CHAPTER 12 - PHYSICAL ASPECTS OF LEACHING

Much of the concern over the management strategies for MSW incinerator ash is based on the perceived potential contamination of water resources through leaching of salts and trace metals from the ash. This focus has been driven by results from regulatory leaching tests designed to simulate a specific worst-case disposal scenario. These tests do not translate to most management practices for the residues. The leaching of MSW incineration residues is a highly complex subject which requires a great deal of background knowledge to interpret leaching data adequately. A more comprehensive approach to understanding leaching phenomena is needed.

12.1 AN INTRODUCTION TO LEACHING

When in contact with a liquid, many solid materials will dissolve to some extent. It is the degree of this dissolution in the contacting liquid that governs the relative strength of the leachate that is produced. Leaching can occur in the field in residues in piles, landfills or granular fill applications, or in the laboratory during column or batch leaching tests. There are a number of factors that can influence the rate at which the solid materials dissolve and these are discussed under two headings: physical aspects and chemical aspects.

For physical aspects influencing leaching, some questions can be posed that help to define the leaching system:

- What is the leaching system being described? Is it landfilled material where an infiltrating leachant flows through the ash (the flow-through system), a batch leaching test where the ash and leaching fluid are agitated together and where the leachant always remains in contact with the ash (the agitated batch system) or is it a batch leaching test without agitation (the non-agitated batch system)?
- What is the leaching time frame (e.g. minutes to millennia)?
- What is the size of particle undergoing leaching?
- Does the particle have a high surface area relative to the volume of the particle, such as in fine-grained particles where the surface area available for dissolution is high?
- Is the particle composed of many different types of minerals or is it homogeneous?
- How does the liquid flow past the particle?

- How fast does the particle dissolve?
- For a flow-through system, is the rate of dissolution faster or slower than the rate of fluid flow past the particle?
- For the agitated batch system, is the rate of dissolution faster or slower than the rates of turbulent mass transfer from the particle to the bulk solution?
- For the non-agitated batch system, is the rate of dissolution faster or slower than the rate of molecular diffusion of the dissolved constituents away from the ash particle?

For chemical aspects influencing leaching, some questions can also be posed that help to define the leaching system further:

- In the flow through system, does the percolating liquid obtain a chemical equilibrium with the dissolving solid phase after some finite percolation distance or fluid velocity?
- In the agitated batch system does the liquid obtain a chemical equilibrium with the dissolving solid phase after some finite length of time and after some mixing energy is used to promote mass transfer between the solid and the liquid?
- In the non-agitated batch system, does the liquid obtain a chemical equilibrium with the dissolving solid phase after some longer finite length of time and after diffusion has resulted in mass transfer from the solid to the liquid?
- For all three scenarios, do some dissolution reactions never reach equilibrium?
- After initial dissolution, do some components reprecipitate?
- How does leachant pH affect dissolution?
- How do leachant complexing agents affect dissolution?
- How does oxidation-reduction potential affect dissolution?
- How do sorption processes redistribute back on the solid phase the originally dissolved solid phase components?

12.1.1 Physical Aspects of Leaching

The physical aspects influencing leaching relate to the manner of contact between the liquid and the solid material. To introduce the concepts related to physical aspects of leaching adequately, the liquid and solid system, referred to here as the leaching system, must be described first.

The Leaching System

There are a number of scenarios that describe potential leaching systems. At one end of the spectrum, an example could be an uncapped landfilled residue which generates a leachate from rainwater percolating through the residue over a one hundred-year period under a field leaching scenario. At the other end of the spectrum could be three examples of leaching occurring in a laboratory setting:

- an artificial acid rain flowing through a residue in a column leaching experiment,
- an artificial acid rain and a residue agitated together in a flask in an agitated batch leaching experiment, and
- an artificial acid rain and a residue added to a batch flask under quiescent conditions in a non-agitated batch leaching experiment.

While the ultimate goal may be predicting and modelling long term field leaching behaviour for disposed, treated or utilised residues, such data are not easily obtained under practical time frames. The use of batch and column leaching tests can simulate such long term scenarios. This is accomplished by increasing the throughput of liquid through columns or increasing the volume of liquid used in batch tests. Both procedures approximate exposure to naturally occurring precipitation over a longer time frame. Batch tests are more readily controlled and subjected to altering influences (temperature, gas partial pressures, complexing ligands, oxidation/reduction potential changes, etc.); column tests frequently better describe field condition fluid flow, mass transfer and dissolution mechanisms.

Many leaching scenarios involve observational time frames of hundreds of years. Many of the leaching tests are operated on the order of hours, days or weeks. For leaching tests to simulate field conditions, the rate of dissolution must be speeded up. This is accomplished by (i) adding mixing energy to promote mass transfer from the solid to the liquid and (ii) using small masses of residues and large volumes of liquid so the solids dissolve into a large "sink" for dissolved constituents.

Consider both the landfilled residue and the column leaching test in a simplified manner. A percolating liquid or leachant flows down through the residue. At the top of the residue, fresh leachant is not in chemical equilibrium with the dissolving solids.

However, as the liquid moves down through the ash material, more and more dissolution occur, increasing the strength of the leachate. At some point, further dissolution cannot occur because the leachate is saturated with respect to dissolved constituents. Residues subjected to a saturated, equilibrated solution will not leach.

The scenarios can be made more complex by allowing the leaching front (the transition zone from the more dissolved region at the top of the column or pile to the undissolved region just below it) to move down through the material. Complexity is also introduced by acknowledging that some ash components that initially dissolve at the top of the pile or column can reprecipitate out from a saturated solution as another mineral further down in the pile or column.

Consider the two batch leaching scenarios in a simplified manner. One is agitated, and the other is static. When the materials are first added together, the liquid or leachant is not in chemical equilibrium with the dissolving solids. Unlike the flow-through system, the leachant and solids remain in contact with each other. There is no renewal, so the dissolving solid can continue to dissolve into the volume of liquid until equilibrium is obtained. The only difference between the agitated and static systems is the energy added to the system that promotes mass transfer from the solid to the liquid. In fact, the agitated system dramatically speeds up transfer; rates are one to two orders of magnitude higher than the flow-through system and many orders of magnitude higher than the static batch system.

