CHAPTER 15 - LEACHING MODELLING

The principles introduced in Chapters 12 and 13, when combined with appropriate field leaching data or leaching test data introduced in Chapter 16, allow for the use of models to verify mechanistic leaching behaviour and to predict leaching behaviour as a function of time, residue management practice, or treatment scheme.

There are numerous advantages associated with the use of models to help understand and simplify complex leaching systems. The fact that complex, heterogeneous, multiphase processes can be accurately described by models with mechanistic bases is, in its own right, an important breakthrough. Such information has been used to show the systematic leaching behaviour for many waste materials, including incineration residues. These models can be used to predict changes in leaching behaviour over much longer time frames of tens to thousands of years. Further, the models can also be used to predict changes in leaching behaviour under different management or treatment scenarios. When coupled with appropriate leaching tests for treated ash products, these models are useful in providing a high level of predictive capability.

Researchers studying ash leaching have used two distinct modelling approaches. The first is based on geochemical thermodynamic equilibrium models that require the leaching system to be at or near equilibrium for all of its dominant solution phase reactions, solution-solid phase reactions, and solid phase-solid phase reactions. This approach describes leaching behaviour under non-flow-through conditions analogous to discrete "snapshots" in the geochemical domain (e.g., a specific pH, Eh, L/S, solution complexation conditions, sorption conditions).

The second approach employs a dynamic multicomponent flow-through leaching model with mass transport, mass balance and mass action constraints. The model is described by boundary conditions and initial conditions for leachable mass fractions. Under plug flow conditions, the system is allowed to evolve and predict phase dissolution and equilibrium-bounded phase reprecipitation. This second approach differs from the first in that the flow-through system, as a function of pore volume or time, can predict longer term leaching behaviour. Again, the dynamic system can be viewed as a series of "snapshots" under changing regimes of pH, L/S and redox.

Both approaches are described in detail below. The reader is provided with references to reviews that offer more detailed information on the two approaches.

15.1 EQUILIBRIUM MODELS

The leaching system (Figure 12.2 in Chapter 12) shows all of the equilibrium reactions (solution complexation, dissolution/precipitation, sorption) occurring amongst the hypothetical solid phase ash particles in a complex, heterogeneous system. To simplify this system slightly, chemical weathering reactions are, for now, neglected because they are kinetically slow reactions that are unlikely to be at equilibrium in the leachates that are studied.

This system may be described as typically containing many different mineral phases, some of which are oxides or aluminosilicates with surface adsorption sites of various affinities for a variety of adsorbing solutes. The leaching solution contains many different solutes in a non-ideal solution with high ionic strength. Each solute can undergo solution complexation reactions, sorption reactions and precipitation/dissolution reactions.

This complex system can approach equilibrium where the free energies of each of these reactions collectively reach a minimum. Researchers are now attempting to employ geochemical thermodynamic equilibrium models to help mechanistically interpret leaching phenomena.

15.1.1 Thermodynamic Equilibrium Models

Numerous reviews of thermodynamic equilibrium models have been published (Kincaid et al., 1984; Kincaid and Morrey, 1984; Morrey et al., 1986; Nordstrom and Ball, 1984). The utility, applicability and limitations of classes of these models are presented here.

The chemical equilibrium condition of a complex system is an attempt to find the most stable state of the system under specified conditions of pressure, temperature and composition. In a thermodynamic sense, it is an attempt to find the Gibbs free energy minimum for the system. This can be done in two ways: by minimising a free energy function or by solving a set of nonlinear equations consisting of equilibrium constants and constraints on the mass balance of participating elements in the system (Nordstrom and Ball, 1984). The major disadvantage in utilisation of a free energy database is these values tend to be less reliable than directly measured equilibrium constants (Nordstrom and Ball, 1984). Invariably, caution is needed in selection of the appropriate model and database and in ensuring the database conforms to the constraints of the studied system.

The numerical algorithms used to solve the nonlinear equations usually involve (i) pure iteration, (ii) Newton-Raphson iteration and (iii) integration of ordinary differential equations. The pure iteration method is a brute approach where the system approaches unity after successful back-substitution iterations. The integration approach is used to solve complex forward and backward kinetic reactions. The Newton-Raphson method is the most widely used; it sometimes does not converge as quickly as the iteration method.

There are more than fifty programs that have been developed for aqueous phase systems. Some are now available for use on a personal computer, however, given their complexity and iterative nature, mainframes are often used. Leachates derived from batch, column or field leaching studies are usually modelled. It should be determined that equilibrium is approached in the leaching test or in the field prior to collection of leachate: the concentration of major and minor constituents in the leachate should be constant over time. Most models input leachate pH, temperature, analyte concentrations, and sometimes Eh and ionic strength. Most models output aqueous phase speciation, species activity, species activity coefficients and saturation indices that describe a tendency for elements to precipitate or stay in solution. The solid phases that can precipitate are usually identified. More recent versions of the models such as MINTEQA2 include surface adsorption reactions and allow for the selection of various sorption models for use in modelling adsorption and desorption. Care is needed in the selection of adsorption constants.

Some limitations to these programs involve the difficulty in which equilibrium constants in the database can be changed, the Gibbs phase rule violations that can occur when too many solid phase constraints are placed on the system, the inability of some models to converge easily and the inability of some models to contain algorithms that reprocess the system at different pH or pE values. The newest version of MINTEQ, MINTEQA2, and the model SOLGASWATER developed by Erickkson (1979) have this iterative capacity.

15.1.2 Use of the Geochemical Thermodynamic Equilibrium Model MINTEQA2

MINTEQA2 is an equilibrium model for dilute heterogeneous aqueous systems. The original MINTEQ, developed by Felmy et al. (1984), was a hybrid of MINEQL, developed by Westall et al. (1976) from REDEQL (Ingle et al., 1978) and WATEQ3, a code developed by the U.S. Geological Survey (Ball et al., 1981). The fundamental mathematical structure of MINEQL and the thermodynamic database of WATEQ3 were combined to produce MINTEQ. The most recent version of MINTEQ, MINTEQA2 (version 3.11) is presently administered by the Environmental Research Laboratory, Office of Research and Development, U.S. Environmental Protection Agency, Athens, Georgia 30613 (Allison et al., 1990).

MINTEQA2 is a much more interactive program than its predecessors. There are more options and features available to the user, the methods of calculation have been improved and the thermodynamic database is more up to date and more readily modified. The database has been deemed to be the most complete, annotated and accurate of the existing current computer codes (Krupka et al, 1986; Morrey et al., 1986; Allison et al., 1990). For ash leaching scenarios the database must be modified to include certain constituent "components" and mineral phases found in residues. MINTEQA2 also uses an interactive program, PRODEFA2, to create input files for MINTEQA2.

The information required to operate MINTEQA2 usually consists of chemical analyses of a leaching solution (at equilibrium) giving total dissolved analytical concentrations

(C_T in units of mg/L, parts per million, molal or molar) and other measurements of the system, including pH, pE (or Eh), gas partial pressures, the presence of mineral phases and the capacity to allow sorption to occur. By specifying gas partial pressures (e.g. CO_2) and finite (potential dissolvable) solid phases, source terms or supplies of these constituents are available to be pulled into the mass action equations. Alternatively, system pH and pE (or Eh) can be set and hypothetical minerals can be input to see if they will dissolve or remain insoluble and produce an aqueous solution similar to a leachate.

MINTEQA2 uses the simultaneous solution of nonlinear mass action expressions (derived from equilibrium expressions) and linear mass balance relationships to solve for the system equilibrium conditions. During iterations it will transfer mass from gas phases or finite solids into these terms to satisfy equilibria. The system can be over-constrained when too many phases or set points are specified, removing degrees of freedom and ultimately causing failure of the program.

MINTEQA2 uses an initial guess of the activity of each component to calculate the concentration of each species according to mass action expressions. The total mass of each component is then calculated from the concentrations of every species containing that component. The calculated mass is compared with the input mass; if it exceeds a tolerance level, a new iteration is conducted (hundreds of iterations can occur). A final aqueous phase concentration for all species is determined once tolerance levels are met.

MINTEQA2 calculates saturation indices during or after the iterative process to see which potential phases can precipitate. The solid phase with the largest positive index can be allowed to precipitate in accordance with reaction stoichiometry. The reverse can also occur if an inputted solid phase is undersaturated with respect to the solution phase saturation index. The whole system is then re-equilibrated through successive iterations until there are no oversaturated possible solids or undersaturated existing solids. The iteration process can be operated for system set points for pH and pE. Sorption models can also be included. They are discussed below.

MINTEQA2 has some system limitations. It is meant for temperatures below 100°C. It uses the van't Hoff equation to modify equilibrium constants for temperatures other than 25°C. It also employs the modified Debye-Hückel and the Davies equations to determine activity coefficients. Thus, its effective range for I is from 0.0001 up to 0.5 molal. Higher ionic strengths require the use of alternative methods for determining activity coefficients, such as the Whitefield modifications to Pitzer's original work discussed in Chapter 13. While MINTEQA2 is not readily modified, models such as SOLMINEQ (Perkins et al.. 1990) and SOLTEQ (Batchelor and Wu, 1993) have these capabilities. Finally, MINTEQA2 also can include in the input some measure of total alkalinity to determine dissolved inorganic carbon [CO_3^{2-}, HCO_3^-, H_2CO_3, $CO_2(aq)$]. These are crucial components that are often neglected.

