constituent release behaviour of the product (Figure 20.2). Several important physical properties of the product are related to the internal pore structure of the material. These include permeability, porosity and tortuosity. Permeability defines the rate at which water can percolate through the product. The difference in the hydraulic conductivity gradient between ash products and the surrounding soil layers generally results in flow around or runoff from a product instead of percolation through the material. Porosity indicates the void space within the material and the potential for water absorption. Tortuosity is the ratio between the actual and apparent geometric path length of a species diffusing through a material. Actual path lengths are longer than apparent geometric path lengths because of the irregular nature of internal pores. Tortuosity is used to estimate the physical restriction to leaching of a leachable constituent.

Figure 20.2 Mechanisms of Release and External Influences During Diffusion Controlled Leaching



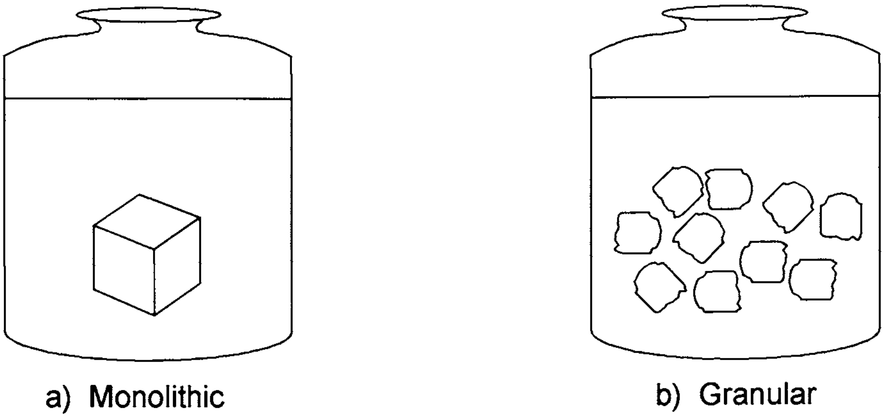
Durability of a product also is a physical property that significantly influences contaminant release. A product which is not durable is subject to erosion and deterioration to a granular material over time and should be evaluated as a granular material with percolation (e.g., solubility) as the controlling release mechanism.

Some of the chemical properties of products which affect constituent release include pH, alkalinity, reducing potential, chemical complexation and sorption. For example, the internal pore water pH of a product greatly influences the solubility of ash constituents in the pore solution, whereas the alkalinity of the material determines the resistance to changes in pH by external influences. The most significant external influences on pH are external applications or acid or alkali, uptake of carbon dioxide, acids produced by biological activity, and acidic precipitation. Uptake of carbon dioxide by alkaline products such as cement blocks typically results in a lowering of pH to between 8 and 9 at the exposed surfaces. The reducing potential is important because subsequent exposure of reduced material to oxidising conditions may result in an increase in the mobility of metallic elements (ie. oxidation of sulphide minerals). Increased metal mobility may also occur when high concentrations of chlorides or organic acids act as complexing agents which sequester the metals and keep them in solution. Conversely, the sorption or cation exchange by an ash's products component may reduce the mobility of leachable constituents. The chemical retention factor is a relative indicator of the cumulative influence of the material's chemical properties on the mobility of contaminants.

20.3 TEST METHODS FOR MONOLITHIC AND COMPACTED GRANULAR PRODUCTS

Test methods used to evaluate diffusion controlled release are frequently referred to as either "monolith leach tests" or "tank leaching tests." Two primary test methods are used for evaluation of monolithic materials. The first test method is the American Nuclear Society Method 16.1 (ANS 16.1, 1986). The second test method is a recent variant of ANS 16.1 that has been adopted in The Netherlands as NEN 7345 (1994). Both tests are operationally very similar (Figure 20.3). A molded and cured test specimen of defined geometry is immersed in distilled-deionised water (leachant). The leachant is replaced with fresh leachant after specified time intervals and the recovered leachant is sampled for chemical analysis. The principal difference between the tests is the basis for data reduction, and the calculation of effective diffusion coefficients and other parameters. A compacted granular leach test was developed to provide diffusion controlled leaching parameters from materials that would be compacted in place to a low permeability (Kosson et al., 1993). In addition, this test permits direct comparison of untreated ash and product properties.

Figure 20.3 Schematic Diagram of Tank Leaching Tests for Monolithic and Compacted Granular Material



20.3.1 ANS 16.1

This leach test uses a cylindrical monolith as the test specimen which is immersed in leachant for defined intervals. At the conclusion of each interval, the resulting leachate is collected and replaced with fresh leachant. A liquid to monolith surface area ratio of 10 is used. Each leachate is analysed individually for species of interest and the cumulative release is calculated as a function of the cumulative leaching interval. A leachability index (pD_e) is then calculated based on the initial concentration in the monolith and the release rate for each species of interest.

20.3.2 NEN 7345

This leach test uses specimens with a minimum diameter of 40 mm which is immersed in leachant (demineralised water) using a closed vessel. The liquid renewal is carried out after 0.25, 1, 2.25, 4, 9, 16, 36 and 64 days. A liquid to product volume of 5 (l/dm^3 of product) is used which corresponds to a liquid to surface area of 80 l/dm^2. In the data processing, the leaching behaviour of constituents is verified to being diffusion controlled (slope ~ 0.5). Subsequently, the effective diffusion coefficient is calculated using the total availability of a contaminant as determined using the NEN 7341, (1994) as the driving force for diffusion. Corrections are made to account for surface wash-off effects. Release after a specified exposure time is expressed in mg/m^2. If the release is not diffusion controlled, alternative methods of assessing release estimates are provided.

20.3.3 Compacted Granular Leach Test

Effective diffusion coefficients for diffusion controlled release from compacted granular materials can be estimated using a compacted granular leach test (Kosson et al., 1993). Granular materials to be tested are compacted at proctor optimum moisture content and a standard compactive effort into a cylindrical mold and allowed to cure prior to testing. The top face of the cylinder is covered with a thin layer of glass beads to avoid erosion during testing. The entire molded sample then is immersed in distilled water for specified time intervals (e.g., 1, 2, 4, 8, 16 and 32 days). The resulting leachate is decanted and replaced with fresh leachant at the conclusion of each leaching interval. Each leachate is analysed separately for each species of interest.

20.4 INTERPRETATION OF DIFFUSION CONTROLLED RELEASE

20.4.1 Characteristic Release Behaviours

Data obtained from monolith or compacted granular leach tests can be used both to identify characteristic release behaviour and to calculate release rate parameters. Characteristic release behaviour can be identified by plotting the cumulative release as a function of contact time on a log-log scale (Figure 20.4). This form of data presentation will be referred to as a "release plot." The following characteristic release behaviours can be distinguished using the release plot:

- Diffusion controlled release
- Depletion of leachable species
- Delayed release
- Surface wash-off
- Washout of mobile species, and
- Changes in chemical conditions

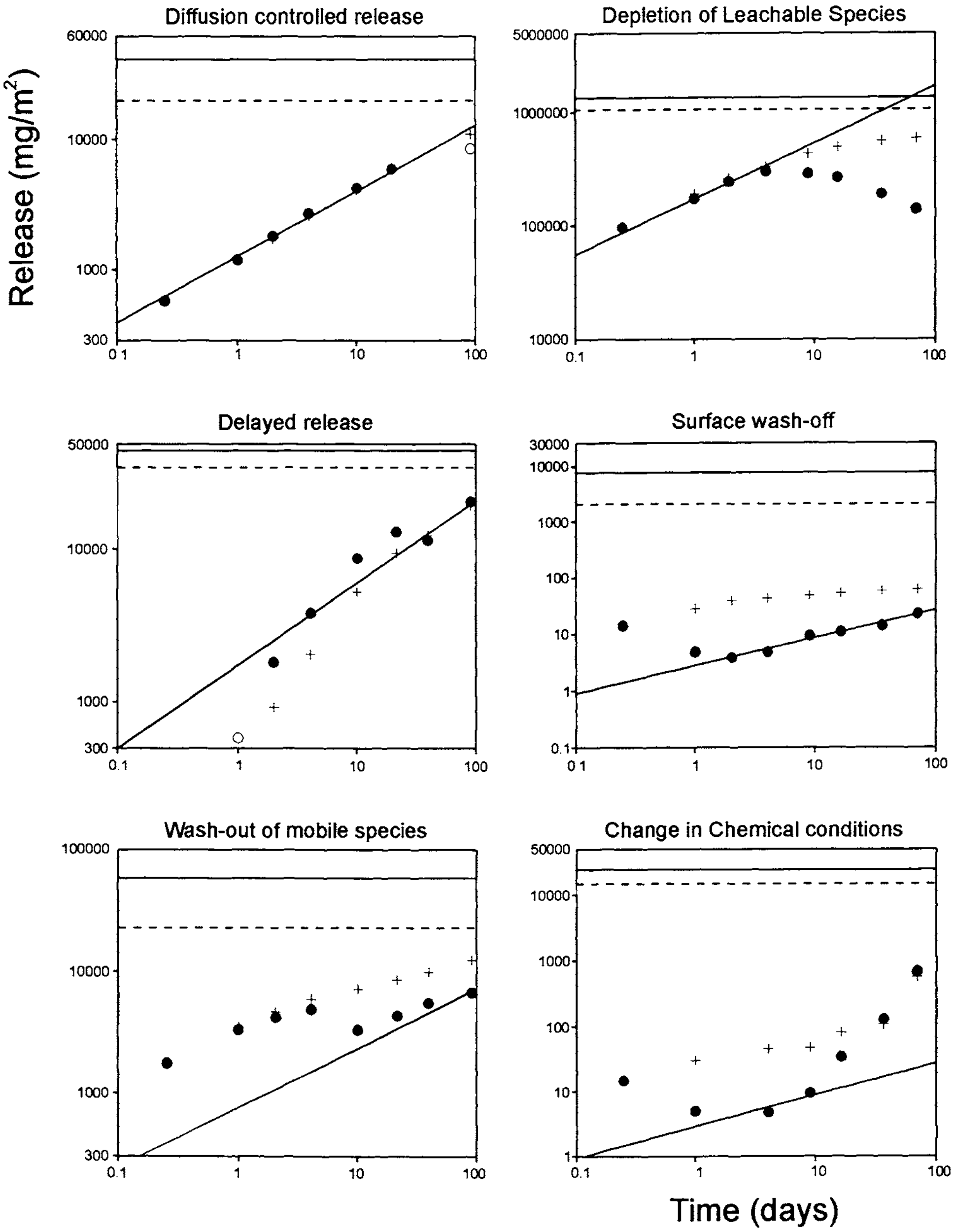
Diffusion Controlled Release

Leaching from most cement-based and asphaltic materials is controlled by diffusion through the solid matrix. Diffusion controlled release is indicated by a slope of 0.5 in the release plot. Diffusion controlled release may be preceded by surface wash off or delayed release. Depletion may occur after an interval of diffusion controlled release. Intrinsic leach parameters, including effective diffusion coefficients, tortuosity, and chemical retention can be derived allowing estimation of release at time scales considerably longer than the duration of the experiment.

Depletion of Leachable Species

Depletion may occur in the later stages of leaching when the concentration of the species of interest within the center of the test specimen is reduced significantly by the

Figure 20.4 Typical Release Profiles Obtained from Tank Leaching Tests for Different Release Mechanisms



cumulative effect of leaching. When this occurs, the initial boundary conditions and experimental assumptions are not met. Depletion may occur when the approximate properties of the material being tested are not known in advance. A slope of less than 0.35 after release in accordance with a slope 0.5 is an indication of depletion. This is verified easily by comparing the cumulative release data with the maximum release quantity obtained from the availability leach test. When more than 50% of the available mass present in the test specimen is leached within the time span of the test, significant depletion can be expected to have occurred.

Delayed Release

A material can be covered with a relatively insoluble or depleted surface layer as a result of process conditions or testing methods. This layer initially retards contaminant release during testing. This behaviour may be observed from the compacted granular leach test because of the presence of the surface layer of beads used to prevent material dispersion.

Surface Wash-Off

A material can be covered with a relatively soluble surface coating as a result of process conditions or condensation processes. This layer can dissolve rapidly during the initial phase of the monolith leaching experiment and is indicated by an initial slope of less than 0.35. In many cases, the subsequent release is diffusion controlled. This type of release is most common for slag type materials.

Wash-Out of Mobile Species (Dissolution)

The solubility of a large fraction of the matrix can be such that dissolution of material from the surface proceeds faster than diffusion through the pores of the matrix. This phenomenon has been observed in products containing very high gypsum loadings (van der Sloot, 1991). In the case of high gypsum content, calcium sulphate solubility is relatively high, which results in an initial theoretical slope of +1 in the release plot. At longer time intervals, the slope decreases as the extract solution becomes saturated with respect to calcium sulphate.

Change in Chemical Conditions

The release rate of a constituent may change during the course of testing because of changing chemical conditions either within the solid matrix or in the extracting solution. This includes changes in redox potential, pH or the depletion of a chemical species which may be limiting the pore water solubility of another species. An example of this type of behaviour is the leaching of Ba, which can be delayed due to an initial high release of sulphate. This causes a low initial Ba leachability, after the sulphate peak Ba starts to leach at a higher level in diffusion controlled mode.

20.4.2 Definition of Leaching Parameters

The leaching behaviour and release rates of constituents from products containing incinerator residues can be modified by changes in one or more of the following factors:

- Total availability, or the fraction of each element not tied up in silicate and relatively insoluble mineral phases (deemed to be not leachable). Availability referred to in this chapter is the quantity of an element extracted based on the NEN 7341 leach test. This quantity typically is less for products because of dilution and treatment effects.

- Physical retention, which is derived from measuring the release rate of an inert component (one which does not chemically interact with the product matrix) from the product matrix. Physical retention is equivalent to tortuosity for cases where the test sample remains physically intact (e.g., no significant cracking or disintegration). In these cases, tortuosity is an approximation of the ratio of the actual mean path length a species travels from within the monolith to the monolith surface for release to the mean direct geometric path length. For cases where the monolith does not maintain physical integrity, the physical retention factor is a relative reference index for the degree of species retention within the S/S matrix by physical encapsulation at the micro-scale. Sodium or potassium are most frequently used as the non-interactive component for estimating of physical retention, and

- Chemical retention, which is a function of each element's chemical interaction with the product matrix. This is derived from the measured release rate of a given component, its free diffusion coefficient in water and the tortuosity as obtained from the inert component release rate. However, differences in redox potential between the testing conditions and actual environmental exposure can result in different release rates

The following parameters are used to quantify release rate information based on monolith or compacted granular leach test results:

- Availability (for NEN 7345) or total solid phase concentration (for ANS 16.1)
- Effective diffusion coefficient (for NEN 7345) and leachability index (for ANS 16.1 only)
- Physical retention factor or tortuosity, and
- Chemical retention factor

Effective diffusion coefficients, leachability indexes, physical retention factors and chemical retention factors are calculated from data obtained during the monolith or compacted granular leach tests in conjunction with either the availability or total solid phase concentrations (van der Sloot, 1991, van der Sloot et al., 1989).

The ion flux through the geometric surface area of a product under diffusion controlled conditions is described by Fick's second law:

$$\frac{\partial C}{\partial t} = D_e \frac{\partial^2 C}{\partial x^2} \tag{20.1}$$

where D_e is the effective diffusion coefficient [m^2/s] and C is the species concentration available in the solid phase. A one dimensional semi-infinite linear diffusion model can be applied to estimate D_e based on data obtained from both monolithic specimens and compacted granular material as long as the boundary conditions for the use of the one-dimensional model are fulfilled. The principal conditions applied to the leaching test are:

- the material is uniform in composition
- no depletion occurs over the duration of the test
- leachant replacement cycles are frequent enough to ensure that the concentration gradient between the solid being leached and the extractant is maximised (e.g., the species concentration in the extract is dilute), and
- monolithic samples maintain physical integrity (e.g., no cracking or disintegration) during testing

For cases where the physical integrity of the monolith is not maintained, estimated values of physical retention and chemical retention factors should be regarded as relative indexes and not be used for extrapolation and estimation of releases over longer time intervals or different physical geometries.

