CHAPTER 14 - LEACHING TESTS

14.0 LEACHING TESTS

Now that the concepts behind leaching phenomena have been introduced, discussing leaching tests is appropriate. Invariably, these tests are involved in the regulation of residues, as well as in the interpretation of leaching phenomena. Careful consideration should be given to the specific "tools" that are selected to characterise ash. Clearly, it is preferable to use a number of tools, rather than a single tool, for work in both science and regulation.

At the end of this section, a unified theory of leaching is presented. This will move away from the strict use of concentration data and toward normalisation of leaching data to release, fractions leached and fluxes from residues. The rationale for using this approach to develop models and management scenarios will be discussed.

Generalised and detailed reviews of leaching tests are found in Jackson et al. (1984), Fällman (1990), Environment Canada (1990), Zachara and Streile (1991) and van der Sloot et al. (1991; 1993). The information from Environment Canada (1990) provides much of the basis for the following discussion.

14.1 PURPOSE OF LEACHING TESTS

In general, a leaching test involves contacting a solid material with a leachant to determine which components in the solid will dissolve in the leachant and create a leaching solution or leachate. To investigate the various processes governing the extent and rate of leaching, endless variations can be introduced by changing test variables, such as leachant composition, method of contact, liquid-to-solid (L/S) ratio, contact time and system control (pH, pE (or Eh), temperature). Leaching tests have a wide range of objectives, the most common of which are presented in Table 14.1.

Leaching tests are typically used to provide information about the constituent concentration or the constituent release from a waste material under reference test conditions, or under conditions that more closely approximate the actual disposal site. This information may subsequently be used in mathematical models to predict long term leaching.

14.1.1 Classification of Leaching Tests

For the purposes of this discussion, leaching tests have been separated into two broad categories on the basis of whether or not the leachant is renewed:

1) extraction tests (no leachant renewal), and
2) dynamic tests (leachant renewal).

Table 14.1
Leaching Test Objectives

Objective	Description
Identification of leachable constituents	Determine which constituents of a waste are subject to dissolution upon contact with a liquid.
Classification of hazardous wastes	Compare wastes against performance criteria for classification of wastes as hazardous or nonhazardous.
Evaluation of process modifications	Determine if modifications to a waste-generating process result in a less leachable waste.
Comparison of waste treatment methods	Determine whether a given waste treatment method/process results in superior containment of contaminants.
Quality control in waste treatment	Verify the efficiency of a treatment process using a simple pass/fail criterion.
Design of leachate treatment systems	Obtain a typical leachate to perform treatability experiments.
Field concentration estimates	Express leaching over time (e.g. to be used as a source term in groundwater modelling).
Parameter quantification for modelling	Quantify partition coefficients and kinetic parameters to be used in transport modelling.
Risk assessment	Estimate potential impact of waste disposal on the environment.

The concept of leachant renewal is based on modifying the leaching system to promote solution control of leaching rather than solid phase control.

Extraction Tests

Extraction tests include all tests in which a specific quantity of leachant is contacted with a specific quantity of waste for a certain length of time, without leachant renewal. (This definition does not include analytical extractions or digestion procedures which are used to measure the total constituent concentration in an ash sample). The leachate is separated from the solid and analysed either at various times during the

test, or, as in most extraction tests, at the end of the test. The analysis of leachates generated at various times can help determine the kinetics of the leaching process or if equilibrium has been attained.

The underlying assumption in this type of test is that an equilibrium condition is achieved by the end of the extraction test (i.e. the concentrations of solutes in the leachate become constant). In this no-flow system, an equilibrium condition occurs when there is no net transfer of components from the solid phase to the leaching solution, or vice versa.

Sampling in an extraction test over time to derive kinetic information or to monitor the attainment of equilibrium is difficult since it must be done without modifying the residue-leachant interactions, which are a function of factors such as the L/S ratio and gaseous exchanges. This can be accomplished in three ways:

- nondestructive sampling and analysis of parameters such as pH, conductivity or specific ions
- removing small volumes (aliquots) that are negligible when compared with the total volume
- preparing as many parallel extraction tests as data points required and performing destructive analyses.

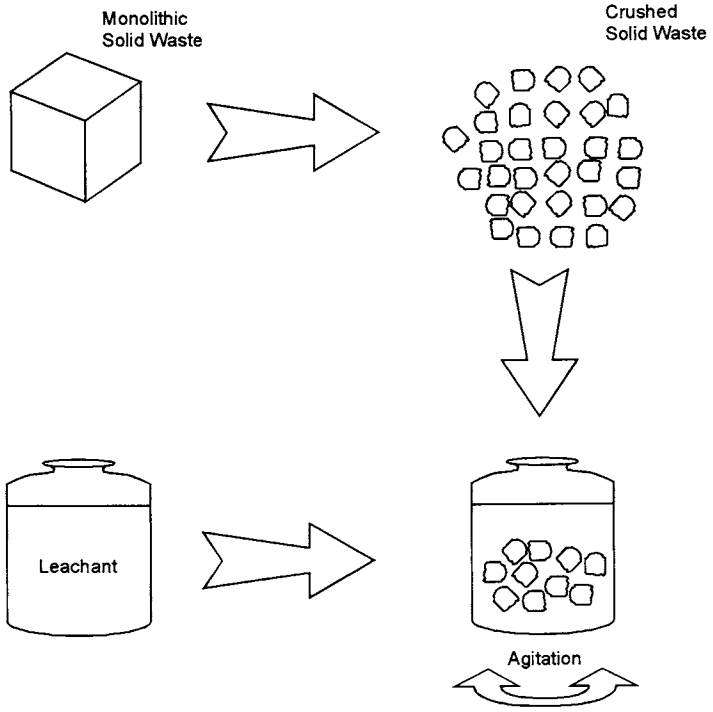
Extraction tests can be further divided into four subcategories:

- agitated extraction tests
- non-agitated extraction tests
- sequential chemical extraction tests
- concentration buildup tests

Agitated Extraction Tests

Agitated extraction tests (Figure 14.1) are performed to reach steady-state conditions as quickly as possible. They measure the chemical properties of a waste-leachant system, as opposed to rate-limiting mass transfer mechanisms. Agitation ensures a homogeneous mixture, promotes contact between the solid and the leachant and reduces boundary layer thicknesses. Sample particle size reduction is often performed to increase the surface area to volume ratio of the solid to enhance liquid/solid phase contact and to eliminate mass-transfer limitations. Generally, this reduces the duration of the test by reducing the time required to reach a pseudo-equilibrium condition in the leachate. This procedure may also have the effect of overestimating the short-term release of constituents. A steady-state leaching environment can also be attained in a column apparatus by recirculating the collected leachate back into the column.

