A Model of pH and Redox Buffer Depletion in Waste Landfills

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quantum potes tantum aude
ABSTRACT

The geochemical processes governing the release of heavy metal contaminants from solid waste materials have been studied experimentally and modelled using a mass balance approach. The aim of the modelling work was to develop calculation tools that can be used to predict the release rate of heavy metals from waste heaps or landfills. The leaching models are based upon the observation that the pH and redox state of the water in contact with waste are the two master variables that control heavy metal mobility in aqueous environments. The models developed are intended to be simple and sufficiently flexible that they may be adapted to different waste types with reasonable ease.

The depletion rates of pH and redox buffering constituents in the waste material are calculated by coupling a description of the geochemical processes occurring within the waste with the in- and out-transport of reactive chemical species. The models of waste leaching require input data to describe the reactive properties of the waste. These data may be obtained from simple laboratory experiments such as pH static titrations and reducing capacity measurements.

The simulation results indicate that oxidation of organic material can improve the quality of solid wastes by way of carbonation processes that transform highly soluble oxide, hydroxide, and silicate forms of Ca into calcite. Calcite buffers leachate at a circumneutral pH level that is optimal for the minimisation of heavy metal leaching. Oxidation of organic material can occur under oxic conditions, or under anoxic conditions using sulphate as an oxidant. Under the anoxic conditions that prevail in a fully water saturated leaching environment, reduction of sulphate also promotes the formation of insoluble heavy metal sulphide minerals. It is concluded that disposal of waste materials in a fully water saturated environment is the best way of minimising environmental impact from these potentially hazardous materials.

Keywords: Leaching, chemical weathering, acid neutralisation, solid waste, combustion residues, pH buffering, redox buffering, geochemical modelling, reactive transport
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This thesis is based in part upon the following papers, referred to by Roman numerals I to IV:


IV Crawford J., Bellander C., and Neretnieks I., 1999. Acid neutralising kinetics of slags and combustion residue waste materials. (submitted for publication)
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Contamination of soils and water by leachate from solid waste heaps and landfills is a growing problem throughout the world today. Several centuries of rapid industrial development have led to a large number of heavily contaminated sites throughout the world. Cleaning up these contaminated sites is a very costly process that may not always be possible and often leads to further problems. In many cases, contamination problems have not yet become apparent owing to the long residence times for water in such systems. These are what are commonly referred to as chemical time bombs.

The term “solid waste” encompasses a large number of different materials both organic and inorganic. This thesis, however, focuses upon wastes that are largely inorganic in nature. The wastes of particular interest in this work are combustion residues from municipal solid waste incineration and slags generated in steel manufacture. The tools and methods developed for predicting the leaching of these wastes are intended to be sufficiently general that they can be applied to other wastes not specifically dealt with in this thesis (such as coal combustion residues and mining wastes).

It is reasonable to expect that proactive management of waste heaps and landfills is both economically and technically more effective than remediation after problems have started to occur. Poor design and siting of a waste landfill can worsen the environmental impact of a waste leaching problem and make the remediation of such a site very expensive. For this reason it is desirable to be able to predict how the waste will behave over a long period of time when exposed to the weathering effects of infiltrating rainwater and the atmosphere.

The leaching processes that take place within a landfill generally occur over such long timescales that it is not possible to carry out laboratory experiments of sufficient duration to adequately observe the long-term behaviour of solid wastes. Leaching processes can be accelerated in the laboratory, but this may give results that cannot be extrapolated to landfill situations as the wastes have been exposed to more aggressive conditions than would exist in natural systems. Even if the leaching processes are not
accelerated, the conditions simulated in the laboratory may not even closely resemble the conditions that would prevail in a natural leaching environment.

Modelling and computer simulation of geochemical processes is a valuable tool, which can be used to gain a greater understanding of waste leaching processes where it is difficult to conduct realistic laboratory experiments. If the major constituents in the waste which govern the chemistry of the water (leachant) can be identified, then changes in the landfill effluent (leachate) composition over time may be predicted with the aid of mass balance models.
2 GENERAL PRINCIPLES OF LANDFILL LEACHING

Large, open systems such as waste heaps or landfills are very complex. Many of the processes that characterise the hydrological and chemical properties of the waste are subject to a great deal of variation at different locations in the landfill. These processes are also influenced heavily by seasonal variations in temperature and rainfall. In spite of the complexity of landfill leaching processes, it is possible to identify some general principles, which can be used as a basis for predicting how the leachate quality may change over long periods of time. This chapter is intended as a brief introduction to the concepts and ideas that are the basis for models of landfill leaching.

2.1 The Landfill as a Chemical Reactor

A waste heap or landfill may be thought of as a large chemical reactor. Oxygen (O\(_2\)), carbon dioxide (CO\(_2\)), and acidic rainwater slowly infiltrate the landfill and react with the waste. Within the landfill, a multitude of chemical reactions occur which influence the composition of the water as it follows a flowpath through the waste. Soluble products from these reactions are washed downstream within the landfill where they may precipitate or take part in additional reactions. The composition of the effluent leachate is usually quite different to that of the leachant water entering the landfill. This difference in composition can tell us a lot about what is occurring inside the waste and is the fundamental basis of mass balance modelling.

The processes that occur within a waste landfill can generally be described by a class of mathematical problems known as coupled transport and chemical reaction problems. In order to model these processes, it is necessary to combine a description of constituent transport within the waste with a description of the chemical transformations that occur along the leachant flowpath. The conceptual problem can be described with the aid of the following mass-balance equation for the aqueous phase:
This equation is essentially a restatement of the principle of mass conservation. Mass is neither created nor destroyed in the system, but transferred between stationary solid and mobile aqueous states. Transport processes such as advection and diffusion determine the rate of inflow and outflow of constituents dissolved in the leachate, while the rates of dissolution and precipitation arise from thermodynamic and kinetic consideration of the mass transfer between the solid phases and the leachant. The system is said to be at steady state if the rate of accumulation is zero.

When the mass balance represented by equation 1 is formulated within a one-dimensional, discretised model the physical problem becomes analogous to a sequence of tank reactors connected in series (as depicted in Figure 1).

Heavy metals are often present in solid wastes at concentrations that are some tens to thousands of times greater than those found naturally in soils. Although they are often present in these wastes in relatively high quantities, their concentrations are generally not high enough to have a great influence upon the leachant chemistry. The chemistry of the leachant, on the other hand, can have a very strong influence upon the mobility of these toxic substances.

Two of the most important variables that influence heavy metal solubility are the pH and redox state of the leachant. Solid wastes generally contain a variety of constituents which react with in-transported acidity and oxidants. Reactions that involve consumption of protons are referred to as pH buffering reactions. The amount of strong acid that can react with the waste is referred to as the pH-buffering capacity, or acid neutralising capacity (ANC) of the waste.
Reactions that consume oxidants, which may be present in the leachant, are referred to as redox buffering reactions. Similarly to pH buffering processes, the total amount of oxidant that can react with the waste is called the redox buffering capacity, or reducing capacity of the waste. Certain redox buffering reactions may generate protons. This can have a considerable impact upon the depletion of the pH buffering capacity, particularly if there is a high rate of oxidant in-transport.

Although not all of the redox reactions occurring in a waste landfill directly involve oxygen, the major oxidant transported into the landfill is atmospheric oxygen. It is often convenient therefore, to describe the redox state of the leachant in terms of oxygen fugacity or oxygen partial pressure ($P_{O_2}$). It is also possible to describe the redox state of the leachant in terms of the relative activity of electrons in the solution ($p\varepsilon$), or in terms of electrode potentials ($E_H$). The $P_{O_2}$ as a measure of the leachant redox state, however, is more intuitively appealing for waste leaching problems and shall be used exclusively in this thesis.

After a period of time, under the influence of in-transported oxygen and acidity, the pH and redox buffering capacity of the waste near the surface of the landfill will become exhausted. As a result, reaction fronts may develop along the leachant flowpath. Upstream of the reaction front, the buffering capacity is depleted, whereas downstream there remains unreacted buffering capacity. There may be reaction fronts existing for both pH and redox buffering constituents in the waste.

The chemical composition of the leachant may change significantly at the reaction front. At a redox reaction front, for example, the oxygen partial pressure in the leachant may decrease rapidly over a short distance. Similarly, for a pH reaction front the leachant pH may suddenly change from being acidic to basic. The sharpness of the leachant composition change depends upon kinetic factors, dispersion, and diffusion. The composition changes may appear to occur very abruptly in a system where rates of dispersion and diffusion are low and the residence time of the leachant is sufficiently high relative to the reaction rate. The effects of slow reaction kinetics, diffusion, and dispersion operate to smooth out these compositional changes.
The reaction fronts slowly recede into the landfill as the buffering capacity of the waste is used up. The rate of movement of the reaction fronts depends upon the rate of mass transport and the initial quantities of reacting constituents present in the waste. As the solubility of toxic metals is strongly dependent upon the pH and redox conditions in the leachant, the rate of heavy metal transport is closely related to the rate of reaction front movement.

Near the surface of the landfill, acidic and oxic conditions may exist in the leachant. Further down in the landfill the conditions may be basic and reducing. Metals dissolved from upstream in the waste may precipitate at reaction fronts downstream where the chemistry of the leachant changes. This may lead to the formation of an enrichment band of the metal that moves through the waste at the same rate as the reaction front. There are many examples of where this kind of process has occurred in nature leading to the formation of mineral ore bodies. One particularly well documented case is that of the uranium ore body formation at the Poços de Caldas uranium mine in Brazil (Cross et al., 1991). The phenomenon of metal accumulation at a reaction front is illustrated conceptually in Figure 2.

![Diagram](image_url)

**Figure 2. Illustration of heavy metal accumulation at a reaction front**

While there is still a pH and redox buffering capacity in the waste material, the rate of heavy metal leaching may be very low owing to the poor solubility of heavy metals.
under basic and reducing conditions. When the buffering capacity of the waste in the landfill is entirely depleted, however, the rate of heavy metal leaching may increase dramatically over a short period of time.

2.2 The Distribution and Leachability of Heavy Metals in Solid Wastes

The concentrations of heavy metals appearing in bottom ashes and slags are typically very different to those to be found in fly ashes and air pollution control (APC) residues. Pollutants such as mercury (Hg), cadmium (Cd), and arsenic (As) are mostly volatilised at temperatures over 1000°C and are carried over into the flue gases where they finally end up in fly ash and APC residues. Copper (Cu) and nickel (Ni), on the other hand, have much higher boiling points and are usually confined to bottom ashes and slags. These non-volatile elements are often referred to as being lithophilic. Some elements such as lead (Pb) have boiling points that are intermediate to those of volatile and lithophilic elements and are often distributed more evenly amongst the various ash and slag fractions.

The partitioning of elements between the bottom ash (or slag) and flue gas fractions depends not only upon their boiling points, but also the operating conditions in the combustion (or smelting) process as well as the speciation of these elements in the original materials (Chandler et al, 1994). Table 1 below, shows typical concentration ranges for some elements found in the bottom- and fly ash fractions from municipal solid waste incineration (MSWI).
Table 1  Typical concentration ranges (mg/kg) for various elements found in MSWI bottom ash and fly ash (Chandler et al., 1994)

<table>
<thead>
<tr>
<th>Element</th>
<th>Bottom ash</th>
<th>Fly ash</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca</td>
<td>3,900 – 120,000</td>
<td>74,000 – 130,000</td>
</tr>
<tr>
<td>Mg</td>
<td>400 – 26,000</td>
<td>11,000 – 19,000</td>
</tr>
<tr>
<td>Na</td>
<td>2,900 – 42,000</td>
<td>15,000 – 57,000</td>
</tr>
<tr>
<td>K</td>
<td>750 – 16,000</td>
<td>22,000 – 62,000</td>
</tr>
<tr>
<td>Al</td>
<td>22,000 – 73,000</td>
<td>49,000 – 90,000</td>
</tr>
<tr>
<td>S</td>
<td>1,000 – 5,000</td>
<td>11,000 – 45,000</td>
</tr>
<tr>
<td>Si</td>
<td>91,000 – 310,000</td>
<td>95,000 – 210,000</td>
</tr>
<tr>
<td>Cl</td>
<td>800 – 4,200</td>
<td>29,000 – 210,000</td>
</tr>
<tr>
<td>Cd</td>
<td>0.3 – 61</td>
<td>50 – 540</td>
</tr>
<tr>
<td>Pb</td>
<td>98 – 6,500</td>
<td>5,300 – 26,000</td>
</tr>
</tbody>
</table>

When we consider MSWI, by far the largest volume of waste material is the bottom ash fraction, which accounts for some 80-95% of the total mass of combustion residues generated. Roughly 70% of the Pb content in the original (non-incinerated) waste material is retained in the bottom ash fraction, whereas only 12% of the Cd content of the original waste is retained in the bottom ash.