The solution of Fick's law of diffusion for the above conditions was presented by Crank for the diffusion from a product with semi-infinite dimensions, in which the initial concentration is uniformly distributed in the product and the concentration on the surface between the product and the leachate is constant with respect to time (Crank, 1989):

$$\frac{C-C_1}{C_0-C_1} = erf\left\{\frac{x}{2\sqrt{D_e t}}\right\} \tag{20.2}$$

where:

$C = C_{(x,t)}$ is the concentration as a function of location within the solid test specimen and time

C_1 is a constant concentration at x=0 (test specimen surface)

C_o is the initial concentration (at t=0) in the product which must be uniformly distributed

D_e is the effective diffusion coefficient [m^2/s]

t	is time [s], and
x	is the distance from the surface [m], positive values

In the monolith leach test, the surface concentration will only be constant as long as no depletion occurs and the mean concentration in the solution does not deviate significantly from zero. These requirements are met by using a product for which the smallest dimension is greater than 5 cm, preventing depletion within the 64 day time frame of the experiment, and by refreshing the leachant at regular time intervals. This size requirement fulfills the assumption of semi-infinite media for most cases. Leachant replacement intervals should be using a geometric time progression:

$$t_n = n^2 t_0 \tag{20.3}$$

where:

t_n	is the leachant replacement time for interval n [days]
n	is the interval number (integer) [-], and
t_0	is the initial leaching interval [days]

Laboratory experiments coupled with model estimations have indicated that use of the boundary condition $C_1=0$ for $t>0$ is appropriate for these experimental conditions as long as the leachate remains dilute relative to leachate saturation element of interest (see Chapters 13 and 15). The resulting diffusion equation derived from Equation (20.2) for this boundary condition is:

$$D = \frac{\pi M_t^2}{4t(\rho C_0)^2} \tag{20.4}$$

where:

D or D_e	is the diffusion coefficient for component x in the product $[m^2/s]$[1]
M_t	is the cumulative release of the component $[mg/m^2]$
t	is the contact time [s]
C_0	is the maximum leachable quantity [mg/kg], and
ρ	is the bulk density of the product $[kg/m^3]$

C_0 also can be interpreted as the "driving force" for diffusion in the solid. In the test method according to ANS 16.1, C_0 is equal to the total solid phase concentration of the product. This may not be accurate for evaluation of some elements in incinerator residue by-products because a fraction of these elements may be in mineral forms which render them unavailable for leaching. Defining C_0 as the total solid phase

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[1] The diffusion coefficient (D) often is referred to interchangeable with the effective diffusion coefficient (D_e) in the literature.

concentration results in smaller values of D and thus can result in the underestimation of the rate of constituent release and the overestimation of the time to depletion. NEN 7435 corrects for this deficiency by defining C_0 as the experimentally determined availability.

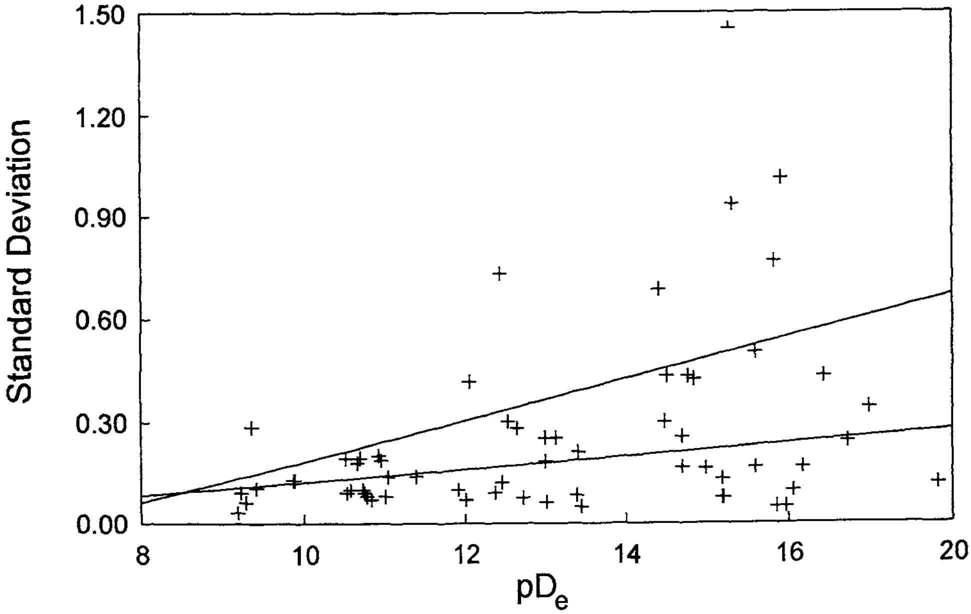
It is often convenient to express D as pD values where D is transformed by the mathematical operator "p" which results in:

$$pD = -\log(D) \tag{20.5}$$

When pD is calculated using the total solid phase concentration equal to C_0 according to ANS 16.1, the resulting value is also referred to as the "leachability index".

Variability associated with the measurement of pD values for monolithic materials as a function of pD is presented in Figure 20.5. Greater standard deviations are associated with larger pD values because of slower rates of release and errors derived from measurement of extract concentrations approaching analytical detection limits. Greater variability associated with larger pD values are of limited concern because of the very slow release rates indicated.

Figure 20.5 The Standard Deviation Associated with Measurement of pD_e as a Function of pD_e



The effective diffusion coefficient can be divided into contributions from the free mobility of the element or species of interest, physical retention factor and the chemical retention factor:

$$D = \frac{D_{o,x}}{R\tau} \tag{20.6}$$

where:

D	is the diffusion coefficient of component x in the product [m^2/s];
$D_{o,x}$	is the diffusion coefficient of component x in water [m^2/s];
R	is the chemical retention factor of component x in the product [-]; and,
τ	is the physical retention in the product [-]

The physical retention or tortuosity reflects the extended path length of a diffusing ion in the pore structure of a product. Values may range from 1 to 10 for stabilised materials and up to 1000 and higher for very dense concrete and bituminous mixes with water repellant properties. A tortuosity value of 1 reflects no physical retention during the leaching process. Physical retention based on sodium as the inert tracer is calculated as:

$$\tau = \frac{D^{o}_{Na}}{D_{Na}} \tag{20.7}$$

where:

τ	is the tortuosity of the product
D^{o}_{Na}	is the diffusion coefficient of Na in water ($pD^{o}Na$ = 8.88 at 22 °C) [m^2/s], and
D_{Na}	is the diffusion coefficient of Na in the product [m^2/s]

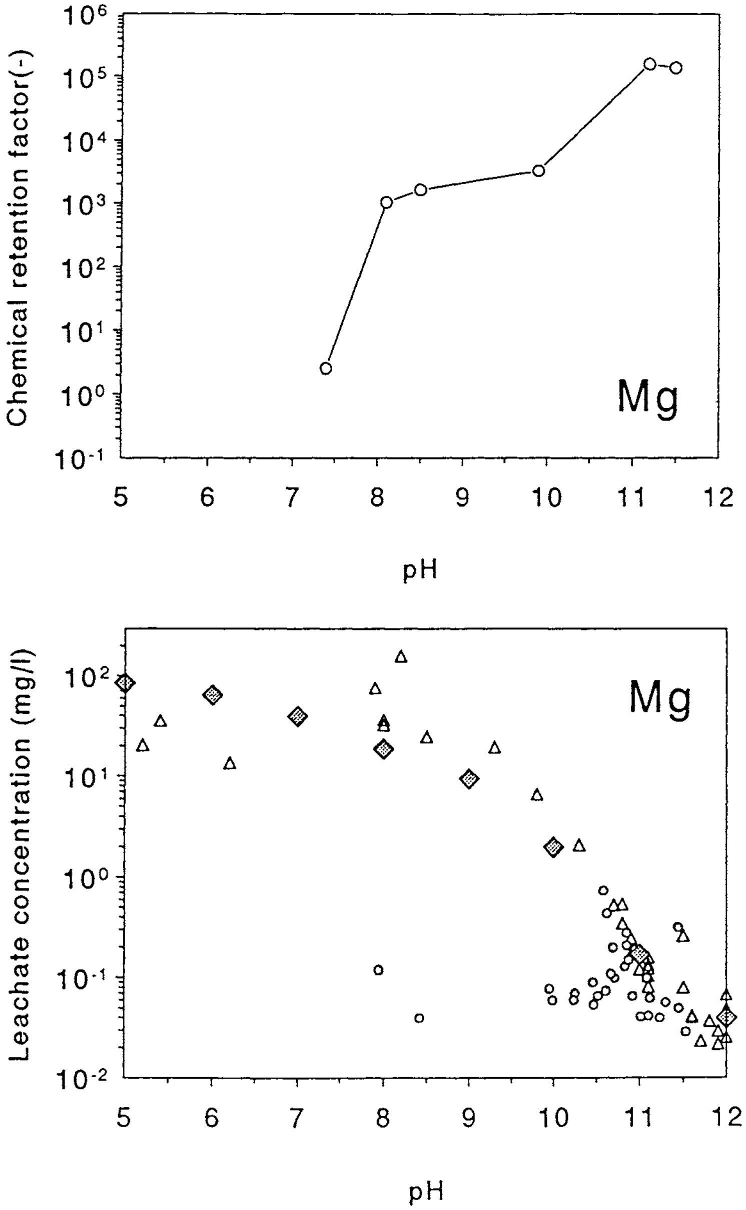
The chemical retention factor quantifies the retardation of the release of a component relative to release of an inert species by chemical interactions of the diffusing ion with the product. The chemical retention factor (R) for the component of interest is calculated from:

$$R = \frac{D^{o}_{x}}{D_{x}\tau} \tag{20.8}$$

where:

R	is the chemical retention factor [-]
D^{o}_{x}	is the diffusion coefficient for component x in water, [m^2/s]
D_x	is the effective diffusion coefficient for component x in the product, [m^2/s],
t	is the tortuosity of the product [-]

Figure 20.6 The Effects of Pore Water pH on Magnesium Chemical Retention and Observed Leachate Concentrations



Pore water composition and the porewater pH are important factors in controlling chemical retention. In other work, relations between porewater pH and retention values have been established. In a number of cases, these relations are strictly based on the solubility as a function of pH of the specific species. Figure 20.6 illustrates the effect of porewater pH on the release of magnesium (de Groot, 1989). The element Mg is an example of an element whose solubility decreases monotonically with increasing pH. Thus, the retention value increases monotonically with the increasing pH. Reactive surface sites also may affect the diffusivity of components in the pore solution. Figure 20.7 presents typical chemical retention profiles from tank leaching tests for several elements. Chemical retention factors may range from 1 to more than 1,000,000, where a value of 1 reflects no chemical retention during the leaching process. The wide range of chemical retention factors reflects that substantial reductions in release rates can be obtained by chemical modifications.

Measures taken to modify the chemical retention of specific components can result in the increased mobilisation of other matrix components. Multiparameter screening is necessary to insure that no adverse effects have been introduced.

In summary, the larger the pD_e at constant availability, the slower the release from the material. Measures to improve the environmental quality of products containing secondary materials can be targeted at any of the three factors (availability, physical retention or chemical retention). Changes in processing parameters can generally lead to a denser product and, consequently, influence the physical retention factor. However, within one category of materials, the range in tortuosity is relatively small. This implies that changes in chemical properties, which influence both availability and chemical retention, have a greater effect on release rates.

20.4.3 Calculation of Effective Diffusion Coefficients from Cumulative Release Data

For the determination of characteristic leaching behaviour, the logarithm of the cumulative release has been plotted versus the logarithm of time. Rearranging Equation 20.4 yields:

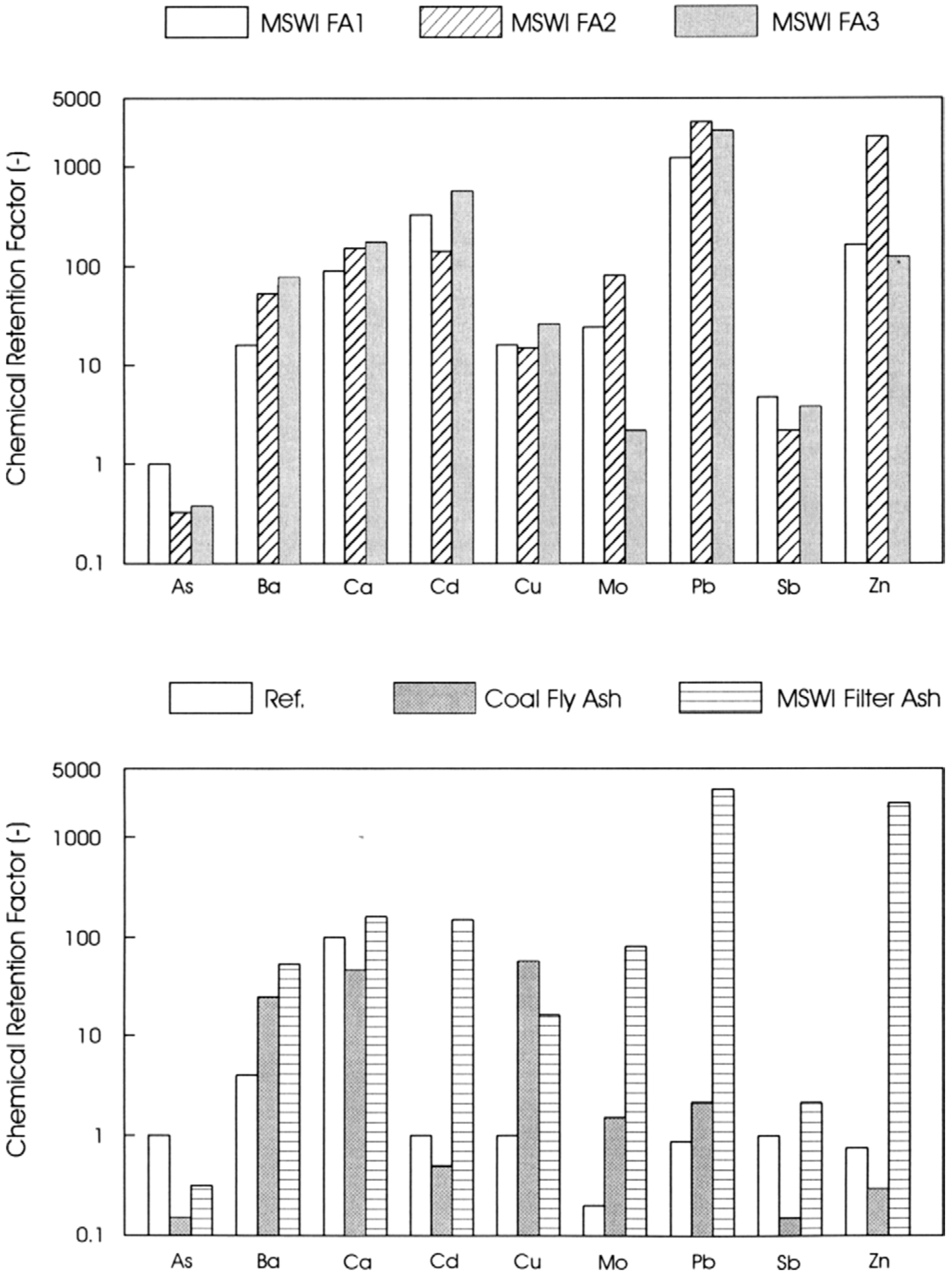
$$M_t = C_0 \rho \left(\frac{4Dt}{\pi} \right)^{1/2} \tag{20.9}$$

and after logarithmic transformation:

$$\log(M_t) = 1/2 \ \log(t) + \log \left\{ C_0 \rho \left(\frac{4Dt}{\pi} \right)^{1/2} \right\} \tag{20.10}$$