MINTEQA2 uses seven different surface adsorption models:

on-Electrostatic Models

- Activity K_d adsorption model
- Activity Langmuir adsorption model
- Activity Freundlich model
- Ion exchange model

Electrostatic Adsorption Models

- Constant capacitance model (CCM)
- Diffuse layer model (DLM)
- Triple layer model (TLM)

These models, described in Chapter 13, are a unique and important feature to MINTEQA2. An excellent source of sorption constants for each of these models can be found in Rai and Zachara (1984) or in Dzombak and Morel (1990). These databases report sorption parameters for a large number of sorptive surfaces, many of which can be modelled in ash systems. Again, caution should be used in the selection and use of these sorption parameters.

15.1.3 Verification of MINTEQA2

Morrey et al. (1986) conducted detailed evaluations of the MINTEQA2 precursor, MINTEQ, for its possible use as a basis for the EPRI FASTCHEM geochemical/ hydrodynamic solute transport code.

Morrey and co-workers were intent on verifying the ability of MINTEQ to properly describe an equilibrated geochemical system containing the minerals malachite, gypsum, gibbsite, cerussite and goethite in equilibrium with coal fly ash leachate solution species. These minerals are important and dominant components of coal fly ash. One approach (the saturated solution approach) was to input the leachate concentrations of these elements as dissolved species in the presence of the five minerals. Could MINTEQ achieve equilibria and predict the continued presence of the five solid phases? The second approach (the solid phase approach) was to input the solid phases as finite (potentially soluble) phases and specify all potential dissolved components as present but at very low concentrations initially. In parallel, these phases were actually solubilised in a laboratory batch leaching test. Could MINTEQ achieve equilibrium and produce solution concentrations similar to the laboratory-derived analytical concentrations?

Table 15.1 describes the master system and solution variables for the first approach. The constituents describe a leachate in equilibrium with the five dominant minerals;

other trace constituents were also present. MINTEQ was run two ways: 1) by allowing additional minerals to form and 2) not allowing additional minerals to form. In the first case, a phase rule violation caused a code termination when the program tried to reprecipitate hematite (Fe_2O_3) when goethite (FeOOH) was already designated as a finite solid. An attempt to precipitate the thermodynamically-preferred hematite caused the phase rule violation. Using the second approach, equilibrium was obtained by extracting 5.8 x 10^{-3} moles of carbon from the infinite gas supply, dissolving small amounts of gypsum and precipitating small additional amounts of cerussite. Gibbsite, goethite and malachite were unchanged. As shown in Table 15.2, their saturation indices remained at 0, indicating their role as controlling phases. The trace constituents did not disrupt the achievement of equilibrium, indicating dominant phases usually control system equilibria.

Table 15.1
Master System and Solution Variables for Evaluating the Saturated Solution Approach to Using MINTEQ

Master Variables:

Alkalinity = 4.3 meq/L
pH = 8.2
CO_2 pressure = 1.58 X 10^{-3} atm
O_2 pressure = 0.2 atm (oxidising)
Temperature = 11°C

Major Cations and Anions (mg/L)

Ca^{2+} = 400
Mg^{+2} = 50
Na^+ = 75
K^+ = 20
SO_4^{-2} = 1,000
Cl^- = 80
NO_3^- = 30
$B(OH)_4^-$ = 20

Minor and Trace Constituents (mg/L)

Al = 0.01
As = 0.01
Cd = 0.03
Co = 0.01
Cr = 0.02
Cu = 0.02
F = 0.50
Fe = 0.20
Mo = 0.01
Ni = 0.02
Se = 0.01
Zn = 0.03
Pb = 0.02

After Morrey et al., 1986

Table 15.2
Results from Saturated Solution Input Verification of MINTEQ

System Variables	
pH	8.200
Sum of Cations (molal)	2.15×10^{-2}
Sum of Anions (molal)	2.31×10^{-2}
Percent Difference (C-A/C+A)	-3.86
Ionic Strength	3.86×10^{-2}
Mineral Saturation Indices	
Aragonite, $CaCO_3$	1.184
Boehmite, AlO(OH)	0.000
Calcite, $CaCO_3$	1.375
Diaspore, AlO(OH)	1.831
Dolomite, $CaMg(CO_3)_2$	1.962
Hematite, Fe_2O_3	4.940
Gibbsite, $Al(OH)_3$	0.000
Goethite, FeOOH	0.000
Gypsum, $CaSO_4 \bullet 2H_2O$	-0.002
Hunite, $CaMg_3(CO_3)_4$	-1.108
Magnesite, $MgCO_3$	0.102
Tenorite, CuO	0.031
Cupricferrite, $(Cu, Fe_2)O_4$	2.970
Cerussite, $PbCO_3$	0.030
Otavite, $CdCO_3$	1.449
Plattnerite, PbO_2	-0.444
Pb_2O_3,	-1.886
Malachite, $Cu_2(OH)_2CO_3$	0.000

After Morrey et al., 1986

Table 15.3 denotes the master system and finite solid variables for the solid phase approach. In parallel, excess masses of ground malachite, gypsum, gibbsite, cerussite and goethite were added to distilled water to produce an equilibrated solution with solids present. Sodium hydroxide was used to control pH at 8.2. MINTEQ was operated with the variables shown in Table 15.3. These solids and their solid phase concentrations were inputted as finite solids while all possible dissolved components were listed but assigned very low concentrations. The addition of the sodium hydroxide titrant was also included as a system parameter.

Table 15.3
Master System and Solid Phase Variables for Evaluating the Solid Phase Approach to Using MINTEQ

Master Variables:			
	Alkalinity	=	9.83 mg/L as CO_3^{-2}
	pH	=	8.2
	Na^+	=	18.75 mg/L[a]
	Total Hydrogen	=	0.8277 mg/L[a]
Finite Mineral Phases			
	Malachite		$Cu_2(OH)_2CO_3$
	Gypsum		$CaSO_4 \bullet 2H_2O$
	Gibbsite		$Al(OH)_3$
	Cerussite		$PbCO_3$
	Goethite		FeOOH

[a]From the NaOH used to control pH
After Morrey et al., 1986

Table 15.4 denotes the results of the modelling run compared to the experimentally derived leachate. Fairly close agreement was seen. Some concern was expressed by the authors about the lack of complete agreement between the predicted and observed leachate concentrations. Experimental non-equilibrium was hypothesised for gypsum and gibbsite. Also a concern was the suspicion that 0.22 μm filters allowed nanocolloid precipitates to pass through the filter, thus overestimating the true dissolved total concentration for some elements.

Table 15.4
Results from Solid Phase Input Verification of MINTEQ

Element	MINTEQ Calculated mg/L	Experimentally Determined mg/L
Sodium	18.75	11.0
Calcium	392.6	590.0
Carbon	9.61	9.93
Aluminum	0.02	0.31
Sulphur (SO_4^{2-})	941.1	1,499.0
Iron	1.69×10^{-8}	NA[a]
Copper	0.263	NA
Lead	0.320	NA
Ionic Strength	2.847×10^{-2}	NA
pH	8.09	7.8

[a]NA = not analysed
After Morrey et al., 1986

Recent efforts by many researchers (DiPietro et al., 1990, DiPietro, 1989; van der Sloot et al., 1992; Theis et al., 1992; Dzombak et al., 1992; Comans et al., 1993; Eighmy et al., 1993) have made use of MINTEQA2 or its precursors in modelling efforts. This model has also been selected by EPRI as a basis for their ECHEM geochemical thermodynamic code for modelling coal ash leachate advection and dispersion in FASTCHEM. Thus MINTEQA2 appears to be, for now, an appropriate geochemical code for modelling.

15.1.4 Recommendations for Utilising MINTEQA2 to Model Leaching Behaviour

There are a number of recommendations that will assist users of MINTEQA2 in making use of this powerful tool for modelling leaching:

For the Saturated Solution Approach

- Input all constituent concentrations in the equilibrated leachate solution; leachates should be from column tests, from longer duration batch tests at lower L/S ratios (to ensure equilibria) and from field leachates or pore waters.
- Set the appropriate temperature.
- Include measures of either total alkalinity or carbonate species (not both); this can also be left unspecified in initial trials if a complex system is being modelled.
- Fix pH to the measured leachate solution value; this can also be left unspecified in initial trials if a complex system is being modelled.
- Fix pE (or Eh) to an oxidised (or reduced) level; this can also be left unspecified in initial trials if a complex system is being modelled.
- Initially do not allow any solids to precipitate.
- Run the program with the intent of it converging to an equilibrium solution. Check cation/anion balances, subtly adjust simple cations (Na^+, K^+) or carbonates as most likely cause of discrepancy (assuming all constituents were quantified).
- Rerun the program; a number of trials may be needed to achieve a good ion balance.

- Rerun the program after reasonable ion balances are achieved and allow the solid phase with the highest saturation indice to precipitate as a finite solid.