In general, there are three different leaching mechanisms that may control the release of a particular constituent from a solid waste in an aqueous environment. These mechanisms are:

- Availability controlled leaching
- Kinetically controlled leaching
- Solubility controlled leaching

Substances that are highly soluble (NaCl, for example) often fall into the category of availability controlled leaching if the concentration released into the leachant is limited only by the amount of the substance present in the waste material. These substances can be expected to leach at high concentrations soon after the beginning of landfill operation, but will generally decrease over time as they are depleted from the waste.
Kinetically controlled leaching is defined to include processes whereby the release of a constituent is limited only by the intrinsic rate of a chemical reaction or diffusional transport resistance. The diffusion of a soluble substance from the interior of a large lump of material is a transport limited process. The slow hydrolysis of a mineral such as feldspar, on the other hand, arises due to the rate of chemical reaction at the mineral surface (Helgeson et al., 1984). Kinetic resistances usually occur in series. A reactant, for example, may need to diffuse through both a laminar boundary layer and the porous internal structure of a lump in order to arrive at a dissolving surface where a slow hydrolysis reaction is occurring.

When there are kinetic resistances in series, the slowest process tends to control the overall release rate. Therefore, if the surface reaction rate of a particular mineral is exceptionally slow, lump size may not make much difference to the rate of constituent release. If the rate of surface reaction is very fast, however, transport resistances may overwhelmingly dominate the release rate of a particular constituent. Over very short timescales (minutes to hours) the dissolution of calcite (CaCO$_3$) is an example of a process that is largely controlled by transport kinetics at low pH (Plummer et al., 1978, 1979; Sverdrup, 1985).

Most constituent release processes are to some extent kinetically controlled until an equilibrium state has become established between the leachant and the solid phases. If thermodynamic equilibrium is attained reasonably quickly in relation to the residence time of the leachant, the release rate may be solubility controlled. Over the timescales encountered in a landfilling environment, the dissolution of calcite may be often described as an equilibrium process. The equilibrium thermodynamics of dissolution and precipitation processes are very well characterised for a great variety of minerals and there are a number simulation programs available that may be used for predicting element solubilities (Allison et al., 1991; Parkhurst, 1995; Truesdell et al., 1974; Wolery et al., 1992).

One drawback associated with these programs is that they cannot tell the user whether the mineral being used to model element solubility is physically realistic, or not.
Databases of thermodynamic data frequently contain minerals that are formed under very special conditions of temperature and pressure and are thus unlikely to form spontaneously in a low temperature, leaching environment. For this reason, some geological common sense needs to be applied when using programs that make use of such databases. This is particularly true when the simulation program automatically selects precipitating minerals.

As mentioned briefly in the preceding chapter, the pH and the redox state of the leachant have a very strong influence upon the solubility of heavy metals. If we take Pb and Cd as two typical examples of heavy metals, it is possible to calculate their solubility using a geochemical simulation program such as PHREEQC (Parkhurst, 1995), provided we can select minerals that are likely to be controlling their release.

Figure 3 below, shows three examples of such calculations where different minerals have been assumed to be controlling the Pb solubility. Under oxidising conditions these minerals were assumed to be Pb(OH)$_2$ and chloropyromorph (Pb$_5$(PO$_4$)$_3$Cl). Under strongly reducing conditions, Galena (PbS) was assumed to control Pb solubility. Reducing conditions were simulated by assuming pyrite (FeS$_2$) co-equilibrium. The maximum contaminant level (MCL) of 0.015 mg/l set by the U.S. EPA is shown in the figure as a broken line.

Figure 3 Pb solubility as a function of pH for Pb(OH)$_2$ (○) and Pb$_5$(PO$_4$)$_3$Cl (▲) [oxidising conditions] and PbS (●) [reducing conditions]. Maximum contaminant level (MCL) set by U.S. EPA shown as a broken line.
Figure 4 below, shows similar examples of such calculations for Cd. Under oxidising conditions the solubility controlling minerals were assumed to be Cd(OH)$_2$ and otavite (CdCO$_3$). Under strongly reducing conditions greenockite (CdS) was assumed to control Cd solubility. As for the examples involving Pb, the MCL of 0.005 mg/l is shown as a broken line.

Whether or not these minerals actually control Pb and Cd solubility is open to question. What these calculations do illustrate, however, is the pH and redox sensitivity of mineral solubilities. Most heavy metals have a field of minimum solubility somewhere between pH 7 and 11. At pH levels below 7 and above 11, the heavy metal solubility tends to increase dramatically. Heavy metals that exhibit this kind of behaviour with increased solubility at both high and low pH are often referred to as being amphoteric. This means that they are able to react both as acids and bases. Sulphur compounds in the leachant may precipitate heavy metals in the form of metal sulphides when the conditions are strongly reducing. These metal sulphides are generally insoluble and the concentrations of heavy metals in the leachant may drop to very low levels.
The presence of complexing agents in the leachant may also have a strong influence upon the solubility of heavy metals. In the case of Cd, for example, the presence of chloride ions (Cl\(^-\)) may increase the Cd solubility by way of complex formation (specifically CdCl\(^+\), CdCl\(_2\), CdCl\(_3\), and CdOHCl\(^+\)).

The solubility of heavy metals may also respond to changes in the leachant chemistry as a consequence of the common ion effect. If Pb\(_5\)(PO\(_4\))\(_3\)Cl is the solubility controlling mineral for Pb, then increasing the concentrations of either phosphate (PO\(_4^{2-}\)) or chloride ion may decrease the Pb concentration in the leachant.

Many minerals have a surface charge that arises due to the hydrolysis of exposed oxide groups on their surfaces. This surface charge is also influenced by the pH of the leachant. The surface charge of hematite (Fe\(_2\)O\(_3\)), for example, is negative at high pH and positive at low pH levels. Around pH 8, hematite has no net surface charge. Heavy metal ions can be adsorbed very strongly to these charged surfaces, particularly at high pH. This is an important mechanism for the retardation of heavy metal movement in solid waste landfills. Owing to competition amongst dissolved ions for adsorption sites, some metals are adsorbed preferentially to others. Pb is often adsorbed preferentially to Cd (van der Sloot et al., 1997). Under such conditions, sorption processes will tend to retard the transport of Pb more strongly than the transport of Cd.

Certain minerals such as aluminium hydroxide (Al(OH)\(_3\)), amorphous silica (SiO\(_2\)), and ferrihydrite (Fe(OH)\(_3\)) may precipitate in the leachant in the form of suspended particles called colloids. Colloids are generally defined as being particles less than about 10 \(\mu\)m in diameter. These suspended solids also have a surface charge and can therefore bind heavy metals strongly. Being freely mobile in the leachant, however, colloids provide a means by which heavy metals can be transported out of the landfill even when their aqueous solubility is low (McCarthy et al., 1989). The extent to which colloidal binding facilitates the transport of heavy metals depends upon the stability of the colloids in the leachant as well as filtration and adhesion processes for these colloids in the waste materials.
3 EXPERIMENTAL AND THEORETICAL DETERMINATION OF SOLID WASTE LEACHING PROPERTIES

The pH and redox buffering capacities of solid wastes can be determined experimentally, or they may be estimated from theoretical considerations when the elemental composition of the waste is known.

Theoretical estimation methods usually assume that all of the buffering constituents present in the waste are in a readily leachable form and will contribute towards the buffering capacity. The buffering capacity of the waste may be overestimated if buffering constituents are present in stable (non-leachable) mineral forms, or if their reaction rates are very slow relative to the residence time of leachate in the landfill.

Experimental methods may give a better idea of the available buffering capacity, but they suffer from the disadvantage that the experimental conditions may be more aggressive than those existing in a waste landfill. This may lead to an overestimation of the buffering capacity if constituents are leached that would normally be unavailable in a landfilling environment. Experimental methods are also highly sensitive to the kinetics of pH and redox buffering processes. Short-term experiments carried out over 24 hours generally give results that differ from those that would be obtained if the same experiment was carried out for a week or more.

Care must be taken when making predictions of landfill leaching behaviour based upon data taken from experimental measurements or theoretical estimation methods. In order to make reliable predictions, it is important to consider both the speciation of different constituents in the solid phases as well as in the leachant. Allowance must also be made for differences in the physical characteristics of the waste between different leaching systems. In experiments, for example, the waste is often ground into small particles and treated at high L/S ratios (liquid to solid mass ratio) in a batch reactor. Under landfilling conditions, the particle size is frequently much larger and water is continually flushed through the system. In a landfill, some of the buffering capacity may not be able to react due to the formation of preferential flowpaths, or
because it is hidden deep inside large lumps and thus isolated from the leachant. Secondary minerals such as gypsum may also precipitate within the pores of large particles and lumps, thus reducing the accessibility of the underlying buffering capacity.

In a flow through system soluble reaction products are flushed downstream along a fluid flowpath. In a batch system, however, these soluble reaction products are retained in the reaction vessel. This fundamental difference between batch and flow through systems can have a considerable impact upon the observed leaching properties of the waste.

Both theoretical and experimental methods give an indication of the maximum available buffering capacity of waste materials when we neglect the influence of physical heterogeneity. This chapter details some of the theoretical and experimental methods that can be used to roughly estimate the maximum pH and redox buffering capacities of solid wastes.

3.1 Acid Neutralisation Properties of Solid Wastes

3.1.1 The Definition of Acidity and Alkalinity

Acidity and alkalinity are two very important concepts when we discuss solid waste leaching problems. In chapter 2, the acid neutralising capacity (ANC) of a solid waste was described as the amount of strong acid that can react with the waste. Actually, the concept of acid and base neutralising capacity was originally developed as a means of distinguishing between the free $H^+$ concentration (or the activity of $H^+$ given by the pH) in an aqueous solution and the reservoir of $H^+$ available for reaction in the solution.

The quantity of protons available for reaction (known as H-acidity, or mineral acidity) is the sum of proton containing species less the sum of proton deficient species in the solution relative to a defined reference speciation level. For most systems of environmental interest, we consider $H_2O$ and $H_2CO_3$ as reference species, and the H-acidity is given by:
neutral (i.e. contain equal numbers of positive and negative charges). Using the electroneutrality principle, it is possible to define a complimentary parameter to the sum of charges for the strong acids and bases in the solution:

\[
[\text{Alk}] = [\text{Na}^+] + [\text{Ca}^{2+}] + 2[\text{Mg}^{2+}] - [\text{Cl}^-] - 2[\text{SO}_4^{2-}] - [\text{NO}_3^-]
\]  

\[
[H-\text{Acy}] = [H^+] - [\text{HCO}_3^-] - 2[\text{CO}_3^{2-}] - [\text{OH}^-]
\]  

In the definitions of H-acidity and alkalinity, minor solution species have been neglected and it is assumed that the chosen reference species are those which would dominate at the reference pH level (usually taken to be pH 4.5). It is possible that other constituents such as Fe, Mn, and Al, make some contribution to the alkalinity of the solution. This may be particularly true in the case of Al, both at pH levels greater than 10 or less than 4, where the solubility of gibbsite (Al(OH)_3) is relatively high. Both of these constituents have been neglected from the definition of alkalinity, and it is assumed that they only contribute to the pH buffering processes after the leachable base cations have been depleted from the solid phases.

By definition, the H-acidity and the alkalinity are always of equal magnitude, but of opposite sign:

\[
[H-\text{Acy}] = [\text{Alk}]
\]  

\[
2)
\]
It is easy to account for solid phase pH buffering processes by considering that the
from the leachant. Similarly, the addition of anionic charge to the leachant is
equivalent to the addition of protons to the leachant. Alkalinity is thus transferred
This principle may be formalised in the following way:

\[ \sum \Delta \text{Ions} + \sum \Delta \text{Conservati} + \Delta [\text{Alk}] = -\Delta [\text{Acy}] \]  

(5)

\[ +\Delta [\text{Alk}] = -\Delta [\text{ANC}]_{\text{waste}} \]  

(6)

Basic oxide, hydroxide, carbonate, and silicate minerals are generally responsible for
the ANC of solid wastes. The ANC is released to the solution, both by weathering and
by ion exchange processes. The ANC may be measured by a pH titration at an
appropriate reference pH level, or it may be estimated directly from the elemental
composition of the waste. If we consider only the basic cations and conservative
anions, the theoretical ANC of the waste is given by:

\[ \text{ANC} = n_{\text{Na}} + n_{\text{K}} + 2n_{\text{Ca}} + 2n_{\text{Mg}} - n_{\text{Cl}} - 2n_{\text{S(IV)}} - n_{\text{N(V)}} \]  

(7)

In equation 7, the parameters \( n_i \) refer to the molar concentrations of each base cation
and conservative anion constituent known to exist in the waste. These concentrations
and the ANC are usually reported in the units of mmol/g or mol/kg. The estimation
method assumes that all of the base cations and conservative anions are leachable and
can contribute towards the ANC. This is probably true for the Ca and Mg content of
wastes as the pH buffering properties are often dominated by weathering processes
involving these two cations (Belevi et al. 1992; Johnson et al., 1995). Leachant
concentrations of Na and K are frequently, but not always, lower than those of Ca and
Mg.