Figure 14.1 Agitation Extraction Test



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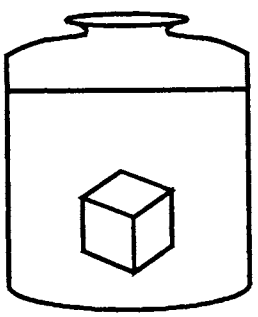
Non-agitated Extraction Tests

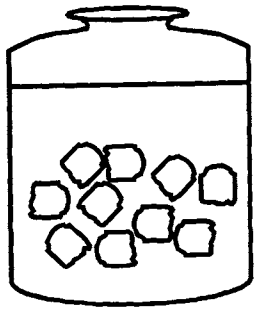
A non-agitated extraction test is performed to study the physical mechanisms that are rate-limiting in leaching. The underlying assumption behind a non-agitated extraction test is that the physical integrity of the solid matrix and mass transfer constraints (both internally within the sample and externally in the boundary layer) affect the amount of contaminants that are leached during the test. Two types of non-agitated tests are illustrated in Figure 14.2. They can be performed on large particle-sized residue samples, concrete-type or monolithic samples.

The disadvantage of running a non-agitated test is that a much longer contact period may be required to reach equilibrium conditions than is required in an agitated test. The advantage of this type of test is that rate-limiting mechanisms of leaching due to the physical integrity of the solid matrix are taken into account. These tests are presented in further detail in Chapter 20.

Figure 14.2 Static Leach Test



A) Static test with monolithic solid waste



A) Static test with nonmonolithic solid waste

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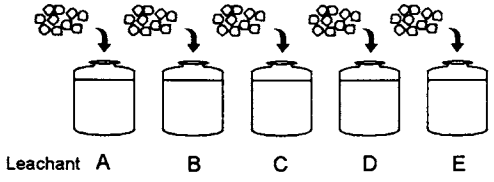
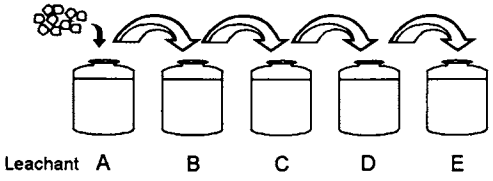
Sequential Chemical Extraction Tests

A sequential chemical extraction test is composed of a battery of non-agitated extraction tests (Figure 14.3). It involves performing sequential elutions of aliquots of a sample with different leachants (i.e. A, B, C, D and E in Figure 14.3), which are increasingly more aggressive in terms of chemical attack toward the residue (Figure 14.3a). One type of method assumes that each successive leachant also extracts the sum of contaminants extracted by all preceding leachants. The other type of method is conducted by subjecting the same aliquot of sample to each leachant (Figure 14.3b). The amount extracted in each elution is associated with a certain chemical form or mineral phase in the solid phase. The Sequential Chemical Extraction Procedure, originally compiled by Tessier et al. (1979), was adapted to sewage sludge incinerator ash by Fraser and Lum (1983), and then further modified for MSW incinerator ash (WTC, 1990). The test has been used in different studies (Wadge and Hutton, 1987) (Tessier Method); Environment Canada, 1993 (modified)), however, results by Khebohian and Bauer (1987) and discussion by Nirel and Morel (1990) (on the Tessier method) have shown that resorption and reprecipitation reactions can dramatically alter the mass fractions that are obtained in the different extractions. This limitation has been recognised and the latest studies using the modified method have based much of their interpretation on the operationally defined extractions (e.g., peroxide extractable) rather than the implied chemical species (Environment Canada, 1993). Consequently, it appears that although the method is not appropriate for determining the chemical species, relating the operationally defined extractions to exposures under different leaching conditions (e.g., fraction available for leaching under acidic leaching conditions versus severe reducing conditions) is an appropriate set of interpretations.

Figure 14.3 Sequential Chemical Extraction Tests



a) With different waste samples



b) With the same waste sample and liquid/solid separation between elutions

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Concentration Buildup Tests

In a concentration buildup test, an extraction is achieved at a very low cumulative L/S ratio. Aliquots of samples are successively contacted with the same leachant (Figure 14.4). The contact of leachate with fresh solid material can be considered as a model for an elemental volume of water flowing through a large body of residue and approaching saturation with respect to specific mineral phases. The purpose of this test is not to collect kinetic information, but to characterise a leachate saturated with soluble residue constituents. In some cases, this may simulate the actual pore water composition of a granular material in column leach tests or in outdoor disposal or utilisation scenarios.

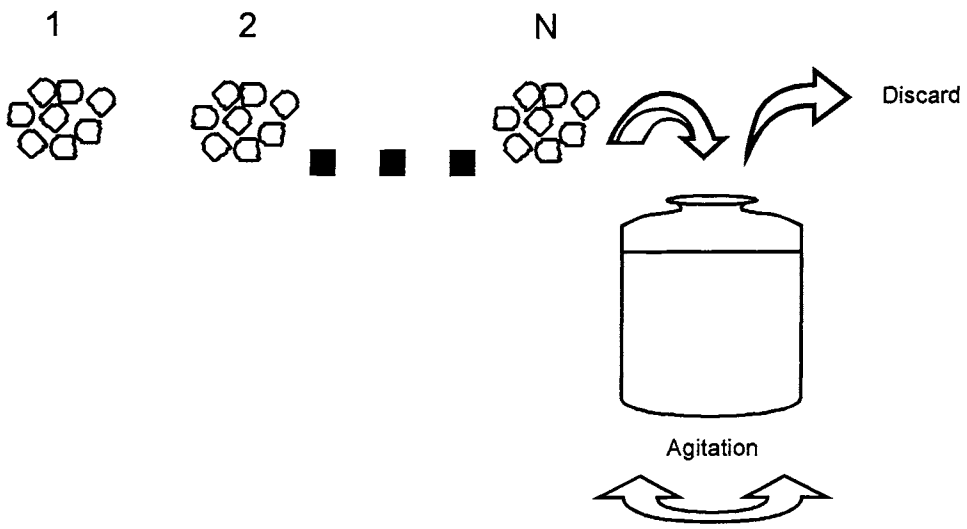
Dynamic Tests

Dynamic tests include all tests in which the leachant is continuously or intermittently renewed to maintain a driving force for leaching that is solution-controlled. The intermittent tests may be conducted by alternating leaching periods with dry periods to study the effects of desiccation or unsaturated flow conditions.

Dynamic tests provide information about the kinetics of solid phase dissolution and contaminant flux. Information is generated as a function of time, and attempts are often made to preserve the residue's physical integrity. These two factors lend this category of leaching tests to the investigation of more complex mechanisms of leaching.