- The possible solid exclusion option may be needed to prevent MINTEQA2 from redissolving a more soluble phase before a more insoluble phase precipitates out or to prevent nonsensical solids from forming.

- Run the program until four or five dominant phases remain as precipitated solids with saturation indices at zero.

- Compare the identity of the precipitated solids with those seen in ash residues using methods described in Chapter 7.

- Try running the program with specified CO_2 partial pressures to see how an infinite supply of CO_2 alters equilibria (if this is appropriate).

- Try varying pH, pE (or Eh), gas partial pressures, solution-phase chelates (organics), the presence of new solid phases, etc. to see how the system responds.

- Attempt to run adsorption subroutines only after the more basic system is described and understood.

For the Solid Phase Approach

- Input all possible or suspected solid phases as finite solids; the thermodynamic database will most likely need modification to include phases not in the database. Data on phase equilibrium constants (e.g. $1/K_{so}$ or K_{so}^{-1} because MINTEQA2 approaches all equilibria constants as dissociation constants so the inverse of the commonly reported K_{sp} or K_{so} is needed), phase enthalpy and reaction stoichiometry are needed.

- For inputted phases, estimates of the finite solid concentration will be needed. These are reported as moles available per one litre of solution. Total Availability Leaching Test data can be used here.

- Identify all possible component dissolved aqueous species of the solid phases and specify their starting concentration at a low value (e.g. 1×10^{-15} molal).

- Include measures of either total alkalinity or carbonate species (not both); this can also be left unspecified in initials trials if a complex system is being modelled.

- Input the total estimated hydrogen ion concentration (as well as its conjugate base concentration) as dissolved constituents to account for the acid used in the leaching test or fix the pH to the measured leachate solution value; this can also be left unspecified in initials trials if a complex system is being modelled.

- Fix pE (or Eh) to an oxidised (or reduced) level; this can also be left unspecified in initial trials if a complex system is being modelled.

- Run the program with the intent of it converging to an equilibrium solution, check cation/anion balances, subtlety adjust solid phase concentrations to correct the balance.

- Rerun the program until a balance is achieved.

- Compare the final solution composition with the leaching solution, examine solution-phase speciation.

- Try running the program with specified CO_2 partial pressures to see how an infinite supply of CO_2 alters equilibria (if this is appropriate).

- Try varying pH, pE (or Eh), gas partial pressures, solution-phase chelates (organics), the presence of new solid phases, etc. to see how the system responds.

- Attempt to run adsorption routines only after the more basic system is described and understood.

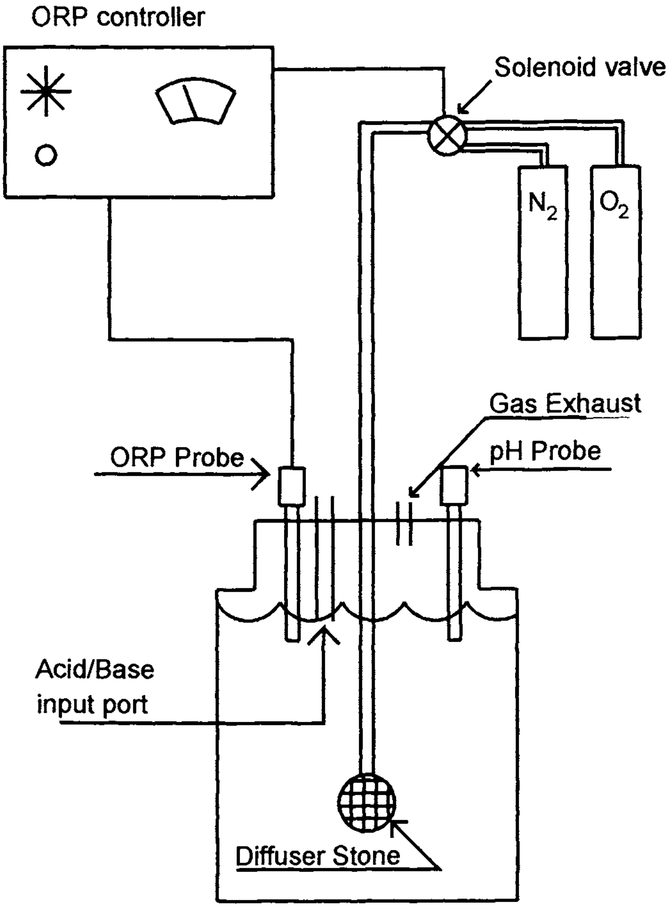
These approaches are demonstrated in the following sections.

15.1.5 Modelling L/S, pH and Redox Control of Leaching

The work of Collins and DiPietro (DiPietro et al., 1990; DiPietro, 1989) evaluated the effects of varying the liquid to solid ratio (L/S), pH and redox potential on leachability on combined bottom ash and boiler ash from a two-stage incinerator.

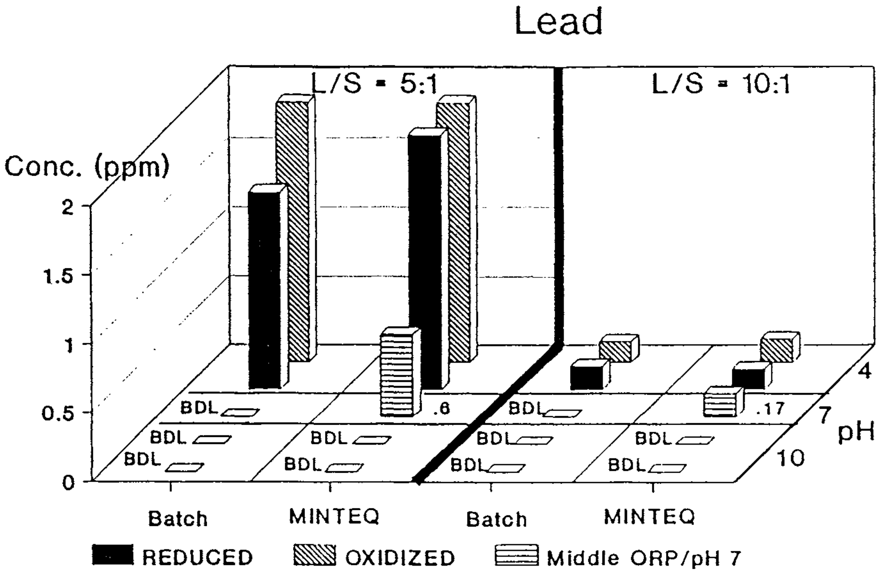
They used the apparatus shown in Figure 15.1 to control redox in an ash/wastewater sludge system at either (i) reducing, intermediate, or oxidising conditions, (ii) pH values of 4, 7, or 10, or (iii) two L/S values of 5 or 10 under presumed equilibrium conditions. The sludge was used to make the matrix slurry initially reducing. The addition of oxygen or nitrogen was used to maintain appropriate redox ranges. After equilibrium was attained (4 to 5 days), leachate samples were collected, filtered and quantified for anions and metal and metalloid elements. The leachate compositional data and system values (pH, redox, ionic strength) were loaded into MINTEQ using PRODEF and the saturated solution approach. After cation/anion balance adjustment, certain phases were allowed to precipitate in equilibria with the solution phase. These predicted precipitates were compared with data on solid phases as determined by X-Ray Powder Diffraction (XRPD). Figure 15.2 shows the results for lead. The data show how at low pH, lead is mobilised. At high L/S, the concentration is decreased, suggesting an extensive solid phase dissolution. Reducing conditions do lower aqueous phase concentrations. The calculated $C_{T,Pb}$ for the solution phase at equilibrium, as predicted by MINTEQA2, was in good agreement with observed data. Data for other elements showed agreements as well. There was not good agreement between the solid phases seen with XRPD and those predicted by MINTEQA2.