The release of each component per time interval can be calculated from the monolith leach test results with the formula:

Figure 20.7 Typical Chemical Retention Profiles from Tank Leaching Tests for Several Elements



$$M_i=\frac{c_iV_i}{1000A} \tag{20.11}$$

where :

M_i is the release during period i [mg/m^2]
c_i is the extract concentration of the component in the ith period [mg/l]
V_i is the volume of the contact solution [l], and
A is the geometric surface area of the specimen [m^2]

The measured release from previous periods is summed to obtain the measured cumulative release. This implies that deviations in a given period accumulate in the subsequent periods, which may hamper interpretation. The cumulative release until the ith period can be calculated only from the release in the ith period, assuming diffusion control in the ith and previous time periods. These values can be used to check whether the release is diffusion controlled. If the measured and calculated cumulative releases are equal, the release is controlled by diffusion. The calculated cumulative release used for all N periods can be derived from:

$$M_{t,i}=M_i\frac{\sqrt{t_i}}{\sqrt{t_i}-\sqrt{t_{i-1}}} \tag{20.12}$$

where:

$M_{t,i}$ is the cumulative release of the component through period i [mg/m^2]
t_i is the contact time after the period i [s], and
t_i-1 is the contact time after the period (i-1) [s]

After plotting the logarithm of the calculated cumulative release ($M_{t,i}$) against the logarithm of the time (t_i) for i=1 to N, the slope of the relation over the complete time interval and three time intervals segments can be determined:

Interval 0 (total range) - leaching extracts 1 to 8
Interval 1 (initial leach range) - leaching extracts 1 to 3
Interval 2 (intermediate range) - leaching extracts 3 to 6, and
Interval 3 (last range) - leaching extracts 6 to 8

The mechanism of leaching during each interval can be derived from the slope of the data from the respective interval. Components dissolving from the surface (slope $\geq$0.8), short initial release of surface deposited components (initial stage slope $\leq$ 0.4) and diffusion controlled release (slope = 0.5) can be distinguished. The meaning of the change in the slopes at different time-intervals is summarised below:

	SLOPE		
Leaching Interval	<0.35	0.35-0.65	>0.65
Initial	Surface wash-off	Diffusion	Lag time/dissolution
Intermediate	Depletion	Diffusion	Dissolution
Last	Depletion	Diffusion	Dissolution

Only in the cases where the slope is approximately 0.5, can effective diffusion coefficient be calculated. When the slope in the entire plot is 0.5 ± 0.15 and the slope in the last range is less than 0.6, data from all leaching extracts can be used for the calculation of the effective diffusion coefficient. If this is not the case, only those intervals in which the slope is 0.5 ± 0.15 can be used for calculation of D(e). The effective diffusion coefficient (D(e)) for the component of interest then is calculated from each period using only those data points for which the slope is 0.5 ± 0.15 by:

$$D_{i,x}=\frac{\pi M^{2}{}_{t}}{(2C_{o}\rho)^{2}(t_{i}-t_{i-1})} \tag{20.13}$$

where:

$D_{i,x}$	is the effective diffusion coefficient of component x calculated from the release in period i [mS(2)/s]
M_i	is the release in period i [mg/m^2]
d	is the bulk density of the product [kg/m^3]
C°	is the maximum leachable quantity [mg/kg]
t_i	is the contact time until period i [s], and,
t_{i-1}	is the contact time until period i-1 [s]

The significance of the availability test for the judgment of the maximum leachability of a given component from waste materials is best illustrated by release data obtained for one product, where depletion of a very soluble component occurs, and the maximum leachable quantity, as determined by the availability leach test, is approached. The data obtained during the monolith leach test are expressed as (mg element leached per m^2 surface area) as a function of time. The availability leach test results are recalculated to the same units by taking the size and shape of the specimens into account. These figures indicate that the release of sodium, chloride, potassium and bromide asymptotically approached the release limit dictated by the availability leach test. Similar observations also have been made in column leaching experiments, indicating the practical significance of this test method as a screening tool for ultimate release at the very long term.

20.4.4 Alternative Release Models for Monolithic Materials

Batchelor and Wu (1993) reviewed a variety of alternative mathematical models for estimating diffusion controlled release from products. Simple models assume:

1. rectangular geometry
2. infinite bath, and
3. semi-infinite solid

The rectangular geometry assumption implies that the surface of the product can be treated as a flat plate. Alternative solutions have been obtained for spherical and cylindrical geometries and coordinate systems. The infinite plate assumption implies that the leaching solution remains dilute with respect to the species or element of interest. This may not always be true and requires careful selection of laboratory conditions and consideration of field boundary conditions. The semi-infinite solid assumption implies that significant depletion of the species of interest does not occur.

Several cases can be defined which meet the above assumptions. These cases include : (i) no reaction, (ii) equilibrium linear sorption, (iii) equilibrium precipitation, and (iv) reaction with a leaching solution component. The mass balance for all of these cases is:

$$\frac{\partial C}{\partial t}=D_e\frac{\partial^2 C}{\partial x^2}-R \qquad (20.14)$$

The solution for the case of no reaction is:

$$C(x,t)=C_0\ erf\left(\frac{x}{(4D_e t)^{0.5}}\right) \qquad (20.15)$$

$$\frac{M_t}{M_0}=\frac{1}{LC_0}\int_0^L (C_0-C)dx \qquad (20.16)$$

$$\frac{M_t}{M_0}=\left(\frac{4D_e t}{\pi L^2}\right)^{0.5} \qquad (20.17)$$

The solution for the case of equilibrium linear sorption is:

$$C_i=K_p C \qquad (20.18)$$

$$\frac{M_t}{M_0}=\left(\frac{4D_{obs}t}{\pi L^2}\right)^{0.5} \tag{20.19}$$

$$D_{obs}=\frac{D_e}{1+K_p}=F_m D_e \tag{20.20}$$

where:

R = reaction term
M_t = cumulative mass released
M_0 = initial mass present in the solid phase
D_{obs} = observed diffusion coefficient
t = time
L = characteristic length
K_p = linear sorption coefficient
F_m = fraction of the constituent that is mobile

The solution for the case of equilibrium precipitation is:

$$\frac{M_t}{M_0}=\left(\frac{4D_{obs}t}{\pi L^2}\right)^{0.5} \tag{20.21}$$

$$D_{obs}=\frac{\pi(F_m-0.5F_m^{\ 2})D_e}{2} \tag{20.22}$$

if $F_m << 1.0$, then

$$D_{obs}=\frac{\pi F_m D_e}{2} \tag{20.23}$$

The solution for the case of reaction with a leaching solution component, e.g., acetic acid (HAc) is

$2HAc + Ca(OH)_2 = Ca^{2+} = 2Ac^- + 2H_2O$

$$\frac{M_t}{M_0} = \left(\frac{4D_{obs}t}{\pi L^2} \right)^{0.5} \qquad (20.24)$$

$$D_{obs} = \frac{\pi \varepsilon C^{b}_{HAc} D_{e,HAc}}{2nC^{0}_{CaOH}} \qquad (20.25)$$

It is important to note that for each of the above cases, the function for cumulative release is of the same form, being related to the D_{obs} and time to the one-half power.

A more complex model for contaminant release was developed by Hinsenveld (1992) and is referred to as the "shrinking core" model. This model was developed to model release from an alkaline S/S product being leached in an acid environment. The model assumes hydrogen ion diffusion into the product matrix and reaction at a boundary between an unleached core and a leached exterior shell. The reaction at the boundary results in release of product matrix components which, in turn, diffuse outward through the reacted shell into the leaching solution. Thus, the model includes time dependent moving boundary between the leached shell and unleached core. The core is depleted (and hence the shell is extended) as a function of the acid concentration in the leaching solution and the acid neutralisation capacity of the S/S product. Diffusion through the shell is assumed to be controlled by the matrix tortuosity. The reaction at the core-shell boundary is controlled by the kinetics of acid dissolution. The two applicable limit cases are (i) when diffusion through the shell is rate limiting, and (ii) when dissolution at the shell-core boundary is rate limiting. This model has been successfully applied to describe the rate of component release when a S/S product is leached using a variety of acid solutions (Hinsenveld, 1992).

20.5. RELEASE FROM PRODUCTS CONTAINING INCINERATOR RESIDUES

20.5.1 Total Availability

The total availability of constituents from a product containing incinerator residues can be modified by the following processes:

- Dilution by treatment or product additives
- Filling of micropores and coating with hydrophobic materials, or
- Chemical respeciation

Dilution occurs when incinerator residues represent only a limited fraction of the product material. Examples of significant dilution effects include partial substitution of grate ash as aggregate substitute in cement or asphalt materials. In these cases, the grate ash may represent from less than 10% to more than 50 wt% of the final material.

Filling of micropores and coating with hydrophobic materials reduces availability by providing a coating over soluble mineral phases that is resistant to aqueous dissolution. An example of when this case occurs is when grate ash (a porous material) is incorporated into asphalt. Hot asphalt cement is absorbed into the micropores of the ash. This asphalt coating may remain even after size reduction for availability testing.

Chemical respeciation may occur as a result of chemical reactions during product production. Respeciation may be the result of a relatively passive process such as hydration and oxidation reactions that occur during ash weathering, or, may result from reaction with process additives. In addition, respeciation may occur through sintering or other thermal processes (e.g., vitrification) of the material during high temperature processing.

In general, the most significant factor affecting availability for low temperature processes is dilution by process additives. Incorporation of trace elements (e.g., lead, zinc, etc.) into alumina-silicate matrices or respeciation during sintering is responsible for the reduction in availability by thermal treatment processes.

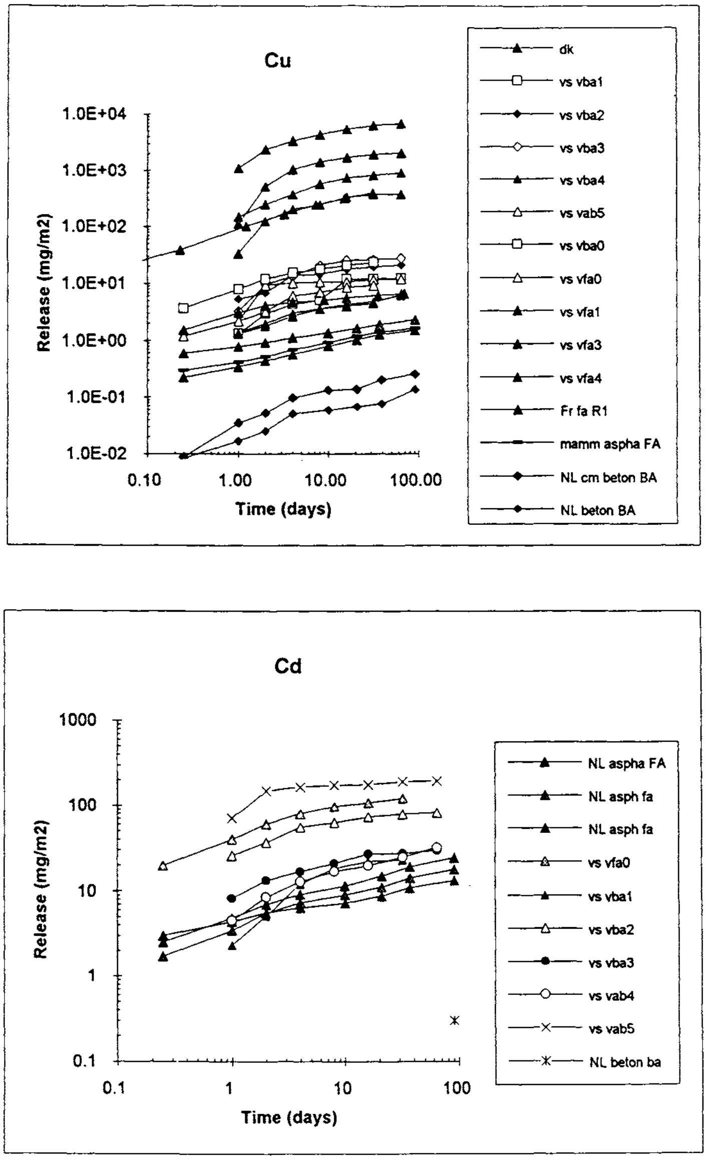
20.5.2 Effective Diffusion Coefficients, Physical Retention and Chemical Retention

Typical tank leaching release profiles for several elements and sulphate from untreated and treated incinerator residues are presented in Figures 20.8 through 20.12 (Kosson et al., 1993).

Copper (Figure 20.8)
Release plots of copper from untreated and treated APC residues, fly ash and bottom ash generally form three groupings. The groupings, from least release to greatest release, are: (a) bottom ash incorporated into pavement blocks; (b) untreated bottom ash, bottom ash treated by S/S processes and untreated APC residue; and, (c) APC residues treated by Portland cement or phosphate addition. In general, treatment of bottom ash tended to decrease release while treatment of APC residues tended to increase release.

Cadmium (Figure 20.8)
Release plots of cadmium from untreated and treated APC residues, fly ash and bottom ash generally also form three groupings. The groupings, from least release to greatest release, are: (a) bottom ash incorporated in paving blocks; (b) fly ash in asphalt and bottom ash treated with Portland cement or phosphate addition; and, (c) untreated APC residue and bottom ash treated with Portland cement. In general, while incorporation of fly ash into asphalt provided consistent results, the effectiveness of S/S treatment of bottom ash was very process specific.

Figure 20.8 Tank Leaching Release Profiles for Copper and Cadmium from Untreated Incinerator Residues and Products Containing Residues



Lead (Figure 20.9)
Release plots of lead from untreated and treated APC residues, fly ash and bottom ash indicate release behaviour very similar to that observed for copper. Generally, the three groupings formed, from least release to greatest release, are: (a) bottom ash incorporated into pavement blocks; (b) untreated bottom ash, bottom ash treated by Portland cement processes, and untreated APC residue; and, (c) APC residues treated by s/s processes. In general, treatment of bottom ash tended to decrease release while treatment of APC residues tended to increase release.

Zinc (Fig. 20.10)
The three groupings observed from release plots for zinc, from least release to greatest release, are: (a) bottom ash incorporated into pavement blocks; (b) bottom ash treated by s/s processes and fly ash used in asphalt; and, (c) bottom ash in asphalt and untreated APC residue. Unlike for all previous cases discussed, zinc release from bottom ash in asphalt does not appear to be diffusion controlled. The principal release mechanism appears to be dissolution from the asphalt binder, as suggested by the significant release from the reference material.

Sodium, Sulphate and Chloride (Figures 20.11 & 20.12)
Release plots for sodium, sulphate and chloride are provided only for bottom ash and fly ash in asphalt and corresponding reference asphalt materials. The release from both incinerator residues in asphalt appears to behave similarly for all three species, with greater sodium release from bottom ash than fly ash containing materials and both cases much greater than the reference materials. This result appears to be directly related to the total loading in the asphalt material. Much greater loadings of bottom ash than fly ash were incorporated in the materials tested. However, the release rates observed for asphalt materials are much slower than that observed for untreated residues and residues incorporated in cement matrices because of much greater tortuosity within the asphalt matrix.