Dynamic tests can be further divided into subcategories according to how the interface between the waste and the leachant is defined. Tests in which individual waste particles are used to define the interface are called serial batch tests. The tests in which a characteristic dimension of the waste, (such as the external geometric surface area or the geometric surface area perpendicular to flow) is used to define the interface include flow-around tests and flow-through or column tests.

Figure 14.4 Concentration Buildup Tests



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Serial Batch Tests

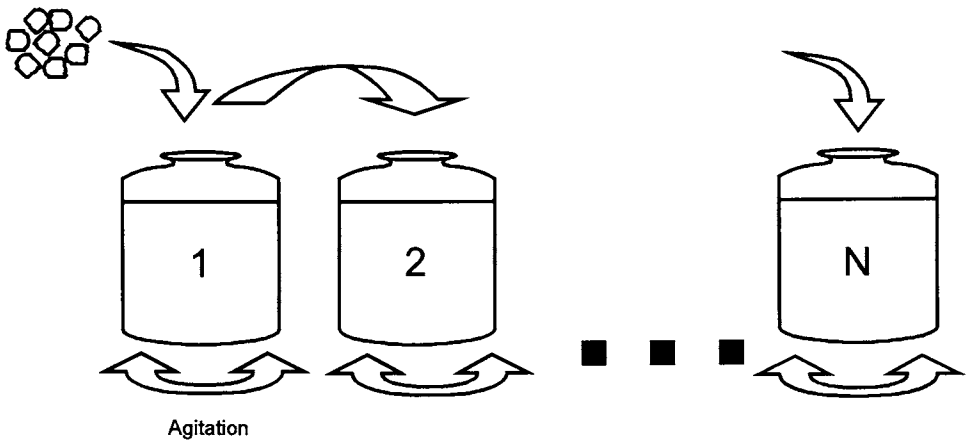
A serial batch test is conducted using a granular or crushed sample which is mixed with leachant at a given L/S ratio for a specified period of time (Figure 14.5). The leachate is then separated from the solids and replaced with fresh leachant until the desired number of leaching periods have been completed. The waste/leachant mixture is normally agitated to promote contact. Kinetic information regarding contaminant dissolution is obtained using the concentrations measured in the leachate from each of the leaching periods. Data from serial batch tests can be used to construct an extraction profile to infer the temporal release of leachable constituents.

Flow-Around Tests

In flow-around tests, a sample of residue is placed in the leaching vessel and the flow of fresh leachant around the residue provides the driving force to maintain leaching. The L/S ratio is modified to express the volume of leachant divided by the surface area

of the solid sample. Samples are usually monolithic, although non-monolithic or crushed residue may be used if it is confined in some manner. Agitation is generally not performed. Leachant flow is either continuous (Figure 14.6a), in which case it is sampled and analysed periodically, or it is intermittently renewed (Figure 14.6b). The latter method is generally simpler from an experimental point of view, but the renewal frequency must be sufficient to prevent a buildup of contaminants at the residue/leachant interface, which may inhibit further leaching by reducing the diffusional gradient.

Figure 14.5 Serial Batch Tests



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Flow-Through Tests

In a flow-through or column test, an open container is packed with a porous solid and leachant is passed through, either continuously or intermittently. The effluent is sampled periodically and analysed for the parameters of interest. The results are used to examine contaminant removal in which the primary transport mechanism is advection. There are two basic types of flow-through tests characterised primarily by the shape and size of the container. The first type is a column test which is performed using a small cylindrical container (Figure 14.7a). The second is a lysimeter test which is conducted in a large rectangular or cylindrical container (Figure 14.7b).

In general, the size of the sample used in a flow-through test tends to be large to minimise the effects of sample heterogeneity and wall channelling effects. The depth of waste in either type of test varies according to the individual experiment.

Figure 14.6 Flow-Around Tests

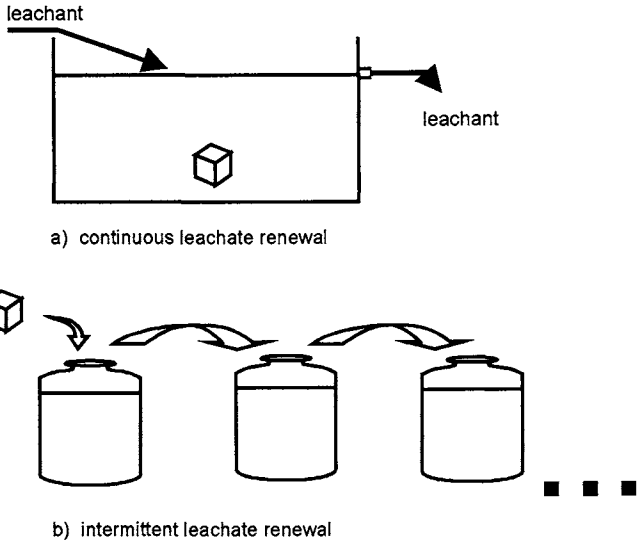

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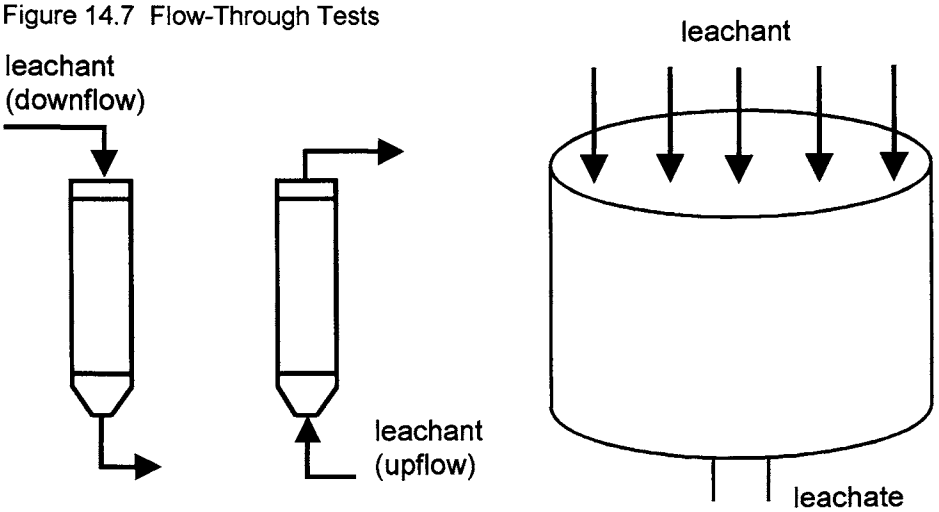
Figure 14.7 Flow-Through Tests



a) Columns

b) Lysimeter

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Columns may be operated either in an upflow or downflow mode, whereas lysimeters are always operated in a downflow mode. Flow through the solid depends upon its hydraulic conductivity, as well as the hydraulic gradient, and varies with the individual test.