A large proportion of the Na and K content of the waste may be sequestered in slowly
dissolving clay (smectite) minerals formed during the initial weathering of glassy
phases. Ca and Mg may also be present in the form of slowly dissolving silicate
minerals, but their rates of weathering are sufficiently slow that fast dissolving minerals mask their influence upon the observed leachant concentrations. Fast dissolving forms of Na and K are most likely to be chloride and nitrate salts that generally do not buffer pH. Slow dissolving minerals tend to have a minor influence upon the leachant chemistry while fast dissolving minerals are still present in the waste and contributing towards the ANC.

The ANC that can be related to the Ca and Mg content of the waste is often more interesting than that involving Na and K. Carbonate forms of Ca and Mg tend to maintain the leachant pH at a level that is ideal for the minimisation of heavy metal solubility. Calcite (CaCO$_3$) is the most important of these minerals as precipitation of magnesite (MgCO$_3$) is rarely seen to occur spontaneously in natural waters (Langmuir, 1997). This suggests that the MgCO$_3$ precipitation reaction may be kinetically hindered.

Although Mg carbonates are unlikely to form as secondary minerals under landfilling conditions, they may be initially present in geological materials such as mining wastes. Carbonate forms of Ca and Mg are usually not present initially in combustion residue and slag-type wastes. Both Ca and Mg may be released by the fast dissolution of oxide and hydroxide forms, but it is only Ca that will form carbonate precipitates. It is worth noting that the dissolution of calcium oxide (or hydroxide) followed by calcite precipitation does not result in the buffering capacity of that element to be available twice. As can be seen from equations 5 and 6, such a process results in a net zero change in leachant alkalinity. More simply: proton equivalents are removed from the leachant by the dissolution of calcium oxide and then returned to the leachant when the dissolved Ca precipitates as calcite.

Since heavy metal solubility is essentially controlled by the presence or absence of carbonate minerals, it is probably cautious to consider only the Ca and Mg content of the waste and neglect the ANC that results from weathering or ion-exchange of Na and K. Assuming that chloride and nitrate are only minor constituents, equation 7 may be simplified to:
\[ \text{ANC}_{\text{CaMg}} = 2C_{\text{Ca}} + n_{\text{Mg}} - n_{\text{S(IV)}} \]  
(8)

Or, if we consider only the Ca-content of the waste:

\[ \text{ANC}_{\text{Ca}} = 2C_{\text{Ca}} - n_{\text{S(IV)}} \]  
(9)

The previously developed definitions of H-acidity and alkalinity may appear to complicate the description of pH buffering processes, but they actually simplify the analysis of leaching problems in one very important respect: The alkalinity of a landfill leachate as determined by an alkalimetric or acidimetric titration is an exact measurement of the amount of pH buffering capacity (ANC) that has been depleted from the waste. By considering the change in alkalinity of the water entering and leaving the landfill, the time required to completely consume the waste ANC may be estimated.

### 3.1.2 pH Titration of Waste Materials

The acid neutralisation properties of solid wastes are most often determined with the aid of experimental pH titrations. A pH titration may be carried out using either a pH-static method or a multiple batch method. A pH-static titration involves the continuous addition of a strong acid to a stirred batch reactor. The rate of acid addition is adjusted so that the pH of the leachant is always maintained at a pre-set level. The pH buffering reactions in waste materials occur relatively slowly and the titrations take some time to perform. This is tedious to do manually, and such titrations are frequently carried out with automatic titrating equipment. By performing a number of such titrations at different set pH levels, it is possible to reconstruct a titration curve.

In the multiple batch method, a number of sample bottles are filled with equal quantities of waste material and water with incremental amounts of acid added. These bottles are left to stand for a period of time, after which the pH of the leachate in each bottle is measured. This method is simpler than the pH-static method as it requires no extra equipment apart from a pH meter. A titration curve is then found by plotting the measured pH against the amount of acid added to each bottle.
In both methods, the slow release of different constituents from the waste leads to a gradual shift in the titration curve over time. In the pH-static titration method, the pH remains constant and the amount of acid added changes continually. In the multiple batch method, however, the amount of acid added is constant in each batch and the pH of the leachate changes. This is illustrated conceptually in figure 5 below:

![Conceptual diagram illustrating movement of the pH titration curve over time owing to slow release kinetics](image)

When constituents are leached from a solid waste, the amount of ANC consumed is given by the change in solution alkalinity according to equation 6. In this definition, it is assumed that the only source of base cations and conservative anions is the waste material itself. This is true when waste is added to a leachant solution of known initial alkalinity (regardless of the initial leachant composition). In a titration experiment, however, we must account for the amount of acid added to the system, as this will comprise part of the measurable alkalinity of the leachant.

If we start with a leachant that is initially neutral and contains no other ions (i.e. de-ionised water) its alkalinity will be zero. When both a strong acid and waste material are added to this system, the resultant alkalinity will be given by the net sum of basic cations and conservative anions in the leachate. The alkalinity of the leachate is thus made up of a contribution from dissolved waste components and a contribution from the acid that has been added to the system. If we have added the waste to a solution of nitric acid ($\text{HNO}_3$) diluted in de-ionised water, the ANC leached from the waste will be given by the following expression:
The alkalinity of the leachate may be determined by filtering the leachate and performing a standard acidimetric or alkalimetric titration to the reference pH used in the definition of alkalinity (usually pH 4.5). This will give an exact measurement of the leachate alkalinity and thus the quantity of ANC depleted from the waste may be calculated.

In most cases this is not practical, and it is usually assumed that the net alkalinity of the leachate solution is approximately zero. This assumption is generally valid if the amount of ANC leached from the waste is large in comparison to the net alkalinity of the leachate. Using this approximation, we can write:

\[-\Delta[\text{ANC}]_{\text{waste}} \approx [\text{Alk}]_{\text{leachate}} + [\text{NO}_3]_{\text{acid}}\]  

Although the ANC at a given pH may be read directly from a titration curve for a batch system, it is meaningless to apply these results directly to field conditions unless additional information about the waste mineralogy is available. The ANC data contained in a batch pH titration curve can be used to predict landfill leaching processes only if the identities of the minerals that control the pH buffering processes are known. In a batch titration, there is a continuous accumulation of aqueous reaction products as acid is added to the system. In a flow through system, however, these reaction products are continually removed by flushing processes. As the solubilities of different buffering minerals are highly dependent upon the chemical composition of the leachate, there will be a large difference in leaching behaviour between batch and flow through systems.

A mineral that is particularly sensitive to differences in experimental conditions is calcite. The equilibrium solubility of calcite is strongly dependent upon the partial pressure of \( \text{CO}_2 \) in the system. Johnson et al. (1995) conducted multiple batch titrations on fresh and aged samples of incinerator ash. In these experiments, dissolved \( \text{CO}_2 \) was removed by bubbling argon gas through the leachate. In doing so, the equivalent solution partial pressure of \( \text{CO}_2 \) is reduced significantly, thereby
increasing the solubility of calcite. Using such a method, we can be almost certain that the entire calcite content of a waste will be dissolved at a pH of about 7.5 with a high L/S ratio, given sufficient time. The rationale behind this procedure can be illustrated by making calculations with a geochemical simulation program, such as PHREEQC. Figure 6 below shows the equilibrium solubility of calcite calculated as a function of $P_{\text{CO}_2}$ at pH 7.5:

**Figure 6** Calcite solubility at pH 7.5 as a function of CO$_2$ partial pressure. Broken line indicates calculated data where the ionic strength exceeds 0.1 mol/kg water (approximate limit of validity for PHREEQC activity model)

In a closed reaction system the solubility of calcite is much less than in a system where gas exchange is allowed to occur with the atmosphere, or where the CO$_2$ is stripped from the leachate using a carrier gas. The ANC measured at pH 7.5 ($\text{ANC}_{7.5}$) therefore does not tell us anything useful unless we also know that there is calcite in the waste and whether, or not, it has been completely dissolved at this pH.

An additional problem, which complicates the interpretation of batch leaching data, is that the measured $\text{ANC}_{7.5}$ may be the result of a number of different mineral dissolution processes. The $\text{ANC}_{7.5}$ may result from calcite dissolution, but a
significant proportion of it may also be attributable to the dissolution of other minerals such as basic oxides, hydroxides, and fast reacting silicate minerals. This presents a problem when we try to make predictions of landfill leaching, as we must specify how much of each mineral is present in the waste in order to calculate their rates of depletion.

Some researchers have adopted a trial and error approach whereby the pH dependent leaching of different minerals is simulated with a geochemical simulation program (Comans et al, 1993, 1994; Garavaglia et al, 1994). By comparing the solubility behaviour of these minerals with analytical measurements of leachate composition, the mineral that is most likely to control the solubility may be determined by the principle of best agreement with the experimental data. This approach can give clues as to which minerals may be present, but it is somewhat speculative, as we cannot rule out the possibility that the agreement with experimental data is purely coincidental.

Occasionally it is possible to determine the presence of a particular mineral by observing the shape of the titration curve and identifying points of inflexion that may indicate the depletion of the mineral. In the great majority of cases, however, it is very difficult to see the points of depletion for any particular buffering minerals in a titration curve for a solid waste. There may be a number of different minerals that give rise to the observed pH buffering behaviour in a batch titration. Some buffering constituents may not be minerals at all, but amorphous (glass-like) phases with variable composition and reactive properties. It is difficult to quantify in any reliable way, how much of the measured ANC results from ion exchange, titration of mineral surface groups, or true weathering processes. Added to these uncertainties are slow changes in leachate chemistry resulting from slow hydrolysis reactions and recrystallisation of secondary minerals. These processes change the shape of the titration curve over time (as illustrated in figure 5) thereby complicating the interpretation of leaching data.

In the absence of detailed information about the quantities and identities of minerals which control leaching processes, it is desirable to model landfill leaching using
minerals that may overpredict the rate of ANC depletion. Using this approach we may not be able to fit the batch titration data well, but conservative estimates will be obtained for the time required to fully deplete the waste of buffering constituents.

### 3.1.3 Experimental Methods and Results

Three different waste materials have been considered as case studies in this project. These materials were a municipal solid waste incineration residue (MSWI), and two different types of steel slag. The MSWI is a non-magnetic fraction of a municipal solid waste bottom ash produced at an incinerator located in Linköping, Sweden. One steel slag (AFS) is a non-magnetic fraction from a scrap based electric arc furnace (Fundia Steel AB, Smedjebacken, Sweden). The other slag is an unsorted blast furnace slag (BFS) originating from an ore based steel production process (SSAB, Oxelösund, Sweden). These waste materials are identical to those used in previous studies by Fällman (1994, 1997), Bäverman (1997), and Yan (1998).