It is evident from the above discussion, that evaluation of release plots can provide important information and comparisons between processes and elements. However, release plots do not provide necessary information for translation of results from one scenario to another or a design basis for treatment process or product development and evaluation. Calculation of effective diffusion coefficients, physical retention factors and chemical retention factors provide this basis.

Figures 20.13 and 20.14 present effective diffusion coefficients for several elements from untreated and treated (S/S with Portland cement) bottom ash and APC residue. The contributions of free diffusion, physical retention and chemical retention to the effective diffusion coefficient are indicated. The "+" symbol at the top of each bar on the figure indicates the effective diffusion coefficient calculated based on the total elemental content of the material instead of the elemental availability. Use of the total

Figure 20.9 Tank Leaching Release Profiles for Lead from Untreated Incinerator Residues and Products Containing Residues

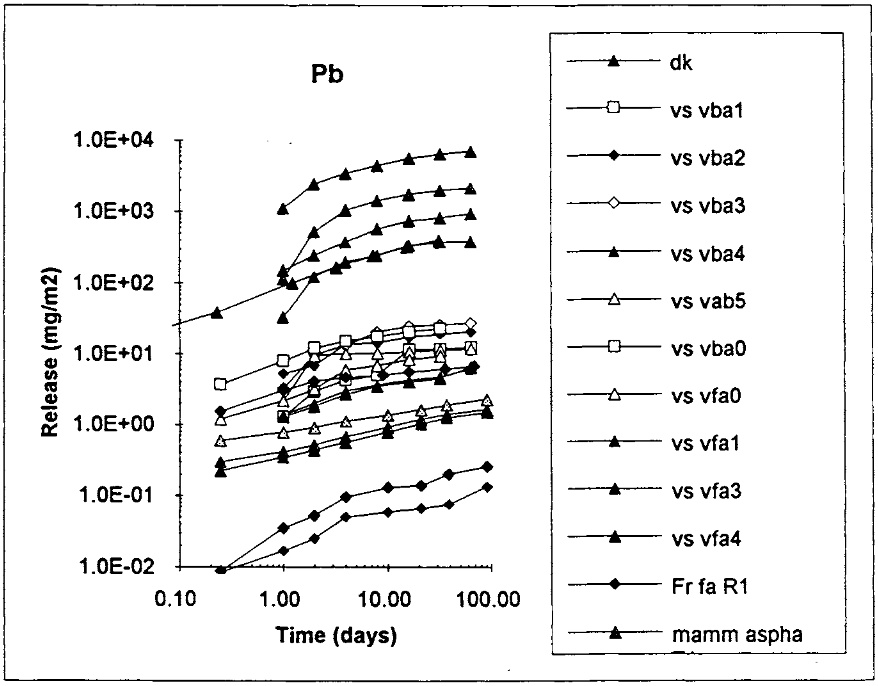


Figure 20.10 Tank Leaching Release Profiles for Zinc from Untreated Incinerator Residues and Products Containing Residues

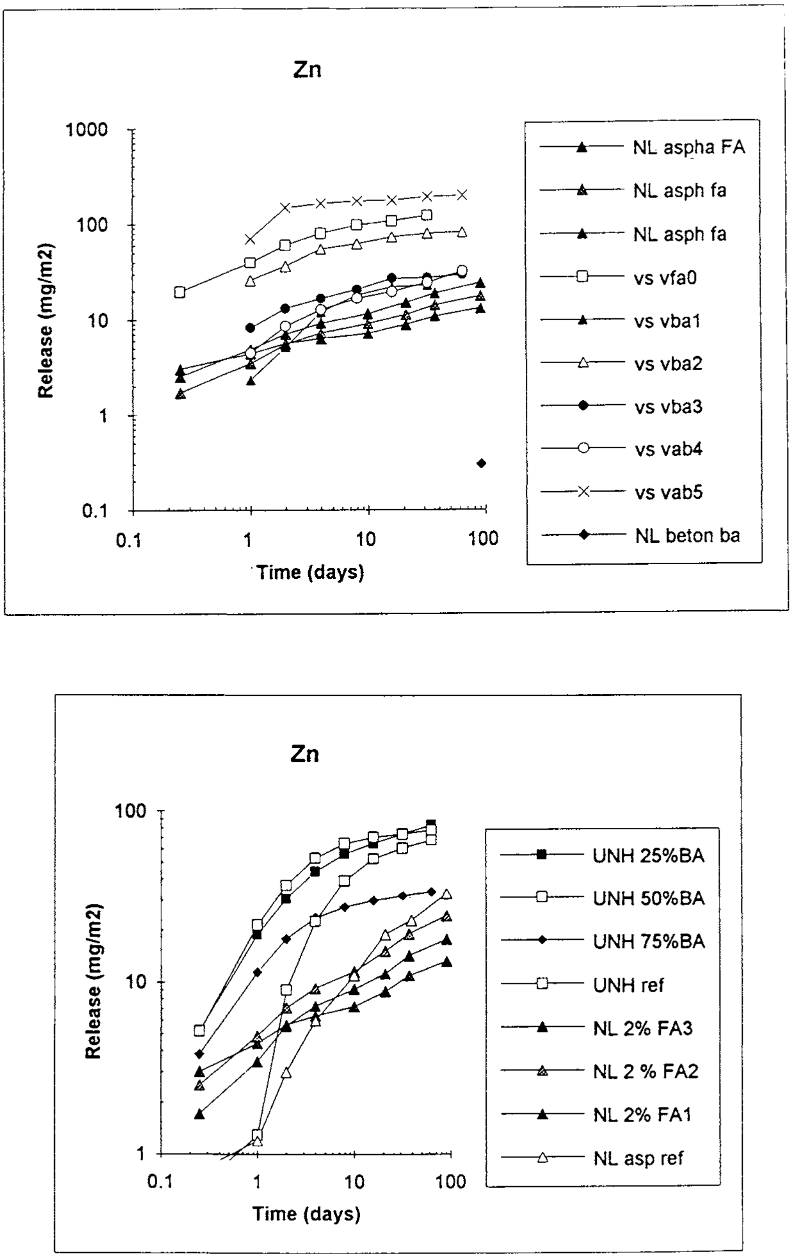


Figure 20.11 Tank Leaching Release Profiles for Sodium from Untreated Incinerator Residues and Products Containing Residues

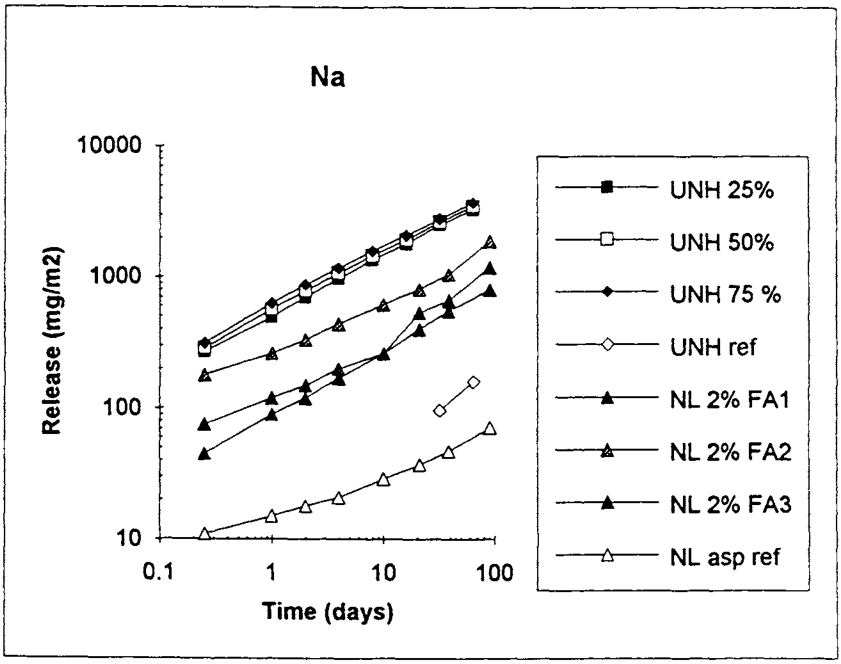
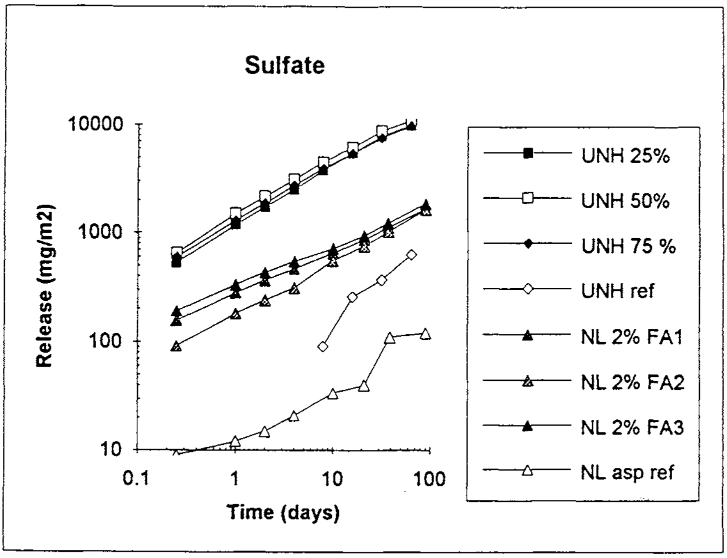


Figure 20.12 Tank Leaching Release Profiles for Sulphate and Chloride from Untreated Incinerator Residues and Products Containing Residues



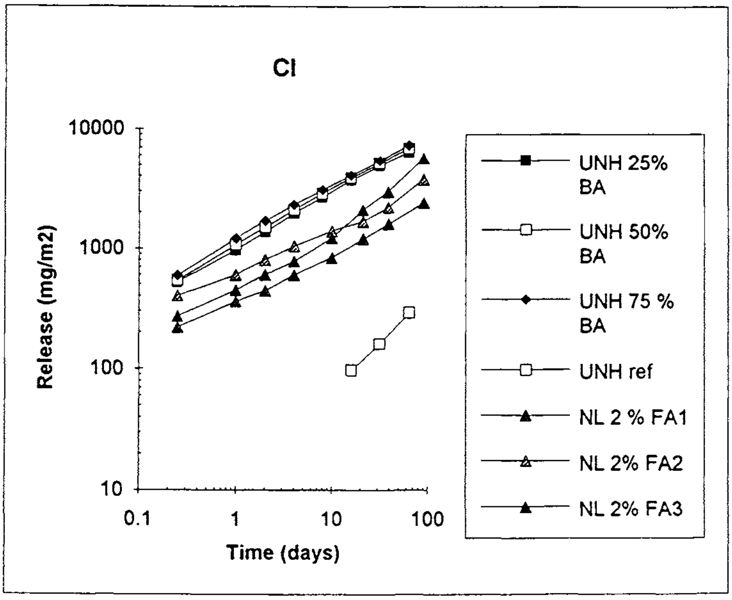
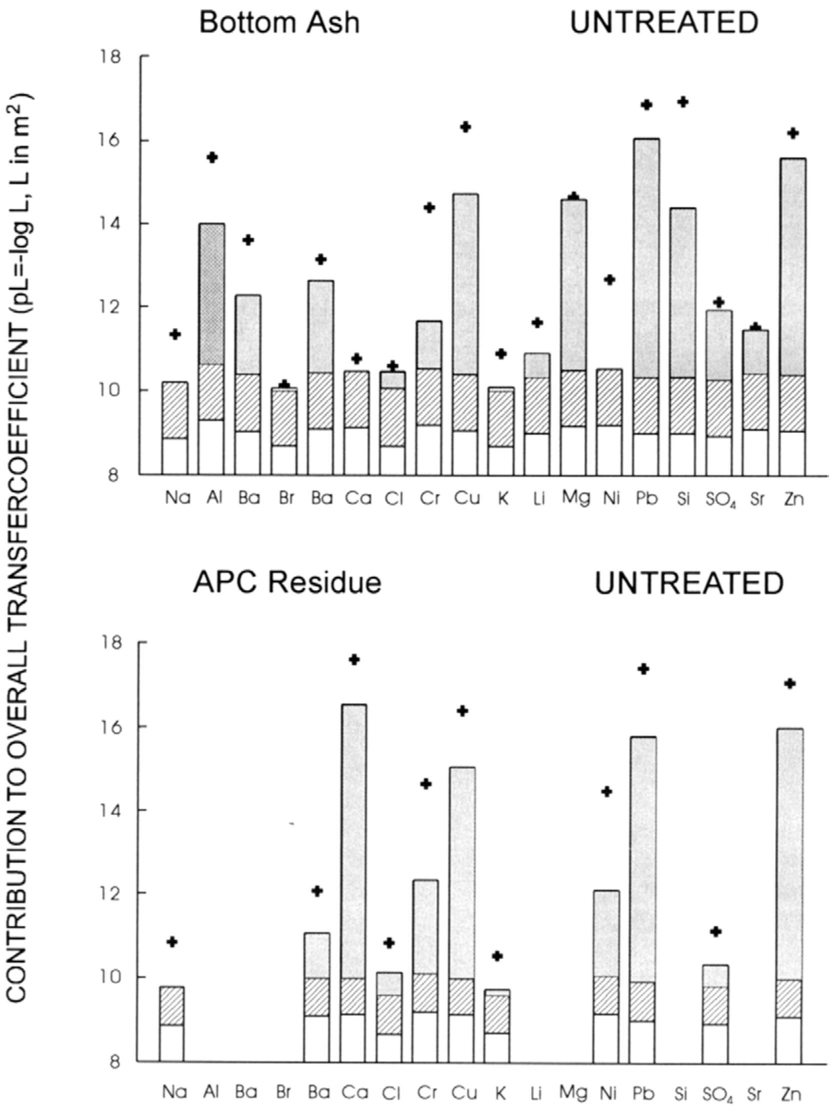


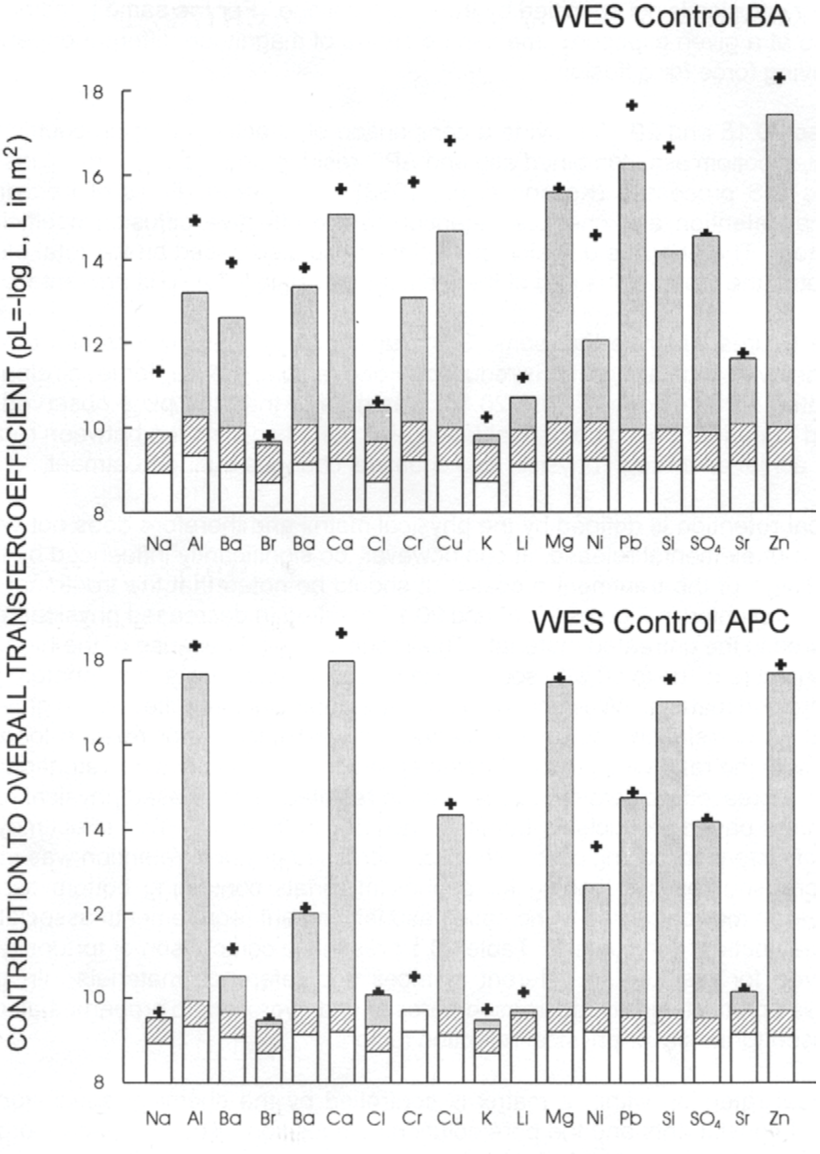
Figure 20.13 Effective Diffusion Coefficients from Tank Leaching Tests on Untreated Bottom Ash and APC Residue for Several Elements