The scenarios can be made more complex by conducting batch tests sequentially. This is accomplished by removing the solid from one flask and adding it to a new flask with a fresh leachant that is not at equilibrium with the solid. Extrapolating further, it is easy to see how a sequential batch system can approximate a flow-through system.

Particle Characteristics

The particle surface area to volume ratio, the average particle size and internal pore structures in the residues all control the surface area where dissolution from the solid to the liquid can occur. Larger surface areas per mass or volume of ash can allow for more rapid dissolution at the surface. Frequently, ash particles exhibit widely different surface area to volume ratios, grain size distributions and internal pore diameters.

Invariably, the ash particles are composed of a number of major and minor minerals. Some are more soluble than others. Leachate pH and oxidation/reduction potential are governed by the predominant phases. Frequently, the dissolution of the more soluble major minerals governs the strength of the leachate.

Fluid Flow Past Particles

In the field and column leaching scenarios, liquid flow past the ash particles is typically facilitated by gravity. The porosity of the ash material and the amount of water above the ash material attempting to flow through governs the velocity of flow of the leachant through the ash particles. Residues with low values of interparticle porosity and high degrees of impermeability will not transmit water. Moreover, the velocity of flow will be quite low. Taken to an extreme, a solidified, impermeable mass of particles will not conduct water; instead, water would be forced to flow around such a monolith.

In an agitated batch leaching scenario, the relative rate of flow of a liquid past a particle is a function of the energy put into the system and the rate of fluid shear between adjacent parcels of water. Agitated systems where the particles remain in suspension and do not settle usually result in very high degrees of mixing and mass transfer.

Fluid flow conditions for liquids that have not yet reached equilibrium with the dissolving solid play an important role in controlling the rate of dissolution by increasing rates of mass transfer from the particle to the bulk solution. For flow-through systems, the rate at which fresh leachant moves through the system can influence whether equilibrium is achieved. For conditions of slow fluid flow and highly soluble solid phases, the rate of dissolution can be faster than the rate that the dissolved constituents are advected or carried away and equilibrium between the liquid and solid can be achieved. Conversely, for conditions of fast fluid flow and relatively insoluble solid phases, the rate of advection is greater than dissolution and equilibrium will not be achieved.

In completely static systems, where diffusion of constituents of dissolving solids are carried into the bulk solution by aqueous diffusive fluxes, the rate of diffusion can be the limiting process for controlling the rate dissolution, thus increasing the time required to achieve equilibrium.

The Local Equilibrium Assumption

For all of the identified leaching scenarios, the relative rates of dissolution and fluid flow or advection must be understood before determining whether there is equilibrium at the local level - between a dissolving particle and fluid in which the particle is situated. Fortunately, most leaching scenarios and tests are in equilibrium for the majority of the principal phases that can dissolve. This has great importance in how we mechanistically describe the chemical aspects of leaching.

12.1.2 Chemical Aspects of Leaching

The chemical aspects influencing leaching relate to the fundamental processes controlling the solubility of solids, including:

- the influence of pH on controlling solubility,
- the influence of solute-phase complexing agents that chemically bind to constituents from dissolved solids and hide them from forces promoting precipitation, thereby increasing dissolution, and

- the role of oxidation-reduction potential in promoting solubilisation. Chemical aspects can also include reprecipitation processes or sorption processes whereby dissolved constituents return to the solid phase.

Equilibrium Versus Kinetic Systems

Many of the dissolution reactions that occur with ash are relatively quick. This permits for the use of equilibrium-based reactions and equilibrium reaction constants to describe the leaching system. Some reactions are relatively slow to extremely slow; equilibrium is never achieved and the reaction describing such a process is based only on kinetics. Kinetic systems are usually described as the rate of appearance of a solute in solution from a slowly dissolving solid as a function of various system parameters (temperature, pH, reaction stoichiometry).

When a system is at equilibrium, it is possible to quantify the mass of an ash constituent that is in solution at equilibrium with the solid phase. As the system approaches equilibrium, the transfer of mass from the solid phase to the solution phase slows. The final equilibrated mass distribution between the two phases describes the equilibrium condition.

Influence of pH on Dissolution

Many solids exhibit a marked increase in solubility at both low and high pH values. Such solids are considered to be amphoteric. Other solids may exhibit maximum solubility at neutral pH values. The pH of the leaching system before leaching occurs is described as the initial pH of the leachant. The leaching system pH at equilibrium is usually governed by the dissolution of the major soluble phases in the ash particles. Frequently, the initial and equilibrium pH values differ widely, particularly if the liquid to solid ratio (L/S) or the mass of dry ash being leached to the mass of leachant, is low and the solid phase dominates the system. When L/S ratios are high, the reverse can hold true; the pH of the initial solution is close to the equilibrium pH because the solution phase dominates.

As discussed below, other chemical aspects that influence leaching (complexation, redox, sorption) are influenced by system pH.

Influence of Complexation on Dissolution

Frequently, constituents in the solution phase of a system can bind to solid phase constituents and form a complex that remains in solution in a dissolved state. Such phenomena, governed by equilibrium reaction constants and susceptible to system pH, can increase the mass distribution of the solute in the solution phase and therefore promote solubilisation.

In the sequestered or complexed state, the bound solute is not available to participate in dissolution equilibria. The solid will then further dissolve to satisfy dissolution equilibria. The unbound free solute and complexed solute, when combined, increase the mass distribution in the solution phase.

Such phenomena can occur when ash is disposed with MSW. Organic complexing agents in solution can bind to dissolving metals and increase the relative solubilisation of the ash solid.

Influence of Oxidation-Reduction Potential on Dissolution

Redox reactions behave like other chemical reactions with the exception that electrons, like protons (H^+ or H_3O^+) or cations or anions, participate in the reaction. Reactions can be described thermodynamically or kinetically; a reduced solid is considered to be electron-rich. An oxidised solid is considered to be electron-poor.