The waste materials were dried and then prepared by crushing until all of the material passed a 0.16mm sieve and most of the material passed a 0.125mm sieve. The materials had been prepared in this way during 1992 and stored in airtight polypropylene bottles since. Fällman (1994) has determined the major elemental composition of these wastes using ICP-AES. These data are given in Table 2 below:
Table 2  Composition, density, and acid neutralising capacity (ANC) of solid waste materials used in this study (Fällman, 1994)

<table>
<thead>
<tr>
<th></th>
<th>MSWI</th>
<th>AFS</th>
<th>BFS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca (mol/g)</td>
<td>2.19×10^{-3}</td>
<td>5.51×10^{-3}</td>
<td>5.59×10^{-3}</td>
</tr>
<tr>
<td>Mg (mol/g)</td>
<td>4.65×10^{-4}</td>
<td>1.86×10^{-3}</td>
<td>4.85×10^{-3}</td>
</tr>
<tr>
<td>K  (mol/g)</td>
<td>3.66×10^{-4}</td>
<td>1.18×10^{-5}</td>
<td>1.25×10^{-4}</td>
</tr>
<tr>
<td>Na (mol/g)</td>
<td>1.15×10^{-3}</td>
<td>1.61×10^{-5}</td>
<td>1.87×10^{-4}</td>
</tr>
<tr>
<td>Al (mol/g)</td>
<td>2.11×10^{-3}</td>
<td>8.12×10^{-4}</td>
<td>2.40×10^{-3}</td>
</tr>
<tr>
<td>Fe (mol/g)</td>
<td>1.93×10^{-3}</td>
<td>4.33×10^{-3}</td>
<td>3.04×10^{-5}</td>
</tr>
<tr>
<td>Si (mol/g)</td>
<td>7.43×10^{-3}</td>
<td>2.05×10^{-3}</td>
<td>5.20×10^{-3}</td>
</tr>
<tr>
<td>S  (mol/g)</td>
<td>2.67×10^{-4}</td>
<td>3.93×10^{-5}</td>
<td>5.33×10^{-4}</td>
</tr>
<tr>
<td>ρ_{bulk} (kg/m^3)</td>
<td>1296</td>
<td>1944</td>
<td>1111</td>
</tr>
<tr>
<td>ANC_{Ca,Mg} (meq/g)</td>
<td>4.78</td>
<td>14.66</td>
<td>19.81</td>
</tr>
<tr>
<td>ANC_{Ca} (meq/g)</td>
<td>3.85</td>
<td>10.94</td>
<td>10.11</td>
</tr>
</tbody>
</table>

Leaching experiments have been conducted upon these three waste materials in order to investigate their pH buffering properties. Half of the experiments consisted of pH-static titrations carried out at pH 4 for a period of 24 hours. In the other half of the experiments, pH-static titrations were first carried out at pH 7 for 24 hours. Following these pH 7 titrations, the remaining solid material was removed by filtration and then titrated for an additional 24 hours at pH 4. The experiments were all carried out open to the atmosphere (no gas sparging) at an L/S ratio of 100. A Metrohm 719S Titriso device with automatic data logging was used for performing the pH-static titrations.

10ml samples of the leachate were taken at various intervals during the titration procedure so that chromatographic analyses could be made. The leachate samples were filtered with a 0.2μm syringe membrane filter to remove fines and possible colloidal material. Analyses were then made with a Dionex DX300 ion chromatograph. An ion exchange suppressor and methanesulphonic acid eluent with conductivity based detection was used for the analysis of the basic cations. Calibration of the system was based upon serial dilutions of external standards. A linear calibration curve forced through the origin was found to give the most reliable results.
In all of the leaching experiments it was found that both Ca and Mg were responsible for the bulk of the measured ANC owing to the high concentrations of these relative to the other basic cations found in the leachate. In all of the experiments, the rate of acid neutralisation was found to be approximately consistent with transport-limited kinetics (see paper IV). The Ca/Mg ratio in the leachate was found to be significantly higher in the experiments involving AFS slag and MSWI than those experiments involving BFS slag. It appears, therefore, that Mg plays a more important role in the pH buffering processes for the BFS slag than for the other waste types examined. For all of the waste materials, the Ca/Mg ratio was higher at pH 7 than at pH 4. This is in agreement with what we would expect from the known solubilities of Ca and Mg oxides (and hydroxides).

The measured acid neutralising capacities of these waste materials after 24 hours of leaching are compared in figure 7 below with the values of $\text{ANC}_{\text{CaMg}}$ and $\text{ANC}_{\text{Ca}}$ estimated from the analytical composition of the waste:

![Graph of ANC values for MSWI, AFS, and BFS](image)

**Figure 7** Results of 24-hour titration experiments compared with theoretically calculated ANC values for the three waste materials. $\text{ANC}_{7.0}$ are measured values at pH 7, $\text{ANC}_{4.0}$ are values measured at pH 4 using untreated waste.
The distribution of the acid neutralising capacity was very different for each of the waste materials tested. For AFS slag, most of the ANC was available above pH 7. For BFS waste, on the other hand, most of the ANC was available below pH 7. MSWI appeared to have a more even ANC distribution with roughly equal amounts available above and below pH 7. No analysis was made for the carbonate content of the waste and the amount of calcite that may be present in these wastes is therefore unknown.

The kinetics of acid neutralisation were generally very fast; between 40 and 60 percent of the theoretically calculated acid neutralising capacity (\(\text{ANC}_{\text{CaMg}}\)) was available within 24 hours of leaching under the given experimental conditions. The release rate of the remaining buffering capacity was not determined in these experiments. Previous studies carried out by Yan (1998), however, indicate that the waste will continue to react at a much-reduced rate for many weeks to months.

### 3.2 Reducing Properties of Solid Wastes

#### 3.2.1 Major Redox Reactions of Importance in Solid Wastes

Ashes and slags are frequently reducing in nature. Ashes from municipal solid waste incineration (MSWI) typically contain 1-5 weight percent of non-combusted organic material (Krebs et al., 1988; Johnson et al., 1995; Zevenbergen, 1994). A proportion of this organic material may be refractory in nature (i.e. non-reactive under landfilling conditions). Very little appears to be known about this residual organic fraction. Krebs et al. (1988) adopted a rule of thumb that 50 percent of the total organic carbon content (TOC) is refractory in order to make scoping calculations. As the nature of this organic residue is poorly characterised, it is often assumed to have the symbolic empirical formula \(\text{C}_2\text{H}_2\text{O}\).

Blast furnace and other, ore based slags generally contain insignificant amounts of organic material, and most of the reducing capacity arises from reduced forms of sulphur. Electric arc furnace slags are unlikely to contain significant quantities of reduced sulphur or organic material as the smelting process is usually scrap metal based. The reducing capacity in these types of wastes may instead be due to the presence of free metals and reduced metal oxides. Metals such as aluminium (Al) can
reduce water to generate hydrogen gas. These reactions tend to dissipate quickly, however, once the metallic aluminium has acquired a surface oxide layer. Hydrogen gas can pose an explosion risk and is one reason why ashes are often stockpiled for some time before landfilling or utilisation.

In many cases, the reducing capacity of a waste may be the result of a combination of different reducing constituents. Redox reactions can also generate acidity. This may lead to a rapid depletion of the pH buffering capacity of the waste, particularly if there is a large flux of oxygen into the system.

Some of the redox reactions that are thought to be of major importance for the waste materials used in this study are:

\[
\begin{align*}
\text{CH}_2\text{O}(s) + \text{O}_2 & \rightleftharpoons \text{CO}_3^{2-} + 2\text{H}^+ & (12) \\
\text{S}(s) + \frac{3}{2}\text{O}_2 + \text{H}_2\text{O} & \rightleftharpoons \text{SO}_4^{2-} + 2\text{H}^+ & (13) \\
\text{CaS}(s) + 2\text{O}_2 & \rightleftharpoons \text{Ca}^{2+} + \text{SO}_4^{2-} & (14) \\
\text{Fe}(s) + \frac{7}{4}\text{O}_2 + \frac{3}{2}\text{H}_2\text{O} & \rightleftharpoons \text{Fe(OH)}_3 & (15) \\
\text{Fe(II)O}(s) + \frac{1}{2}\text{O}_2 + \frac{1}{2}\text{H}_2\text{O} & \rightleftharpoons \text{Fe(OH)}_3 & (16)
\end{align*}
\]

In these reaction pathways, the amount of oxygen consumed and the amount of acidity generated depends upon the end products of the redox reactions. Here, it is assumed that the end products are fully oxidised, but this may not always be the case.

Under oxidising conditions in a basic environment, Fe$^{3+}$ ions formed as a reaction product in the oxidation of metallic Fe or Fe(II)O are rapidly precipitated as ferrihydrite (Fe(OH)$_3$). As there is no net change in the cation/anion balance in the leachate, this results in no production or consumption of protons and therefore no change in the leachate alkalinity. In strongly reducing, acidic environments, however, the conversion of Fe$^{2+}$ to Fe$^{3+}$ is hindered and the oxidation of metallic Fe may result in an increase of leachate alkalinity (i.e. protons are consumed). Under such conditions, Fe(II)O may not be oxidised at all.
The oxidation of calcium sulphide to produce Ca$^{+2}$ and SO$_{4}^{-2}$ has no net influence upon the leachate alkalinity as both ions are released in a 1:1 stoichiometric ratio. The oxidation of free sulphur, on the other hand, results in an unbalanced addition of SO$_{4}^{-2}$ to the leachate and will thus decrease the alkalinity. It has been observed that the oxidation reactions for reduced forms of sulphur may not necessarily go to completion in a landfill environment. In many cases, the dominant redox reaction product may be the metastable thiosulphate ion (S$_{2}$O$_{3}^{-2}$) rather than SO$_{4}^{-2}$ under basic, mildly oxidising conditions (Bäverman, 1997; Goldhaber, 1983). If we assume that thiosulphate is the end redox reaction product rather than sulphate, equation 13 and 14 may be rewritten as:

$$S(s) + \frac{1}{2}O_2 + \frac{1}{2}H_2O \leftrightarrow \frac{1}{2}S_2O_3^{-2} + H^+ \quad (17)$$

$$CaS(s) + O_2 + H^+ \leftrightarrow Ca^{+2} + \frac{1}{2}S_2O_3^{-2} + \frac{1}{2}H_2O \quad (18)$$

The incomplete oxidation of elemental sulphur actually produces more proton equivalents per mole of oxygen reacted (2 eq/mol O$_2$) than the complete pathway (1.33 eq/mol O$_2$). It is important to realise, however, that the overall reducing capacity of elemental sulphur is less when it is only partially oxidised to thiosulphate. A greater quantity of protons is therefore generated per mole of elemental sulphur by the complete oxidation pathway than by the incomplete pathway.

The oxidation of organic material presents an interesting problem, as the amount of proton equivalents generated varies according to which carbonate species is dominant in the leachant. The overall reaction pathway for the oxidation of organic material may therefore be written in three different ways:

$$CH_2O \text{ (s)} + O_2 \text{ (g)} \leftrightarrow HCO_3^- + H^+ \quad 6.3 < pH < 10.3 \quad (19)$$

$$CH_2O \text{ (s)} + O_2 \text{ (g)} \leftrightarrow CO_3^{-2} + 2H^+ \quad pH > 10.3 \quad (20)$$

$$CH_2O \text{ (s)} + O_2 \text{ (g)} \leftrightarrow H_2CO_3^+ \quad pH < 6.3 \quad (21)$$

The reducing capacity of a given quantity of organic material is the same for each of the three reactions given above; it is only the apparent amount of acidity generated
that varies as a function of leachate speciation. The definition of Alkalinity given in
the previous chapter is useful for making sense of this problem. In a strictly
mathematical sense, alkalinity in a carbonate-buffered system is defined as a
measurement of the proton deficiency with respect to the reference proton level
$\text{H}_2\text{CO}_3^- - \text{H}_2\text{O}$ (Stumm and Morgan, 1996; Morel and Hering, 1993). The addition or
removal of carbonate from the leachate, either by gas exchange with the atmosphere
or by oxidation of organic matter, does not affect the alkalinity provided there is no
change in the net balance of basic cations and conservative anions in the leachate (i.e.
no dissolution or precipitation of acid neutralising capacity).

If other ions such as $\text{NO}_3^-$, $\text{NH}_4^+$, $\text{HPO}_4^{2-}$ are released during the oxidation of organic
material, there will be a change in the leachate alkalinity. The imbalance in release
and assimilation of these ions is why forest soils and peat bogs are often acidic in
nature.

If we consider other non-organic redox processes, the release of ionic constituents
will generally lead to a change in leachate alkalinity. This will vary, depending upon
whether the oxidation goes to completion or not. It is possible to extend the definition
of alkalinity (remembering that alkalinity and H-acidity are equal, but of opposite
sign) to include non-carbonate species such as partially oxidised (and reduced) forms
of sulphur and iron. This quickly becomes a complex task, as we must consider the
very detailed chemistry of a multitude of different aqueous species. Using certain
simplifying assumptions, however, it is possible to avoid this complexity and still be
able to use an alkalinity balance to analyse the depletion of acid neutralising capacity.

The definition of alkalinity and H-acidity are convenient to work with, as they allow
us to separate aqueous pH buffering (by dissolved carbonate) from the pH buffering
that arises due to the release of ionic constituents from the solid phase. This permits a
fixed definition of solid phase acid neutralising capacity based upon the waste
composition.

In the discussion thus far, it has been assumed that leaching occurs either under
strongly oxidising conditions, or mildly oxidising conditions in the case of the
incomplete reaction pathways. In reality, the redox conditions in the leachate leaving the landfill may be strongly reducing. This will be particularly true if the landfill is fully water saturated. Under these conditions, reducing equivalents may be flushed from the landfill in the form of dissolved Fe(II), Mn(II), HS⁻, H₂S, NH₄⁺, and organic acids. Reducing equivalents may also be lost in the form of partially oxidised sulphidic and organic colloids suspended in the leachate, or gases formed during nitrate reduction, fermentation, and hydrogen generation reactions.

