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Waste Materials in Construction: Putting Theory into Practice

A GENERALISED MODEL FOR THE ASSESSMENT OF LONG-TERM LEACHING IN COMBUSTION RESIDUE LANDFILLS

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Summary

A generalised solid waste leaching model (GSWLM) has been developed which may be used to simulate the changes in leachate chemistry which occur in a waste landfill over long periods of time without considering detailed weathering processes. The model simulates the reactive properties of the waste and how these change in time as the pH- and redox-buffering capacities of the waste are exhausted. Reactions that control the solubility of heavy metals may be included in the reaction and transport model to ascertain the mobility of heavy metals and thus leachate pollution loads as a function of time. The model is intended to be simple and flexible enough that it can be adapted to different waste types with relative ease. A particular advantage of the model is that it can use data from rather simple experiments such as pH and redox titrations.

1.0 Introduction and Background

Pollution of groundwater by contaminants released from hazardous wastes is a serious and growing problem. The prediction of the long-term leaching behaviour of combustion residues is thus becoming an increasingly important issue as awareness grows of the future pollution risks associated with landfills of such wastes. It is not entirely clear if landfill effluent concentrations of heavy metals decrease over time or whether they may be very low for a long time and then increase dramatically when the pH- and redox-buffering capacities of the waste are exhausted. Such a sudden increase in leachate concentration is the scenario for what is commonly referred to as a chemical time bomb.

Hydrogeochemical modelling may be used to provide an answer to this question as phenomena that can be observed in the laboratory or in the field are, for all practical purposes, instantaneous from a geological time perspective. This paper deals with a methodology that may be used to gain valuable insights into long-term leaching processes and ascertain whether chemical time bombs are likely to occur.

A waste landfill containing ash from municipal solid waste incineration (MSWI) may be thought of as a large chemical reactor. Carbon dioxide, oxygen, and acidic rainwater slowly infiltrate the landfill and react with the waste. Soluble products from these reactions are transported downstream with the water. Further down in the landfill, these soluble species may precipitate as new, secondary minerals, or they may take part in additional reactions. After a long time, the waste near the surface of the landfill will be exhausted with respect to its pH- and redox-buffering capacity, and be depleted of its readily soluble constituents. Downstream along the fluid flowpath there may still be an unreacted buffering capacity. When the leachant passes from a depleted zone to an unreacted zone, the chemistry of the leachant may alter considerably.

The region separating these zones is often referred to as a reaction front. These reaction fronts move slowly through the waste as the buffering capacity is used up in an on-going process. At the reaction front, the composition of the leachant may change very suddenly. At a pH-front, for example, the pH of the leachant can change from acidic to alkaline over a short distance. Upstream of the pH-front, the buffering capacity of the waste is exhausted, whilst downstream there remains unreacted buffering capacity. This process is illustrated schematically in figure 1, below:

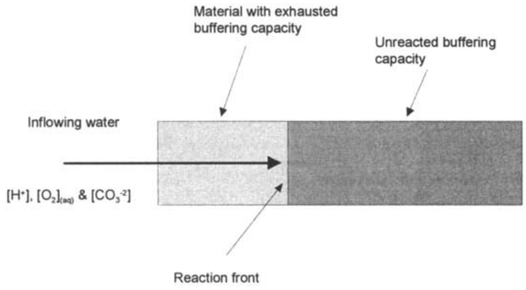

Figure 1. **Schematic diagram of a reaction front**

The width of the reaction front depends upon reaction rates, dispersion, and the effects of diffusion. If we assume that chemical reactions are fast and advective flow dominates, the reaction fronts may appear razor sharp. If, on the other hand, there is a lot of dispersion, the reaction fronts may be very diffuse and the chemistry of the leachant will vary more gradually from zone to zone.