Mini-columns may be used to achieve a relatively rapid breakthrough of leached species. Since head losses may be large and a rapid breakthrough is desired, the leachant is usually delivered under pressure and at a constant flow rate. The advantages of minicolumns include:

- L/S ratios that are similar to those of real waste-leachant systems
- a known and easily varied average fluid velocity
- negligible axial dispersion or spreading of the solute
- a simple estimation of both equilibrium and kinetic coefficients
- automation permitting the rapid output of data.

These tests are not applicable when large volumes of leachate are needed for a variety of analytical tests. Care should also be taken when conducting flow-through tests to avoid unnatural channelling of water and clogging by fine material or biological growth. In lysimeter tests, channelling cannot be avoided. It is a factor that occurs in the field, and its influence should be modelled in the laboratory, although quantifying it is difficult. Biodegradation of organics can also be a problem in columns, although in some cases experiments are intentionally set up to measure the effects of biological activity. Flow-through tests can also be modified to examine other site-specific influences, such as vegetation on the surface of the container, or layered media, such as ash and geological material.

14.1.2 Leaching Test Variables

There are several experimental variables which are common to all extraction and dynamic tests. These variables need to be considered when designing a leaching test for specific purposes.

Sample Preparation

Depending on the nature of the waste and the test to be performed, the sample may require one of the following preparatory steps:

- liquid/solid separation
- sub-sampling
- particle-size reduction
- surface washing
- compaction
- preservation
- curing
- aging

Liquid/solid separation may be performed on residues containing a free liquid phase. The leaching test is conducted only on the solid portion of the sample. The free liquid phase constitutes the initial leachate, which may be analysed separately to estimate the pore-water concentration or it can be included with the final leachate for analysis. Liquid/solid separation can be accomplished by various methods, including settling and decanting, centrifugation or pressure filtration through filter media of various types.

Sub-sampling is generally required when several different tests or replicates are to be performed on the same sample. Waste samples should be thoroughly mixed before sub-sampling is performed. (See Chapter 6).

Particle-size reduction is required for most extraction tests. The goal is to reduce the time required to reach steady-state conditions by increasing the contact surface area between the solid and the leachant. However, care should be taken to prevent the loss of volatile compounds in the solid if they are of interest. Particle-size reduction is usually carried out by grinding (e.g. mortar and pestle, centrifugal grinder or hammer mill). These issues are also discussed in more detail in Chapter 6 and 7.

Surface washing may be performed prior to testing small monolithic samples in flow-around tests. The surface is washed to remove small detachable particles and readily soluble salts by quickly dipping the sample in an aqueous solution.

Compaction or remolding is often required for flow-through tests. Reproducibility and field simulation considerations require that samples be compacted to a pre-specified density using methods such as vibration, proctor compaction or modified proctor compaction.

Sample preservation is performed to avoid biological activity. This is a greater problem in tests of long duration, such as column tests. Various chemical treatments are available, such as the addition of sodium azide, however, none offer complete efficacy.

Curing may be performed on samples that have been transformed into a solidified mass using various chemical additives, such as Portland cement. It allows the waste sample to gain physical and engineering properties, i.e. high unconfined compressive strength and low permeability, that are considered to be important in reducing leachability. Curing can be used to achieve a variety of chemical reactions within the waste, although this term usually refers to cement hydration reactions.

Aging may be promoted on any type of waste sample to account for the physical, chemical and biological alterations that a waste might undergo in the field. Chapter 13 discusses classes of aging reactions that can occur in residues.

Leachant Composition

The release of contaminants from a waste in any leaching test may be strongly influenced by the initial leachant composition, especially at high L/S ratios, or with the

use of an aggressive solution. Chemical properties of the leachant that influence contaminant mobilisation are indicated in Table 14.2. Examples of three types of commonly used leachants, i.e. water, site liquid and chemical solution, are identified in Table 14.3. Several advantages and disadvantages of these leachants are outlined in Table 14.4.

Table 14.2
Important Factors in Leachant Composition

Factor	Release Mechanism Affected
pH	Dissolution/precipitation of metals, speciation of inorganic species Adsorption/desorption of solutes
Eh, redox potential	Oxidation/reduction of inorganic species
Ionic strength	Ionic exchange of metals, speciation chemistry and solubility products
Chelating and complexing agents	Metal solubility
Buffering capacity	All above properties

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Table 14.3
Commonly Used Leachants

Type of Leachant	Common Uses	Examples
Water	Nonaggressive, baseline medium without buffering capacity	Distilled, deionised and tap water
Site liquid (real or synthetic)	Simulates site-specific leaching conditions	Rainwater, groundwater, surface water, landfill leachant, seawater
Chemical solution	Examines metal speciation and organic compound binding	Strong chemical solution (acidic, basic, reducing, oxidising, complexing, solvent,etc.)

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Table 14.4
Advantages and Disadvantages of Commonly Used Leachants

Leachant	Advantages	Disadvantages
Pure water	Reliable, simple standard	Lack of background composition may result in dissolution of common ions
Site liquid	Best field case model	Requires characterisation (to obtain leaching results by subtraction)
	Several synthetic liquids available	Results not comparable with other leaching studies
		Labour intensive (sampling and preservation)
Chemical solution	Allows for the study of waste chemistry	Aggressive, difficult to relate data to field conditions

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Method of Contact

Since a leaching test is primarily a system to study the transfer of contaminants from a residue to a liquid, it is important to consider the aspects of the test conditions that promote mass transfer, such as agitation, and to consider the effect of mass exchange with other components of the system, primarily the leaching vessel and the atmosphere.

Agitation of the leachant-solid slurry generally hastens reaching equilibrium conditions by maintaining maximum contaminant concentration gradients at the leachant-solid particle interface. Different methods can be used to agitate the waste, including

- shaking (wrist action or reciprocation)
- stirring (magnetic or paddle)
- tumbling
- gas bubbling.

In static or non-agitated tests, the leachant-solid interface is usually the geometrical surface area of the solid form. There is usually no provision for mixing because diffusion of leached constituents within the leachate is assumed to be much faster than the rate of release by mechanisms such as dissolution from the surface or diffusion from within ash particles. Ensuring that the leachate is well mixed before sampling is important, however.

It may be important to identify and quantify exchanges of chemical species other than between the solid and the leachant. Exchanges between the leachant and the leaching vessel are always undesirable, whereas exchanges with the atmosphere depend in large part upon the objectives of the test, such as leaching with carbonic acid.

To minimise exchanges with the leaching vessel, glass or stainless steel should be used for organic contaminants and plastic for inorganic contaminants. If the cost is not prohibitive, polytetrafluoroethylene is considered to be acceptable for both. For the purpose of verifying the mass of constituents adsorbed to the container wall, the emptied leaching vessel can be extracted with a strong solvent.