If the waste initially contains a mixture of reduced and oxidised constituents, the oxidised constituents may function as a source of oxidant in the system. This will be most important for waste materials where organic matter is found in combination with Fe(III) or sulphate containing minerals (MSWI bottom ash is a good example of this). Under strongly reducing conditions, the main oxidation reactions involving organic matter are likely to be:

\[
\text{CH}_2\text{O} (s) + 4\text{Fe}^{3+} + 2\text{H}_2\text{O} \iff \text{CO}_3^{2-} + 6\text{H}^+ + 4\text{Fe}^{2+} \quad (22)
\]

\[
\text{CH}_2\text{O} (s) + \frac{1}{2}\text{SO}_4^{2-} \iff \frac{1}{2}\text{HS}^- + \text{CO}_3^{2-} + \frac{3}{2}\text{H}^+ \quad (23)
\]

In the case of ferric reduction, the dissolved Fe²⁺ reaction product may precipitate in the form of siderite (FeCO₃) or Fe(OH)₂. The overall mineral reactions for ferric reduction could then be written as:

\[
\text{CH}_2\text{O} (s) + 4\text{Fe(OH)}_3(s) \iff 4\text{Fe(OH)}_2(s) + \text{CO}_3^{2-} + 2\text{H}^+ + 2\text{H}_2\text{O} \quad (24)
\]

\[
\text{CH}_2\text{O} (s) + 4\text{Fe(OH)}_3(s) + 3\text{CO}_3^{2-} + 6\text{H}^+ \iff 4\text{FeCO}_3(s) + 10\text{H}_2\text{O} \quad (25)
\]

If the reduction of sulphate were to result in the precipitation of elemental sulphur, we could write the overall mineral reaction for sulphate reduction in the following way:

\[
\frac{1}{2}\text{CH}_2\text{O} (s) + \text{SO}_4^{2-} \iff \text{S} (s) + \frac{3}{2}\text{CO}_3^{2-} + \text{H}^+ + \text{H}_2\text{O} \quad (26)
\]

The reduction of Fe(III) or sulphate does not result in the creation or destruction of reducing capacity, but merely a transfer of organic reducing equivalents to a ferrous or sulphide form. The ferrous and sulphidic precipitates may be subsequently oxidised
by in-transported oxygen from the atmosphere. By examining the stoichiometry of the oxidation reactions, however, it is easy to see that the same amount of oxygen is required to oxidise the waste regardless of whether the oxidation occurs directly, or via a sequence of redox reactions involving transfer of reducing equivalents from one form to another.

In a flow through system it is possible to make a mass balance over the amount of reducing capacity depleted from the waste irrespective of whether the redox reactions occur in the solid phase or in the aqueous phase. If we consider the molal concentrations (i.e. mol/kg) of oxidising and reducing equivalents transported across the system boundaries, we can write the following mass balance equation:

\[
\sum \text{oxidising equivalents} + \sum \text{reducing equivalents} = \frac{\rho_{\text{bulk}} L}{\rho_{\text{H}_2\text{O}} V} \int dn_R dt
\]  

(27)

where \( n_R \) is the reducing capacity of the waste at time \( t \), \( \rho_{\text{bulk}} \) is the bulk density of the waste, \( \rho_{\text{H}_2\text{O}} \) is the density of water, \( L \) is the depth of the landfill, and \( V \) is the leachant flux. By a slight modification of this mass balance, we define a term that is called the operational reducing capacity (\( n_R^e \)) of the waste. This is equal to the initial reducing capacity of the waste (\( n_R^0 \)) less the reducing capacity that is lost through flushing processes:

\[
n_R^e = n_R^0 - \frac{\rho_{\text{H}_2\text{O}} V}{\rho_{\text{bulk}} L} \int \text{reducing equivalents} dt
\]

(28)

In this equation, \( t_r \) is the length of time required to completely deplete the reducing capacity of the waste under the influence of in-transported oxidant. The operational reducing capacity is thus the net reducing capacity of the waste that is consumed within the landfill, when we account for the out-transport of reducing equivalents in the form of reduced or partially oxidised constituents. If we assume that the types and extent of the redox reactions are constant throughout the lifetime of the landfill, it is possible to calculate both the overall reducing capacity (\( n_R^0 \)) and the operational reducing capacity (\( n_R^e \)) from theoretical considerations without the need to calculate the integral in equation 28.
It should be noted that the term “operational reducing capacity” used here is not in any way related to the term “operational valence” used in the PHREEQE geochemical simulation program (Parkhurst et al., 1990).

In all the reaction pathways for incomplete oxidation, the total reducing capacity of the waste is less than that for the full oxidation reaction, as products are transported out of the waste in the leachate without being completely oxidised. Although the amount of proton acidity generated per mole of oxygen consumed may be greater for the incomplete oxidation pathways, the overall quantity of proton acidity generated by the reaction of a given amount of reducing material is generally highest for the complete oxidation pathways.

The principal oxidant transported into the waste landfill is molecular oxygen. If we use the rate of oxygen in-transport as a measure of the reducing capacity depletion rate, it is not necessary (from a mass balance point of view) to examine the detailed geochemistry of the individual redox reactions. For this reason, the individual oxygen consuming reactions may be lumped together into an overall reducing capacity.

If we assume that reaction products leached from the waste are fully oxidised, an overall reducing capacity can be defined for the waste if we also assume that CH$_2$O, S, CaS, Fe, and Fe(II)O are the only reducing constituents likely to be present in non-negligible quantities. It is difficult to predict how much of the waste reducing capacity will be lost by flushing processes without examining the detailed geochemistry and kinetics of individual redox reactions. For this reason, it is assumed here that the organic, ferrous, and sulphide reducing capacities are relatively immobile and reducing equivalents can only be lost in the form of thiosulphate.

From the stoichiometry of the oxidation reactions we shall define an overall reducing capacity ($n^0_R$) and proton generation capacity ($n^0_H$) based upon the equivalent number of moles of O$_2$ that can be consumed per mole of each reducing species in the waste:

$$n^0_R = n_{\text{CH}_2\text{O}} + \frac{3}{2} n_{\text{S}} + 2 n_{\text{CaS}} + \frac{3}{2} n_{\text{Fe}} + \frac{1}{4} n_{\text{Fe}(\text{II})O} \quad (29)$$

$$n^0_H = 2n_{\text{CH}_2\text{O}} + 2n_{\text{S}} \quad (30)$$
The terms \( n_i \) in the equation above, refer to the molal concentrations of each reducing constituent \((i)\) in the waste expressed in moles per gram of waste.

If we were to assume that thiosulphate is the main reaction product resulting from the oxidation of reduced forms of sulphur, equation 29 and 30 would need to be defined as:

\[
\begin{align*}
    n_R^e &= n_{\text{CH2O}} + \frac{1}{2} n_S + n_{\text{CaS}} + \frac{3}{4} n_{\text{Fe}} + \frac{1}{4} n_{\text{Fe(II)O}} \\
    n_H^e &= 2n_{\text{CH2O}} + n_S - n_{\text{CaS}}
\end{align*}
\]

(31) (32)

If we combine the different redox reactions together to make a generalised, symbolic reaction equation, we can write:

\[
R_0 + O_2 + H^+ + b CO_3^{2-} + R_{\text{diss}}^{(2b-a)} \leftrightarrow a H^+ + b CO_3^{2-} + R_{\text{diss}}^{(2b-a)}
\]

(33)

In this reaction equation, \( R \) represents the overall reducing capacity of the solid and \( R_{\text{diss}}^{(2b-a)} \) represents a dissolved reaction product resulting from the oxidation of one mole of \( R \). The superscript \((2b-a)\) refers to the charge on this dissolved species and is included only to ensure that the reaction is electrostatically balanced. It is important to include carbonate ion \( (CO_3^{2-}) \) explicitly in the generalised redox reaction as it is central to the definition of H-acidity.

The reaction product \( R_{\text{diss}}^{(2b-a)} \) may be interpreted as a conservative anion and could be included in the definition of alkalinity change given by equation 6. For the complete redox reaction pathways we may write:

\[
[\Delta [\text{Alk}]]_{\text{diss}} = -[\Delta [\text{ANC}]]_{\text{waste}} - b a R_0^{0} - a R_{\text{diss}}^{0}
\]

(34)

Or, for the incomplete oxidation pathways:

\[
[\Delta [\text{Alk}]]_{\text{diss}} = -[\Delta [\text{ANC}]]_{\text{waste}} - b a R_0^{0} - a R_{\text{diss}}^{e}
\]

(35)

For the complete oxidation pathways, the following relations give the stoichiometric coefficients in equation 33 (a and b):

\[
a = \frac{n_R^0}{n_R^e} \quad ; \quad b = \frac{n_{\text{CH2O}}}{n_R^e}
\]

(36)
If the oxidation reactions involving reduced sulphur do not go to completion, the stoichiometric coefficients are given instead by:

\[
a = \frac{n_H^e}{n_R^e} ; \quad b = \frac{n_{CH_2O}}{n_R^e}
\]  

(37)

The relative quantities of each of the reducing species in the waste must be known in order to calculate these variables. It is difficult to know these quantities in the absence of an extensive mineralogical investigation. In spite of this apparent difficulty, there is often indirect evidence to support certain simplifying assumptions about the reducing capacity of the waste.

Some information about the organic content of the waste may be obtained by the standard mass loss on ignition (LOI) test carried out at 550°C. Depending upon how much of the organic fraction is considered to be non-refractory, this data can be used to specify the amount of organic material comprising the total reducing capacity of the waste.

The amount of reduced sulphur is difficult to specify a priori. It does seem, however, that wastes likely to contain appreciable quantities of reduced sulphur often have low metallic Fe, Fe(II)O, and organic contents (at least for the wastes examined in this study). Previously, we have used the total concentration of Ca in the waste to define the acid neutralising capacity. When we consider the reducing capacity of the waste, which may include CaS, this definition is strictly incorrect. As Ca and S are present in the stoichiometric ratio 1:1 in CaS, however, it makes no difference to the estimated ANC provided we do not include free sulphur (nS) in the calculation:

\[
\text{ANC}_{\text{CaMg}} = 2d_{\text{Ca}} + n_{\text{Mg}} - n_{\text{S(IV)+CaS}}
\]  

(38)

\[
\text{ANC}_{\text{Ca}} = 2d_{\text{Ca}} - n_{\text{S(IV)+CaS}}
\]  

(39)

The overall reducing capacity of the waste upon complete oxidation (nR^o) can be determined by a redox titration. In this thesis, the difference between the measured overall reducing capacity and that given by the estimated amount of non-refractory organic carbon and reduced sulphur is assumed to be either Fe or Fe(II)O.
Although there are many assumptions implicit in this representation of the reducing properties of the waste, different case studies can be defined to explore the possible theoretical ranges of redox buffering behaviour. In this way it is possible to approximately describe the reducing properties of the waste, even in the absence of detailed analytical data.

### 3.2.2 Experimental Methods and Results

A redox titration method suggested by van der Sloot (1993) has been used to measure the reducing capacity of the waste materials examined in this project. In this method, finely ground waste material is oxidised with an excess quantity of Ce(IV). After the waste has stopped reacting, the suspension is filtered and a potentiometric titration performed upon the filtered reaction solution using Fe(II) as a reductant. The amount of Fe(II) added to the solution at the equivalence point is equal to the amount of Ce(IV) which remains unreacted after the waste oxidation step. The reaction equation for the reduction of Ce(IV) to Ce(III) using Fe(II) is:

\[
\text{Ce}^{4+} + \text{Fe}^{2+} \leftrightarrow \text{Ce}^{3+} + \text{Fe}^{3+} \tag{40}
\]

The difference between the initial amount of Ce(IV) added to the waste and the amount of Fe(II) required to reduce the excess Ce(IV) gives the reducing capacity of the waste in terms of electron equivalents. This may be converted to a reducing capacity in terms of oxygen consumption, using the half electrode reaction for water:

\[
\text{O}_2(g) + 4\text{H}^+ + 4\dot{e} \leftrightarrow 2\text{H}_2\text{O} \tag{41}
\]

The reducing capacity in moles of O₂ that can be consumed by the waste is calculated by dividing the molar reducing capacity specified in electron equivalents by four. As an excess of oxidant is used in these measurements, it is reasonable to expect that all the redox reactions go to completion.