There may be a number of different constituents in the waste which buffer the leachant at different pH levels. Minerals that buffer at high pH values (e.g., CaO) are generally exhausted before those that buffer at lower pH values (e.g., Kaolinite). There may be a number of different pH reaction fronts along a flowpath where different minerals control pH-buffering. If the leachant flow is dominated by advective transport and there is little dispersion, the pH-profile will vary in a stepwise fashion along the flowpath.

Similar reaction fronts may also be seen for redox processes. The concentration of dissolved oxidant in the leachant (generally oxygen in natural systems) may thus be seen to decrease significantly downstream from a redox front. Many oxidation reactions (e.g. oxidation of residual organic or sulphide materials) generate acidity.

Depending upon the amount and type of reducing material initially present, acidity-generating redox reactions may consume the pH-buffering capacity of the waste rapidly if gaseous diffusion of oxygen is a dominating transport mechanism. If the landfill is saturated and there is very little gaseous diffusion, the solubility of oxygen in the infiltrating leachant and the flowrate of the leachant will limit the amount of acidity which is generated.

The mobility of heavy metals is dependent upon a number of controlling variables that determine their solubility. The pH and the redox state of the leachant, as well as the concentration of complexing agents (both organic and inorganic) are arguably the most important of these. Sorption of metal ions to oxides and humic material is important, but this is a process that tends to retard leaching. A model that does not include sorption processes will thus give a worst case scenario for leaching (i.e. where there are no retardation processes).

It has been observed that binding of metal ions to colloidal material (having essentially the same binding properties as the solid phase) may be a very important mechanism for transport of contaminants (McCarthy *et al.*, 1989). Colloidal materials are typically suspended particles of less than 2μm diameter. Colloids may be inorganic substances (e.g. clay particles), organic humic substances, or even bacteria.

Techniques developed for geological systems can be used to simulate the geochemical evolution of a waste repository, provided that the mechanisms of leaching are understood in sufficient detail. This type of modelling is valuable as it allows us to evaluate scenarios and anticipate leaching processes that may be impossible to observe in the laboratory or in the field due to the long time-scales involved.

2.0 Methodology

Complex geochemical models require very detailed knowledge about the mineralogy and reactive properties of the waste material. Combustion residue-type wastes are notoriously difficult to characterise owing to the different origins of the waste and variations in the combustion processes used to make them. Moreover, a large proportion of the waste (Yan, 1995) may consist of glass phases that have poorly defined compositional and reactive properties. Dissolution of these glass phases over time gives rise to secondary minerals in a process, which is similar to clay formation in nature (Zevenbergen, 1995).

Because of the chemical complexity of combustion residues, the emphasis is upon simple methods that rely on relatively uncomplicated laboratory experiments to obtain input parameters. By examining the fluxes of only the most important reactants and buffering constituents, it is possible to construct a simple mechanistic model for the leaching system.

The generalised solid waste leaching model (GSWLM) uses hypothetical minerals to describe the reactive properties of the waste (Crawford, 1996). A simple version of this model that has been used to simulate the reactive properties of MSWI reasonably closely is one that contains three pH-buffering minerals and one redox-buffering mineral. The generalised pH- and redox-buffering reactions are:

$$AOH_{(s)} + H^+ \Leftrightarrow A^+ + H_2O \qquad (1)$$

$$BOH_{(s)} + H^+ \Leftrightarrow B^+ + H_2O \qquad (2)$$

$$COH_{(s)} + H^+ \Leftrightarrow C^+ + H_2O \qquad (3)$$

$$R_{(s)} + O_2 \Leftrightarrow CO_3^{-2} + 2H^+ \qquad (4)$$

In addition to the mineral reactions, there are also three aqueous reactions accounted for in this simple model:

$$CO_3^{-2} + H^+ \Leftrightarrow HCO_3^- \qquad (5)$$

$$CO_3^{-2} + 2H^+ \Leftrightarrow H_2CO_3 \qquad (6)$$

$$H_2O \Leftrightarrow H^+ + OH^- \qquad (7)$$

The quantities and thermodynamic constants for the pH-buffering reactions may be obtained by fitting a numerical titration of the generalised model to an experimental pH titration curve. Figure 2 shows the experimental pH titration characteristic and the generalised pH-buffering model (optimised in the least-squares sense) for a typical bottom ash from municipal solid waste incineration (MSWI BA):