Figure 15.1 Apparatus Used for pH and Redox Control



After DiPietro, 1989

Figure 15.2 Lead Leachability as a Function of L/S, pH and Redox



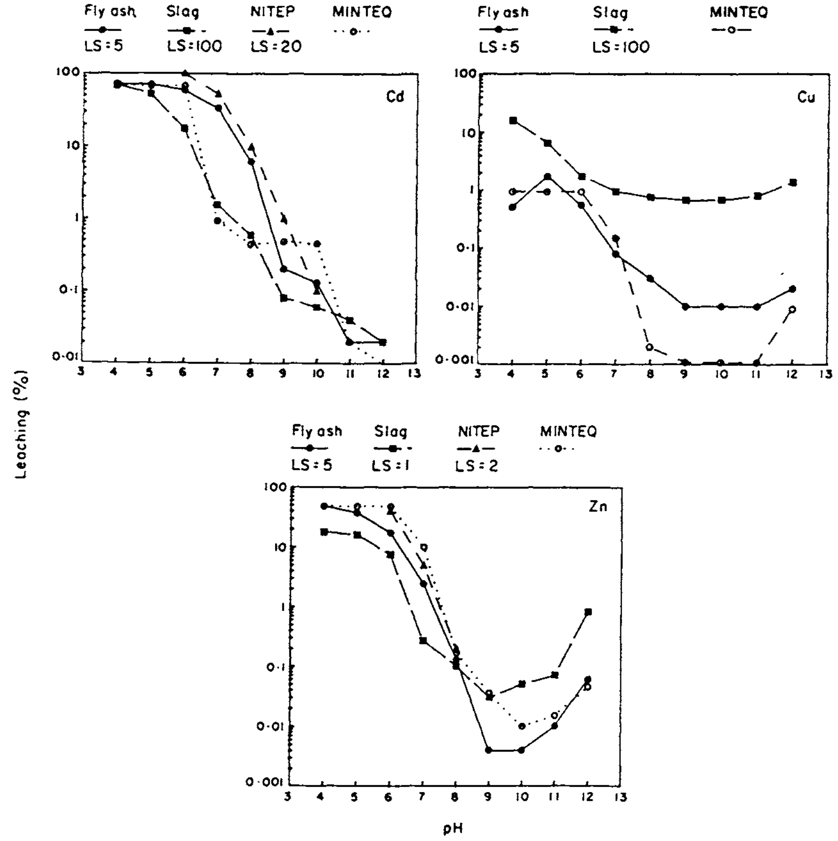
After Dipietro, 1989

15.1.6 Modelling L/S, pH, Redox and Complexation Control of Leaching

Van der Sloot (1990) evaluated the effects of L/S, pH and solution phase complexation for bottom ash and ESP ash from a Dutch mass burn incinerator. Leaching tests based on the Dutch column percolation experiment and the Dutch multiple batch extraction test (NVN 2508) were used to evaluate three L/S ratios: 1, 5 and 100. pH was controlled over the entire pH range using either H_2SO_4 or CaO in the extraction solutions. The effect of aqueous phase chloride complexation was investigated by using a high chloride content fly ash that would presumably leach more chloride into the extraction solution than the bottom ash. The systematic leaching behaviour of cadmium, copper and zinc was investigated. The equilibrium concentration of leachates from the fly ash (L/S = 5) and the bottom ash (L/S = 1 or 100) were input into MINTEQA2 along with other system parameters (final pH, temperature) using the saturated solution approach. The solid phases were not allowed to precipitate in the model.

The results for the leaching of cadmium, copper and zinc are shown in Figure 15.3. The results are presented as mass fractions leached (%) as a function of final leachate pH. In most cases, as discussed in Chapter 13, the presence of significant concentrations of chloride (as a complexing ligand) in the fly ash helped to increase the mass fraction released for cadmium and zinc. MINTEQA2 was able to accurately predict the mass fraction released by successfully modelling significant chloride compiexation of Cd and Zn in the aqueous phase, thus promoting solubilisation. Both Cd and Zn exhibited minimum solubilities associated with hydroxide or carbonate phases.

Figure 15.3 Cd, Cu and Zn Leachability



From van der Sloot, 1990 with permission of Waste Management and Research

Copper, on the other hand, did not exhibit an increased solubilisation in the presence of increased solution phase chloride complexation. The presumed high levels of organic acids in the bottom ash tended to promote solubilisation of copper out of the bottom ash. Copper forms strong complexes with soluble organic carboxylic ligands. MINTEQA2 was less successful in predicting mass fractions released because organic ligand concentrations were not inputted into the modelling run.

15.1.7 Modelling Sorption Reactions Influencing Leaching

Dzombak et al. (1992) evaluated the effects of solution pH and sorption for petroleum sludge fluidised bed fly ashes. The fly ashes were obtained from a venturi wet scrubber. Thus, the residues contained both fly ash and scrubber residues. XRPD was used to verify the presence of amorphous $(FeOH)_3$ and $Al(OH)_3$, SiO_2, Fe_3O_4, $CaCO_3$, $CaSO_4$ and $CaHPO_4$ in the solids.

Leaching tests were conducted under batch-agitated conditions at an L/S of 100. The tests were run for 16 hours. The chemical equilibrium program MINEQL, a prototype to MINTEQA2, was used. The generalised diffuse layer model (DLM), a feature of both source codes, was employed to examine sorption/desorption in addition to precipitation/dissolution and solution phase speciation. The database generated by Dzombak and Morel (1990) for sorption of ions onto hydrous ferric oxide was added to MINEQL. The scrubber solids were considered to be dominated by metal oxides which were modelled as amorphous hydrous ferric oxide. Leachate analytes, solid phase concentrations, ionic strength and activity coefficients were inputted into the model using the solid phase approach. During modelling, solid phase formation was suppressed.

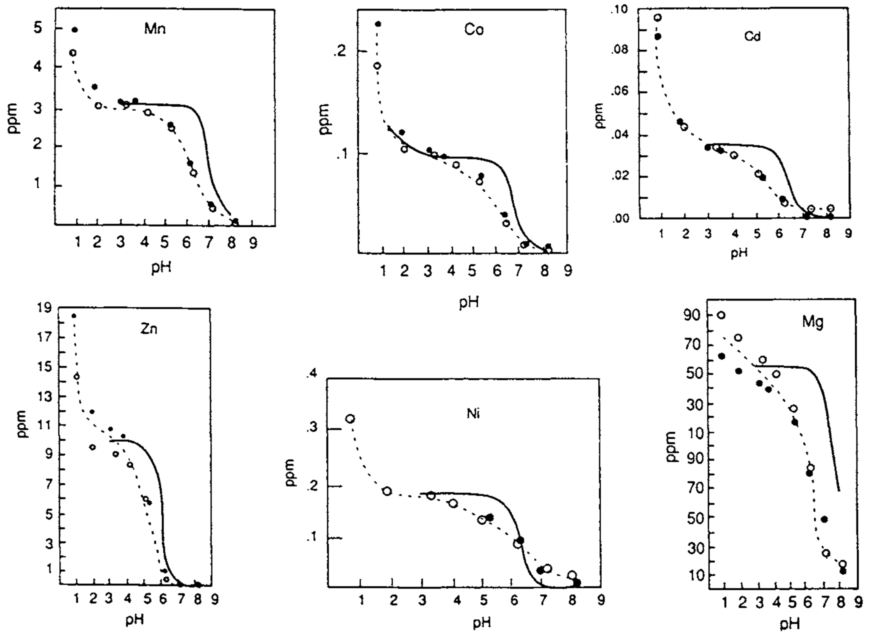
The data for a variety of elements with strong dependence of pH are shown in Figure 15.4. As pH decreases, Mn, Zn, Co, Ni, Cd and Mg exhibit a plateau behaviour consistent with a sorption edge from an oxide surface that occurs near a pH of 3 to 6. For the most part, model predictions for solution phase concentration for Mn, Co, Cd, Zn, Ni and Mg were close to observed values.

The data for a variety of elements with a weak dependence on pH are shown in Figure 15.5. As pH decreases, Pb, Sn, Mo, Sb, Be, Ba and Ag do not exhibit a strong plateau or pH dependency for dissolution. The model was not as successful in predicting behaviour, possibly because of the high carbonate content of the solid phase and the poor binding constant for ion sorption to carbonates.

15.1.8 Modelling Solid Phase Control of Leaching in Conjunction with Solid Phase Speciation Studies

Comans et al. (1993) used MINTEQA2 to model the solid phase control of leaching of bottom ash as a function of pH. A pH stat system was used to control pH between 4 and 13. Three L/S ratios were investigated (2,5,10). A 24-hour equilibration period was used; kinetic studies revealed this was a reasonable time frame. They used a combined solid phase - solution approach to model the solid phase control. They inputted the equilibrated leachate constituents into the model and then tested a variety of minerals to see which mineral produced a solubility plot in agreement with the laboratory data. The solids were introduced as infinite solids in the model.

Figure 15.4 Sorption/Desorption Processes on Ash Surfaces for Elements Exhibiting a Strong pH Dependence

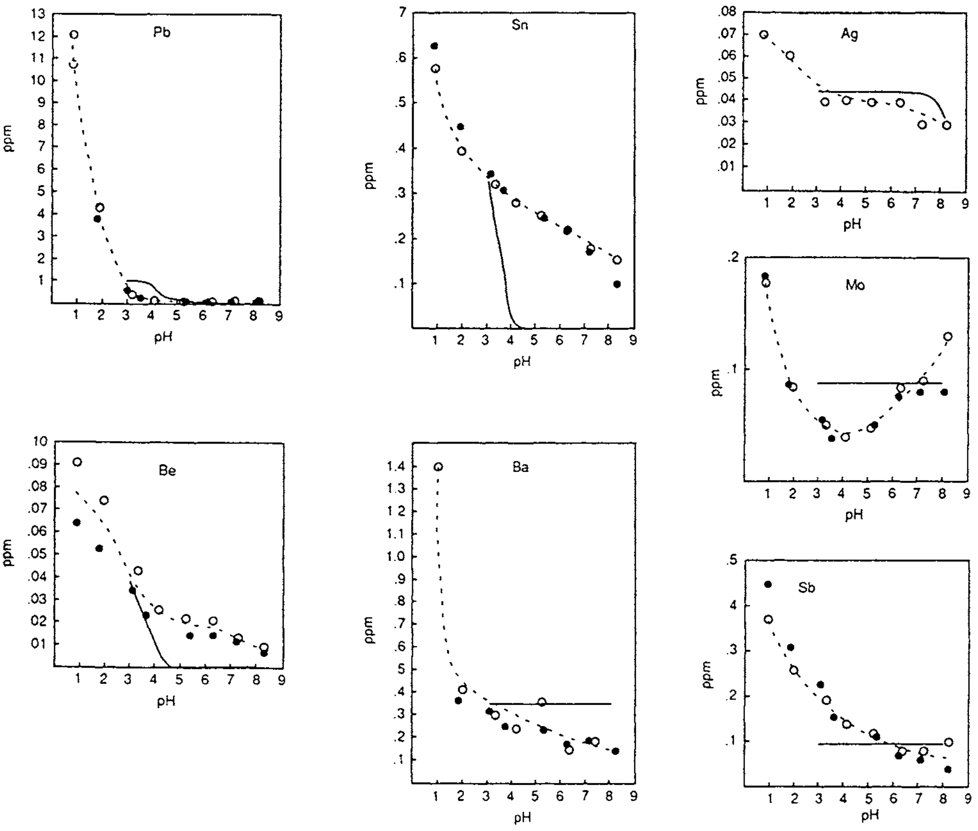


Solid Line = Model-Predicted Distribution
After Dzombak et al., 1992 with permission of author