"+" indicates the effective diffusion coefficient if it were estimated based on the total elemental concentration in the solid phase

The contributions to the effective diffusion coefficient of chemical retention, tortusoity and free diffusion are indicated

Figure 20.14 Effective Diffusion Coefficients from Tank Leaching Tests on Bottom Ash and APC Residues S/S with Portland Cement for Several Elements



"+" indicates the effective diffusion coefficients if it were estimated based on the total elemental concentration in the solid phase

The contributions to the effective diffusion coefficient of chemical retention, tortusoity and free diffusion are indicated elemental content can result in under estimation of the effective diffusion coefficient by up to two orders of magnitude (or under estimation of pD_e by two units). Thus, use of the leachability index described by ANS 16.1 is not recommended, because the driving force for diffusion is not specified by the L factor alone. For the same L factor, the net release at a given exposure time can be orders of magnitude different depending on the driving force for diffusion.

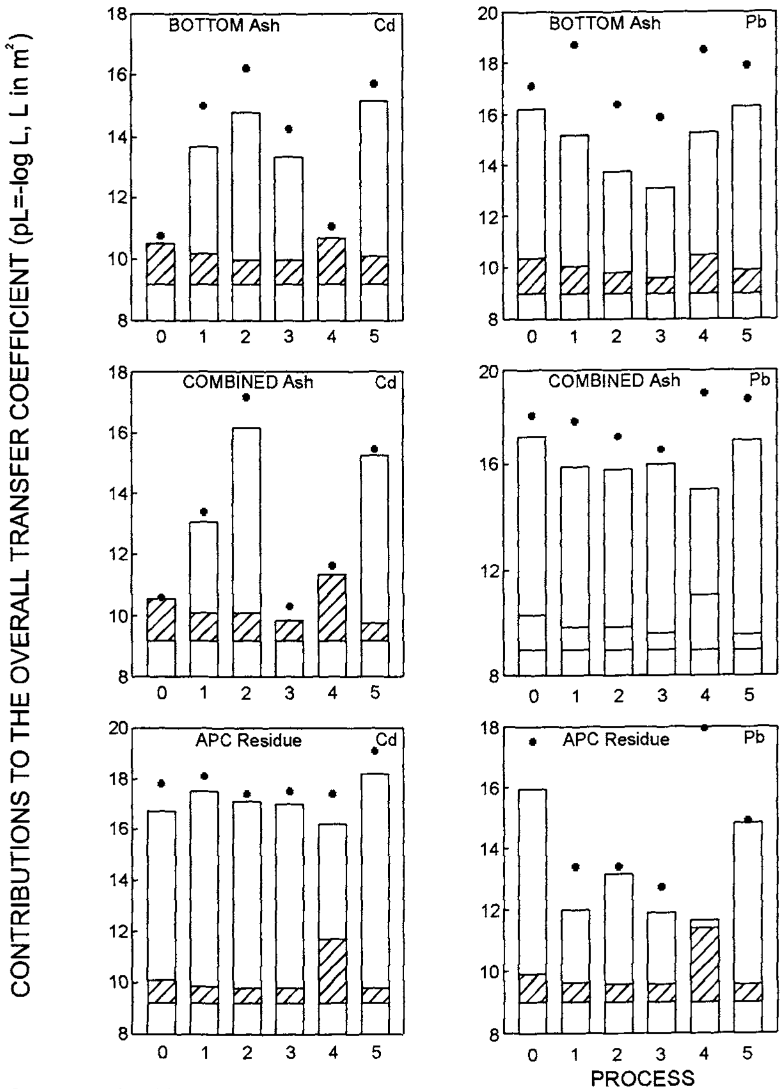
Figures 20.15 and 20.16 provide a comparison of effective diffusion coefficients for untreated bottom ash, combined ash and APC residue and the same residues treated by five S/S processes (Kosson et al., 1993). The contributions of free diffusion, physical retention and chemical retention to the effective diffusion coefficient are indicated. The effective diffusion coefficient calculated based on the total elemental content of the material instead of the elemental availability also is presented.

These figures illustrate that some S/S treatment may actually increase the rate of diffusion even if the availability is reduced. For example, the pD_e for lead release from untreated APC residue (Figure 20.16) was greater than the pD_es observed for the treated material. This type of evaluation also permits distinction between reductions in pD_e achieved through physical and chemical changes during treatment.

Physical retention is defined by the physical matrix and therefore does not vary as a function of elemental release. It can however, be significantly influenced by the type and design of the treatment process. It should be noted that the treatment of APC residue presented in Figures 20.16 and 20.17 resulted in decreased physical retention compared to the untreated material. This result occurred because of the high soluble salt content (e.g., up to 50 wt% sodium and potassium chlorides and sulphates) present in the treated material. Wash out of the highly soluble salts resulted in a highly porous matrix. A correlation has been observed between incinerator residue loading (or, conversely the relative quantity of treatment additives) and physical retention (Figure 20.17). Increased incinerator residue loading resulted in decreased physical retention for cement-based products for both filter ash and bottom ash. This effect may be the result of increased loading of soluble salts. Increased physical retention was indicated for increased residue loading for asphalt materials containing bottom ash. This observation may be related to increased asphalt cement requirements associated with increased bottom ash content. Table 20.1 presents a comparison of tortuosity values observed for residues in different matrices and reference materials. In general, increased product density, decreased porosity and hygroscopic properties all result in increased tortuosity or physical retention factors.

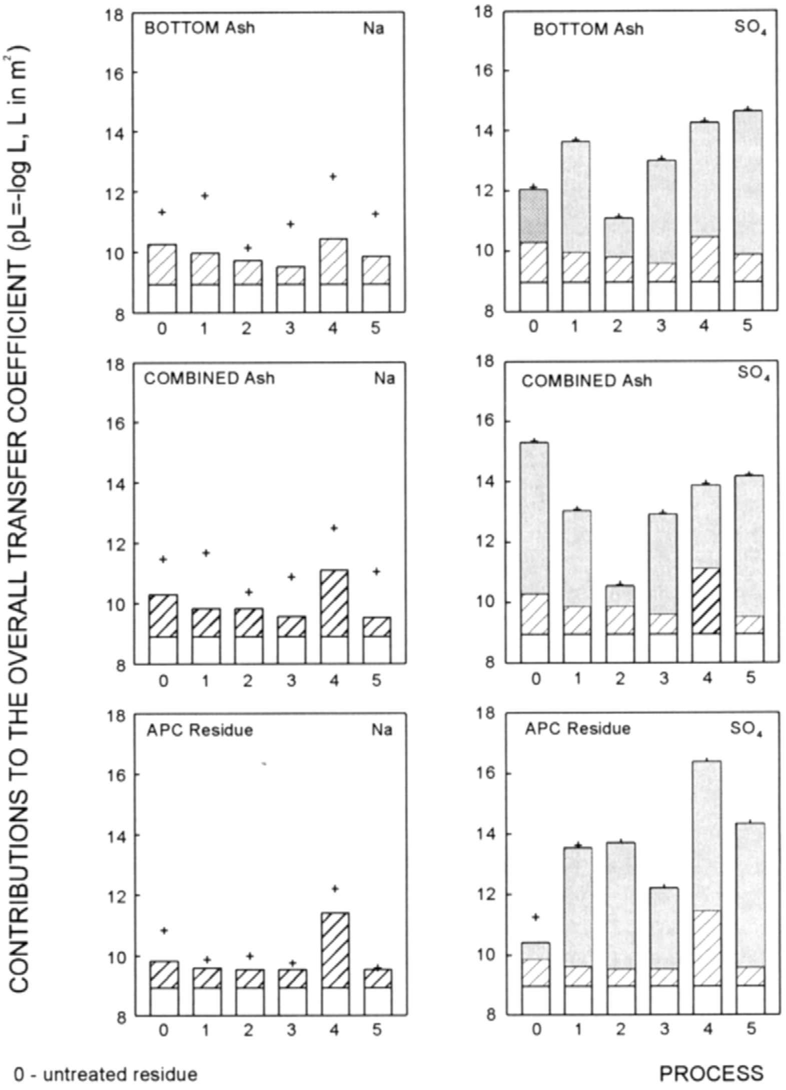
Chemical retention within a matrix is controlled by the chemical speciation of the material constituents and the pore solution composition. Thus, treatment processes may effect changes in chemical retention either by respeciation or alteration of the pore solution. The principal effect of the treatment process presented in Figures 20.15 and 20.16 is the most likely the result of increased matrix alkalinity and attention buffering of pore solution pH. In general, increased chemical retention values are associated

Figure 20.15 A Comparison of Effective Diffusion Coefficients from Tank Leaching Tests on Untreated and S/S Bottom Ash, Combined Ash and APC Residue for Cadmium and Lead



0 - untreated residue
1 - S/S with Portland cement and polymeric additives
2 - S/S with Portland cement and soluble silicates
3 - S/S with cement kiln dust
4 - S/S with soluble phosphates
5 - S/S with Portland Cement only

Figure 20.16 A Comparison of Effective Diffusion Coefficients from Tank Leaching Tests on Untreated and S/S Bottom Ash, Combined Ash and APC Residue for Sodium and Sulphate



0 - untreated residue
1 - S/S with Portland cement and polymeric additives
2 - S/S with Portland cement and soluble silicates
3 - S/S with cement kiln dust
4 - S/S with soluble phosphates
5 - S/S with Portland cement only

Figure 20.17 The Effect of Residue Loading on Tortuosity for Filter Ash and Bottom Ash Incorporated into Various Product Materials

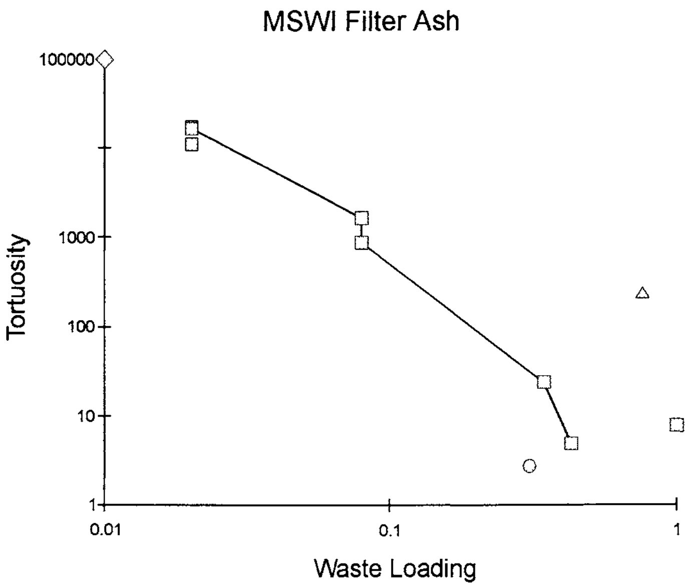


Table 20.1
Ranges of Tortuosity Values Measured for Untreated Incinerator Residues, Products Containing Residues and Reference Materials

Material	Tortuosity
Unconsolidated granular Waste[1]	2 - 4
Compacted Bottom Ash[2]	20 - 25
Compacted Fly Ash[2]	
Stabilised Bottom Ash[2]	5 - 10
Stabilised Fly Ash[2]	1 - 6
Stabilised Fly Ash[6]	25 - 35
Stabilised Fly Ash[3]	200 - 210
Pavement Blocks Containing Bottom Ash[4]	7 - 19
Pavement Block Reference[4]	35
Asphalt Concrete Containing Bottom Ash[4]	1900 - 3300
Asphalt Concrete Reference[4]	24000
Asphalt Concrete Containing Fly Ash[5]	450 - 1400
Asphalt Concrete Reference[5]	> 3000

1. ECN Work, Various Wastes
2. ECN Study
3. BCR intercomparison
4. Mammoet
5. UNH Whitehead
6. Mehu/vdSloot Record

with decreased aqueous solubility of the element of interest either as a function of pore solution pH or the presence of a solubility limiting species. Elements or species that are highly soluble (e.g., chloride, sodium) have relatively little or negligible chemical retention. Table 20.2 provides a comparison of chemical retention values observed for several elements in untreated and treated residues and reference materials. Note that relatively high chemical retention values are observed for untreated residues and low values are observed for asphalt matrices.