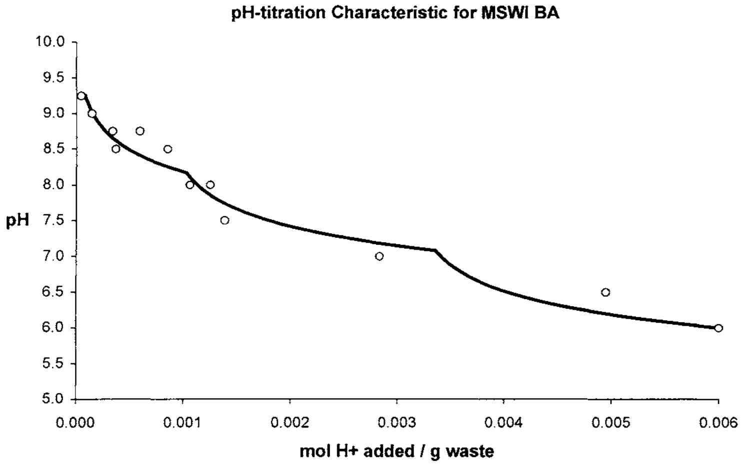

Figure 2. **Acid Neutralising Capacity of a typical MSWI BA**

In figure 2, experimentally determined data (from pH-static experiments) are given as scattered points and the solid line corresponds to the simulated generalised model. The MSWI BA used in this investigation comes from a waste incineration plant located in Linköping, Sweden. This bottom ash has been used as a "benchmark" waste for a number of projects in a collaborative effort between the Swedish Geotechnical Institute in Linköping, and the Royal Institute of Technology in Stockholm, Sweden.

As there are few experimental points and some spread in the data for this titration characteristic, there may be a number of different parameter combinations that fit the batch data almost equally well. It has been found that these sub-optimal parameter combinations exhibit roughly the same characteristics when a flow-through system is simulated. This uncertainty seems to only have a minor influence on the observed leaching behaviour.

The partial pressure of oxygen in reducing wastes, sediments, or groundwater is generally very low if there is little diffusive transport (gaseous diffusion) of oxygen into the system. Under reducing conditions, the partial pressure of oxygen (P_{O2}) may be as low as 10^{-30} - 10^{-70} atm. For a redox buffer mass balance, however, it makes little difference whether the equilibrium partial pressure is 10^{-30} atm or 10^{-70} atm. The equilibrium partial pressure of oxygen in the pore water may influence the solubility of heavy metals present in trace quantities in the waste, but it will not influence the rate of redox buffer exhaustion.

For all practical purposes, the oxygen concentration in the pore water may be considered as zero and the rate of redox buffer exhaustion is equal to the rate of oxygen transport into the waste. For this reason, the equilibrium constant for the redox-buffering reaction is set to give an arbitrarily low equilibrium P_{O2}, and we consider only the total reducing capacity of the waste in the mass balance.

It is difficult to directly measure the reducing capacity of a combustion residue waste material as would exist in a landfill-leaching environment. Oxygen is an impractical reagent to work with as it has relatively slow reaction kinetics and is a major atmospheric constituent. In a method originally proposed by Van der Sloot (1993), and further developed by Dziwniel *et al.* (1996), Ce(IV) is used as an oxidant. In this method, an excess of acidified Ce(IV) is added to a slurry of the waste material. After the waste has been allowed to equilibrate with the solution, the supernatant fluid is filtered and the amount of remaining Ce(IV) oxidant is determined by potentiometric titration with an Fe(II) reductant. Simple arithmetic then gives the reducing capacity of the waste as the difference between the amount of oxidant initially added to the waste, and the amount remaining after reaction (determined by titration). Ce(IV) was chosen as its oxidisting potential lies closer to that for oxygen than stronger oxidising agents such as permanganate ion (MnO_4^-), for example.