The data, some of it shown in Figure 15.6, show some solid phases clearly control the pH-dependent leaching behaviour. The controlling solids (e.g. $CaSO_4{\bullet}2H_2O$, $Cd(OH)_2$, ZnO) are typically found in bottom ash.

Eighmy et al. (1993) have utilised a number of spectroscopic and analytical methods to identify solid phases in a variety of ash residues. As part of that study, total availability leaching studies were conducted to allow leaching modelling of these residues with MINTEQA2. One aspect of the study was to use the solid phase approach and to input ESP ash solid phases and their molal concentrations into MINTEQA2 to see if the model would (i) dissolve the soluble phases in the ash, (ii) partially dissolve more insoluble phases in the residue, (iii) keep insoluble those non-dissolving phases, (iv) reprecipitate new phases, and (v) produce a final equilibrium aqueous phase concentration of dissolved constituent close to the actual leaching test data. In effect, MINTEQA2 was asked to predict the observed leaching behaviour of solid phases determined by various spectroscopic methods such as X-ray powder diffraction (XRPD) or X-ray photoelectron spectroscopy (XPS).

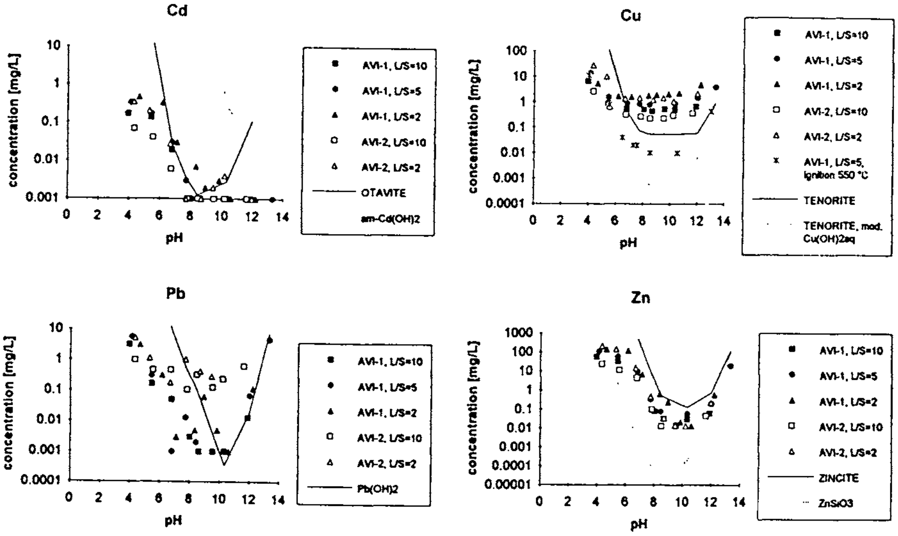
Figure 15.5 Sorption/Desorption Processes on Ash Surfaces for Elements Exhibiting a Weak pH Dependence



Solid Line = Model-Predicted Distribution
After Dzombak et al., 1992 with permission of author

Suspected major mineral phases and their estimated molar concentrations were inputted into MINTEQA2 along with very low concentrations (1 x 10^{-15} molal) of all component species. Table 15.5 shows the inputted information. The databases to MINTEQA2 had to be adjusted to include new phases (K_2ZnCl_4, Cd_5ClAsO_4). Inverse solubility products were calculated from thermodynamic or solubility data for modification of the Thermo.dbs and Type6.dbs databases.

Figure 15.6 Solid Phase Control of Bottom Ash Leaching as a Function of pH



After Comans et al., 1993

Table 15.5
Solid Phase Approach to MINTEQA2 for ESP Ash

Phase	Source	Moles/L[a]
K_2ZnCl_4	XRPD, XPS	3.53 x 10^{-3}
NaCl (Halite)	XRPD, XPS	5.50 x 10^{-3}
$CaAl_2Si_2O_8$ (Anorthite)	XRPD, XPS	6.04 x 10^{-4}
$CaCO_3$ (Calcite)	XPS	3.86 x 10^{-3}
$MgSO_4{\bullet}7H_2O$ (Epsomite)	XRPD, XPS	7.42 x 10^{-4}
$Pb_3O_2SO_4$	XRPD, XPS	4.00 x 10^{-4}
Cd_5ClAsO_4	XRPD, XPS	5.00 x 10^{-6}
$CaSO_4{\bullet}2H_2O$ (Gypsum)	XPS	3.85 x 10^{-3}
$Pb_5(PO_4)_3Cl$ (Chloropyromorphite)	XRPD	8.62 x 10^{-5}
$KAl(SO_4)_2$ (K-Alum)	XRPD, XPS	4.00 x 10^{-4}
$PbSO_4$ (Anglesite)	XPS, XRPD	7.12 x 10^{-4}
ZnO	XPS, XRPD	8.80 x 10^{-4}
$KAlSi_3O_8$ (Microcline)	XRPD, XPS	8.81 x 10^{-4}

[a] Based on stoichiometry and total composition data, the model inputs the total moles of a mineral and assumes a volume of one litre.

After Eighmy et al., 1993

The results of the modelling effort are presented in Table 15.6. Reasonably good agreement was seen between model-predicted equilibrium aqueous phase total concentrations and the analytical data. The lack of perfect agreement most likely reflects the presence of amorphous phases for $CaCO_3$ or $CaSO_4 \bullet 2H_2O$, or solid solutions for aluminosilicates with activities or solubilities that are not amenable to modelling with the present database in MINTEQA2. The solubility of gypsum had to be increased slightly and kaolinite had to be excluded to allow the program to converge to equilibrium. This usually took more than 400 iterations. Gypsum, chloropyromorphite and anglesite were the only finite solids to remain as solids. All the others, including NaCl and K_2ZnCl_4, dissolved in general agreement with XPS and XRPD data. Quartz (SiO_2), diaspore [AlO(OH)] and alunite $[KA1_3(SO_4)_2(OH)_6]$ precipitated out. All six of the solids presented at equilibrium were detected with either XRPD or XPS in the leached ash. The final mass distributions of all solids were close to the insoluble fraction determined for the residue. The final equilibrium pH was close to the experimental value (4.69 vs. 4.00) and the cation-anion differences were virtually balanced (0.04% difference).

Table 15.6

Verification of Solid Phase Approach for ESP Ash

Constituent	Leaching Test Data (mg/L)	MINTEQA2 Output (mg/L)
Al	7.56 ± 1.48	0.02
H_4AsO_4	0.815 ± 0.60	0.72
Ba	0.14 ± 0.01	not inputted
Ca	281.5 ± 3.75	178.7
Cd	4.50 ± 0.05	2.80
Cl	620 ± 0.0	694
Cu	4.92 ± 0.05	not inputted
K	406.5 ± 0.71	271.0
Pb	4.60 ± 0.35	8.35
Mg	18.41 ± 0.49	18.0
H_4SiO_4	107.4 ± 0.15	9.40
SO_4^{2-}	890 ± 10.0	424
Na	117.5 ± 0.1	126.4
Zn	221.7 ± 1.70	230.8

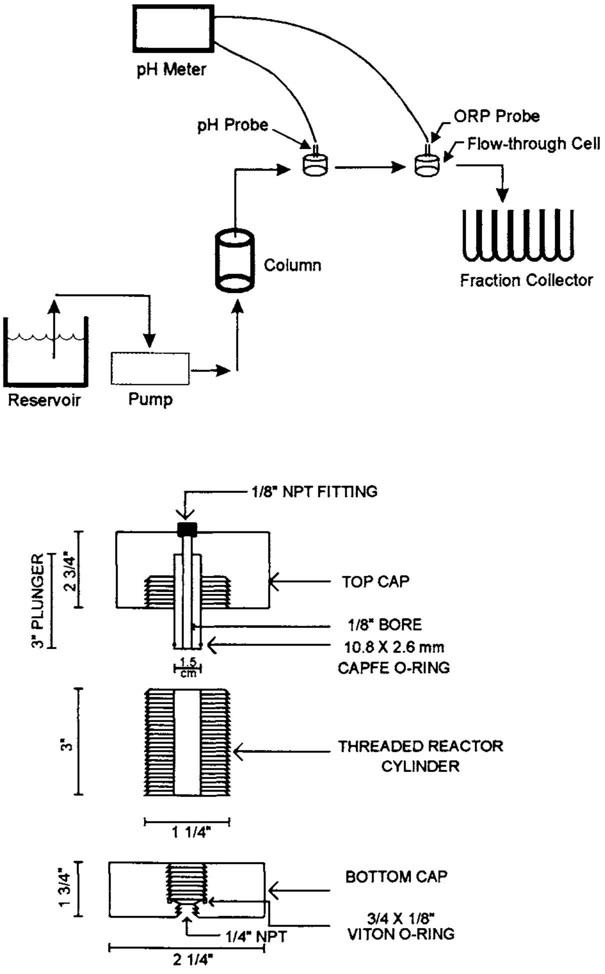
[a] All constituents in aqueous phase were entered at 1×10^{-15}M, except for NO_3^- and H^+ (added at 1.6×10^{-3} M) as acid used to drop pH to 4.0 for the test. Phosphate was also added at low concentration (8.0×10^{-6} M) based on ICAP, SEM/EDS, and STEM/EDS analysis.