Table 20.2
Ranges of Chemical Retention Values Measured for Untreated Incinerator Residues, Products Containing Residues and Reference Materials

Material	Chemical Retention Values				
	Cd	Cu	Pb	Zn	Cl
a	n.a	32,000	3.1×10^6	4×10^5	2.9
b	5×10^5	8×10^4	$1{,}300 - 9 \times 10^4$	$1.5 \times 10^5 - 4 \times 10^6$	1.2 - 1.5
c	2×10^5	7×10^5	$2 \times 10^5 - 2 \times 10^6$	$3 \times 10^6 - 3 \times 10^7$	1 - 5
d	1.6×10^8		13,800		2.5
e	3×10^8		70,000 - 98,000		1.5 - 2
f	40,000		13,900	790,000	2
g	>30,000	$>2 \times 10^4$	1.5×10^6	7×10^5	92
h	(220)	(780)	(820)	(17,800)	(110)
i	150 - 600	17 - 26	1,300 - 3,100	100 - 200	2 - 3
j	1	1	1	1	1
k	n.d.	n.a.	n.a.	n.d.	1.4 - 2
l	n.d.	n.a.	n.a.	n.d.	n.d.

a. Compacted Bottom Ash
b. Compacted Fly Ash
c. Stabilised Bottom Ash
d. Stabilised Fly Ash
e. Stabilised Fly Ash
f. Stabilised Fly Ash
n.d. - not detected

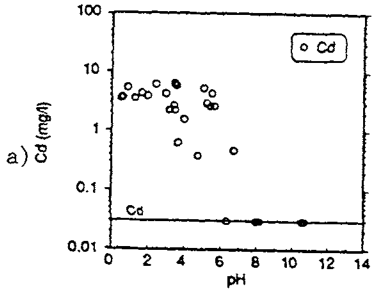
g. Pavement Blocks Containing Bottom Ash
h. Pavement Block Reference
i. Asphalt Concrete Containing Bottom Ash
j. Asphalt Concrete Reference
k. Asphalt Concrete Containing Fly Ash
l. Asphalt Concrete Reference
n.a. - Not analysed

20.5.3 Solubility

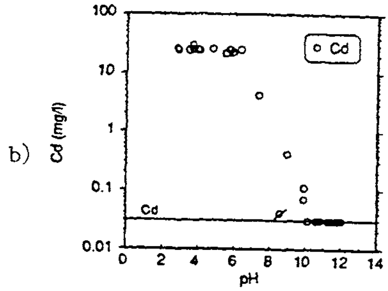
Cadmium solubility as a function of pH is presented in Figure 20.18 for untreated APC residue from a semi-dry scrubber/fabric filter unit and the same APC residue S/S treated with Portland cement and treated with soluble phosphate (Kosson et al., 1993). It can be seen that the effect of treatment on solubility was minimal. Similar information is presented in Figure 20.19 for chromium in untreated and treated APC residue and bottom ash, and for lead in Figure 20.20. The characteristic solubility curves for chromium were the same for untreated bottom ash, cement stabilised bottom ash and

Figure 20.18 The Effect of S/S Processes on the Solubility of Cadmium for Bottom Ash and APC Residues

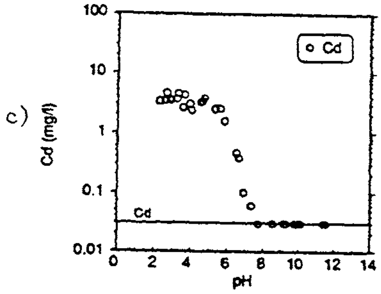
Bottom ash, untreated



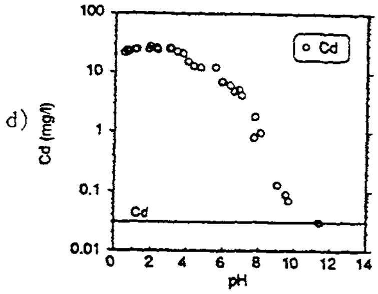
APC residue, untreated



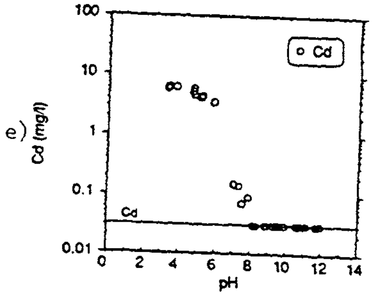
Bottom ash, phosphate treatment



APC residue, phosphate treatment



Bottom ash, Portland cement treatment



APC residue, Portland cement treatment

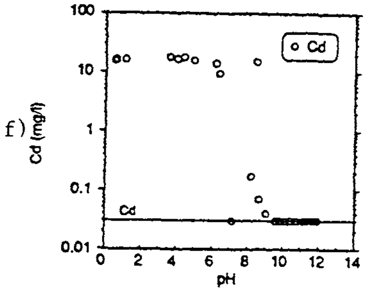
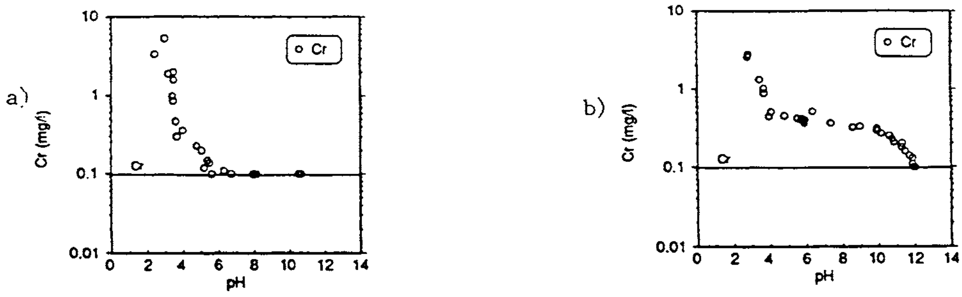
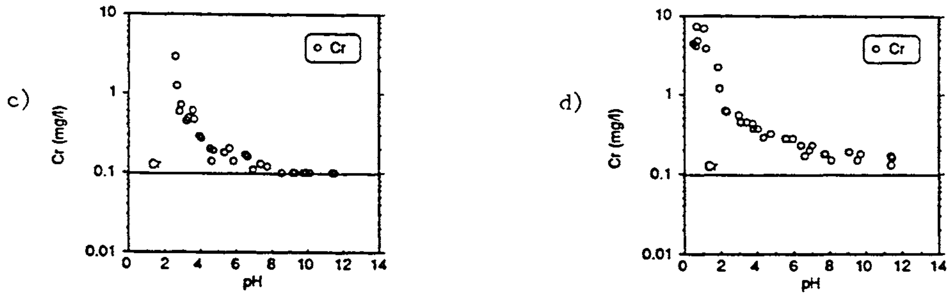


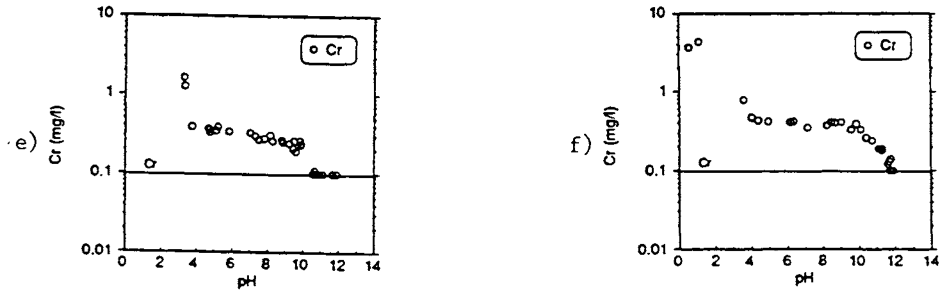
Figure 20.19 The Effect of S/S Processes on the Solubility of Chromium for Bottom Ash and APC Residues


Bottom ash, untreated

APC residue, untreated


Bottom ash, phosphate treatment

APC residue, phosphate treatment

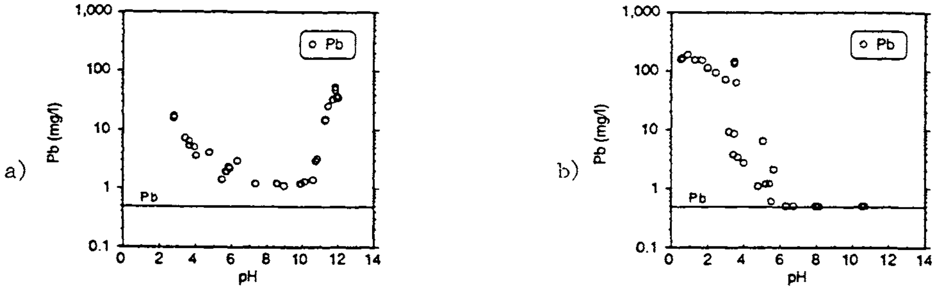

Bottom ash, Portland cement treatment

APC residue, Portland cement treatment

Figure 20.20 The Effect of S/S Processes on the Solubility of Lead for Bottom Ash and APC Residues

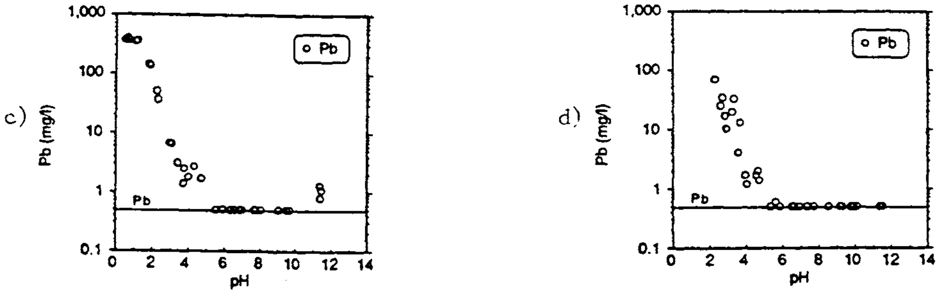
Bottom Ash, Untreated

APC Residue, Untreated



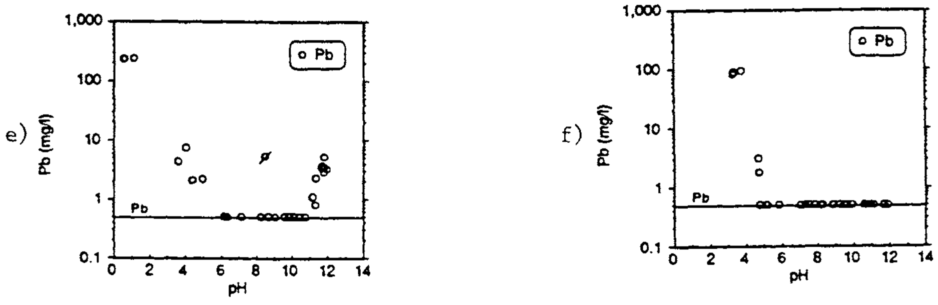
Bottom Ash, Phosphate Treatment

APC Residue, Phosphate Treatment



Bottom Ash, Portland Cement Treatment

APC Residue, Portland Cement Treatment



cement stabilised APC residues. These curves exhibited a regime of intermediate solubility between pH 5 and 10, and sharply increasing solubility with pH decreasing below 5. The solubility between pH 5 and 10 may be indicative of chromate (Cr+6). The curves for untreated APC residue, APC residue treated with soluble phosphate and bottom ash treated with soluble phosphate indicate increasing solubility only at pH less than 5. This suggests that treatment with phosphate may have facilitated conversion of chromium to less soluble speciation, while cement-based treatment of APC residue facilitated the formation of more soluble chromium species. For lead, treatment of APC residue resulted in decreased solubility between pH 5 and 11 while treatment of bottom ash had limited effect.

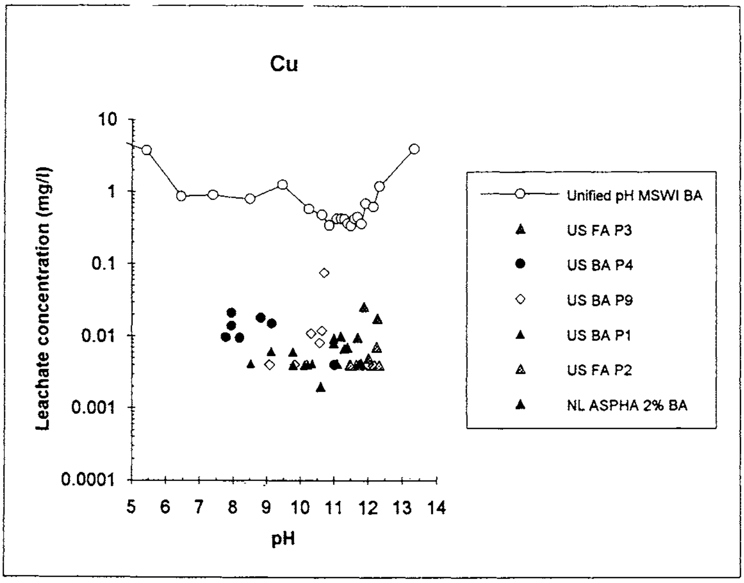
The solubility of an element or species of interest also can significantly effect the testing protocols required for estimating diffusion controlled release. A critical assumption in the tank leaching protocols is that the leachant remains dilute with respect to species of interest during each leaching interval. Figures 20.21 and 20.22 present the measured leachate concentrations for copper, cadmium, lead and zinc from several studies. The unified pH solubility curves for bottom ash (see Chapter 16) are provided for comparison. For the case of copper, all observed leachate concentrations were significantly less than the unified solubility curve. However, for most data sets, the observed leachate concentrations of Cd, Pb and Zn are below or equal to the solubility curve. In a few cases, data above the solubility curve have been measured. In these cases, the dilute solution criteria have not been met and the release data have to be interpreted with caution. Future testing for these cases should be carried out either with increased liquid to solid surface area ratios or with shorter leaching intervals. If release is controlled by solubility, other means of assessing long term release are needed. The use of release assuming an effective diffusion coefficient based on the highest pDe measured during testing is a worst case assessment of release. For the purpose of evaluating acceptability of release, this may already be adequate in view of the limit values concerned.

20.6 INTEGRATED INTERPRETATION OF pD_e AND AVAILABILITY

Reductions in constituent release from a treated material can be achieved either through reducing the fraction of that constituent available for release, through reduction of the rate of release (increased pD_e), or through modification of both critical parameters. In addition, the pD_e can be modified either through physical or chemical effects of treatment. A useful mechanism for evaluating the combined effects of both availability and pD_e is needed.

Estimation of diffusion controlled release from specific geometries and conditions over prolonged time periods can be accomplished through use of intrinsic leaching parameters and application specific geometries and exposure conditions. An important advantage to the use of intrinsic leaching parameters derived from the availability and diffusion release test data is the ability for prediction of release under conditions other

Figure 20.21 A Comparison of Tank Leaching Concentrations for Various Products as a Function of Solution pH and the Unified pH-Solubility Leaching Curves for Cu and Cd



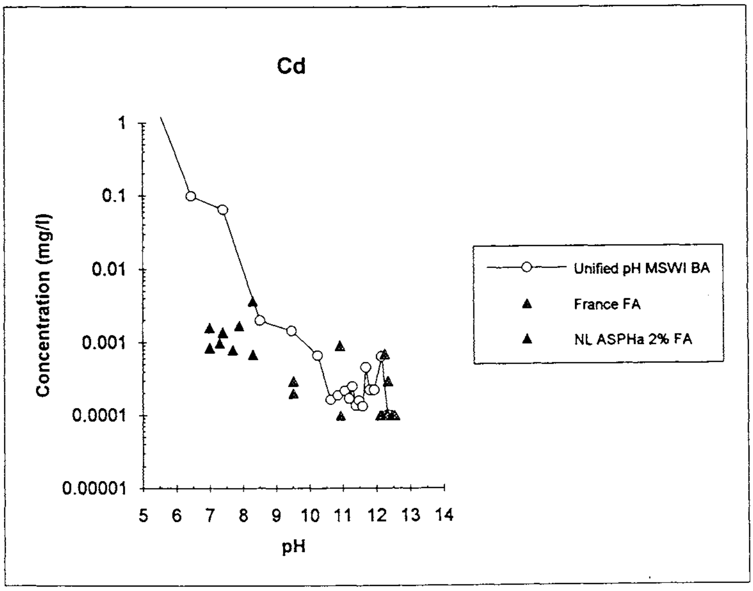
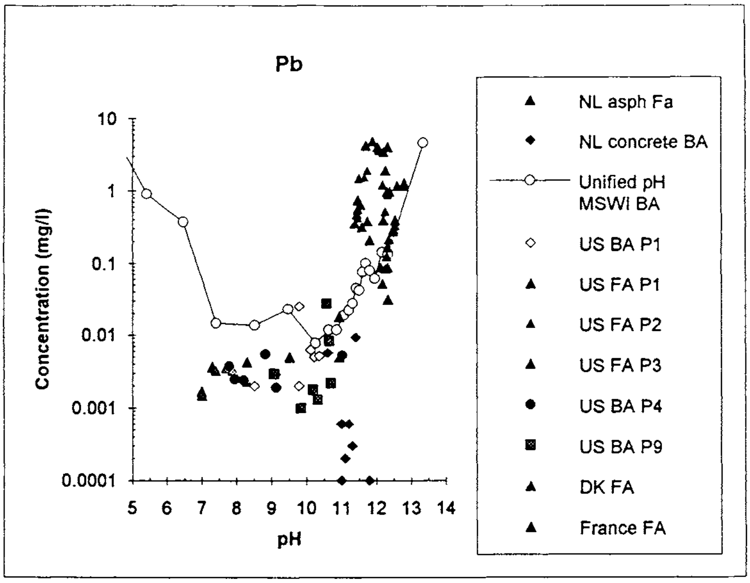
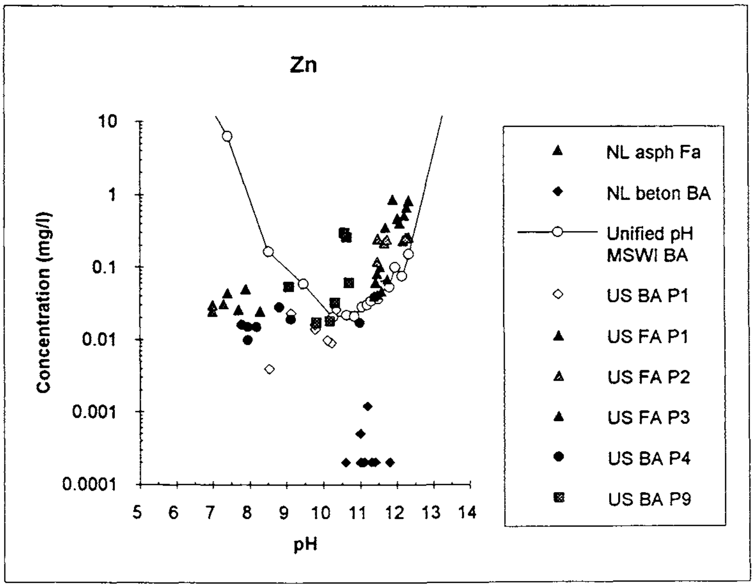


Figure 20.22 A Comparison of Tank Leaching Concentrations for Various Products as a Function of Solution pH and the Unified pH-Solubility Leaching Curves for Pb and Zn





than those studied in the laboratory. Many factors affect the translation of laboratory results to prediction of field behaviour. Field environmental conditions that are important include residue aging, contact with infiltration and precipitation frequency, temperature cycles, direct abrasion or erosion and the specific application scenario. Thus, estimates of field releases must be carefully derived. However, simplified models can be used to indicate relative releases and provide order of magnitude or limit case assessments.