The reducing capacity of the MSWI BA was estimated to be 1.22 equivalent moles O_2/kg of waste when Ce(IV) was used as an oxidant. When MnO_4^- was used as an oxidant, the measured reducing capacity was 2.75 equivalent moles O_2/kg of waste. The stronger MnO_4^- oxidant thus gives an estimate which is 2.26 times that estimated by oxidation with Ce(IV). This result shows clearly, the importance of choosing an appropriate oxidising reagent when measuring the redox-buffering capacity of the waste material.

The loss on ignition (LOI) for this waste material at 550°C is roughly 4.3% by mass. We may write the empirical formula of the organic content as n-CH_2O, if we assume the average composition of possible organic phases in the waste. If we also assume that the loss on ignition is due solely to pyrolysis of organics, there is a reducing capacity of approximately 1.43 equivalent moles O_2/kg of waste. Considering that a proportion of the organic material may be refractory (non-oxidisable) under landfilling conditions, the assumed organic content correlates well with the reducing capacity as measured by oxidation with Ce(IV).

It is actually uncertain, how much of the measured reducing capacity is organic, and how much is due to oxidation of metallic Fe, or Fe(II) compounds present initially in the waste. Organic material, however, has a much greater capacity for oxidative generation of acidity than the Fe compounds which are likely to exist in the waste. For this reason, assuming that the reducing capacity is largely organic gives a worst case scenario for acidity generation in the model.

3.0 Coupled Transport and Reaction Simulation Results

The generalised model describing the reactive properties of the waste was simulated using the CHEMFRONTS advective transport and reaction simulation program (Bäverman, 1993). This program was designed to simulate flow-through systems where there is negligible dispersion or diffusion. The program has the ability to simulate the kinetic dissolution of minerals, but owing to the absence of appropriate kinetic data for the waste reactions, local equilibrium has been assumed for the simulations.

It was considered important that the influence of a gaseous phase in the waste be investigated as this may have a significant influence upon the leaching characteristics of the waste when diffusion is the dominating mechanism for transport of O_2 and CO_2. As the program cannot simulate diffusional processes directly, a method first adopted by Strömberg *et al.* (1995) was employed in order to simulate a constant gaseous partial pressure in the landfill. The equilibrium constants for the reactions were chosen so that the P_{CO2} and P_{O2} would correspond to the normal atmospheric partial pressures of these gases.

Two cases have been investigated: a saturated landfill scenario, and a partially saturated scenario (P_{O2}= 0.21 atm, and P_{CO2}= $10^{-3.5}$ atm). As a case study, certain assumptions were made concerning the pH of leachant entering the system, as well as its infiltration rate. Because the local equilibrium assumption has been used in these simulations, the results can be scaled to arbitrary landfill depth and leachant flux. The leaching parameters assumed for the coupled reaction and transport simulation are summarised in table 1:

Table 1. **Leaching parameters assumed for coupled reaction and transport simulation**

Parameter	Value
Incoming leachant pH	5.5
Leachant dissolved O_2 concentration	10 mg/l
Waste depth	1 m
Leachant flux	0.1 m^3/m^2year

In addition to the generalised mineral reactions, a number of reactions describing the solubility of lead (Pb) were included in the simulation model. The Pb solubility model was kept relatively simple and the influence of organic complexation, or colloid binding has not been considered. The following aqueous species were assumed to exist for dissolved Pb: $PbCO_3$, $Pb(CO_3)_2^{-2}$, $PbHCO_3^{+}$, $PbOH^{+}$, $Pb(OH)_2$, $Pb(OH)_3^{-}$, Pb_2OH^{+3}, $Pb_3(OH)_4^{+2}$, $Pb(OH)_4^{-2}$, $PbSO_4$, $Pb(SO_4)_2^{-2}$. The possible solubility-controlling minerals for Pb were presumed to most likely be: $PbCO_3$ (Cerrusite), PbO (Litharge), PbO_2 (Plattnerite), $Pb(OH)_2$, $PbSO_4$ (Anglesite), and PbS (Galena). The thermodynamic constants for these reactions were obtained from the MINTEQA2 database (Allison *et al.*, 1991). Figure 3 shows the effluent pH, and the concentration of Pb and dissolved oxygen as a function of time for a saturated landfill as predicted by the 1-dimensional coupled reaction and transport model:

