IMMOBILIZATION OF MIXED WASTE[a]

T. Michael Gilliam
Oak Ridge National Laboratory
Oak Ridge, Tennessee 37831

ABSTRACT

A fundamental relationship between ANS 16.1 and EP-Tox leach results has been developed and experimental data presented verifying the relationship for solidified waste products. The relationship can be used as a powerful tool for quality assurance during disposal operations; to guide formulation development efforts; and to expand existing data bases to a wider variety of mixed wastes.

INTRODUCTION

Cement-based materials are the most widely used hosts for the immobilization of radioactive low-level waste (LLW) streams because (1) the cost of materials is low; (2) the processes run at low temperature, use standard "off-the-shelf" equipment, and are adaptable to a wide variety of disposal scenarios; (3) the resulting waste forms are highly resistant to chemical, biological, thermal, and radiation degradation; and (4) high waste loadings are achieved with a minimum waste volume increase when the waste host formulas are tailored to the specific waste streams.

Formulation development for the immobilization of wastes containing both radioactive and chemically hazardous constituents is complicated by the sometimes conflicting waste form requirements of the U.S. Nuclear Regulatory Commission (NRC) and the Environmental Protection Agency (EPA) (1). The greatest perception of conflicting performance requirements is in the area of leachability.

The EPA requires that the waste form pass the EP-Toxicity Extraction Procedure commonly referred to as the EP-Tox test (2). This procedure is a 24-h static leach test in pH 5 acetic acid solution. The resultant leachate concentrations must be less than specified threshold values (currently 100 times drinking water standards) for selected priority pollutants. If the concentrations are below the threshold values, then the waste may be disposed of as a nonchemically hazardous waste.

On the other hand, the NRC requires that the waste form be characterized by Leachability Indices >6 for all radionuclides as prescribed by the ANS 16.1 Leach Protocol (3). ANS 16.1 is a quasi-dynamic test in deionized water with leachant replacement at 2, 7, 24, 48, 72, 96, 120, 456, 1128, and 2136 h. The resulting leachate concentrations are modeled by a fundamental mass transport equation to obtain an effective solid-diffusion coefficient in units of square centimeters per second. The Leachability Index is then defined as the negative log of the diffusion coefficient.

The use of Leachability Indices is well established in the LLW disposal industry. As such, extensive data bases exist with vendors, universities, and the U.S. Department of Energy laboratories for the control and enhancement of these indices. However, the seemingly incongruent relationship between Leachability Indices and EP-Tox requirements serves as an impediment to the application of these data to the immobilization of mixed waste. The relationship between Leachability Index and EP-Tox requirements is described in this paper.

ANS 16.1 Leach Procedure

The ANS 16.1 Leach Procedure is designed to determine the effective solid diffusion coefficients for species of interest. In general, solid-diffusion-controlled leaching represents the maximum release rates for the species of interest (4).

The ANS 16.1 procedure utilizes periodic leachant replacement to simulate a continuous-flow system. The procedure is designed so that the results can be modeled by the fundamental mass transport equation:

$$\left(\frac{\Sigma a_n}{A_o}\right)\left(\frac{V}{S}\right) = 2\left(\frac{D_e}{\pi}\right)^{1/2} t^{1/2} , \qquad (1)$$

where

Σa_n = cumulative mass of species released through cumulative time, t;

A_o = original mass of species in the waste form;

V = external volume of the waste form;

S = external surface area of the waste form;

D_e = effective solid diffusion coefficient.

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The Leachability Index, L, of a species is defined as

$$L = - \log (D_e) \ . \qquad (2)$$

It has been shown that, with the diffusion coefficient established, Eq. (1) can be used to predict release for a variety of solid geometries, leachant compositions, and cumulative leach times (5). For example, utilizing Eq.(1), the release in a 24-h period from a 7.1 cm-long, 3.3-cm-diam, right-circular cylinder becomes

$$\frac{a_n}{A_o} = 495.4 \sqrt{D_e} \ , \qquad (3)$$

where

a_n = mass of species released in the initial 24-h leach interval, mg;

A_o = original mass of species in waste form, mg;

D_e = effective solid diffusion coefficient of species, cm^2/s.

Relationship to EP-Tox

Significantly, Eq. (3) models the release from the sample size and leach interval specified by the EP-Tox test. Thus, Eq. (3) provides the means to relate Leachability Index and EP-Tox requirements. For pumpable grouts, such as those developed for the Oak Ridge National Laboratory (ORNL) hydrofracture process (6) and the Rockwell-Hanford Transportable Grout Facility (7), Eq. (3) can be modified to (8)

$$\frac{C}{C_o} = \frac{(30.87)\ 10^{-L/2}}{M + \rho_w} \qquad (4)$$

where

C = EP-Tox leachate concentration, mg/ℓ;

C_o = original waste concentration, mg/ℓ;

M = grout mix ratio, kg/ℓ;

ρ_w = density of original waste, g/cm^3.

Although the EP-Tox Procedure requires an acetic acid solution as the leachant, previous laboratory experience at ORNL has shown that, generally, results from leaching in distilled water are similar for grouts that pass the structural integrity test. Therefore, the Leachability Index used in Eq. (4) can be obtained using distilled water, the ANS 16.1 standard leachant.

Extrapolation Calculations

Thus, Eq. (4), combined with Leachability Indices as determined by the standard ANS 16.1 protocol, becomes a powerful tool which can be used to predict EP-Tox test results. To verify the equation's applicability, ANS 16.1 and EP-Tox tests were performed on a hydrofracture grout.