The test system may be either open or closed to the atmosphere. The choice depends on the specific leaching problem being examined. For example, a closed system provides a better simulation of the saturated groundwater environment, whereas an open system models problems like a storage pile and unsaturated disposal environments more accurately.

An open system facilitates sampling, leachant renewal and periodic or continuous adjustment of the pH or redox potential. However, a system that is open to the atmosphere allows for the loss of volatile compounds, including water and organics, and the introduction of CO_2 and O_2 from the air. Losses due to evaporation may have to be accounted for in an open system.

Although volatile organics are generally not a concern with incinerator ash, there are several apparatus configurations that will prevent volatile contaminants from escaping. If there is no headspace in the leaching vessel, volatiles will remain in either the solid phase or the leachate. If there is a headspace, volatiles will be partitioned in the gas phase. Analysis of the headspace allows for an evaluation of this loss.

Even for experiments carried out in closed containers and under controlled conditions, penetration of gases through plastic container walls can have a significant effect, especially over long durations. This is seen in reaction vessels kept at a low redox potential when oxygen diffuses into the vessel.

Liquid-to-Solid Ratio

The L/S ratio is the ratio of the amount of leachant in contact with the residue to the amount of waste being leached. Although this definition appears straightforward at first glance, it can become confusing because of the many ways in which the two variables in the ratio have been defined.

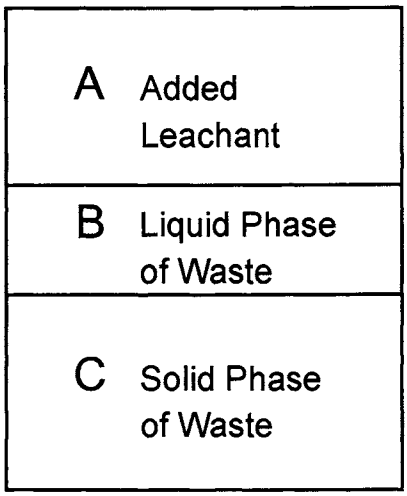
The L/S ratio has been expressed as:

- volume of leachant/mass of solid
- mass of leachant/mass of solid and
- volume of leachant/surface area of solid (for monolithic material).

Furthermore, when using the first two expressions, the mass of solid being leached can be calculated on a wet weight or a dry weight basis. Another problem arises because of the various ways that the volume or mass of leachant can be calculated, depending on whether or not the liquid phase of the solid is included in the total leachant volume. The preferred way to report L/S is the mass of leachant to the dry mass of solid.

Figure 14.8 illustrates how these various ways of defining the amounts of waste and leachant can give different L/S ratios for the same system. The three fractions shown in Figure 14.8 include the amount of leachant added, the liquid phase associated with the solid, and the solid phase.

Figure 14.8 Liquid and Solid Fractions of the Waste Leachant System



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If the residue is dry, then the L/S ratio is simply A/C. If the residue is wet, there are three ways to define the L/S ratio:

1) the residue is the sum of the liquid and solid phases, i.e. L/S = A/(B+C).

2) the leachant is the sum of the amount of leachant added plus the liquid phase associated with the solid, i.e. L/S = (A+B)/C

3) the liquid phase associated with the solid is excluded from the calculations, and residue is the solid phase only, i.e. L/S = A/C.

Leachate concentrations of highly soluble species (e.g. sodium, potassium) are generally inversely proportional to the L/S ratio of all of the species which have been removed from the solid. However, if the release of a species is limited by solubility, the final concentration is independent of the L/S ratio and simply equals the maximum solubility concentration.

In general, the leachate concentration will be controlled by a number of competing factors, namely, the amount of contaminant available, solubility and kinetically controlled chemical reactions. Thus, the relationship between the L/S ratio and concentration is complex, and different for each species of interest.

Selection of an appropriate L/S ratio depends on the objectives of the leaching test, the solubility of species of interest and analytical constraints. The ratio should be low enough to avoid dilution of contaminants to less than analytical detection limits. However, the ratio also must be high enough to prevent solubility constraints from limiting the amount of contaminants that can be leached from the waste. The selected ratio should be somewhere between these two limitations. Practical values for the L/S ratio range from 0.1 to 100:1. To place these values into perspective, most landfilled residues are exposed to L/S values of less than 3:1 during the operational life (10 to 20 years) of a disposal facility. After closure, the type and integrity of the cap will influence further increases in the L/S.

Contact Time

The total amount of time that a leachant is in contact with a solid sample before the attainment of equilibrium will influence the amount of contaminant released. In extraction tests, the contact time is equivalent to the duration of the test, whereas in dynamic tests, it is a function of the flow rate, or the number of elutions, in addition to the test duration.

The contact time for extraction tests should allow equilibrium conditions to be reached for the contaminants of interest. This is generally in the order of hours to days for samples that have undergone particle-size reduction. For concrete-based or monolithic samples, it can be in the order of weeks to months.

The contact time for dynamic tests should be sufficient to allow for observation of the processes of interest. Diffusion processes may be quantified within a few weeks, although several months may be required to study slow chemical reactions.

Temperature

Temperature affects the results of extraction and dynamic tests. Both the van't Hoff relationship, which applies to thermodynamic equilibrium constants and solubility products, and the Arrhenius relationship, which applies to kinetic processes such as adsorption and diffusion, indicate that properties or mechanisms relevant to leaching vary exponentially with temperature.

For convenience, most leaching tests are performed at room temperature. Higher temperatures may be used to accelerate the rate of leaching (although this may also change the properties of the waste) or to simulate the effects of biological activity in a landfill or the self-heating from exothermic reactions.

Leachate Separation

Leachates are commonly separated from agitated non-monolithic wastes by filtration using a 0.45 μm membrane filter (a convention used to define soluble species). However, very small colloid particles can pass through a 0.45 μm filter. A smaller pore size filter (0.2 μm) should be used if these particles are to be removed. The use of the smaller filter size should be reported with the data.

Glass fibre filters are chosen when hydrophobic, low solubility organic molecules are expected in the leachate since they may have a high affinity for filters composed of an organic polymer. Membrane filters, such as cellulose acetate, should be used for metal species in place of glass. The same care used to select a leaching vessel should be applied when selecting the filter material.

Filtering the leachate from non-agitated monolithic samples may not be necessary if the method of contact generates only dissolved species. This should be verified before sampling.

14.1.3 Compilation of Leaching Tests

The leaching tests presented in Environment Canada (1990), Fällman (1990), and van der Sloot et al. (1991, 1993) serve as the basis for the compilation of various leaching tests presented here. The reader can refer to these references for precise details of each method.