The availability and pD_e leach parameters can be used to predict the release of contaminants during a given time period for a variety of application geometries. A 3-dimensional diffusion model enables one to take actual dimensions into account, so differences in leaching from a product with a cubic versus a flat rectangular shape can be described. With the 3-D model, release from only one side of the material also can be modelled.

A 3-dimensional model is based on the analytical solution of the linear diffusion from a parallelepiped, which initially is at a constant concentration, to an infinite region outside with a constant surface concentration (Crank, 1989; de Groot, 1993). The diffusion profile is calculated in all three dimensions according to the equation:

$$\frac{C(x,y,z,t)}{C_0}=\frac{64}{\pi^3}\sum_{l=0}^{\infty}\sum_{m=0}^{\infty}\sum_{n=0}^{\infty}\frac{(-1)^{l+m+n}}{(2l+1)(2m+1)(2n+1)}\cos\frac{(2l+1)\pi x}{2a}$$

$$x\cos\frac{(2m+1)\pi y}{2b}\cos\frac{(2n+1)\pi z}{2c}\exp(-t\alpha_l,m,n)$$

where: (20.26)

$$\alpha_{l,m,n}=\frac{\pi^D}{4}\left\{\left(\frac{2l+1}{a}\right)^2+\left(\frac{2m+1}{b}\right)^2+\left(\frac{2n+1}{c}\right)^2\right\} \tag{20.27}$$

Integration of the constituent flux across the surface boundary with respect to time results in an expression for calculation of cumulative release (Crank, 1989):

$$M_t=\int_0^t\left\{\left(\frac{64}{\pi^3}\right)^2\rho C_0abc\sum_{l=0}^{\infty}\sum_{m=0}^{\infty}\sum_{n=0}^{\infty}\frac{\alpha e^{-t\alpha}}{(2l+1)^2(2m+1)^2(2n+1)^2}\right\}dt \tag{20.28}$$

Application of Equation 20.10 permits estimation of the cumulative release of a constituent as a function of time. The cumulative release, expressed as fraction of the total leachable quantity (R_{max}), can be calculated using the 3-D model for different product configurations and bulk applications based on the effective diffusion coefficient measured during laboratory testing or in the field under well-defined boundary conditions. The usual boundary condition applied for field translation is that the surface concentration of the leaching constituent is effectively zero.

The cumulative release, expressed as fraction of the total leachable quantity (R_{max}), can be calculated using the 3-D model for different product configurations and bulk applications based on the effective diffusion coefficient measured under well-defined boundary conditions. The relative release from standard sizes with dimensions of 10 x 10 x 10 cm and 15 x 15 x 45 cm were calculated as a function of time for different effective diffusion coefficients ranging from pD_e=9 to pD_e=15 (pD_e = -log D_e with D_e in [m^2/s]). The cumulative release-time curves are provided in Figure 20.23. Between blocks of increasing size, the difference is largely a shift of the cumulative release for a given pD_e to a longer timescale. It takes longer to reach the maximum leachable quantity, but the leachable quantity may ultimately be reached unless the chemistry or other release controlling factors change. A significant shift in the cumulative release curve is apparent for the roadbase simulation. For a base of 15 cm thickness, 50% of the highly mobile components (pD_e=9) will be leached from the slab in less than approximately one year, assuming permanent contact with water. A 45 cm thick slab will reach the same level of relative release in about 6 years. It is important to consider that translation of lab data to field conditions further involves several factors such as corrections for the ambient temperature and degree of contact with water.

Estimating release during utilisation must consider adjustments to the pD measured in the laboratory to reflect anticipated field conditions (Kosson et al., 1995). Temperature, the fraction of time the surface is wetted, and the degree of water saturation are important considerations. While the diffusion coefficient is a function of the diffusivity of the constituent of interest in water, tortuosity, and chemical retention, only diffusivity (D_0) is significantly a function of temperature. The temperature dependence of diffusivity in dilute ionic solutions can be considered to be proportional to the absolute temperature over limited temperature ranges [20.28], e.g.,

$$D_{T2}=\frac{D_{T1}T_2}{T_1} \qquad (20.29)$$

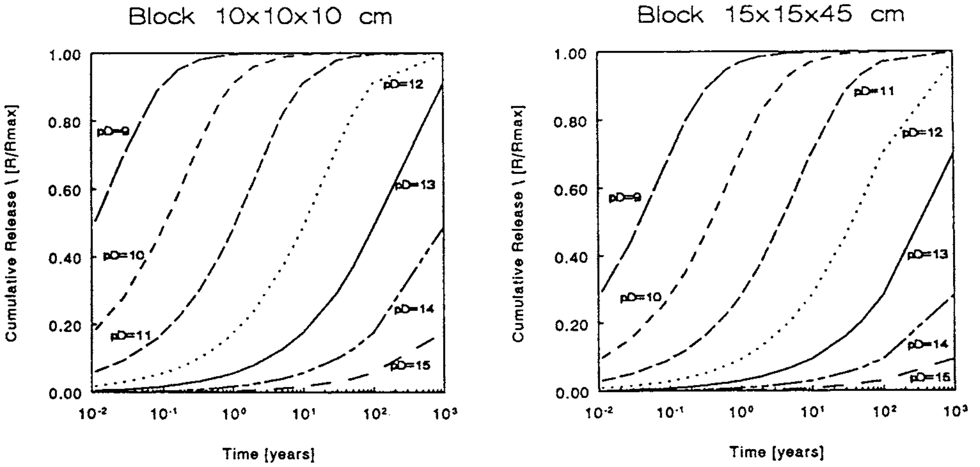
The above relationship assumes that the viscosity of the pore water (leachate) does not change significantly over the temperature range of interest. Alternatively, the effect of temperature on D has been correlated for release from cement stabilised products containing waste materials according to [20.29]:

$$pD_1-pD_2=0.71\left(\frac{1}{T_1}-\frac{1}{T_2}\right) \qquad (20.30)$$

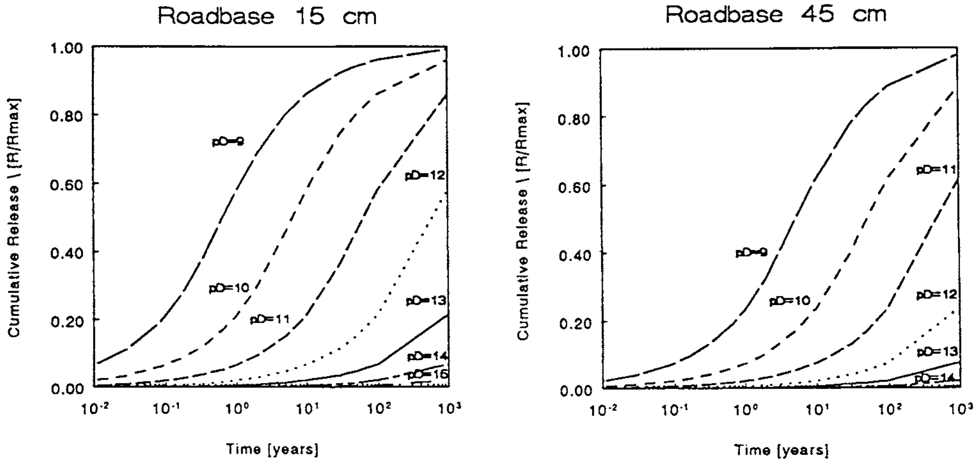
The cumulative release for a series of wet dry cycles can be approximated based on Equation 20.24 by:

Figure 20.23 Estimation of Fractional Cumulative Release as a Function of Time and Effective Diffusion Coefficient (pDe)

MONOLITHIC CONSTRUCTION MATERIALS



DIFFUSION CONTROLLED COMPACTED GRANULAR LAYER



$$\frac{M_t}{M_{t,w/d}} = \left(\frac{t}{t_{w/d}}\right)^{0.5} \tag{20.31}$$

or

$$M_{t,w/d} = M_t \left(\frac{t}{t_{w/d}}\right)^{-0.5} = M_t F_{w/d} \tag{20.32}$$

Note that the calculation of M_t assumed a continuously water saturated material. Figure 20.24 illustrates the effects of temperature and wet/dry cycles on diffusion controlled release from a 45 cm thick roadbase (Kosson, 1995). The cumulative effect of these conditions can be significant over long time intervals.

Calculation of cumulative release curves for a variety of geometries and applications is impractical on a routine basis. A simple one-dimensional diffusion model, assuming a constant source, can be used as an approximation. The advantage of this approach is that cumulative release is only a function of availability, pDe and the exposed geometric surface area. The one-dimensional model is independent of application specific geometry. This approach is valid as long as the concentration in the material has not decreased substantially, avoiding species depletion. If depletion does occur over the time period of interest, the one-dimensional model will over predict release, providing a conservative estimate for decision making. However, the amount of a specific element released will not exceed the availability of that element for all cases.

The one-dimensional model is based on the "semi-infinite slab" solution of the diffusion equation provided by Crank (1989):

$$M_t = 2\rho C_o \left(\frac{Dt}{\pi}\right)^{1/2} \tag{20.33}$$

where:

M_t = cumulative release [mg/m^2]

C_o = availability [mg/kg]

D = effective diffusion coefficient [m/s^2]

t = time [s]

r = density [kg/m^3]

This is the same basis which was used to estimate the pD from tank leaching data. The initial and boundary conditions for this solution are (i) the initial constituent concentration is uniformly distributed in the matrix; (ii) the exposed surface for leaching has a liquid concentration which is maintained essentially at zero; and (iii) depletion does not occur. Figure 20.25 provides a comparison of cumulative release estimated using the three-dimensional model and the one-dimensional model applied to a 10 x 10 x 10 cm block and a 45 cm thick roadbase (one surface exposed) for two different values of pDe. The effect of depletion on release is indicated by the greater predicted release by the one-dimensional model. However, in all cases the release estimated by the one-dimensional model will be equal to, or greater than the release predicted by the three-dimensional model. This confirms that the one-dimensional model provides a conservative estimate of release, provided that no significant changes in chemistry occur.

Figure 20.24 The Effect of Intermittent Wetting and Temperature on Diffusion Controlled Release of Product Constituents

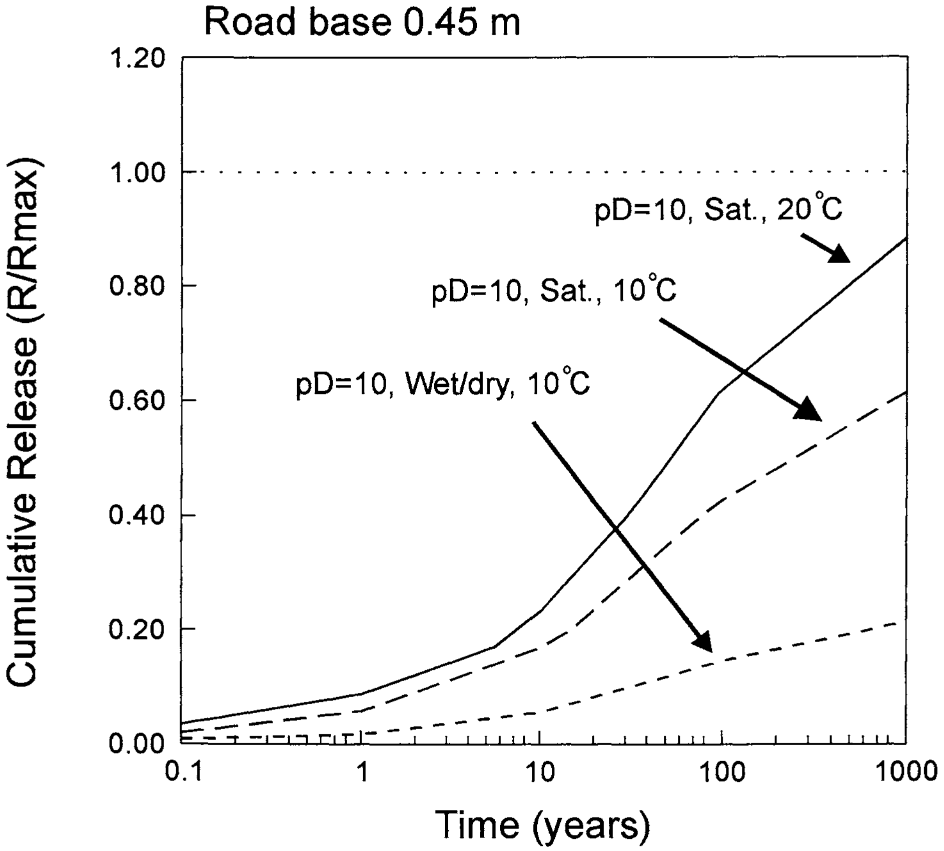
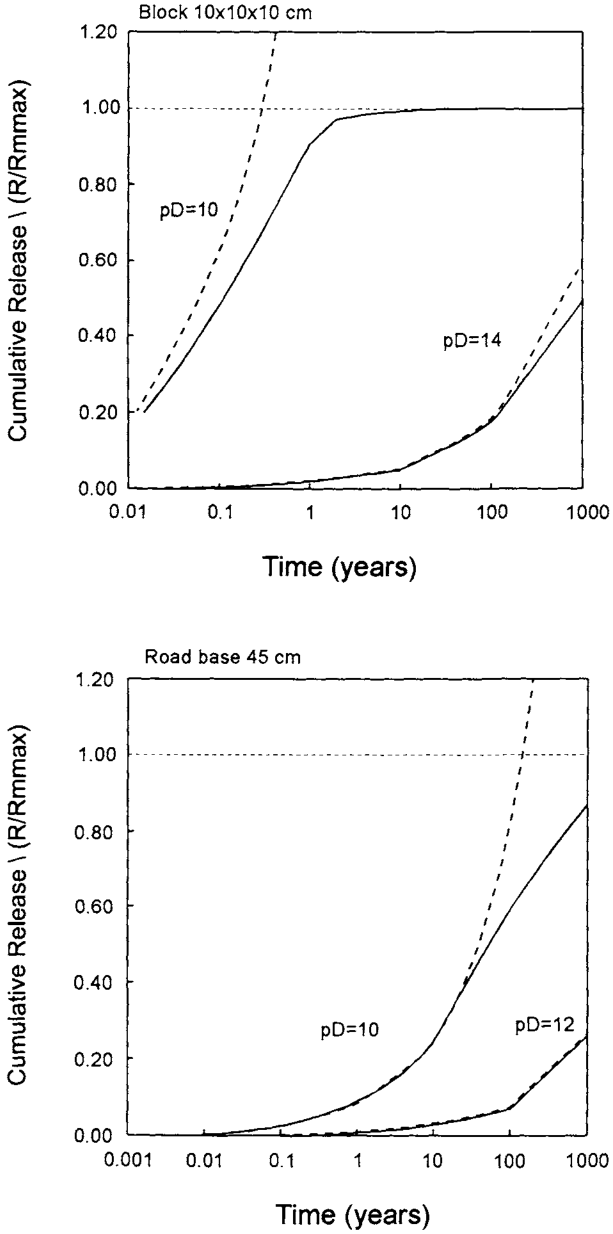