The presence or absence of oxygen or the presence or absence of oxidised or reduced mineral species can have an important influence on the stability of solids in ash. Under oxidising conditions, metal oxides remain an important phase for immobilising metals. Under reducing conditions, when oxygen is absent, metal sulphides become an important phase for immobilising metals. Metal sulphides are one of the most insoluble phases that can be created geochemically. The transition back and forth between oxidising and reducing environments can result in transitional redox states that promote the solubilisation of both oxides and sulphides.

Influence of Sorption on Leaching

Many of the solid phases in ash are very sorptive and are capable of immobilising dissolved constituents from the ash onto the ash surface via a number of sorption reactions. Sorption reactions can involve the formation of bonds that are relatively weak to those that are relatively strong. Strong binding implies that the adsorbing solute would rather stay on the particle surface than go back into solution.

Many sorption processes are very pH dependent. For example, at a specified pH edge, a sorbed solute will be displaced by a proton or a hydroxyl ion. Below (or above) that pH edge, the solute remains sorbed.

The distribution of trace constituents in ash is such that sorption can easily immobilise the dissolving solute. Frequently, aged ash has a high degree of sorptive surfaces which promote trace metal immobilisation.

12.1.3 Leaching Tests

Leaching tests are employed to simulate field leaching scenarios. The three basic leaching concepts, the flow-through column, the agitated batch system and the non-agitated batch system form the basis for most scientific and regulatory leaching tests that are used.

In almost all cases, a number of tests are required to describe leaching behaviour. One concept that is important to note is that leaching data from many tests show a rather uniform leaching behaviour when ash leaching data are normalised. Raw leaching data in the form of concentration has little meaning until it is transformed into units which are comparable between leaching tests. The normalisation process requires that all data be reported as a function of the L/S ratio. Additionally, the mass of an ash constituent that is leached is also reported as a function of the dry weight of ash leached. This is usually termed "release" (mass of element leached per dry weight of ash) or "fraction leached" (mass of element leached per mass of element in the dry residue). Such normalisation processes are needed to look at mass fractions released from ash as a function of time or the L/S ratio. This then equates to "flux" (discrete mass of element released per unit time) and "cumulative flux" (total mass of element released per unit time).

Leaching tests employ a number of reactor configurations and control measures for stabilising pH, pE (or Eh), temperature, etc. The tests are conducted for specific periods of time. A number of initial leaching solutions can be used. The researcher or regulator must select the types of tests that describe the leaching system to be studied and are amenable to leaching modelling efforts.

12.1.4 Leaching Modelling

The ultimate goal for the selection of an appropriate leaching test or the evaluation of field leaching data is the ability to interpret the observed leaching behaviour mechanistically. By understanding field leaching behaviour, predictions can be made and modelled for how leaching behaviour will change over time and under various management scenarios. This ultimately provides the researcher or regulator with the ability to develop management options based on predicted leaching behaviour.

Two principal approaches are used to model leaching. One involves the use of computer codes that use an iterative technique to simultaneously solve equilibrium expressions and mass balances. Such thermodynamic equilibrium models rely on the assumption that equilibrium will occur between the solid phase and the liquid. These models are valuable in predicting how the alteration of leaching system pH, redox potential, solution-phase complexation and sorption can control the equilibrium of the system.

The second approach couples the equilibrium-based phenomenon of the first approach with an advecting fluid flow through the ash material. Such models usually employ mass transfer and dissolution/reprecipitation mechanisms. The multicomponent approach is particularly useful in predicting long term leaching behaviour.

It is anticipated that thermodynamic equilibrium models and multicomponent advection models will be merged with fate and transport models so as to provide better larger scale modelling capabilities for ash utilisation, storage or disposal sites.

12.1.5 Unified Approach to Leaching

A unified approach to leaching involves the careful characterisation of the residues to be leached, the thoughtful selection of appropriate leaching tests, and the modelling of leaching behaviour. When such approaches are used, systematic leaching behaviour of waste materials is usually observed.

12.2 THE SOLID PHASE/LEACHANT/SOLUTE LEACHING SYSTEM

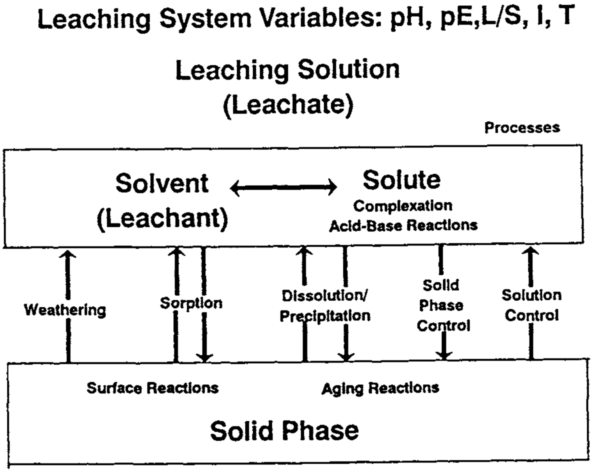
12.2.1 The Leaching System Concept

Leaching can be broadly defined as the mobilisation, extraction or washing of soluble constituents from a solid phase by a contacting solvent. To discuss the phenomena of leaching appropriately, it is necessary to define the system and provide nomenclature. As shown in Figure 12.1, the residue constitutes the solid phase. The leaching of the solid phase by a solvent (or leachant) causes solid phase constituents to become solutes in the solvent. The solute-solvent system, initially described by the characteristics of the leachant, becomes more solute-dominated and takes on the characteristics of a leachate. Adherence to this style of nomenclature in the text will hopefully provide clarity and precision in the presentation.