Table 14.5 summarises the various agitated batch extraction tests that are used for regulatory purposes or for research into leaching characteristics of waste. All the methods specify the type of leaching vessel to be used, the type of sample preparation that is required, the amount of sample that is needed, the type of leachant to be employed, the L/S ratio that is used, the type of agitation that is required and the duration of the test. Most methods also specify the type of filtration that is to be employed to allow for quantification of total dissolved constituents in the leachate.

Table 14.6 specifies two non-agitated extraction tests that are commonly used to examine sequential dissolution of mineral phases in a solid or the fundamental dissolution and effective diffusion parameters of a solid dissolving under static conditions.

Table 14.5
Agitation Leach Tests

Test Name and Proponent	Status of Development	Leaching Vessel	Sample Preparation	Sample Mass	Leachant	L/S Ratio	Agitation	Duration	Leachate Separation
-EP Tox U.S. EPA Method 1310	Standard regulatory method (1980)	Unspecified	Non-monolithic waste; phase separation Monolithic waste; particle-size reduction	100 g	Deionised water 0.5 N acetic acid (max. 2.0 meq H+/g solid)	20:1	Unspecified, continuous	24 to 28 hours	0.45 µm filtration
-LEP MOE (Ontario)	Standard regulatory method (1985)	Wide mouth, 1250 mL cylindrical bottle	Phase separation by 0.45 µm membrane filter	50 g of dry solids	Distilled water Acetic acid (2.0 meq H+/g dry solids)	20:1	End over end (10 rpm)	24 hours	0.45 µm filtration
-TCLP U.S. EPA Method 1311	Standard regulatory method (1986)	Any material compatible with waste, zero head-space extractor (ZHE) for volatiles	Cutting/crushing and grinding Solid/liquid phase separation No structural integrity	100 g (25 g for ZHE)	Buffered acetic acid 1) pH = 4.93 2) pH = 2.88	20:1	End over end (30 rpm)	18 hours	0.6 to 0.8 µm borosilicate glass fibre filter combines liquid phase with extract
-Q.R.S.Q. MOE (Quebec)	Standard regulatory method (1987)	>1 L bottle	No phase separation Grinding No structural integrity	100 g dry solids 50 g for volatiles	Inorganics: buffered acetic acid (0.82 meq H+/g dry solids) Organics: distilled water	10:1	End over end (10 to 20 rpm)	24 hours	30 min decantation, 0.45 µm filtration
-WET California	Standard regulatory method (1985)	Polyethylene or glass container	Milling, 0.45 µm filtration	50 g	0.2 M sodium citrate at pH 5.0	10:1	Table shaker Rotary Extractor	48 hours	Centrifugation 0.45 µm filtration
-X31-210 French Leach Test AFNOR (France)	Proposed standard for waste (Dec 1992)	Straight wall, 2 L bottle	Remove free liquid Reduce particle size to <4 mm	100 g	Demineralised water	10:1	Roller or shaker	16 hours	0.45 µm filtration

Test Name and Proponent	Status of Development	Leaching Vessel	Sample Preparation	Sample Mass	Leachant	L/S Ratio	Agitation	Duration	Leachate Separation
-EE Environment Canada	Published research method	Inorganic: wide mouth, plastic sample bottle (250 mL); Organic: glass (500 mL)	Grinding (inorganic) Mortar and pestle (organic)	Inorganics : 40g Organics: 80 g	Distilled water	4:1	NIST rotary extractor	7 days	0.45 µm vacuum screen
-ASTM D3987 ASTM	Standard research method	Round, wide mouth bottle	As received	700 g	Distilled water (ASTM Type IV)	4:1	Shaking	48 hours	0.45 µm filtration
-MBLP Environment Canada	Published research method	Square, polyethylene or glass bottle, 1 to 2 L	Remove free liquid Reduce particle size to <9.5 mm	Variable to fill 90% of bottle	1) Distilled water 2) acidic water buffer to pH 4.5 3) synthetic leaching media	4:1 or 2:1	Slow rotary tumbling	24 hours	0.45 µm filtration
-MCC-35 Materials Characterisation Center, England	Standard regulatory method (radioactive wastes)	Teflon container, 20 mL to 1 L	Crush waste form into two fractions: 74 to 149 µm 180 to 425 µm	>1 g	Choice of high purity water, silicate water, brine, repository water	10:1	Rolling and rocking	Variable: 28 days to several years	N/A
-DEVS4 Germany	Standard regulatory method	2L container	Ground specimen, <4 mm	100 g	deionised water	10:1	Table shaker	24 h	0.45 µm filtration
-TVA Switzerland	Standard regulatory method	Bottle	Not specified	100-200 g	CO_2 saturated water	10:1	Bubbling, 100 mL CO_2/ minute	24 h	0.45 µm filtration
-Total Availability NVN 7341 The Netherlands	Standard regulatory method	1 L beaker	Ground specimen, <300 µm	8g	deionised water at pH 7 then pH 4 with nitric acid	100:1 Total	Magnetic stirrer	4h	0.22 µm filtration

Table 14.6
Non-Agitated Extraction Tests

Test Name and Proponent	Status of Development	Leaching Vessel	Sample Preparation	Leachant	L/S Ratio	Duration	Leachate Separation
-Sequential Chemical Extraction	Research	100 ml Teflon	<300 µm	Varies	Varies	Varies	0.22 µm
-Granular Diffusion Test The Netherlands	Under Development	2 L Plastic	Granular material	pH 4.0 Nitric	Varies, Sequential	64 days	0.22 µm

Table 14.7 identifies a number of serial batch tests that are used to provide for the successive renewal of leachant for a given mass of a solid material. Such tests can approximate flow-through leaching tests. Information is provided on the sample preparation, the type of leachant, the leaching vessel, the type of agitation, the sample mass and L/S ratio that is used, the contact time, the number of elutions that are generated, and the method of filtration. A number of researchers also employ a reverse cascade leaching test where the L/S ratio goes from 10 to 1 (Fällman, 1990). This is accomplished by renewing the solid to be leached rather than the leachant.

Table 14.8 identifies a number of flow-around tests. These methods are used more for surfaces of monolithic-like materials. Information is provided on sample surface preparation, sample size, leachant, leaching vessel, volume to surface area and leachant renewal specifications.

Table 14.9 provides details on a few flow-through or column leaching tests that are frequently employed by researchers. The type of column, the sample preparation, the sample mass, the cumulative L/S ratio, the means of providing the percolation, the times for sample collection and the filtration method are specified in the table.

Table 14.10 discusses specifications that are used to establish outdoor field lysimeters by a number of institutions involved in ash research. Lysimeter construction, sample mass, and typical L/S ratios are specified in the table.