After Eighmy et al., 1993

15.1.9 Modelling Solid Phase Control of Leaching in Dynamic Flow-Through Systems

Gardner (1991) and Theis et al. (1992) employed small minicolumns to look at the dissolution of a variety of bottom ashes and fly ashes. A large throughput of leachant through the minicolumn (Figure 15.7) allows for high seepage velocities and high Peclet numbers in the system. The number of pore volumes pumped through the minicolumn was quite high (sometimes more than 1,000).

Figure 15.7 Apparatus Used for Minicolumn Experience



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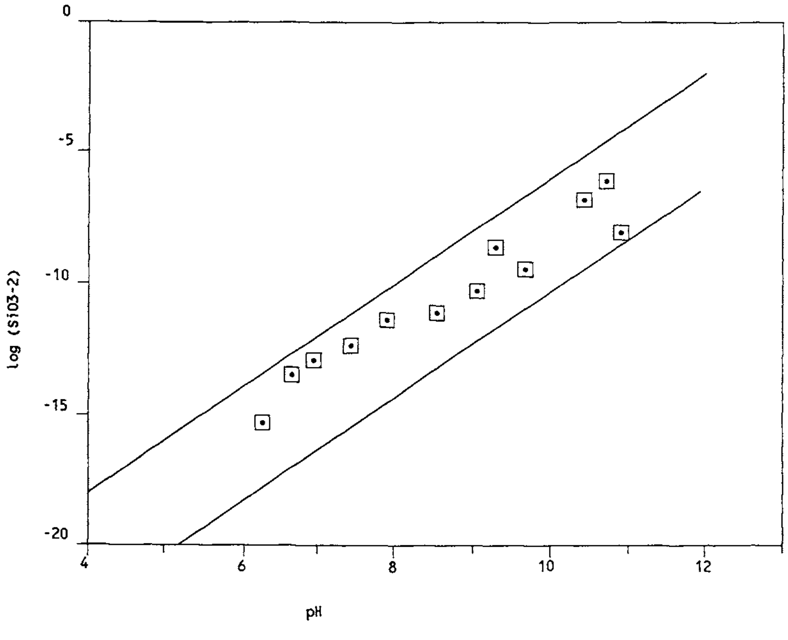
The researchers measured minicolumn effluent pH and Eh. Periodically, effluent leachate samples were quantified for dissolved constituents. The geochemical code HYDRAQL was used to calculate the activities of the dissolved leachate constituents using the saturated solution approach. IAPs could then be calculated and compared to published solubility products.

The data generated for fly ash (Figure 15.8) show the leachate Zn^{2+} and SiO_3^{2-} activity products fall within the region of available solubility products reported in the literature. The utility of the geochemical code in this application was to calculate activities and allow comparison of IAPs to solubility products. In this case, Zn^{2+} solution phase activity and concentration were controlled by $ZnSiO_3$.

Figure 15.8 Log SiO_3^{2-} versus pH as Compared to Theoretical $ZnSiO_3$ Solubility Plots



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15.1.10 Modelling Field Leaching Behaviour

Fruchter et al. (1990) collected pore water samples from a combined bottom ash and fly ash disposal site. Ceramic cup suction lysimeters were used to collect leachates with depth in the disposal mass. The L/S ratio that the ashes were exposed to was considered to be less than one.

The collected pore water leachates were analysed for elements and anions. The analytical concentrations, along with pH, were input into MINTEQA2 using the saturated solution approach so the model could calculate ionic strength, ion speciation, single ion activity coefficients, single ion activities for aqueous solute species, ion activity products and saturation indices for mineral solids. Activity-pH or activity-activity plots were used to identify the solid phases controlling pore water chemistry.

The results for aluminum, iron and calcium are shown in Figure 15.9. For aluminum, both $Al(OH)_3$ (crystalline) and amorphous $Al(OH)_3$ appear to control aluminum activity in the pore water. For iron, amorphous $Fe(OH)_3$ appeared to play a limited role in controlling iron activity in the pore water. For calcium, gypsum rather than anhydride was the controlling phase.

15.2 DYNAMIC MULTICOMPONENT MODELS

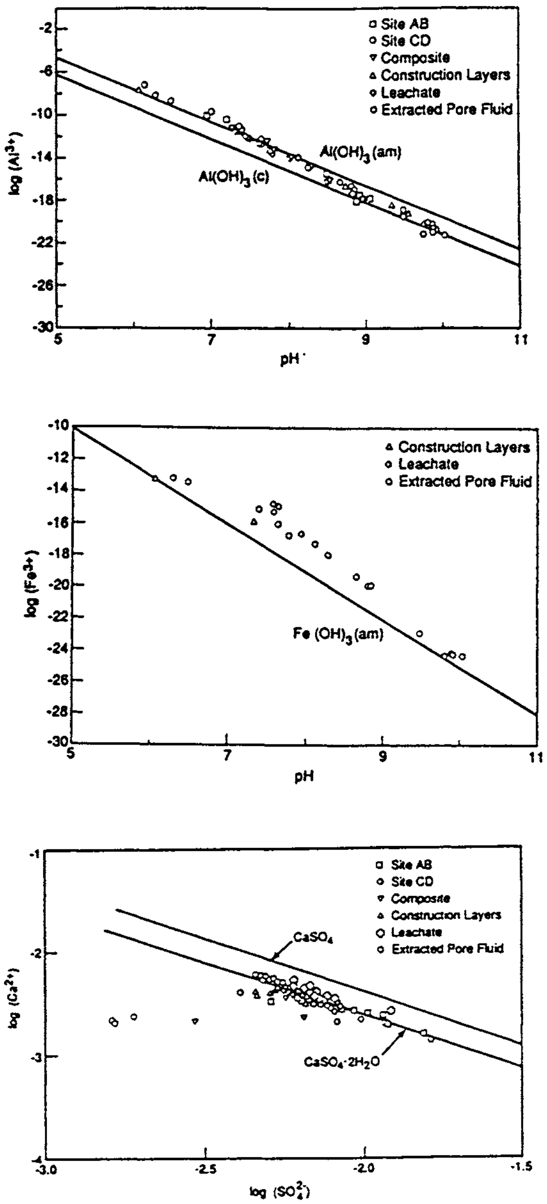
Many of the leaching modelling efforts described in Section 15.2 examine the role of precipitation/dissolution, sorption, and solution phase complexation under discrete conditions of L/S, pH and redox. As such, they mechanistically describe leaching behaviour as "snapshots" within the potential leaching spectrum. Frequently, the leaching tests used to generate data to be input into the model are done under agitated conditions so mass transfer limitations are reduced.

A second generation approach to modelling leaching behaviour has been developed that incorporates, or can incorporate, elements of dissolution, reprecipitation, sorption, desorption and mass transfer phenomena on residues subjected to leaching under realistic seepage velocities. The dynamic multicomponent model developed by Theis and coworkers (Theis et al., 1992) is particularly attractive to this second generation approach because of the mechanistic basis it employs, the ease with which parameter estimation can be used to refine the parameters and the predicative capability the model employs if minicolumn leaching data over sufficiently large L/S ratios are used to challenge the model.

15.2.1 Dynamic Multicomponent Models

Under many field leaching scenarios, a leachant is flowing through and/or around residue material. Accurate modelling requires the coupling of chemical behaviour with transport behaviour. Since field leaching involves both phenomena, a multicomponent model is needed. Transport and chemistry model components ultimately are coupled using source/sink terms of the time- and space-dependent mass balance equations for each chemical component. Simple partitioning coefficients describing dissolution/ reprecipitation and sorption/desorption are used in both the transport and chemistry components of the model (Theis et al., 1992).