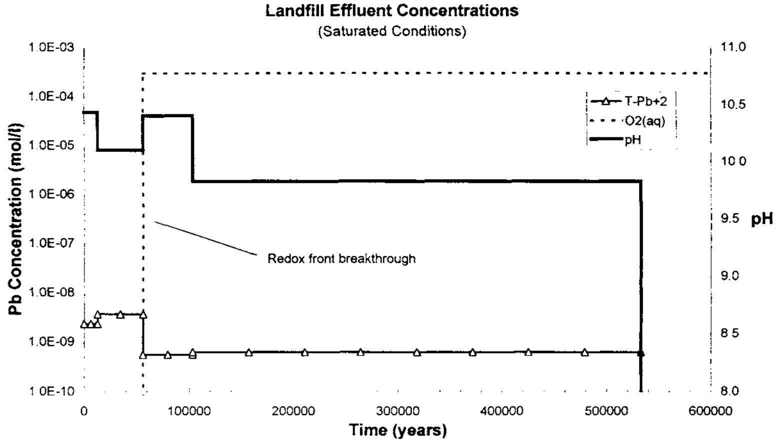

Figure 3. **Leaching of Pb in a flow-through system under saturated conditions**

Figure 4 shows the effluent pH, and the concentration of Pb and dissolved oxygen as a function of time for a partially saturated landfill as predicted by the 1-dimensional coupled reaction and transport model:

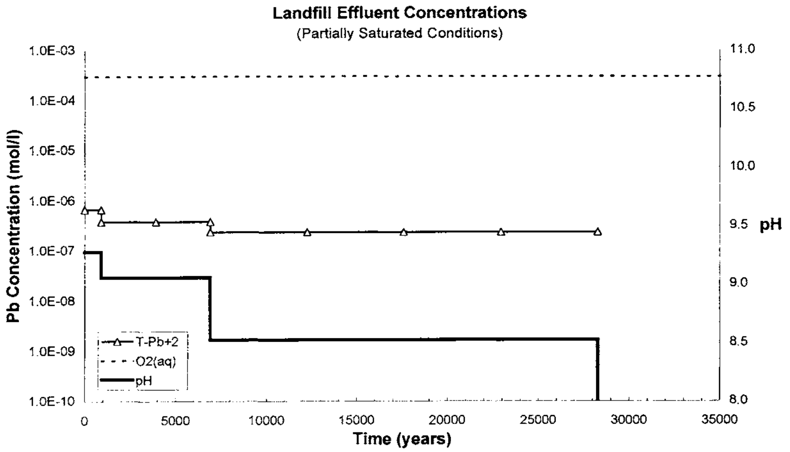

Figure 4. **Leaching of Pb in a flow-through system under partially saturated conditions**

Because we have assumed local equilibrium and neglected dispersion, the breakthrough characteristics shown in figures 3 and 4 appear rectangular. In reality, the concentration fronts can appear much more gradually in the leachate than what these diagrams may suggest. In spite of this, however, the results should be roughly the same for the depletion time of the pH and redox-buffering capacity in the waste material.

4.0 Discussion

As may be seen from the results, the pH-buffering capacity in the partially saturated case is depleted roughly 20 times faster than in the saturated case. The equilibrium pH levels are also noticeably lower under partially saturated conditions. This is due to aqueous dissolution of atmospheric CO_2, which is a source of protons in the pH-buffer mass balance.