14.2 A UNIFIED APPROACH TO LEACHING TESTS

As indicated in previous chapters, examining leaching phenomena on a normalised basis is important. The normalisation process uses a ratio of instantaneous or cumulative mass of an element released to the dry weight of residue being leached. This is reported as a function of the L/S ratio which incorporates the dry weight of residue. The use of mass fractions leached and L/S ratios ultimately allow for examining mass fluxes from residues. Fluxes are more descriptive of leaching as a function of time than discrete measures of concentration.

Because leaching behaviour can change dramatically over time and under different leaching conditions, it is recommended that more than one test (ie. more than one type of extract analysis) be used to provide the information necessary to characterise the potential leaching behaviour. A general evaluation framework, or a unified approach to leaching, includes use of the total elemental composition, an availability leaching test and pH-dependent leaching to provide reference levels for comparison. It is suggested that a series of basic characterisation leaching tests be selected, including determination of:

- the total availability for leaching;
- the elemental solubility as a function of pH; and
- the effect of increased L/S ratio or time on cumulative release.

Table 14.7
Serial Batch Tests

Test Name and Proponent	Status of Development	Sample Preparation	Leachant	Leaching Vessel	Agitation	Sample Mass	L/S Ratio	Contact Time	Number of Elutions	Leachate Separation
-MEP U.S. EPA Method 1320	Standard test method (1986)	Same as EP Tox	Acetic acid Synthetic acid Distilled water	Same as EP Tox	Same as EP Tox	Same as EP Tox	Same as EP Tox	Same as EP Tox	10	Same as EP Tox
-MWEP U.S. EPA	Technical resource document (1986)	Particle-size reduction to <9.5 mm or structural integrity	Distilled water Site water	Wide mouth sample bottle	Rotary tumbler	Unspecified	10:1	18 hours	4	Settling and filtration
-Graded Serial Batch U.S. Army	Research method for waste and soil (1987)	-	Distilled water	Unspecified	Periodic gentle shaking (4/5 times daily)	300 g	2/3/6/12/24/48/ 96:1	Until steady-state conditions attained	>7	Vacuum filtration
-SBE D4793-88 ASTM	Standard method (proposed) (1988)	Drying, Phase separation	Reagent water (Type II D1193)	2 L, wide mouth bottle	None	100 g	20:1	24 hours	10	0.45 µm membrane filter
-WRU Leach Test Harwell Laboratory United Kingdom	Standard method (1982)	Crushing Vacuum filtration	Distilled water Dilute acetic acid buffered (pH = 5)	50 mL, wide necked flask	Mechanical flask shaker	100 g	One bed volume (first five elutions) 10 bed volumes (more than six elutions)	2 to 80 hours Steady state	5	Vacuum filtration
-SLT Cascade Test SOSUV Netherlands	Standard research method for incinerator residues (1984)	Crushing/ sieving Dry	Distilled water Nitric acid (pH = 4.0)	1 L polyethylene bottle	Shake/roll	40 g	20:1	23 hours	5	Settling and 0.45 µm filtration

Table 14.8
Flow Around Tests

Test Name and Proponent	Status of Development	Sample Preparation	Sample Size	Leachant	Leaching Vessel	Volume: Surface Area	Leachant Renewal Rate
-MCC-4S MCC	Standard (1983)	Individual fabrication or surface washing or cut sample	400 mm^2	Pure water, bicarbonate-silicate water, repository water	1 L teflon cylinder	10 cm	Flow rate = 0.1, 0.001, and 0.001 mL/min
-IAEA Dynamic Leach Test IAEA	Past standard (1971)	One circular face is prepared for leaching	Cylinder, 5 cm x 5 cm	Demineralised water Site water	Compatible with sample and leachant	<10 cm	Daily (1st week), weekly (8 weeks),monthly (6 months), biannually
-ISO Leach Test ISO	Past standard (1986)	Surface polishing	Surface area = 0.5 to 0.001 m^2	Deionised water Synthetic seawater Site water	Cylinder: unreactive, radiation resistant	10 to 20 cm	1, 3, 7, 10, 14, 28, 35, 42, 72, 102 days
-ANSI/ANS 16.1 ANS (American Nuclear Society	Standard (1986)	Surface washing	Cylinder, length/diameter = 0.2 to 5.0	Distilled water	Cylinder: unreactive material, sized to immerse sample	10 cm	2, 7 hours; 1, 2, 3, 4, 5, 14, 28, 43, 90 days
-NEN 7345 (NVN 5432) Monolith Leaching Test	Draft Standard (1993)	Curing and surface washing	Cylinder, 4.5 cm diameter x 7.5 cm long	Distilled water	Large, wide mouth jar	Allows contaminant detection, diffusion modelling	0.5, 1, 2, 4, 8, 12, 16, 32, and 64 days

Table 14.9
Flow Through or Column Tests

Test Name, Proponent	Status of Development	Leaching Vessel	Sample Preparation	Sample Mass	L/S Ratio	Percolation	Leachate Collection	Leachate Separation
-Column Extraction Method, ASTM	Proposed method	10 cm x 30 cm column	field samples	500 g	Simulate field, 0-3 (cumulative)	Pumped up flow	At 1, 2, 3, 8 pore volumes	0.22 µm filtration
-Column Method SOSUV, The Netherlands	Standard regulatory method	5 cm x 20 cm column	<3 mm	500-800 g	0-10 (cumulative)	Pumped up flow	Periodically over 10 d	0.45 µm filtration
-Mini-Column, (Clarkson University)	Research method	1.5 cm ID, Piston controlled length	<300 µm	2g	0-1,000 (cumulative)	Pumped up flow, 0.1 to 2 ml/min	Periodically over hours to days (up to 1000 pore volumes)	0.45 µm filtration

Table 14.10
Field Lysimeter Tests

Test Name, Proponent	Status of Development	Structure	Sample Mass	L/S Ratio	Leachate Collection	Leachate Separation
-Field Lysimeter, University of New Hampshire, USA	Research; Bottom Ash, Combined Ash	2m x 3mX 4m Roll off lined with HDPE Liner, geonet, geofabric and drainage sand	5,000-10,000 kg	0-5	Periodically pumped out after precipitation	0.22 µm
-Field Lysimeter, AVR, The Netherlands	Research; Bottom Ash	2.5m x 2.5m x 12m containers	100,000 kg	0-1	Periodic collection; pore water analysis; run-off analysis	0.45 µm
-Field Lysimeter, VKI, Denmark	Research; Many Ash Types	3m x 3m x 1.5m or 3m x 3m x 2.5m prefab concrete with LDPE liners and drainage system	6,000 - 18,000 kg	0-4	Drain to automatic collection system	0.45 µm
-Field Lysimeter, SGI, Sweden	Research; Consulting; Many Ash Types	3m x 3m x 1.2m or 4m x 4m x 1m; lined with HDPE with geotextile drainage system	15,000 - 20,000 kg	0-2	Periodically drained to tipping bucket under argon gas	0.45 µm
-Field Lysimeter, KfK, Germany	Research; Bottom Ash, ESP Ash	cylindrical ø=63cm, h=1m cylindrical ø=80cm, h=1m acrylic columns	300-400 kg 140 kg	0-1 0-15	Periodically removed (~2 weeks)	0.45 µm