12.2.2 A Multiphase Heterogeneous System

This simplified system is much more complex in controlled leaching tests and infinitely more complex in dynamic flow-through field leaching scenarios. As depicted in Figure 12.2, the solid phase is a structurally and mineralogically complex heterogeneous material. Basic reactions such as acid-base chemistry and redox chemistry are governed by numerous interactive equilibrium-based reactions that are sometimes kinetically dissimilar. Precipitation, dissolution and sorption phenomena are also kinetically controlled and interactive. Kinetics can govern the appearance of solutes in the leaching solution. Both slow kinetic mechanisms and mass-transfer constraints can prevent equilibria from being attained. The internal porosity, tortuous path lengths of particles and internal reaction mechanisms constitute an internal resistance to diffusion of solutes or solvents into and out of the particle. The fluid boundary layer external to the particle constitutes an external resistance to diffusion of solutes of solvents between the particle surface and the bulk liquid.

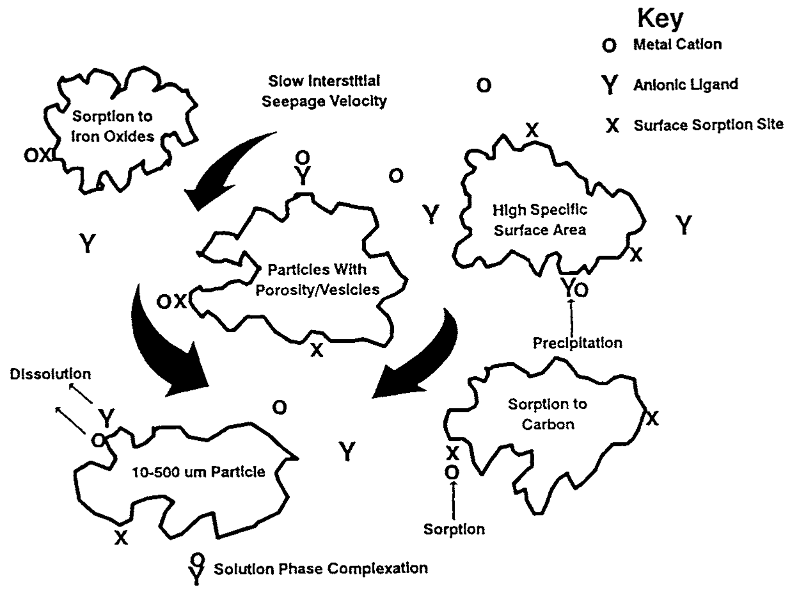
Figure 12.1 The Leaching System



In fact, the leaching of incineration residues probably constitutes one of the more complex solid phase/leachant/solute systems that has ever been studied. For example, a typical leaching scenario can involve a solid phase containing multiple mineral and amorphous principal phases that exhibit differential solubility and are thus incongruent with each other. The leaching solution, in equilibrium with these phases, can contain a multitude of dissolved or colloidal constituents that are also in equilibrium with each other. The system can be exposed to dynamic hydraulic flow conditions where the velocity of the fluid relative to the particle varies and thus boundary layer thicknesses and mass transfer rates vary between the bulk liquid and the particle. The presence of a leaching solution can be intermittent because of the cyclic nature of precipitation or infiltration. The system pH and redox potential (pE or Eh) can dynamically vary. Given the fact that interest in this topic in the scientific and engineering communities increased only ten to fifteen years ago, much inference must be drawn from the work in fields of coal ash leaching, aquatic chemistry, marine geochemistry and terrestrial geochemistry to assist in the comprehension of leaching phenomena and in the design, selection and interpretation of leaching tests. This bridge can be made because the leaching system shown in Figures 12.1 and 12.2 is not that different from soil-porewater systems, soil-contaminated groundwater systems, marine sediments, mine tailing piles or coal ash piles.

Central to leaching phenomena is the concept of solid phase control (see Figure 12.1). During solid phase control, the relative mass (or chemical poise) of the solid phase to that of the leachant is high. The inherent chemical characteristics of the solid phase dominate the solvent, producing saturated solutions. Under such situations, the residue is viewed as controlling leaching. Under certain leaching scenarios, solid phase control can transition into solution control (see Figure 12.1). Under solution control, the mass (or chemical poise) of the solid phase to that of the leachant is small. The infinite volume characteristics of the solvent dominate the nature of leaching solution, acting as a sink for the leaching solutes. More precise descriptions of solid phase or solution control are discussed in Chapter 14. The other aspects of leaching shown in Figure 12.1 are solution behaviour, precipitation, dissolution, weathering and adsorption, as well as controls on that system. The pH, redox, liquid-to-solid ratio and time are the topics of Chapter 13.

Figure 12.2 Schematic of Heterogeneous Complex Leaching System



After Kirkner et al., 1986

12.2.3 Leaching Scenarios

There are a number of leaching scenarios that can be envisioned for incineration residues. As shown in Table 12.1, scenarios range from piled or landfilled material where some type of regulatory and engineering control is imposed, to utilisation applications where beneficial use is envisioned, to various leaching tests. For each scenario, typical leaching time frames, leaching regimes and leachants are shown. The scenarios depict whether the flow-through, agitated batch, or non-agitated batch systems apply. It is important to note that many potential leaching scenarios can assume a time frame of geologic time (e.g. 10,000 years). The examples in no way