Figure 20.25 A Comparison of Fractional Cumulative Release for Products Estimated Based on the "Infinite Slab" Approximation and Accounting for the Product Geometry and Depletion



Interpretation of the availability and pD information can be further simplified if a fixed time interval is defined over which to consider release. For example, a 100 year interval may be considered as the useful life for roadbase or other construction applications. Use of the one-dimensional model permits the development of charts which provide estimated cumulative release per unit area as a function of only availability and pD. These charts are referred to in this text as "cumulative release nomographs". Examples of cumulative release nomographs are provided for several elements in Figures 20.26 through 20.28. Availability and pD are presented on the x-axis and y-axis, respectively. Diagonal lines indicate lines of constant cumulative release (e.g., 10, 100, 1000, etc. mg/m^2 over a 100 year interval). Lines of constant cumulative release decrease in value from lower right to upper left of each figure. Data plotted above and to the left of a line of constant cumulative release provide less release than the indicated value; data below and to the right provide greater release than the indicated value.

Cumulative release nomographs provide a straightforward method of interpretation for evaluation of data from laboratory testing of diffusion controlled release. An acceptable cumulative release can be defined for specific applications or locations based on evaluation of the potential impacts of that release. Data for applications which result in release less than the defined limit would be considered acceptable. Thus, diffusion controlled release information can be readily incorporated into a regulatory framework.

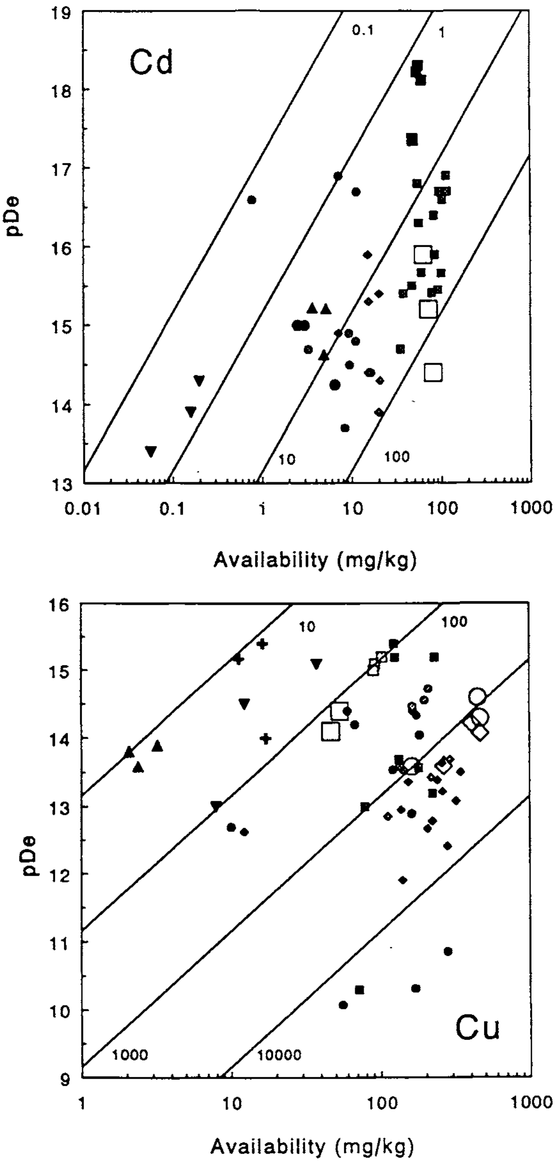
Consideration of the cumulative release nomographs presented in Figures 20.26 through 20.28 also provide information about the effectiveness of various treatment processes and products for incinerator residues. Observations are summarised in the paragraphs that follow.

Cadmium (Figure 20.26)
Cumulative release for bottom ash incorporated into cement pavement blocks was between 0.1 - 1.0 mg/m^2. S/S treated bottom ash and fly ash incorporated in asphalt had release between 1.0 - 10 mg/m^2. Untreated APC and S/S treated residue typically had cumulative release > 10 mg/m^2.

Copper (Figure. 20.26)
Cumulative release for fly ash in asphalt, bottom ash in paving blocks and residue from the 3R process was between 10 and 100 mg/m^2. Untreated and S/S treated APC residue cumulative release was between 100 and 1000 mg/m^2. Untreated and S/S treated bottom ash and combined ash generally had cumulative release in excess of 1000 mg/m^2.

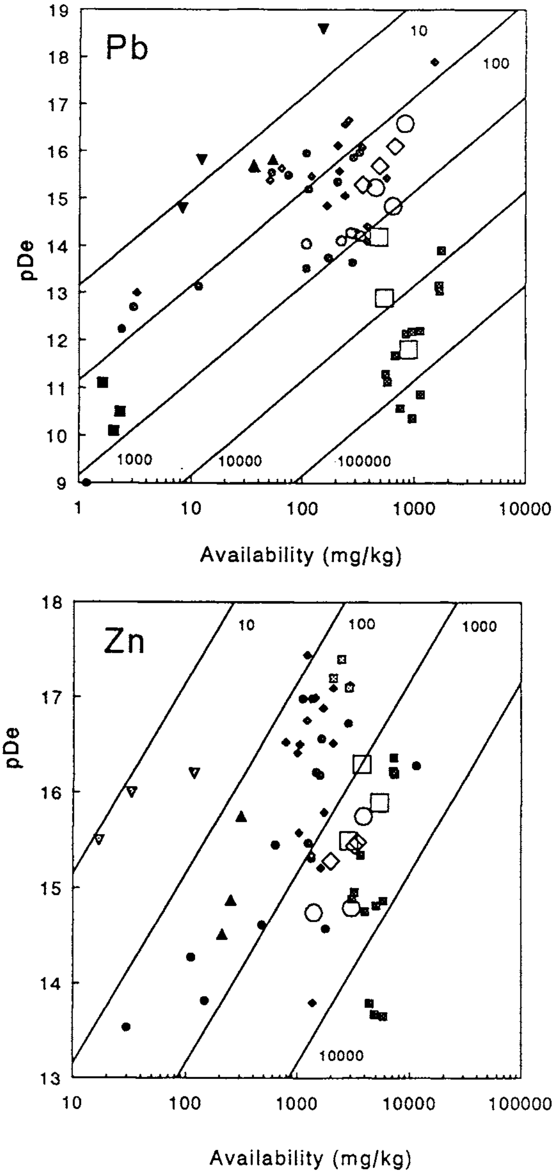
Lead (Figure 20.27)
S/S treated bottom ash, bottom ash in cement pavement blocks and fly ash in asphalt generally had cumulative release less than 100 mg/m^2. Untreated bottom ash,

Figure 20.26 Availability-pDe Plot of Release Parameters for Cadmium and Copper from Tank Leaching Tests on Untreated Incinerator Residues and Several Product Materials Containing Residues



Diagonal lines represent constant cumulative release (mg/m^2) estimated for 100 yrs using the "infinite slab" approximation

Figure 20.27 Availability-pDe Plot of Release Parameters for Lead and Zinc from Tank Leaching Tests on Untreated Residues and Several Product Materials Containing Residues



Diagonal lines represent constant cumulative release (mg/m^2) estimated for 100 yrs using the "infinite slab" approximation

untreated combined ash, S/S treated combined, S/S treated fly ash, and fly ash in asphalt had cumulative release between 100 and 1000 mg/m^2. Untreated APC residue and S/S treated APC residue generally had cumulative release in excess of 10,000 mg/m^2. Phosphate treated APC was the exception to this with cumulative release between 100 and 1000 mg/m^2.

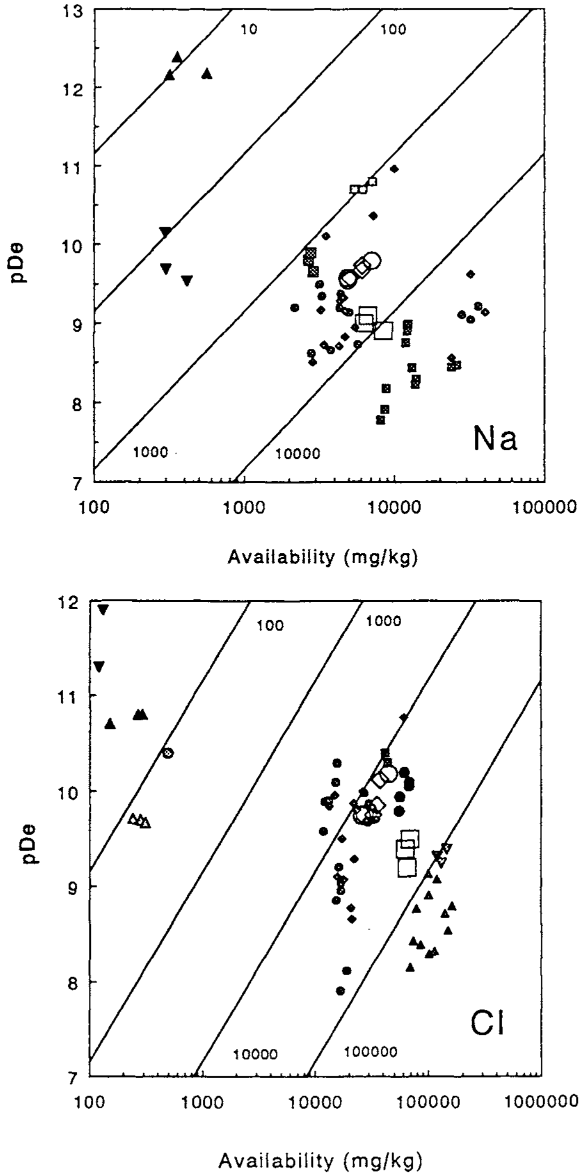
Zinc (Figure 20.27)
Bottom ash in cement pavement blocks had cumulative release between 10 and 100 mg/m^2. S/S bottom ash, S/S combined ash and fly ash in asphalt had cumulative release between 100 and 1000 mg/m^2. Untreated bottom ash, combined ash and APC residue, and S/S treated APC residue generally had cumulative release in excess of 1000 mg/m^2.

Sodium (Figure 20.28)
Bottom ash in cement pavement blocks had cumulative release of approximately 10 mg/m^2. Bottom ash in asphalt had release between 100 and 1000 mg/m^2. All untreated residues and other treatment conditions had release in excess of 1000 mg/m^2. Several processes resulted in cumulative release in excess of 10,000 mg/m^2. It is important to recognise that because the pD_e for sodium is less than 10.5 for most cases, the majority of the cumulative release will occur during the first ten years of application with subsequent depletion (see Figure 20.24).

Chloride (Figure 20.28)
Bottom ash in asphalt, fly ash in asphalt and bottom ash in cement paving blocks all had cumulative release of approximately 100 mg/m^2 or less. Untreated and S/S treated bottom ash and combined ash generally had cumulative release between approximately 10,000 and 100,000 mg/m^2. S/S treated APC residue and fly ash had cumulative release in excess of 100,000 mg/m^2. As with sodium, the majority of the release will occur during the first few years of application.

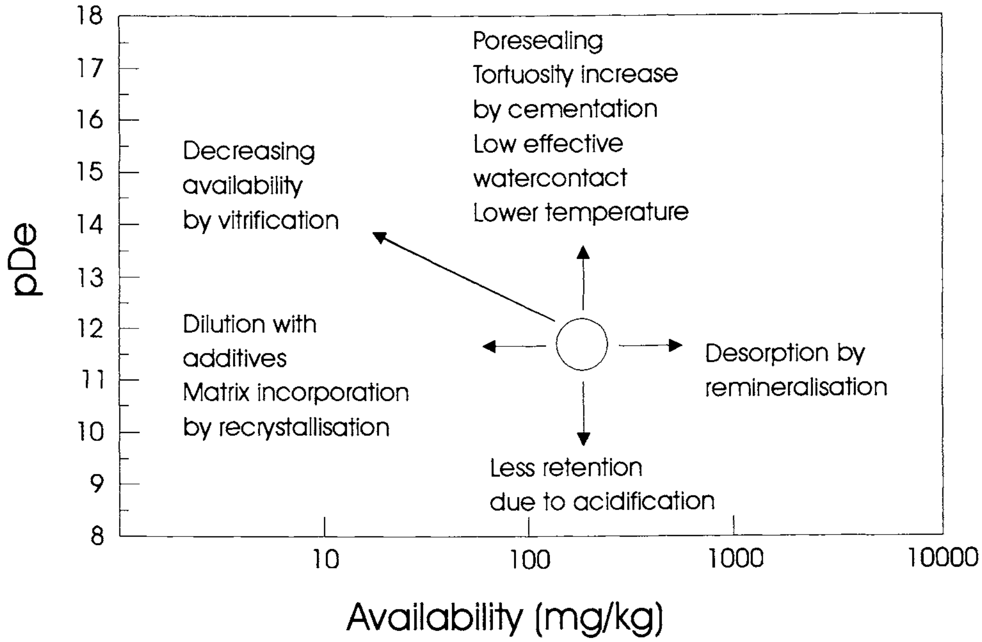
Figure 20.29 summarises the affects of various treatment processes on diffusion controlled release from incinerator residues. In general, incorporation of residues into asphalt decreases release through increased physical retention. Therefore, the process can be effective for both highly soluble salts and trace metals. Treatment of residues by S/S processes decreases release through chemical respeciation and modification of the matrix alkalinity. Therefore, S/S processes may be effective for reducing release of trace metals but are generally ineffective for reducing release of highly soluble salts, although release may be delayed. S/S processes also may be ineffective when highly soluble salt loadings are so great, as in the case of APC residues, that a highly porous matrix remains after depletion of the salts. Availability of all of the residue constituents may be reduced by any of the above processes by having limited residue loading in the final product (dilution effects).

Figure 20.28 Availability-pDe Plot of Release Parameters for Sodium and Chloride from Tank Leaching Tests on Untreated Residues and Several Product Materials Containing Residues



Diagonal lines represent constant cumulative release (mg/m^2) estimated for 100 yrs using the "infinite slab" approximation

Figure 20.29 A Schematic Illustration of Treatment Process and Environmental Conditions Effects on the Availability-Effective Diffusion Coefficient Relationship



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