Figure 15.9 Solid Phase Control of Al, Fe and Ca in a Field Leaching Scenario



After Fruchter et al., 1990

The minicolumn leaching apparatus forms the basis for developing a dynamic multicomponent model. The device, shown in Figure 15.7, is modelled as a plug flow reactor with non-steady balances on residue components derived in the axial direction of the column (Theis et al., 1992):

$$\underset{\text{(Term 1)}}{\frac{\partial u_i}{\partial t}} + \underset{\text{(Term 2)}}{\sum_{j=1}^{Np} A_{ij} = \frac{\partial P_j}{\partial t}} = \underset{\text{(Term 3)}}{-V\frac{\partial u_i}{\partial x}} + \underset{\text{(Term 4)}}{\frac{\partial C_{si}}{\partial t}\left[\frac{i-\varepsilon}{\varepsilon}\right]} + \underset{\text{(Term 5)}}{\frac{\partial \bar{C}_p}{\partial t}} \qquad (15.1)$$

where

u_i = the total soluble concentration component [i] that is mobile,

P_j = the total concentration of precipitate [j] that is immobile,

C_{si} = the concentration of available component [i] on the ash particle surface,

C_p = the average concentration of component [i] in the interior matrix of the ash particle that can be released by diffusive flux,

t = time,

x = axial distance,

N_p = the number of discrete precipitates in the ash,

N_c = the number of discrete components in the ash,

A_{ij} = the stoichiometry of component [i] in precipitate [j],

ϵ = bed porosity or porosity of the ash particles in the minicolumn, and

v = interstitial or seepage velocity of leachant flow in the column.

The two terms on the left-hand side of equation (15.1) describe the change in mobile constituents (Term 1) and immobile precipitates (Term 2) with respect to time. Term 2 relates to fast dissolution and reprecipitation. The terms on the right-hand side of equation (15.1) describe the change in mobile constituents with respect to axial distance (Term 3), the change in leachable constituents on the surface of the ash particles with respect to time (Term 4) and the change in particle interior constituents with respect to time (Term 5). Terms 4 and 5 relate to sorption/desorption and slow dissolution, respectively.

Mass balance constraints are placed in context with equation (15.1) that constrain mass over the iterative process that is used to provide time and space solutions to equation (15.1). The mass balances are:

$$\frac{\partial C_{si}}{\partial t} = aK_c\,(C_{si} - u_i) \text{ for } i = 1 \text{ to } N_c\text{, and} \qquad (15.2)$$

$$\frac{\partial \bar{C}_p}{\partial t} = \frac{\pi^2 De}{R_p^2}\,(\bar{C}_\pi - u_i) \text{ for } i = 1 \text{ to } N_c \qquad (15.3)$$

where

a = the ash particle specific area (area/volume),

k_c = the mass transfer coefficient,

D_e = the effective diffusion coefficient, and

R_p = the ash particle radius.

Equation (15.2) is a mass balance constraint on constituents leaving or going to the ash particle surface. Equation (15.3) is a mass balance constraint on constituents diffusing out of the ash particle itself.

A chemical mass action constraint is also used to constrain equation (15.1) with regard to reaction stoichiometry as the iterative process is used to provide time and space solutions. The chemical mass action constraint is:

$$K_j^{sO} = \sum_{i=1}^{N_c} [F(u_i, u_2, \ldots, u_{N_C}, A_{ij}] \text{ for } j = 1 \text{ to } N_p \tag{15.4}$$

where

K_j^{sO} = partition coefficient for precipitation/dissolution or sorption/desorption, and

F = mass fractions for components involved in the partition.

Finally, boundary and initial run conditions are needed to start the iterative solution process and further constrain equation (15.1). These conditions are:

$$u_i(x, t=0) = 0 \quad \text{for} \quad i = 1 \text{ to } N_c \tag{15.5}$$

$$v_i(x=0, t) = 0 \quad \text{for} \quad i = 1 \text{ to } N_c \tag{15.6}$$

$$P_j(x, t=0) = 0 \quad \text{for} \quad j = 1 \text{ to } N_p \tag{15.7}$$

$$P_j(x=0, t) = 0 \quad \text{for} \quad j = 1 \text{ to } N_p \tag{15.8}$$

$$C_{si}(x, t=0) = C_{si0} \quad \text{for} \quad i = 1 \text{ to } N_c \tag{15.9}$$

$$\bar{C}_{ri}(x\ t=0) = C_{pi0} \quad \text{for} \quad i = 1 \text{ to } N_c \tag{15.10}$$

$$C_{si0} > \frac{1}{V_s} \int_{o}^{t_1} q \cdot u_{ti} dt \quad \text{for} \quad i = 1 \text{ to } N_c, \text{ and} \tag{15.11}$$

$$C_{pi0} > \frac{1}{V_s} \int_{t_i}^{t_2} q \cdot u_{ti} dt \quad \text{for} \quad i = 1 \text{ to } N_c \tag{15.12}$$

where

u_{ti} = column leaching curve from the minicolumn experiment for component [i],

V_s = the volume of ash in the column, and

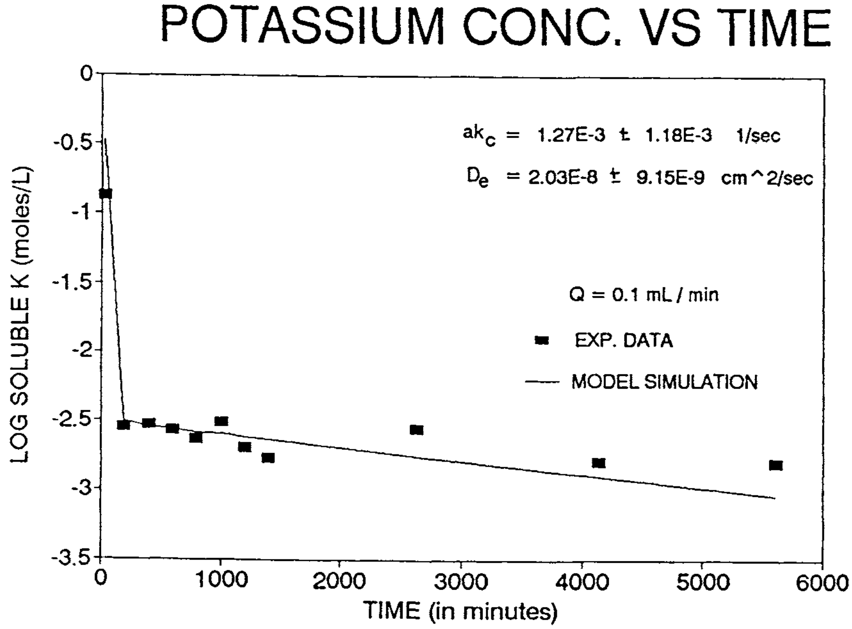
q = the flow rate.

15.2.2 Modelling Solid Phase Dissolution

Theis et al. (1992) used their approach to model minicolumn leaching experiments for a number of MSW incineration residues. Results for a soluble constituent (potassium) from an ESP ash are discussed further.

The data are shown in Figure 15.10. Potassium in the ESP ash is readily soluble, it initially appears in high concentration in the minicolumn leachate and declines precipitously over time without any reprecipitation. The column was operated over 30,000 pore volumes during the one hundred-hour run. The model simulated the observed data quite well.

Figure 15.10 Potassium Leaching and Modelling from Minicolumn Experiments



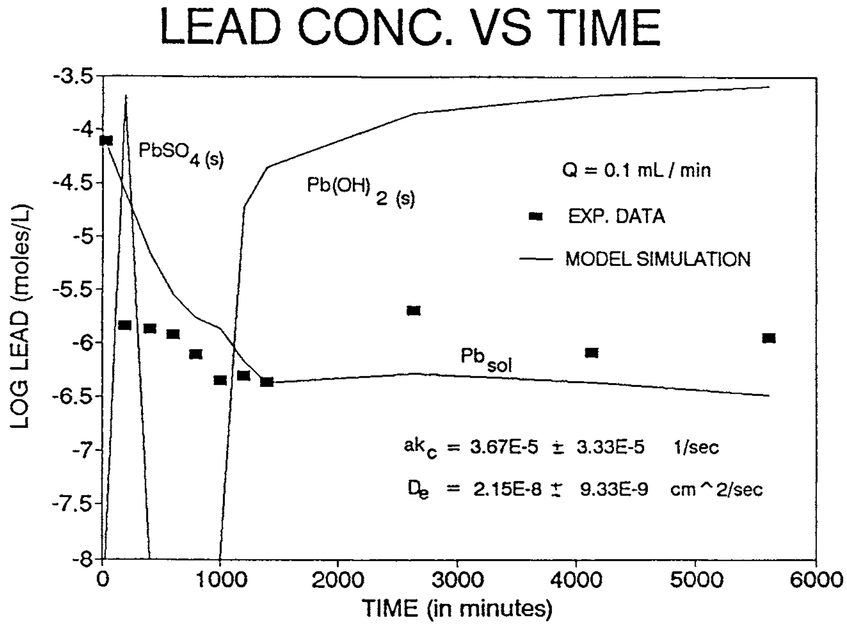
After Theis et al., 1992 with permission of the Air and Waste Management Association

15.2.3 Modelling Solid Phase Reprecipitation and Solubility Control

The data for lead are shown in Figure 15.11. Lead in the ESP ash is less soluble than potassium. It appears in an initially high concentration in the minicolumn leachate and declines over time. The model simulates soluble lead in the leachate quite accurately.