Table 12.1
Leaching Scenarios for Incineration Residues

Scenario	Leaching Time Frame (years)	Leaching Regime	Solid Phase or Solution Control		Initial Solvent (Leachant)	Initial Solvent pH
			Short Term	Long Term		
•Piled Residue (no cap, 100 year application	0-100	Flow Through System, Intermittent Saturation, Granular Material	Solid Phase	Solid Phase	Precipitation	4.0-6.0
•Landfilled Residue (leachate removal, cap after 3-10 yr)	3-15	Flow Through System, Intermittent Saturation, Granular Material	Solid Phase	Solid Phase	Precipitation	4.4-6.0
•MSW/Residue Codisposal (leachate removal, cap after 3-10 yr)	3-15	Flow Through System, Intermittent Saturation, Granular Material	Solid Phase	Solid Phase	Landfill Leachate	4.5-5.5
•Granular Fill (no cap, saturated groundwater 100 yr application)	0-100	Flow Through System, Continuous Saturation, Granular Material	Solid Phase	Solid Phase	Groundwater	6.0-8.5
•Road Subbase Utilisation (15 yr application)	0-15	Flow Through System, Very Intermittent Saturation, Granular Material	Solid Phase	Solid Phase	Road Run-off/ Groundwater	5.5-6.5 (run-off) 6.0-8.5 (groundwater)
•Road Paving Utilisation (15 yr application)	0-15	Very Intermittent Saturation, Monolithic Material	Solid Phase	Solid Phase	Precipitation	4.4-6.0
•Column Lysimeter	0-1	Flow Through System, Intermittent Saturation, Granular Material	Solid Phase	Solid Phase	Artificial Precipitation	4.0
•Agitated Batch System	1-2 days	Agitated Batch System, Saturated, Granular Material	Solution Phase	Solution Phase	Artificial Precipitation	4.0
•Non-Agitated Batch System	64 days	Non-Agitated Batch System, Saturated, Granular Material	Solution Phase	Solution Phase	Artificial Precipitation	4.0

represent all residue leaching scenarios, yet they illustrate how the systems can vary and how the perspective of time must be considered.

12.3 RESIDUE PARTICLES AS A SOLID PHASE

It is important to have a clear understanding of ash particle size, porosity and morphology and the role they play in influencing the ash leaching system. These particle characteristics influence the relative surface area available for chemical reactions to take place. They also influence the magnitude of the diffusion path length and the type of internal and external mass transfer resistances that occur as solutes or solvent diffuse into or out of particles.

12.3.1 Particle Characteristics

Theis and Gardner (1990) have assembled pertinent information from the literature on particle size, specific surface area, specific gravity and bulk density for MSW fly ashes and bottom ashes. The data are shown in Table 12.2. The fly ash residues are characterised as fine grained with high levels of specific surface area. The bottom ash residues are characterised as lightweight, medium-grained particles with very high levels of specific surface area.

Table 12.2
Physical Properties of Ash Particles

Property	MSW Fly Ash	MSW Bottom Ash
Particle Size Range, mm	0.01-230	295-9500
Specific Surface Area, m^2/g	2.83-36.93	9.4-46.3
Specific Gravity	2.1-4.04	1.52
Bulk Density g/cm^3	0.78-1.04	0.37-0.73

Theis and Gardner, 1991

Gardner (1991) conducted detailed BET surface area analyses and mercury porosimetry studies on fly and bottom ashes from RDF, rotary kiln mass burn and starved-air mass burn incinerators. The data are presented in Table 12.3. The data indicate that the bottom ashes, though larger in particle size, contain significantly higher specific surface areas, larger total pore areas (based on mercury intrusion) and smaller average pore diameters. The bottom ashes studied typically had specific surface areas of 4 to 30 m^2/g, total pore areas of 1.41 to 19.56 m^2/g and average pore diameters of 0.07 to 2.11 μm. These data strongly suggest that internal diffusional resistance and chemical retardation can be significant in bottom ashes.

Table 12.3
Physical Properties of Selected Fly Ashes and Bottom Ashes

Property	MSW Fly Ash	MSW Bottom Ash
Specific Surface Area, m^2/g	3-18	4-30
Bulk Density, g/cm^3	0.61-1.69	0.7-1.2
Skeletal Density, g/cm^3	0.89-2.83	1.74-2.48
Total Intrusion Volume, cm^3/g	0.23-0.71	0.21-0.74
Total Pore Area, m^2/g	0.06-0.28	1.41-19.56
Average Pore Diameter, μm	9.0-15.5	0.07-2.11

Gardner, 1991

Fly ashes had lower specific surface areas (3.18 m^2/g), significantly lower total pore areas (0.06 to 0.28 m^2/g) and significantly higher average pore diameters (9.0 to 15.5 μm). Such data suggest that internal diffusional resistances can be much less severe in fly ashes.

12.3.2 Particle Morphology

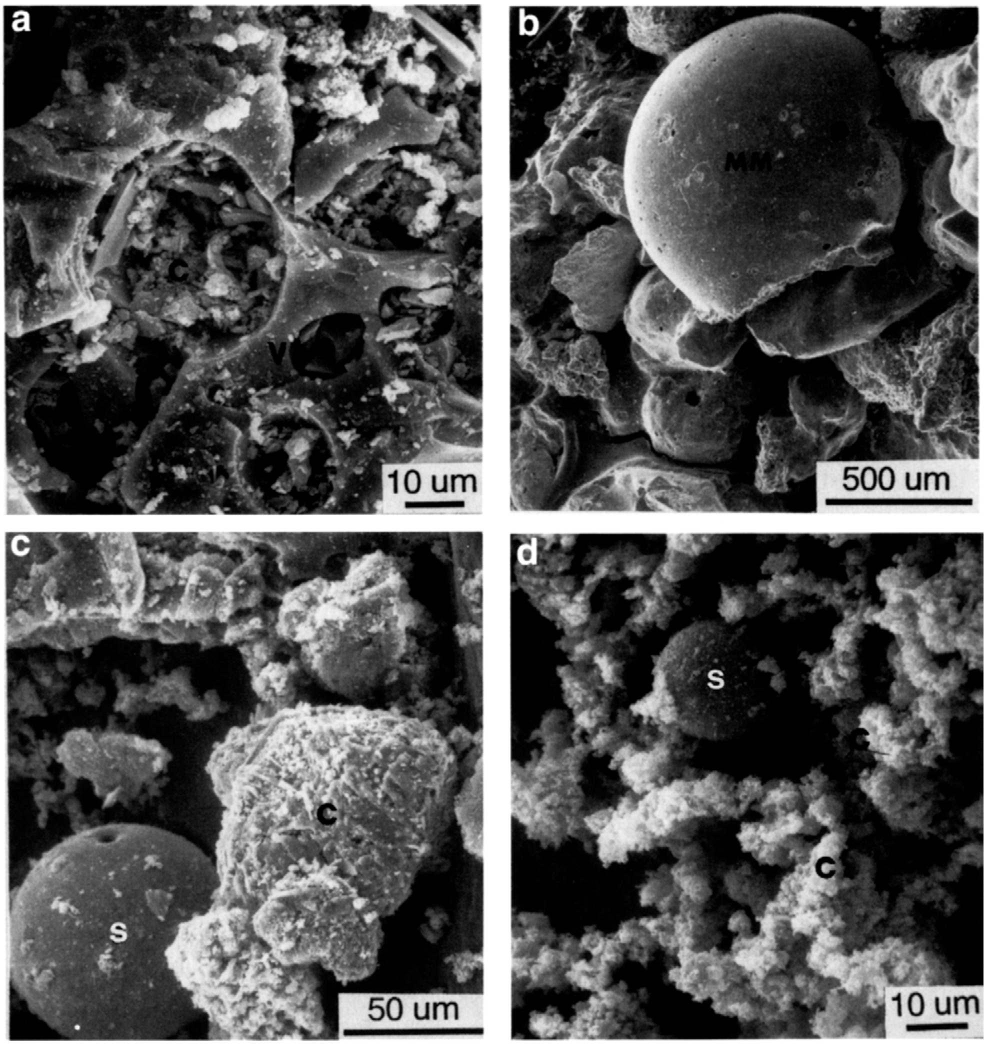
Figure 12.3 is a composite of SEM micrographs of grate ash, grate siftings, boiler ash and dry scrubber residue.