The oxidising reagent was prepared as a 0.1M solution of Ce(SO₄)₂ in 1M H₂SO₄. The reducing solution for the potentiometric titration was prepared as a 0.1M solution of FeSO₄ in 0.1M H₂SO₄. A 0.1M solution of oxalic acid (C₂H₂O₄) was used as a
primary standard to calibrate the Ce(IV) solution. By performing a titration using the calibrated Ce(IV) solution, the Fe(II) solution could also be calibrated indirectly.

To determine the optimal oxidant/waste ratio for these experiments, some preliminary tests were carried out on the three waste materials. The optimal mass of waste was deemed to be that which would reduce roughly half of the oxidant solution. An optimal oxidant/waste ratio is necessary to obtain accurate results during the Fe(II) titration procedure.

In the experiments, 50ml of the acidified Ce(IV) oxidising solution was added to the optimal mass of waste as determined in the preliminary tests. The reacting suspensions were kept in airtight, glass Erlenmyer bottles and left to stand for nine days after which the solid material was removed by filtration using a glass fibre filter. 20ml samples of the filtered fluid were titrated with the Fe(II) reducing solution. The titration was carried out using a manually operated burette and a Metrohm redox electrode with voltmeter.

The initial oxidising capacity of the Ce(IV) solution was also measured by a control titration with the Fe(II) solution. The difference between the initial oxidising capacity of the solution and that remaining after reaction was taken to be the reducing capacity of the waste with which it had reacted. As only 20ml samples of the initially 50ml reaction solutions were titrated, the results had to be multiplied by a factor of 2.5 to obtain the correct reducing capacity for the waste. The measured reducing capacities of the three waste materials are given in table 3 below:
Table 3 Reducing capacity of solid waste materials used in this study

<table>
<thead>
<tr>
<th></th>
<th>$n_R^0$ (mol O$_2$/g waste)</th>
<th>$\rho_{\text{bulk}} n_R^0$ (mol O$_2$/m$^3$ waste)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MSWI</td>
<td>$1.03 \times 10^{-3}$</td>
<td>1335</td>
</tr>
<tr>
<td>AFS</td>
<td>$5.6 \times 10^{-4}$</td>
<td>1089</td>
</tr>
<tr>
<td>BFS</td>
<td>$3.4 \times 10^{-4}$</td>
<td>378</td>
</tr>
</tbody>
</table>

In order to draw conclusions about the type of reducing constituents, which may be active in a waste material, it is useful to consider both the origin and the elemental composition of the waste.

The measured reducing capacity of MSWI correlates well with the estimated organic content of the waste based upon the LOI at 550°C (4.3 wt%). It is likely, however, that a sizeable fraction of measured reducing capacity is actually in the form of metallic Fe or Fe(II)O. The MSWI waste has been observed to become a brownish, rust colour over time in batch experiments where the leaching vessels have been exposed to the atmosphere. This is a good circumstantial indicator for the presence of oxidisable Fe species in the waste. It is thought that the sulphur content of this waste is probably oxidised in the form of anhydrite (CaSO$_4$) or gypsum (CaSO$_4 \cdot 2H_2O$) and is unlikely to be initially present in a reduced state.

For BFS, the amount of organic material based upon the LOI is negligible (< 0.1 wt%). The Fe content of the waste is also known to be low. The observed reducing capacity is therefore most likely to be due to the presence of reduced sulphur compounds. If the reducing capacity were to be in the form of elemental sulphur, this would require about 20 percent more sulphur than is known to be present in the waste. If the main reducing component of the BFS is assumed to be CaS, on the other hand, about 97 percent of the sulphur content would need to be in this form to account for the measured reducing capacity. The bottles used for the oxidation of the BFS slag had a distinct odour of H$_2$S. This is a good circumstantial indicator for the presence of reduced sulphur compounds in the waste.
In steel manufacture, desulphurisation is usually achieved by direct injection of Ca and Mg compounds into the molten iron ladle (Elvers et al., 1994). This results in the formation of CaS and MgS which, being insoluble in the metal phase, are rapidly transferred into the slag phase. For this reason, it is thought that CaS is the most likely reducing species in BFS.

In field lysimeter tests carried out by Fällman (1997), the pH of the leachate from BFS was observed to fall to low levels (ca. pH 3). This is a circumstantial indicator for the presence of free elemental sulphur as the oxidation reactions for CaS should not result in the production of acidity. The pH of the leachate was also observed to fluctuate from summer (low pH) to winter (high pH) indicating microbial activity. Owing to the excellent agreement between the measured reducing capacity and the hypothesis of CaS being the major reductant, it is thought that elemental sulphur can only account for a small part of the observed reducing capacity.

For AFS, the amount of organic material based upon the LOI is also negligible (< 0.1 wt%). The sulphur content of the waste is also low and the reaction bottles had no odour of H$_2$S as was the case for BFS. For this reason it is probably safe to assume that the observed buffering capacity of the waste originates almost exclusively from metallic Fe or Fe(II)O.

In the reducing capacity measurements, a large excess of Ce(IV) oxidant is used and it is therefore assumed that the aqueous reaction products are completely oxidised. As discussed previously, these redox reactions may not necessarily go to completion in a landfill environment even under atmospheric oxidising conditions. It follows that the reducing capacity measurements may overpredict the available reducing capacity in a landfill environment. If we assume that it is only the oxidation reactions involving reduced sulphur that do not go to completion, it is possible to calculate the operational/measured reducing capacity ratio and the generalised stoichiometric coefficients (equation 36 and 37) for each of the waste materials investigated. These results are given in table 4 below:
<table>
<thead>
<tr>
<th></th>
<th>MSWI</th>
<th>AFS</th>
<th>BFS</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\frac{n^e}{n^0}$</td>
<td>$n^e / n^0 \approx 1$</td>
<td>$n^e / n^0 \approx 1$</td>
<td>$\frac{1}{3} \leq \frac{n^e}{n^0} \leq \frac{1}{2}$</td>
</tr>
<tr>
<td>$a$</td>
<td>$0 \leq a \leq 2$</td>
<td>$a \approx 0$</td>
<td>$-1 \leq a \leq 2$</td>
</tr>
<tr>
<td>$b$</td>
<td>$0 \leq b \leq 1$</td>
<td>$b \approx 0$</td>
<td>$b \approx 0$</td>
</tr>
</tbody>
</table>

Based upon the assumptions about the nature of the reducing constituents likely to be present in these waste materials, it is thought that the MSWI and AFS waste materials probably have operational reducing capacities that are close to those measured experimentally. For BFS waste the operational reducing capacity may be as little as 1/3 to 1/2 of the measured reducing capacity if there is only partial oxidation of the reduced sulphur species in the leachate.
Many of the heavy metal mobilisation processes that were discussed in chapter 2 depend, in one way or another, upon the pH and redox state of the leachant. Accordingly, the depletion rate of pH and redox buffering constituents in the waste will determine to a large extent how the leachate quality is likely to change over long periods of time. Although it may not be possible to exactly quantify many of the parameters that influence the transport of heavy metals, it is possible to construct simple models of pH and redox buffer depletion that may be used for scoping calculations. This chapter details some simple mathematical tools that can be used to make such calculations.

4.1 Rates of pH Buffer Depletion

The rate of pH buffer depletion in a waste heap or landfill depends upon the alkalinity of the leachant both entering and leaving the waste as well as the leachant flowrate. In this study of landfill leaching, we have chosen to consider only the processes that will maintain the leachate at circumneutral pH levels or higher.

Belevi et al. (1992) have proposed that the most important reactions involving Ca in a fresh MSWI bottom ash are the hydrolysis of lime (CaO) followed by precipitation of portlandite (Ca(OH)$_2$). These reactions occur immediately after quenching with water and continue over a period of time during storage. Over longer timescales, the indiffusion of atmospheric CO$_2$ as well as that produced by the oxidation of residual organic carbon leads to the precipitation of calcite. CaO is thermodynamically unstable under landfilling conditions and is transformed into portlandite irreversibly. Both portlandite and calcite, however, can dissolve and precipitate reversibly.

Some researchers have suggested (Comans, 1994) that minerals such as ettringite ($\text{Ca}_6\text{Al}_2\text{(SO}_4)_3\text{(OH)}_{12}\cdot2\text{H}_2\text{O}$) may be responsible for the observed solubility behaviour of Ca in the range of pH 10-12. As there is some doubt about which secondary minerals are actually responsible for Ca solubility control in this pH range,
it is probably safe to assume the presence of portlandite as this will tend to over-predict the leachability of Ca and give a conservative estimate of Ca depletion.

In order to make a simple model of pH buffer depletion we shall assume that portlandite, calcite, and gypsum (CaSO₄) are the three most important minerals controlling the Ca solubility. The dissolution and precipitation rates of these minerals are very fast, and it is therefore reasonable to assume equilibrium between the leachant and solid phases.

Portlandite is a highly soluble mineral that buffers at pH 12.4. Calcite is somewhat less soluble and buffers at a pH that is strongly dependent upon the partial pressure of CO₂. Gypsum, containing stoichiometrically balanced quantities of Ca²⁺ and SO₄²⁻, does not buffer pH. Because of the common ion effect, however, it can influence the solubility of other pH buffering minerals containing Ca.

Using a geochemical simulation program such as PHREEQC, it is possible to calculate both the pH and alkalinity of leachant in equilibrium with portlandite, calcite, and gypsum. These data are presented in figure 8 and figure 9, where the minerals are allowed to equilibrate with an initially acidic rainwater (pH 4) containing both dissolved carbonate and sulphate ions.
Figure 8  Alkalinity [Alk] of leachant in contact with portlandite/calcite/gypsum (thick line) and portlandite/calcite (thin line) under various conditions of CO₂ partial pressure ($P_{CO_2}$). Symbols (Δ and ○) give alkalinity of leachant where gas exchange is neglected.

Figure 9  pH of leachant in contact with portlandite/calcite/gypsum (thick line) and portlandite/calcite (thin line) under various conditions of CO₂ partial pressure ($P_{CO_2}$). Symbols (Δ and ○) give pH of leachant where gas exchange is neglected.
The simulation results indicate that both the leached alkalinity and the pH of the leachant are higher when gypsum is neglected. Neglecting gypsum will thus give a conservative estimate of pH buffer depletion in a flow through system such as a waste heap or landfill.

The broken vertical lines in figure 8 and figure 9 indicate the stability limit for portlandite ($P_{\text{CO}_2} \approx 10^{-13}$) as well as conditions corresponding to equilibrium with the atmosphere ($P_{\text{CO}_2} \approx 10^{-35}$). For CO$_2$ partial pressures greater than $10^{-13}$ atm, portlandite is thermodynamically unstable and is transformed into calcite. When the partial pressure of CO$_2$ exceeds the hydrostatic pressure in the leachant, bubbles of gas form spontaneously. This is a phenomenon known as ebullition. If the hydrostatic pressure is 1 atm, the point of ebullition coincides with the left-hand limit of the horizontal axis in the figures (i.e. $\log_{10} P_{\text{CO}_2} \approx 0$).

When the system is allowed to reach equilibrium without any gas exchange processes, the points corresponding to the symbols in figure 8 and figure 9 give the alkalinity and pH of the leachant. The circular markers (○) indicate the alkalinity and pH for the portlandite/calcite system and the triangular markers (△) indicate the alkalinity and pH for the portlandite/calcite/gypsum system.

It is possible to calculate the rate of pH buffer depletion using the description of the leachant chemistry given in figure 8. In this calculation we can include the rate of portlandite and calcite depletion due to flushing of water through the system, as well as conversion of portlandite to calcite under the influence of in-transported carbonate. Figure 10 below, illustrates how Ca is depleted from the waste over time owing to these leaching processes:
In general, the rate of portlandite depletion in the waste will be equal to the rate at which alkalinity is flushed out of the system added to the rate of carbonation. From mass balance considerations and assuming fast reaction kinetics, the rate at which the portlandite depletion front recedes into the waste is given by:

$$\frac{dz_p}{dt} = \frac{J_c + 0.5 V \rho_{\text{H}_2\text{O}} \Delta[\text{Alk}]_p}{\rho_{\text{bulk}} n_{\text{Ca(OH)}_2}^0}$$

(42)

where,

$$\Delta[\text{Alk}]_p = [\text{Alk}]_p - [\text{Alk}]_0$$

(43)

where $z_p$ is the depth to which the portlandite depletion front has receded in the waste, $J_c$ is the net carbonate flux that is consumed within the waste, $V$ is the leachant flux, $n_{\text{Ca(OH)}_2}^0$ is the molar concentration of portlandite initially in the system, $\rho_{\text{bulk}}$ is the bulk density of the waste, and $\Delta[\text{Alk}]_p$ is the alkalinity difference between the inflowing ($[\text{Alk}]_0$) and out-flowing leachant ($[\text{Alk}]_p$) when portlandite controls the leachant chemistry. This variable is a measure of the rate of portlandite depletion due to flushing processes.
The initial molar concentration of portlandite is given by:

\[ n_{\text{Ca(OH}_2)}^0 = 0.5 \cdot \text{ANC}_{\text{Ca}} \cdot g \cdot n_{\text{CaCO}_3}^0 \]  

(44)

where \( \text{ANC}_{\text{Ca}} \) is the acid neutralising capacity of the waste based upon its known Ca content, and \( n_{\text{CaCO}_3}^0 \) is the initial molar concentration of calcite in the system. For a fresh bottom ash or slag, the initial concentration of calcite may be assumed to be small in comparison to the amount of leachable calcium.