However, in the case of lead, at two different positions in time and space, two solids are predicted to precipitate out and control lead dissolution. The first solid to appear is anglesite ($PbSO_4$) early in the column run. The second, lead hydroxide [$Pb(OH_2)$], controls later in the run. In support of these observations, earlier pC-pH plots of lead data from the column showed aqueous phase lead to be in equilibrium first with anglesite and then with lead hydroxide.

Figure 15.11 Lead Leaching and Modeling from Minicolumn Experiments



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The utility of the Theis model is that (i) many residues can be easily modelled, (ii) the basic tenets of equations 15.1 to 15.3 can be modified to include other partitioning reactions as well as soluble phase partitioning, and (iii) the model can be used to predict behaviour over geologic time (e.g. thousands of years).

15.3 FUTURE DIRECTIONS IN MODELLING

It is likely the next decade will see a better melding of ash solid phase and leaching solution speciation data with both equilibrium and dynamic multicomponent models. The speciation data on ash solids will allow better quantification of initial soluble phases, insoluble phases, geochemically unstable phases, sorptive surface areas and surface adsorption site densities. The speciation data on solution phase ligands will allow for better quantification of binding constants in solution. Improvements in understanding sorption are also expected.

All of these refinements in the knowledge base of ash will allow for more accurate modelling using both approaches. In fact, the dynamic multicomponent approach can be modified to include more components that exhibit equilibrium-like behaviour in the context of dynamic leaching. The multicomponent model is likely to be used for more predictive capabilities under various geochemical scenarios with ash management, treatment or disposal.

Recent developments by EPRI have resulted in the creation of a dynamic-empirical leaching code for fossil fuel waste leaching, denoted as FOWL (Hoestetler et al., 1988). FOWL uses empirical observations on solubilisation as a function of pH as well as estimates of total available fractions to predict leachates generated from geometrically-defined ash masses. Additionally, the geochemical code ECHEM, a modification of the original MINTEQ, is the basis of a coupled leaching-hydrologic transport-geochemical reaction dynamic multicomponent model termed FASTCHEM (Morrey, 1988). ECHEM also contains dissolution kinetic rate constants for a number of relatively insoluble minerals. The approaches used in these two EPRI efforts are excellent bases for developing similar approaches with MSW residues. Finally, Batchelor and Wu (1993) have made extensive modifications to MINTEQA2 to model leaching from monolithic material. Their model, SOLTEQ, incorporates Pitzer-based activity coefficients and cement chemistries.

REFERENCES

Allison, J.D., D.S. Brown and K.J. Novo-Gradac. MINTEQA2/PRODEFA2, A Geochemical Assessment Model for Environmental Systems: Version 3.0 User's Manual. Environmental Research Laboratory, U.S. EPA, Athens, GA, 1990.

Ball, J.W., E.A. Jenne and M.W. Cantrell. WATEQ3: A Geochemical Model with Uranium Added. U.S.G.S. 81-1183, U.S. Geological Survey, Menlo Park, CA, 1981.

Batchelor, B. and K. Wu. Effects of Equilibrium Chemistry on Leaching of Contaminants from Solidified/Stabilized Wastes. In Chemistry and Microstructure of Solidified Waste Forms. Edited by R.D. Spence. Lewis Publications, Boca Raton, FL, 1993.

Comans, R.N.J., H.A. van der Sloot and P.A. Bonouvrie. Geochemical Reactions Controlling the Solubility of Major and Trace Elements During Leaching of Municipal Solid Waste Incinerator Residues. Proceedings of the 1993 International Conference on Municipal Waste Combustion, March 30-April 2, Williamsburg, VA. Edited by J. Kilgroe. AWMA, Pittsburgh, PA, 1993.

DiPietro, J.V. Municipal Solid Waste Combustion Residue Leachate Composition: The effect of Selected Environmental Parameters and an Assessment of Geochemical Modelling Predictions. Masters Thesis, University of New Hampshire, Durham, NH, 1989.

DiPietro, J.V., M.R. Collins, M. Guay and T.T. Eighmy. Evaluation of pH and Oxidation-Reduction Potential on Leachability of Municipal Solid Waste Incineration Residues. Proceedings of the International Conference on Municipal Waste Combustion, April 11-14, Hollywood, FL, 2B, p. 21, 1990.

Dzombak, D.A. and F.M.M. Morel. Surface Complexation Modeling, J. Wiley and Sons, N.Y., 1990

Dzombak, D., F. Morel, J. Mundt, E. Hirschberg and G. Huff. Modelling the Leaching of Metals from Hazardous Waste Incineration Ash. Proceedings of the 1992 Incineration Conference, May 11-15, Albuquerque, NM, 1992.

Eighmy, T.T., D. Domingo, J.R. Krzanowski, D. Stämpfli and D. Eusden . The Speciation of Elements in Incineration Residues. In Proceedings of the 1993 Municipal Waste Combustion Conference, March 30 - April 2, Williamsburg, VA. Edited by J. Kilgore. AWMA, Pittsburgh, PA, 1993.

Erikkson, G.A. An Algorithm for the Computation of Aqueous Multicomponent Multiphase Equilibria. Anal. Chem. Acta 112, pp. 375-383, 1979.

Felmy, A.R., D.C. Girvin and E.A. Jenne. MINTEQ-A Computer Program for Calculating Aqueous Geochemical Equilibria. EPA-600/3-84-032, U.S. EPA, Athens GA. NTIS, Washington, DC, 1984.

Fruchter, J.S., D. Rai and J.M. Zachara. Identification of Solubility-Controlling Solid Phases in a Large Fly Ash Field Lysimeter. Environ. Sci. Technol. 24, pp. 1173-1179, 1990.

Gardner, K.H. Characterization of Leachates from Municipal Incinerator Ash Materials. Masters Thesis, Clarkson University, Pottsdam, NY, 1991.

Hoestetler, C.J., R.L. Erickson and D. Rai. The Fossil Fuel Combustion Waste Leaching (FOWL™) Code: Version 1, User's Manual. EPRI EA-5742-CCM, EPRI, Palo Alto, CA, 1988.

Ingle, S.E., M.D. Schuldt and D.W. Shults. A User's guide for REDEQL.EPA. A Computer Program for Chemical Equilibria in Aqueous Systems. EPA 600/3-78-024, U.S. EPA, Corvallis, OR. NTIS, Washington, DC, 1978.

Kincaid, C.T., J.R. Morrey and J.E. Rogers. Geohydrochemical Models of Solute Migration, Volume 1: Process Description and Computer Code Selection. EPRI EA-3417, EPRI, Palo Alto, CA, 1984.

Kincaid, C.T. and J.R. Morrey. Geohydrochemical Models of Solute Migration, Volume 2: Preliminary Evaluation of Selected Computer Codes. EPRI EA-3417, EPRI, Palo Alto, CA, 1984.

Krupka, K.M., R.L. Erikson, S.V. Mattigod, J.A. Schramke, and C.E. Cowan. Thermochemical Data Use the FASTCHEM Package. EPRI EA-5872, EPRI, Palo Alto, CA, 1988.

Morrey, J.R., C.T. Kincaid and C.J. Hoestefler. Geohydrochemical Models for Solute Migration, Vol. 3: Evaluation of Selected Computer Codes. EPRI EA-3417, EPRI, Palo Alto, CA, 1986.

Morrey, J.R. FASTCHEM™ Package Volume 4: User's Guide to the ECHEM Equilibrium Geochemistry Code. EPRI EA-5870-CCM, EPRI, Palo Alto, CA, 1988.

Nordstrom, D.K. and J.W. Ball. Chemical Models, Computer Programs and Metal Complexation in Natural Waters. Edited by C.J.M. Kramer and J.C. Duinker. Martinus Nijhoff/Dr. J.W. Junk Publishing Co., Dordrecht, The Netherlands, 1984.

Perkins, E.H., Y.K. Kharaka, W.D. Gunter and J.D. DeBraal. Geochemical Modelling of Water-Rock Interactions Using SOLMINEQ.88. Chemical Modelling of Aqueous Systems II. Edited by D.L. Melchior and R.L. Bassett. ACS, Washington, DC, 1990.

Rai, D. and J.M. Zachara. Chemical Attenuation Rates, Coefficients and Constants in Leachate Migration Volume 1: A Critical Review. EPRI EA-3356, EPRI, Palo Alto, CA, 1984.

Theis, T.L., R. Iyer and K.H. Gardner. Dynamic Evaluation of Municipal Solid Waste Ash Leachate. Emerging Technologies for Hazardous Waste Management. Edited by D.W. Tedder. American Chemical Society, Washington, DC, 1992.

van der Sloot, H.A., Leaching Behavior of Waste and Stabilized Waste Materials; Characterization for Environmental Assessment Purposes, Waste Man. Res., **8**, pp. 215-228, 1990.

Westall, J.C., J.C. Zachary and F.M. Morel. MINEQL: A Computer Program for the Calculation of Chemical Equilibrium Composition of Aqueous Systems. MIT Tech. Note 18, MIT, Cambridge, MA, 1976.