Figure 12.3 depicts the morphology and crystalline nature of a typical grate ash particle. The sample is from a large Canadian mass burn facility. The grate ash was collected prior to quenching. The particle is large and contains a high degree of externally-connected vesicles. These are formed by trapped gases that escape from material in a plastic state as it cools during quenching. Many of the vesicles have relatively large diameters, on the order of 100 to 1000 μm in size. There are a number of crystalline phases on the particle surface and in the vesicle. Some of the phases exhibit high degrees of crystallinity, whereas some are more glassy, indicating that melting and rapid cooling have occurred. Coupling this information with mercury porosimetry data suggests that diffusion path lengths are long (up to 10,000 μm) and highly tortuous. These data are consistent with the Gardner (1991) data which suggest a very high degree of internal diffusional resistance. Diffusional leaching processes are therefore much more complex in bottom ash.

Figures 12.3 also depict the morphology of grate siftings, boiler ash and dry scrubber residue. The grate siftings are similar in characteristic to bottom ash; however, typical grain sizes are smaller and molten metal beads, glass fragments, soil, and metal pieces are commonly found. Slag particles are also present. The boiler ash and dry scrubber

Figure 12.3 SEM Micrographs of Grate Ash (a), Grate Sifting (b), Boiler Ash (c), and Dry Scrubber Residue (d)

V=vesticle, S=spherical particle, C=crystalline particle, MM=melted metallic materials



residue are characterised by large specific surface areas because of their relatively small particle size and highly polycrystalline nature. The pore sizes are relatively large because of the agglomeration of very fine particles. Diffusion path lengths are relatively short (100 μm).

12.4 FLUID FLOW, DIFFUSION AND MASS TRANSFER

In field and laboratory column leaching scenarios, the ash particle is stationary and a leachant flows through or around the ash particles and carries away dissolved ash constituents. In certain batch leaching scenarios, agitation is used to cause fluid to flow past particles and accelerate the dissolution of constituents in the ash. In other batch leaching scenarios, fluid flow or agitation is absent, which permits only strict molecular diffusion and Brownian motion to carry away dissolving constituents. The rate at which constituents are carried away (via advection) plays a fundamental role in influencing chemical reactions associated with leaching.

An appreciation for the concept of fluid flow and advection is needed to characterise the interactive roles of diffusion and mass transfer in leaching phenomena.

12.4.1 Fluid Flow Through Residues

In many field leaching scenarios, a leachant flows through or around a pile of ash. The flow can be approximated in the laboratory with columns or outdoors in small lysimeters. For most leaching scenarios, the flow of a leachant through or around incineration residues is governed by Darcy's Law. Typically, the flow is unsaturated. Examples include landfill leaching, road-base leaching, pile leaching and column leaching of residues. Flow, however, can be saturated under certain landfill, pile, road sub-base and column leaching scenarios.

The factors describing saturated fluid flow in porous media are derived from Darcy's Law:

$$Q = KA\left(\frac{dh}{dl}\right) \tag{12.1}$$

where

Q is the quantity of water moving through an incremental volume per unit time (m^3/d),

K is the hydraulic conductivity constant; it is a function of porosity and leachant kinematic viscosity and density (m/d),

A being the cross-sectional area of the incremental volume through which flow is occurring (m^2),

dh/dl is the hydraulic or gravitational gradient or headloss across a depth or length of the incremental volume through which flow is occurring (m/m).

Rearranging equation (12.1) produces:

$$K = \frac{Q}{A}\frac{dl}{dh} = v\frac{dl}{dh} \tag{12.2}$$

where v is a measure of saturated velocity or specific discharge.

There are limits to which Darcy's law is valid for flow through porous media. For fine grained, impermeable materials there are threshold hydraulic gradients below which flow does not occur. At very high rates of flow, Darcy's law is also invalid. The dimensionless "Reynolds number" is used to determine when this happens. The Reynolds number (Re) is a ratio of inertial to viscous forces during flow. It is used to determine whether flow past a particle is laminar or turbulent. Typically mass transfer to or from a particle surface is much higher under turbulent conditions. The Reynolds number is defined as:

$$Re = \frac{\rho v d}{\mu} \tag{12.3}$$

where

ρ is fluid density (kg/m^3),
v is fluid specific discharge (m/s),
d is particle diameter (m), and
μ is dynamic viscosity(kg/m.s).

Darcy's law is valid when the Re is below values ranging from 1 to 10.