The rate of carbonation is equal to the net advective flux of dissolved carbonate added to the diffusive flux of gaseous \( CO_2 \) into the waste. If we assume a roughly linear carbonate concentration profile between the surface of the landfill (\( P_{\text{CO}_2} = 10^{-3.5} \text{ atm} \)) and the portlandite reaction front (\( P_{\text{CO}_2} \approx 0 \text{ atm} \)), we can write for the rate of carbonation:

\[ J_c = \frac{D_{e CO_2 - \text{Air}} P_{\text{CO}_2}^0}{RT} + \nabla \rho_{\text{H}_2\text{O}} C_T^0 - C_T^p h \]  

(45)

where \( D_{e CO_2 - \text{Air}} \) is the effective diffusivity of gaseous \( CO_2 \) in the waste, \( P_{\text{CO}_2}^0 \) is the atmospheric partial pressure of \( CO_2 \), \( C_T^0 \) is the total carbonate concentration in the infiltrating rainwater, \( C_T^p \) is the total carbonate concentration in the out-flowing leachate, \( R \) is the universal gas constant, and \( T \) is the temperature.

Equation 42 may be integrated to obtain the time required (\( t_p \)) for the portlandite reaction front to penetrate from the surface to a given depth (\( L \)) of waste:

\[ t_p = \frac{\rho_{\text{bulk}} n_{\text{Ca(OH}_2)}^0}{c_2} \left[ C_L + c_1 \log_c \left( c_1 + c_2 L \right) \right] \]  

(46)

where

\[ c_1 = \frac{D_{e CO_2 - \text{Air}} P_{\text{CO}_2}^0}{RT} \]  

(47)

\[ c_2 = \nabla \rho_{\text{H}_2\text{O}} C_T^0 - C_T^p + 0.5 \Delta [\text{Alk}] \]  

(48)

For a fresh waste, the calcite content may be assumed to be negligible. Equation 46 may therefore be written as:
After the portlandite content of the waste has been completely exhausted, calcite will become the solubility-governing mineral for Ca depletion. The time required to completely deplete all Ca from the waste ($t_c$) may then be calculated with the aid of a total mass balance for Ca:

$$t_c = \frac{L \rho_{\text{bulk}} \text{ANC}_{Ca} - V_{\text{H}_2\text{O}} \Delta[\text{Alk}]_p - \Delta[\text{Alk}]_t}{V_{\text{H}_2\text{O}} \Delta[\text{Alk}]_t}$$

(50)

where,

$$\Delta[\text{Alk}] = [\text{Alk}] - [\text{Alk}]_0$$

(51)

The variable $\Delta[\text{Alk}]$ is the alkalinity difference between the in-flowing ($[\text{Alk}]_p$) and out-flowing leachant ($[\text{Alk}]_t$) when calcite is the solubility controlling mineral.

If we normalise equations 49 and 50 with respect to the volumetric Ca content of the waste (i.e. $\rho_{\text{bulk}} \text{ANC}_{Ca}$), a generalised depletion time may be calculated that is independent of the Ca content of the waste. The generalised depletion time for portlandite has been calculated as a function of the effective diffusivity ratio ($D_{e\text{CO}_2-\text{Air}} / D_{0\text{CO}_2-\text{Air}}$) for CO$_2$ in air (see appendix 1), assuming a rainwater infiltration rate of 0.5 m$^3$/m$^2$/y. These results are presented in Figure 11 below:
The rate at which the calcite fraction is leached depends upon the CO$_2$ partial pressure in the landfill, as this will influence the solubility of calcite and thus the alkalinity leached. The presence of other minerals, such as gypsum, will also have an influence upon the solubility of calcite. If we assume that there is no exchange of CO$_2$ with the atmosphere after portlandite has been exhausted, the alkalinity and pH of the leachant will be given by the points in figure 8 and figure 9 that are labelled with symbols ($\triangle$ and $\circ$). The time taken to completely deplete the Ca content of the waste may then be calculated using equation 50. The results of these calculations are shown in figure 12 below, where the depletion time has been given in a generalised form for the system where gypsum is neglected:
Figure 12  Generalised depletion times (y m$^3$/mol) for total Ca content of waste as a function of waste depth and effective diffusivity ratio (calcite in equilibrium with leachate). Leachant flux assumed constant at 0.5 m$^3$/m$^2$y

Using the estimated value of the volumetric pH buffering capacity ($\rho_{\text{bulk ANC}_{\text{Ca}}}$) for each of the wastes, the actual depletion times for the portlandite and calcite fractions ($t_p$ and $t_c$) may be calculated. These results are shown in figure 13 below for each of the three waste types investigated, where a waste depth of 5 m has been considered:
The Mg content of each of these wastes (particularly BFS) is relatively high and will contribute towards the available ANC in a leaching environment. The calculations made thus far assume that only the Ca content of the waste contributes towards the ANC. Calculations made using this assumption will therefore tend to underestimate the time required for total depletion of the ANC.

When portlandite controls the leaching of Ca from the waste, alkalinity is consumed roughly 100-300 times faster by flushing processes than when calcite is the solubility controlling mineral. The more calcite that can be formed, the longer it takes to deplete the Ca content of the waste. From the standpoint of reducing heavy metal leaching, it would be advantageous to minimise the length of time where the leachate is buffered at a high pH and maximise the length of time where the leachate has a circumneutral pH.

By a slight modification of equation 50, it is possible to calculate an efficiency factor for the carbonation process. This factor is defined as the percentage of the buffering capacity that is transformed into calcite, in relation to the total ANC of the waste:
Using equation 52, the carbonation efficiency can be calculated as a function of landfill depth and effective diffusivity. These results are shown in figure 14 below:

![Graph showing carbonation efficiency as a function of waste depth and effective diffusivity ratio](image)

**Figure 14** Carbonation efficiency (%) given as a function of waste depth and effective diffusivity ratio (calcite in equilibrium with leachate). Leachant flux assumed constant at 0.5 m$^3$/m$^2$y

The results of these calculations suggest that the buffering capacity of the waste is used ineffectively when we consider that only a small fraction of the leachable Ca is actually transformed into calcite and a large proportion is lost due to flushing processes. This is particularly true for deep landfills, where there may be considerable resistance for CO$_2$ transport. If all of the Ca content of the waste were to be transformed into calcite, the ANC depletion times would be considerably longer than the results shown in figure 13.
4.2 Rates of Redox Buffer Depletion

In the proposed model of redox buffering it is assumed that a number of basic redox reactions may be lumped together in the form of a single, generalised oxygen consuming reaction (equation 33). It is difficult to assign a meaningful equilibrium constant to this generalised redox reaction as the system is in reality comprised of a number of redox couples, which may not necessarily be in equilibrium. In spite of this, the partial pressure of oxygen ($P_{O_2}$) in reducing systems is frequently very low and of only minor importance from a mass balance viewpoint.

As the rate of oxygen consumption is the result of a multitude of different competing redox reactions, the kinetics of oxygen consumption are actually quite complex. In this analysis, the rate of oxygen consumption is assumed to be a first order rate process. Upon first glance, this may seem to be an unrealistic assumption. In fact, the assumption of a first order rate process is probably about as complex as the nature of the problem allows. The actual kinetics of oxygen consumption may depend upon surface reaction rates, homogeneous reaction rates, bio-catalysis, particle and film diffusional resistances, or combinations thereof. The amount of physical heterogeneity in the system, which is difficult to characterise with any degree of certainty, will strongly influence these rate-limiting processes. A first order reaction rate, although a much simplified representation of the actual behaviour, does exhibit roughly the same characteristics as a more complex description of the kinetics (i.e. a maximum rate of oxygen consumption that decreases in proportion to the oxygen availability).

If we consider a generalised redox mineral that consumes oxygen in accordance with a first order rate law, we can write a one-dimensional mass balance for oxygen where oxygen transport results from a combination of advective and diffusive processes in a hypothetical, semi-infinite column of waste. In this mass balance we shall also neglect the small enhancement of mass transfer that arises due to the consumption of oxygen at the redox front and assume that the quasi stationary state approximation is approximately valid for the system (see paper III).
After some period of leaching, all reducing matter will have been depleted at the surface of the landfill. Over time this depletion zone will advance further into the hypothetical column of waste as the reducing capacity is depleted. The boundary between where there is, and where there is no reducing material is referred to as the redox front. The oxygen concentration profile may thus appear as shown conceptually in figure 15 below:

Figure 15  Conceptual diagram of waste leaching system showing the redox front and its associated oxygen concentration profile

In terms of dissolved oxygen concentration (Q), the one-dimensional, unsteady-state mass balance is:

\[-D_e^{\infty} \frac{\partial^2 Q}{\partial z^2} + V \frac{\partial Q}{\partial z} + kQ = -e^{-\frac{S}{\text{RT}}} + \frac{S}{Q} \]  

In this equation $D_e^{\infty}$ is the effective diffusivity of oxygen based upon aqueous concentrations, k is a first order kinetic constant for oxygen consumption, $K_q$ is the equilibrium constant for dissolution of oxygen in water, R is the universal gas
constant, $S$ is the degree of saturation, $t$ is time, $T$ is the absolute temperature, $V$ is the advective flux of leachant, $z$ is the waste depth, and $\varepsilon$ is the total porosity.

When the quantity of reducing material in the waste is large in relation to the dissolved concentrations of oxygen, many volumes of leachant need to be transported through the system until there is a noticeable change in the mass distribution of unreacted reducing material. If the time taken to establish a steady state concentration profile in the leachant is significantly less than the length of time required to completely dissolve a constituent in the solid phase, the quasi-stationary state approximation may be applicable. Lichtner (1988) discusses criteria for when this approximation may be valid. The quasi-stationary state approximation has been shown to be valid for advective, diffusive, and combined advective-diffusive systems. It can also be shown that the approximation is valid for the cases studied in this thesis (see paper III). The assumption of a quasi-stationary state permits setting the accumulation term on the right hand side of equation 53 to zero. In this case we can write:

$$\frac{d^2 Q}{dz^2} - \frac{V}{D_e^w} \frac{dQ}{dz} - \frac{k}{D_e^w} Q = 0$$

(54)

From mass balance considerations, we may also define the following relation (see appendix 1) between the overall effective diffusivity based upon gaseous partial pressure ($D_e^a$) and that based upon dissolved aqueous concentrations ($D_e^w$):

$$D_e^w = \frac{D_e^a}{K_q RT}$$

(55)

The dimensionless term $K_q RT$ is calculated to be approximately $3.1 \times 10^{-2}$ at 298 K. Equation 55 is a useful conversion formula as effective diffusivity is most frequently reported in terms of the free diffusivity for oxygen in air.