Consider the normalised plot of the pH dependent leaching of copper from an APC residue (dry scrubber) as shown in Figure 14.9a. On the y-axis is the mass fraction released in mg/kg. This can also be reported as concentration in mg/L. On the x-axis is pH of the leachate at equilibrium. For reference purposes, two horizontal lines are shown depicting the total and available copper concentration in the residue. A region is shown where the pH dependent data fall. The graph indicates the amphoteric leaching behaviour of the metal. Also note that at very low or high pH, the pH dependent test releases the same amount of copper as the availability test. The various single point data depicted in the plot are derived from regulatory agitated batch extraction tests, as shown in the key. These data are plotted as release versus final extraction pH. What is apparent is the uniformity of the leaching behaviour in spite of the various tests that were used. The regulatory test data fall within the range of the pH dependent data. Normalisation helps to reduce variability associated with concentration measurements and variable L/S ratios.

Figure 14.9b brings together the principles shown in Figure 14.9a as well as from other tests in a unified plot. The y-axis shows either instantaneous or cumulative release of copper from an APC residue (dry scrubber, in mg/kg) as a function of either the instantaneous or cumulative L/S ratio.

Depicted in the plot are the two horizontal lines for total and available copper in the residue. Both asymptotes are useful references for evaluating the results of various leaching tests. Also shown on the plot are cumulative release plots for serial batch extraction, upflow column leaching tests and the results from various regulatory agitated batch extraction tests. One important question to ask is how quickly or slowly these cumulative release plots approach the total available asymptote. By using an L/S of 100, the serial batch and upflow column tests have clearly removed most of the available Cu fraction, although this behaviour may be different for elements.

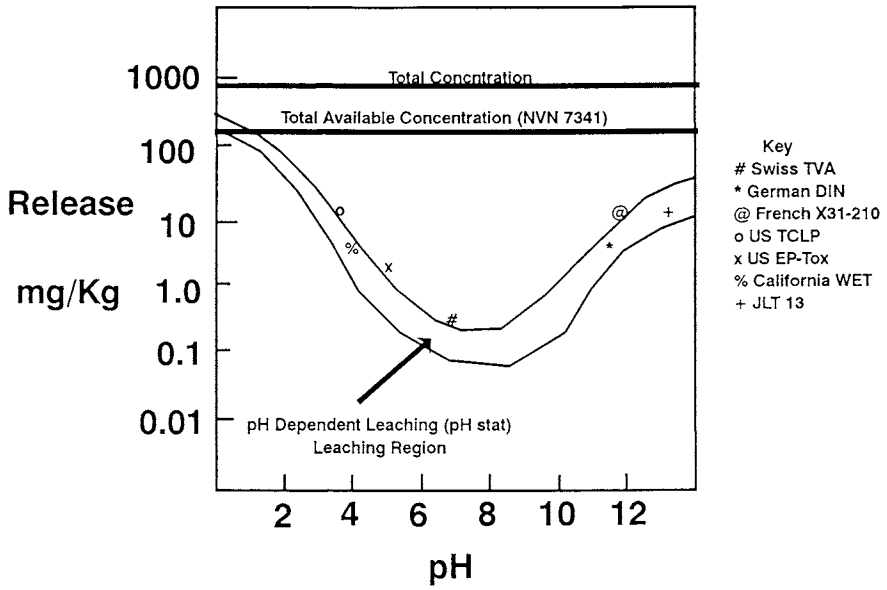
Also shown on the plot are the ranges of data seen in the pH dependent leaching (Figure 14.9a) at an L/S of 20. The values close to the asymptote are the regions where copper is very soluble (pH 4 and 12). The values situated well below the asymptote are for pH values where copper is insoluble (pH 7-10).

A particularly useful approach is to relate the data shown in Figure 14.9b to actual field leaching data. Questions to pose include how the cumulative release plots approximate the field scenario? Alternatively, has the field plot also approached the total available asymptote?

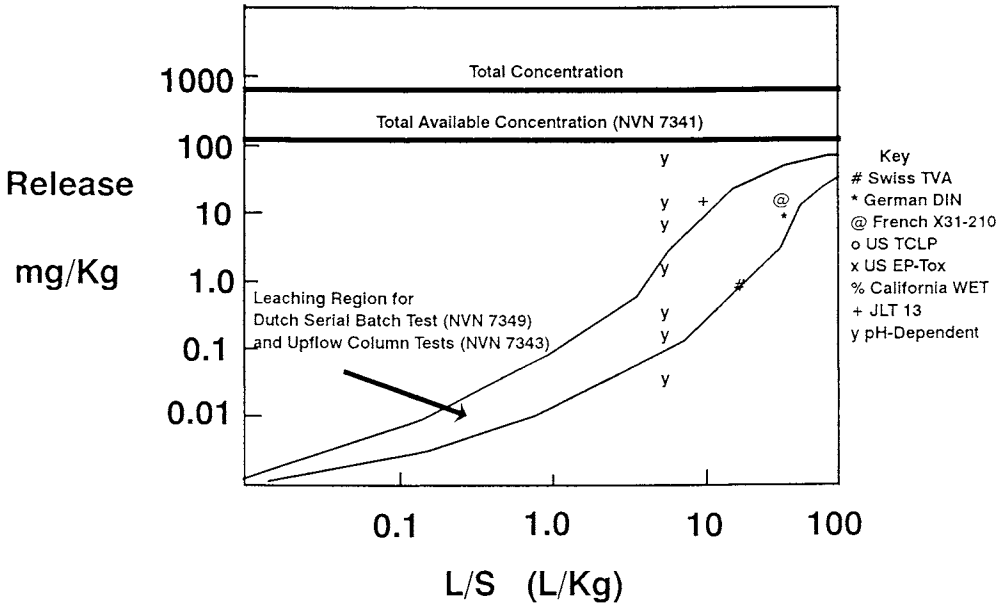
Data from many of the leach tests described in Section 14.1.3 can be incorporated into the unified plot of Figure 14.9b. The data can also be used with modelling efforts discussed in Chapter 15.

Figure 14.9 A Unified Approach to Leaching

a) pH Dependent Leaching



b) cumulative leaching



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