A number of studies have characterised saturated hydraulic conductivities of combustion residues. Hartlén and Elander (1986) documented saturated hydraulic conductivities (K) of 10^{-5} to 10^{-7} m/s for bottom ashes, $10^{-6.5}$ to $10^{-9.5}$ m/s for fly ashes and $10^{-8.5}$ to $10^{-10.5}$ m/s for scrubber residues.

The steady-state unsaturated flow of a leachant through and around porous ash particles can be determined from a modified form of Darcy's law:

$$Q = K_e A\left(\frac{h_c - z}{z}\right) \pm \left(\frac{dh}{dl}\right) \tag{12.4}$$

where

Q is the quantity of water moving through an incremental volume per unit time (m^3/d),
K_e is the hydraulic conductivity under unsaturated conditions (m/d),
A is the cross-sectional area of the incremental volume through which unsaturated flow is occurring (m^2),
(h_c-z)/z is the capillarity or surface tension gradient (m/m), and
dh/dl is the hydraulic or gravitational gradient through which unsaturated flow is occurring. (m/m)

Typically, K_e approaches K logarithmically as saturation approaches 100%. During unsaturated conditions the effective hydraulic conductivity of a residue is a function of particle size, capillarity and moisture content. There are no published effective hydraulic conductivities (K_e) for combustion residues.

For typical hydraulic gradients and typical saturated conductivities, one would expect fluid velocities to range from 1×10^{-7} to 1×10^{-4} cm/s, which are low enough to maintain low Reynold's numbers (<5) and laminar flow during saturated conditions.

For typical hydraulic gradients and typical unsaturated effective hydraulic conductivities, one would expect lower seepage velocities. Such values would range from 1×10^{-9} to 1×10^{-6} cm/s. These values are well within the range of low Reynold's numbers (10^{-2} and less) and laminar flow conditions.

The implication of laminar flow through and around combustion residues is that fluid and chemical boundary layers are large, constituting an external resistance to diffusion that may limit fast reactions. Such rate-limited reactions have been observed by Theis et al. (1992, 1993). For slow reactions at or inside particles, external diffusional resistance is probably not rate limiting.

12.4.2 Fluid Flow Past Particles in Suspension

In non-agitated suspensions, particles settle at a terminal velocity according to their buoyant weight and the resisting forces resulting from drag. Stoke's Law describes particle settling velocities:

$$V = \frac{(\rho_p - \rho_f)\, g\, d^2}{18\mu} \qquad (12.5)$$

where

V is the settling velocity,
ρ_p and ρ_f are particle and fluid density, respectively,
g is the gravitational constant, and
d is the particle diameter
and μ is the dynamic viscosity of the fluid.

Stokes law can be used to approximate velocities for tumbled agitation systems. In continuously agitated suspensions, the weight of the suspended particles is continuously supported by the fluid. Any inclination toward settling is counterbalanced by random upward movements of fluid parcels during turbulent flow. The intensity of turbulence, the scale of turbulence and kinematic eddy viscosity of the turbulent fluid parcels keep the particles suspended. Kinematic eddy viscosity is used to describe fluid shear between turbulent parcels and therefore between parcels and particles.

For most continuously agitated systems, kinematic eddy viscosity and shear is high. This means that fluid and chemical boundary layers are very compressed and not likely to constitute a resistance to diffusion or limit fast reactions at the particle surface. By increasing mixing energy, external diffusional resistances can be virtually abolished.

12.4.3 Diffusional Processes and Internal Mass Transfer Considerations in Residues

It is useful to examine the role of bulk diffusion and internal mass transfer resistance on leaching (Hinseveld, 1991). As shown in Figure 12.4, Fick's second law of diffusion is applicable for leaching from a small unit area in a hypothetical ash particle:

$$\frac{\partial C}{\partial t} = D_e \frac{\partial^2 C}{\partial x^2} \qquad (12.6)$$

where

C is the concentration of a potential solute in the particle (mole/cm^3),
t is the leaching time frame (seconds),
x is the distance from the leaching region in the particle to the particle shell (cm), and
D_e is the effective diffusion coefficient (cm^2/second).

As indicated previously, the diffusion path length in the particle may be tortuous and long and therefore should not be expressed as a radial distance. Assuming an area through which diffusion out of the particle is proportional to the porosity (ϵ) in the particle, it is evident that the effective diffusion coefficient relates to the true molecular diffusion coefficient:

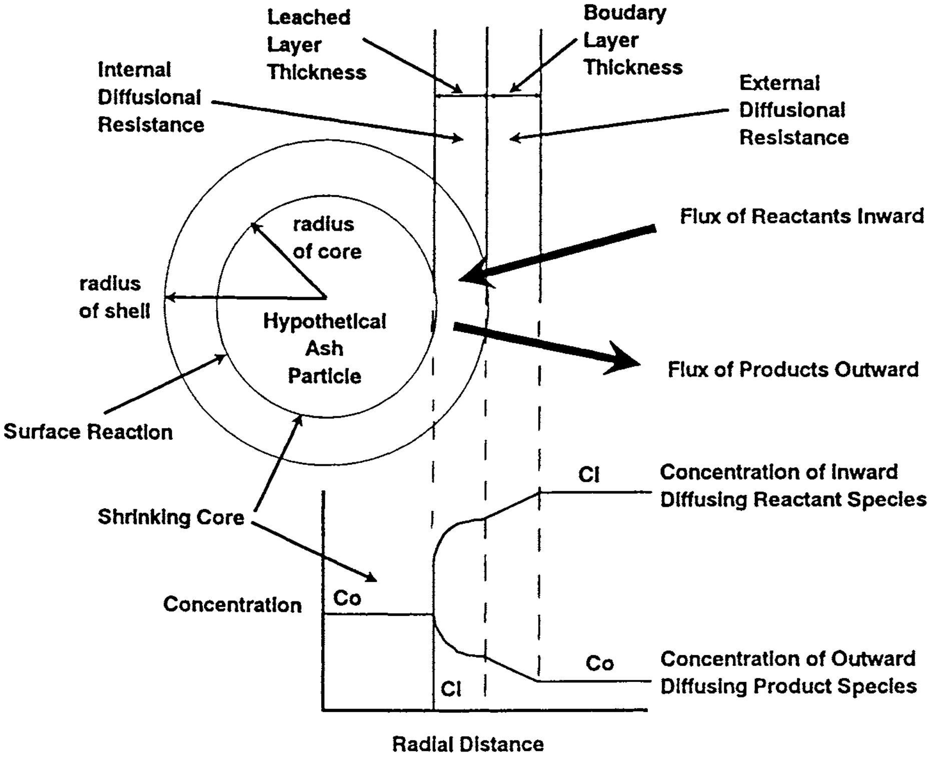
$$D_e = \frac{D_m \varepsilon}{\tau} \qquad (12.7)$$