The grout samples were mixed at a ratio of 0.84-kg dry-solids blend per liter of waste. The dry-solids blend used in preparing the grout samples consisted of 42 wt % Type I Ideal Portland Cement, 34% ASTM Class F fly ash, 16% Attagel-150 clay, and 8% Indian Red Pottery Clay. The liquid waste concentration is shown in Table I.

TABLE I

Salts Used in Simulated Waste Solution

Salt	Concentration (mg/ℓ)
Major Components	
$Al(NO_3)_3 \cdot 9H_2O$	2780
$NaCl$	5430
Na_2CO_3	20140
$NaNO_3$	68860
$NaOH$	7200
Na_2SO_4	13350
NH_4NO_3	240
Minor Components	
As_2O_5	307
$Cr(NO_3)_3 \cdot 9H_2O$	3846
$Pb(NO_3)_2$	320

Right circular cylindrical samples were prepared in triplicate with dimensions of 2.5 cm in diameter and 4.5 cm in length. The samples were then subjected to the 5-d abbreviated ANS 16.1 leach protocol with distilled-water leachant replacement at 2, 7, 24, 48, 72, 96, and 120 h. Resulting Leachability Indices for arsenic, chromium, and lead are shown in Table II.

TABLE II

Summary of Leachability Results

Constituent	Leachability Index	EP-Tox Concentrations (mg/ℓ) Predicted	Actual
As	>11.13	<0.009	<0.005
Cr	>11.37	<0.017	<0.010
Pb	11.06	0.009	0.013

Right circular cylindrical samples of 3.3 cm in diameter and 7.1 cm in length were similarly prepared and subjected to the EP-Tox protocol. Resulting leachate concentrations, as well as predicted results using Eq.(4) and Leachability Indices obtained from the ANS 16.1 experiments are shown in Table II.

Significantly, the predicted values closely approximate the actual EP-Tox concentrations, thereby verifying the applicability of the mathematical relationship. The relationship thus becomes a useful tool which can be used to guide formulation development efforts, as well as a quality assurance guide during operations.

Typically, liquid wastes are stored in large tanks, from which a truly representative sample is difficult to obtain. Nonetheless, grout formulation development is routinely predicated on a "representative" sample from these large tanks. In addition to formulation development, regulatory leach testing, such as ANS 16.1 and EP-Tox, are performed on these same samples. However, during waste disposal operations, it is not uncommon to see significant concentration deviations from the representative samples, particularly with the trace levels of priority pollutants (arsenic, chromium, lead, etc). Because Leachability Indices are insensitive to relatively large variations in trace element waste concentration, the mathematical relationship in conjunction with these Indices provides a means to assess waste variations on EP-Tox results immediately after waste analyses. This relationship provides a significant time savings because to perform an EP-Tox test, one must allow the sample to set and cure (up to 28 d) prior to performing the leach test.

In addition, the mathematical relationship expands the applicability of existing (and ever increasing) Leachability Indices data bases to a greater variety of mixed wastes. For example, if the Leachability Index for lead has been reported for a grout developed to immobilize a nitrate waste containing 10 ppm of lead, then the relationship can be used to quickly assess the grouts applicability to a similar waste containing 500 ppm of lead. The relationship can further aide formulation development by establishing the minimum Leachability Index required to meet a desired EP-Tox concentration. This can be accomplished by substituting the desired EP-Tox concentration into Eq. (4) (or 3) along with the maximum anticipated waste concentration. The calculated Leachability Index (or diffusion coefficient) then becomes the minimum acceptable Index. Formulation efforts would be directed to meet or exceed this Index.

SUMMARY

A fundamental relationship between ANS 16.1 and EP-Tox leach results has been developed and experimental data presented verifying the relationship for solidified waste products. The relationship can be used as a powerful tool for quality assurance during disposal operations; to guide formulation development efforts; and to expand existing data bases to a wider variety of mixed wastes.

It should be noted that although the release of some organics from solidified waste have been shown to be diffusion controlled (9), the relationship presented here is intended primarily for inorganic pollutants. In addition, a statistical treatment of the input data to the relationship will greatly enhance its accuracy and usefulness.

For example, the relationship presented here was developed from mass transport theory as applied in the ANS 16.1 protocol. For this theory to be valid, a plot of $[(\Sigma a_n/A_o)(V/S)]$ vs $\sqrt{t}$ must result in a straight line which passes through the origin. Effective diffusivities have been reported from data which, though linear with the square root of time, did not go through the origin (10). A positive intercept may represent a surface phenomena where salts are washed off over a relatively short period of time. A negative intercept may correspond to a delay in leaching caused by a passive surface layer.

Typically, this intercept represents a small fraction of the total amount released during the experiment. As such, it can be ignored for qualitative comparisons of competing waste forms or for predicting long-term release. However, for predicting a 24-h release, as with the relationship presented here, it may become significant. Therefore, before applying ANS 16.1 data in this relationship, a statistical treatment of the leach data may be necessary to assess the magnitude of the intercept. If significant, the fundamental mass transport equation (Eq. 1) can be simply modified to:

$$\left(\frac{\Sigma a_n}{A_o}\right)\left(\frac{V}{S}\right) = \left[\left(\frac{\Sigma a_n}{A_o}\right)\left(\frac{V}{S}\right)\right]_o + 2\left(\frac{D_e}{\pi}\right)^{1/2} t^{1/2} \,. \quad (5)$$

The correct relationship between Leachability Index and EP-Tox concentration can then be derived from Eq. (5) in a manner similar to that presented in this paper.

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