When there is a constant partial pressure of CO_2 and O_2 in the waste (as in the partially saturated case), the organic redox buffer has no influence on the proton mass balance as the dissolved concentration of carbonate is determined by the P_{CO2}. When the landfill is water saturated, however, acidity generated by the redox reaction influences both the effluent pH and the rate of pH buffer depletion. This explains why the effluent pH increases slightly after the redox-buffering capacity is exhausted in figure 3.

Another feature of interest, which is revealed in the coupled reaction and transport simulations, is that the pH-buffering minerals take proportionately longer to deplete at lower pH levels. As may be seen from the discontinuities in the simulated pH-titration curve (figure 3), the three generalised pH-buffering minerals are present in roughly equal quantities. The breakthrough times for the pH-reaction fronts, however, differ significantly when the waste is leached in a flow-through system.

The rate of pH-buffer depletion is related to the difference in the total proton concentration entering and leaving the system. At high pH levels, the dissociation of water to form hydroxyl ion (OH^-) is a source term in the proton mass balance and the pH-buffer is thus exhausted at a faster rate than would occur at a lower pH-buffering level. This also means that a pH-buffering mineral, which buffers at the same pH as the infiltrating leachant, will (in principle) never be exhausted.

In both leaching scenarios, the concentration of dissolved Pb generally decreases over time. In the saturated case, the solubility controlling mineral for Pb was found to be $Pb(OH)_2$ under reducing conditions and PbO_2 (Plattnerite) when the redox-buffering capacity was depleted. As may be seen from figure 3, the Pb solubility is actually higher under reducing conditions when $Pb(OH)_2$ is controlling. In the partially saturated case, the solubility-controlling mineral for Pb was found to be PbO_2 over the entire leaching time. At no point was PbS_2 found to be solubility controlling, even though the equilibrium P_{O2} was roughly 10^{-60} atm under reducing conditions.

The predicted Pb concentrations are higher under partially saturated conditions than for saturated conditions. This is largely due to the increased carbonate (CO_3^{-2}) complexation that occurs under partially saturated conditions. Neither chloride (Cl^-), nor sulphate (SO_4^{-2}) complexation was found to influence the Pb solubility appreciably over the pH ranges encountered in the simulations.

5.0 Conclusions

The results obtained from the coupled reaction and transport modelling seem to indicate that a chemical time bomb for Pb does not exist. Outside of the range of pH buffering, which was examined in the model (i.e. beyond the experimental pH-titration end point), it is not possible to say with absolute certainty how the Pb leaching may change. As the depletion time for pH-buffering minerals increases with decreasing pH, however, it is likely that any eventual increase in leachate Pb concentration will be very gradual.

The solubility model, which was used in the simulations, may over predict the aqueous concentrations of Pb as precipitation with phosphate (PO_4^{-2}) has been neglected. On the other hand, transport of colloidal Pb may be a very important mechanism and the total Pb pollutant loads may actually be higher than those predicted by the model, which gives only the dissolved Pb concentrations.

The amount of colloidal Pb in the leachate will depend upon filtering processes in the landfill, as well as in the underlying aquifer. Notwithstanding this, however, the amount of Pb transported as colloidal material is not likely to increase dramatically after the depletion of the pH- and redox-buffering capacity of the waste. This means that the leachate Pb concentrations, which are to be observed soon after the commencement of leaching (i.e. after breakthrough of the first leachant pore volume), should decrease over time and will not increase catastrophically as would be the case in a chemical time bomb scenario.

As may be appreciated from this simple example for Pb leaching, coupled reaction and transport modelling can be a useful tool for predicting changes in landfill leachate composition over geologically significant periods of time. The generalised model, although very simple, can also give insights into how the leaching of heavy metals is related to the chemistry of the leachant, as well as the eventual depletion of the pH- and redox-buffering capacity of the waste material.

Acknowledgement

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