where

D_m is the molecular diffusion coefficient (cm^2/sec),
ϵ is the porosity in the particle (cm^3/cm^3), and
τ is a tortuosity factor (unitless).

Estimates of porosity (0.10 to 0.30) and tortuosity (1 to 1000) means the effective diffusion coefficients are up to 10^4 times smaller than molecular diffusion in dilute solutions. Li and Gregory (1974) provide a table of D_m values for simple anionic and cationic species in dilute solutions at different temperatures.

Figure 12.4 Conceptual Model of Ash Particle Dissolution



After Hinseveld, 1991

An analytical solution to equation (12.6) is available in Crank (1975). As noted by Hinseveld (1991), the underlying assumptions of applying Fick's second law (flat element, infinite medium, one-dimensional diffusion, equimolar diffusion, constant surface concentration, constant D_e) make this an overly simplistic approach to modelling leaching.

The bulk diffusion process can be modified for internal mass transfer resistance inside the ash particle in two steps (Hinseveld, 1991). The first part is accomplished through the use of a unitless linear distribution coefficient, K_D,:

$$K_D = \frac{C_{mobile}}{C_{immobile}} \tag{12.8}$$

where

C_{mobile} is the concentration of the mobile solute in the particle and
$C_{immobile}$ is the concentration of the immobile solute in the particle.

The new form of equation (12.6) is therefore:

$$\frac{\partial C}{\partial t} = \frac{D_e}{(1+K_d)} \frac{\partial^2 C}{\partial x^2} \tag{12.9}$$

Second, equation (12.9) can then be further modified with a dissolution constant, k, for the immobile phase so that:

$$\frac{\partial C}{\partial t} = D_e \frac{\partial^2 C}{\partial x^2} - \frac{\partial C_{immobile} + k(C_s - C_{mobile})}{\partial t} \tag{12.10}$$

where

k is dissolution constant (molal) and
C_s is the surface concentration of the solute (molal).

Both linear distribution and dissolution decrease the internal flux of constituent solutes out of the ash particle. Hinseveld (1991) provides a solution to equation (12.10). The use of this approach theoretically demonstrates that internal diffusional resistances can act as a rate-limiting step to leaching phenomena. Unlike external resistances, these internal resistances cannot be abolished unless residues are dramatically size reduced.

12.4.4 External Mass Transfer Considerations in Residues

Consider the nature of the fluid flow past a hypothetical ash particle as depicted in Figure 12.4. Molecular diffusion, advection and hydrodynamic dispersion are three transport processes governing external mass transfer between the bulk fluid, the boundary layer and the particle surface (Zachara and Streile, 1991).

The Peclet number (P_e) is a useful parameter to investigate the relative role of fluid velocity and diffusion on transport processes. P_e is defined as:

$$P_e = \frac{dv}{D_m} \tag{12.11}$$

where

d is the average particle diameter (cm),
v is fluid velocity (cm/s), and
D_m is the molecular diffusion coefficient (cm^2/s).

Rose (1977) makes use of the Peclet number for characterising the influence of fluid flow on the nature of transport mechanisms between particles and the bulk liquid. The five regimes are depicted in Table 12.4. Also shown in Table 12.4 are likely fluid velocities for APC residues of characteristic diameter of 0.01 cm (100 μm) and bottom ash residues of characteristic diameter of 0.1 cm (1000 μm) associated with each domain (assuming a typical solute diffusivity of 10^{-7} cm^2/s). The results indicate that molecular diffusion is the predominant transfer mechanism for anticipated fluid velocities through residues.

Table 12.4
Peclet Numbers and External Mass Transfer Mechanisms

		Typical Seepage Velocities (cm/sec)	
Regime	Dominant Process	APC Residues[a]	Bottom Ash[b]
$P_e < 0.3$	Molecular Diffusion	$3x10^{-6}$	$3x10^{-7}$
$0.3 < P_e < 5$	Molecular Diffusion & Advection	$3x10^{-1}$ to $5 x 10^{-5}$	$3x10^{-7}$ to $5x10^{-6}$
$5 < P_e < 1000$	Advection But Molecular Diffusion Cannot be Neglected	$5x10^{-5}$ to $1x10^{-2}$	$5x10^{-6}$ to $1x10^{-3}$
$1000 < P_e <$ 150,000	Advection	Not Likely	$1x10^{-3}$ to $1.5x10^{-1}$
$P_e > 150,000$	Dispersion	Not Likely	Not Likely

[a] Based on characteristic lengths of 0.01 cm, and on diffusion coefficients of 10^{-7} cm^2/sec.
[b] Based on characteristic lengths of 0.1 cm and on diffusion coefficients of 10^{-7} cm^2/sec.

12.5 THE LOCAL EQUILIBRIUM ASSUMPTION

It is important to note how fluid flow past a particle can influence our estimate of the local equilibrium assumption (LEA). Conceptually, for sorption reactions at surfaces, if a chemical reaction at the particle surface is fast relative to the rate of advection from fluid flow, then pointwise equilibrium may be obtained and the LEA is valid. If a reaction is slow, however, advection will sweep reactants away from reaction sites

(Jennings, 1987). This condition is likely to occur for many surface reactions processes. It is outlined in more detail in Chapter 13.

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