Equation 54 has the standard solution:

$$Q = \alpha_e \exp \left( \frac{D_e^a}{K_q RT} \right) \exp \left( \alpha_e \exp \left( \frac{D_e^a}{K_q RT} \right) \zeta \right)$$

(56)

where,
\[ \lambda_1 = \frac{V}{2D_e^w} + \sqrt{\frac{V^2}{4D_e^w} + \frac{k}{D_e^w}} \]  
(57)

\[ \lambda_2 = \frac{V}{2D_e^w} - \sqrt{\frac{V^2}{4D_e^w} + \frac{k}{D_e^w}} \]  
(58)

(\(\alpha_1\) and \(\alpha_2\) are constants)

As the redox reaction is absent upstream of the redox front, equation 56 is subject to the following restrictions:

\[ k = 0 \quad 0 < z < z_R \]  
(59)

\[ k > 0 \quad z_R < z < \infty \]  
(60)

The mass balance for oxygen also requires that there is no discontinuity of oxygen flux (\(J_z\)) or concentration at the redox front:

\[ J_z\big|_{z_R} = J_z\big|_{z_R} \]  
(61)

\[ Q\big|_{z_R} = Q\big|_{z_R} = Q_R \]  
(62)

In addition to these restrictions, we have the boundary conditions:

\[ z = 0 \quad Q = Q_0 \]  
(63)

\[ z = \infty \quad \frac{dQ}{dz} = 0 \]  
(64)

Applying these conditions and restrictions to equation 56 gives the following expressions for the aqueous oxygen concentration profile in the waste:

\[ Q = Q_0 - b_o - Q_R \exp\left(-\frac{V}{D_e^w} - \frac{z}{z_R}\right) \quad 0 < z < z_R \]  
(65)

\[ Q = Q_R \exp\left(\alpha_2 b - z_R\right) \quad z_R < z < \infty \]  
(66)

The oxygen concentration at the redox front is then given by:
where,

\[
\phi = \frac{V - D_e \lambda_2 h R}{1 - \exp \left( - \lambda_2 z_R \right)}
\]  

As the redox front recedes into the waste, the concentration of oxygen at the redox front decreases owing to the diffusional resistance for mass transport in the depleted zone upstream of the redox front.

The flux of oxygen anywhere in the system is equal to the sum of advective and diffusive fluxes. The flux of oxygen at the redox front may therefore be shown to be:

\[
J_R = \nabla - D_e \lambda_2 h R
\]  

The flux of oxygen at a distance \( L \), downstream of the redox front is:

\[
J_L = \nabla - D_e \lambda_2 h R \exp \left( \lambda_2 L - z_R \right)
\]  

For an infinitely fast redox reaction \( (k \rightarrow \infty) \), the rate of oxygen transport approaches a limiting value:

\[
J_R^\infty = -D_e \phi Q_0
\]

\[
J_L^\infty = 0
\]

After a stationary state is established, the concentration of dissolved oxygen downstream from the redox front is proportional to the concentration of oxygen at the redox front (equation 66). If the oxygen concentration at the redox front were to remain constant, the concentration profile for oxygen (and the reducing agent in the solid phase) would have a constant pattern and move without changing shape. Although this is not strictly true in our case owing to the fact that the oxygen concentration at the redox front \( (Q_R) \) changes slowly with time, we use this
simplification to allow for the use of simple analytical solutions. This gives a better insight into the main processes than the use of numerical solutions.

Using this simplification, the instantaneous velocity of the redox front is given by:

$$\frac{dz_R}{dt} = \frac{J_R}{\rho_{bulk} n_R^0} \quad (73)$$

Rearranging this equation and integrating the resultant expression gives the time required for the redox front to recede from the surface of the landfill to the depth $z_R$:

$$t - \tau_0 = \rho_{bulk} n_R^0 \int \frac{dz_R}{J_R} \quad (74)$$

The parameter $\tau_0$ is the time initially required for the formation of a steady state concentration profile before the redox front begins to move. It should be noted that $\tau_0$ approaches a value of zero for an infinitely fast reaction. The time required to establish this steady state is given by:

$$\tau_0 = \rho_{bulk} n_R^0 k Q_0 \quad (75)$$

The integral in equation 74 may be solved analytically to obtain:

$$\frac{t - \tau_0}{\rho_{bulk} n_R^0} = \frac{D^w_s}{V^2 Q_0} \frac{\lambda_2}{\lambda_1} \exp \left( \frac{V}{D^w_s} z_R \right) - \frac{z_R}{V Q_0} \quad (76)$$

It may be also shown that there is a maximum rate of redox buffer depletion when the redox reaction is infinitely fast. In this case $\lambda_2 / \lambda_1 \approx -1$ and the resultant equation for redox buffer depletion time is:

$$\frac{t}{\rho_{bulk} n_R^0} = -\frac{D^w_s}{V^2 Q_0} \exp \left( \frac{V}{D^w_s} z_R \right) - \frac{z_R}{V Q_0} \quad (77)$$

If the advective flowrate decreases to zero and there is only diffusional transport of oxygen, equation 77 reduces to:

$$\frac{t}{\rho_{bulk} n_R^0} = \frac{z_R^2}{2 D^w_s Q_0} \quad (78)$$
This result is identical to that given by a shrinking core model with an instantaneous reaction at the redox front (Romero, 1995). If the oxygen transport is purely advective, as might be the case in a saturated landfill, equation 76 reduces to:

\[ \frac{t - \tau_0}{\rho_{\text{bulk}} n_R} = \frac{z_R}{V Q_0} \quad (79) \]

It should be noted that under purely advective flow conditions, the rate of redox front movement (after the formation of a steady state mineral concentration profile) is independent of the redox reaction rate and is dependent only upon the reducing capacity of the waste and the rate of advective oxygen transport into the landfill. This is the same conclusion reported by Lichtner (1988, 1993). Furthermore, in the absence of diffusional transport, the oxygen concentration at the redox front will be constant and equal to that in the rainwater infiltrating the landfill.

As discussed previously, it is difficult to estimate the first order rate constant (k) for the generalised redox reaction. Equation 77 shows that for fast redox reactions there is a maximum theoretical rate of oxygen transport into the landfill, which limits the rate of oxidation. The kinetics of organic oxidation processes in MSWI bottom ash have been examined in paper II. In this previous investigation, it is speculated that the aqueous, first order reaction rate constant (k) probably lies somewhere in the range from $10^{-2}$ to $10^5$ year\(^{-1}\), depending upon the volumetric reducing capacity of the waste ($\rho_{\text{bulk}} n_R^0$) and the first order rate constant for organic depletion ($k_c$). From mass balance considerations, the value of k is given approximately by the following expression:

\[ k = \frac{k_c \rho_{\text{bulk}} n_R^0}{K_q P_{O_2}^0} \quad (80) \]

where $P_{O_2}^0$ is the partial pressure of oxygen in air under ambient conditions (i.e. 0.21 atm). The variable $k_c$ is the rate constant for organic depletion that is most often reported in the literature and usually lies between 0.01 year\(^{-1}\) and 20 year\(^{-1}\) for most non-refractory organic materials.
Of the three waste materials examined in this project it is known that only the MSWI is likely to contain organic reducing material. As discussed in chapter 3.2.2, it is thought that the reducing capacity of the BFS waste is predominantly CaS and that of AFS is Fe or Fe(II)O. There is very little literature data that can be used to estimate the value of the rate constant k for these other materials that do not contain organic matter.

Using the experimentally determined reducing capacity (or the estimated operational reducing capacity), it is possible to calculate the length of time required to totally deplete the reducing capacity of a waste using equation 76. In order to do so, however, the transport properties of the landfill, the leachant flux, and the first order kinetic constant need to be determined. As the current analysis centres upon a hypothetical landfill, these parameters are chosen to reflect what are considered to be conservative scenarios for leaching. In the calculations presented here, an effective diffusivity ratio of $D_r^* / D_o^* \approx 0.05$, and a leachant flux of 0.5 m/year have been assumed.

If the time calculated for the depletion of the waste reducing capacity is normalised as in equation 76-79, the value of $\mathcal{D} - \tau_0 \mathcal{G} \rho_{\text{bulk}} n^0_R$ is general for all reducing capacities, provided that the quasi-stationary state approximation is valid. Figure 16 below, shows the value of $t / \rho_{\text{bulk}} n^0_R$ plotted against the redox front depth in the waste material for a range of different kinetic constants and for purely advective flow conditions:
Figure 16   Generalised reducing capacity depletion time as a function of redox front depth (corrected for initial transient period). Assumed effective diffusivity ratio is 0.05

The results in figure 16 have been corrected for the formation time of the initial steady state mineral concentration profile ($\tau_{\text{rho}}/\rho_{\text{bulk}}n_{R}^{0}$) and therefore represent the total leaching time.

The depletion time under purely advective flow conditions is much longer than for the combined advection-diffusion case with a high effective diffusivity. The advective flow case corresponds to the situation where the landfill is completely water saturated (perhaps below the water table) and the effective diffusivity is thus very low. If the landfill is designed to minimise the flow rate of leachate, the redox buffer depletion time may be even longer than these results suggest for the advective flow case.

For the combined advection-diffusion case, the depletion time approaches that for an infinitely fast redox reaction with increasing depth. This indicates that the rate of redox buffer depletion becomes increasingly transport controlled at greater depths in the waste. For purely advective flow, the depletion rate is entirely transport controlled and after the formation of a steady state mineral concentration profile, it is only the reaction front width that depends upon the reaction rate.
In previous chapters, mass balance techniques have been used to predict the depletion rates of buffering constituents along a leachant flowpath. In the model of pH buffer depletion developed in chapter 4.1, no consideration has been given to the possibility that redox processes may generate carbon dioxide or mineral acidity. Oxidation reactions can accelerate the depletion of the pH buffering capacity if there is a significant amount of reducing material in the waste. This is particularly important if the waste is only partially saturated with water, as the in-transport of oxygen will be much greater under such conditions.

This chapter deals with the development of a generalised model for pH buffer depletion that incorporates the model of redox buffering developed in chapter 4.2. The model is more complex than those presented thus far, as a fully analytical solution is not available for the coupled pH and redox buffer depletion problem. Wherever possible, however, analytical solutions have been used in the numerical calculation procedure. This allows predictions of pH buffer depletion times to be generated quickly for leaching scenarios where more advanced geochemical simulation programs may require very long calculation times. An additional advantage of this approach is that the use of simple models gives results that are more transparent and thereby more easily understood than complex numerical models.

As in the previously developed models, the generalised solid waste leaching model (GSWLM) is based upon a mass balance of reactive constituents in the aqueous phase, combined with dissolution and precipitation of buffering constituents at the pH and redox reaction fronts. The model incorporates a rigorous description of the leachate chemistry together with carbonation processes resulting from organic oxidation reactions.
5.1 Organic Oxidation Reactions and Leachate Chemistry

When the residual organic matter in a waste material is oxidised in an aqueous environment, dissolved carbonate is generated. As a result, soluble Ca minerals such as portlandite will be transformed into calcite. Once the portlandite content of the waste has been exhausted, either by flushing or carbonation processes, the carbonate concentration and the \( \text{P}_{\text{CO}_2} \) in the leachate will increase if organic material continues to be oxidised. If this continues to the point where the \( \text{P}_{\text{CO}_2} \) exceeds the local hydrostatic pressure, gaseous CO\(_2\) may be generated. It was shown previously in figure 8 that the \( \text{P}_{\text{CO}_2} \) has a strong influence upon the solubility of calcite. As the solubility of calcite can be directly related to the leachate alkalinity, the \( \text{P}_{\text{CO}_2} \) will also have a significant influence upon the rate of pH buffer depletion.

Organic oxidation reactions can be simulated by adding fixed quantities of carbonate to the leachate. The geochemical simulation program, PHREEQC is ideally suited for this type of calculation as it has the capability of adding specified quantities of chemical species to, or from, reaction solutions. Simulations have been made using this program to calculate the Alkalinity, pH, and \( \text{P}_{\text{CO}_2} \) of initially acidic rainwater (\( \text{pH} 4 \)) that is equilibrated with calcite. These data are presented in figure 17 and figure 18 where carbonate has been added to the leachate in fixed quantities (\( \text{mol} \text{CO}_3^{2-} \) / kg \( \text{H}_2\text{O} \)):
The simulations indicate that the solution alkalinity (and thus the solubility of calcite) increases with increasing quantities of carbonate added to the reaction solution. When the $P_{CO_2}$ reaches 1 atm (the assumed hydrostatic pressure), the solubility of calcite is
at a maximum. When additional carbonate is added to the leachate, CO₂ gas is generated and the chemistry of the leachate remains unchanged. This also means that the pH of the leachate cannot decrease below about pH 6 when the reducing capacity results largely from residual organic material (when calcite is also present). This is not true for reactions that generate mineral acidity such as elemental sulphur or pyrite (FeS₂) and in these cases the pH can decrease to very low levels.

From the stoichiometry of the organic oxidation reaction given in equation 12, the molar quantity of carbonate added to the leachate is equal to the molar quantity of organic material oxidised. Consequently, the independent variable (Xc) in the figures above is the equivalent molar quantity of organic oxidation reaction added to the leachate. The data contained in figure 17 can therefore be used in a mass balance to calculate the depletion rate of calcite if we can estimate how much carbonate is added to the leachate as a result of organic oxidation reactions.

5.2 Coupling of pH and Redox Buffering Sub-Models

When we consider the weathering of a waste material containing a number of different pH and redox buffering constituents, they will tend to be depleted in an order that depends upon the amount of mineral present in the waste and the rate of in-transit of reactants. In the model of pH buffering presented in chapter 4.1, the process of carbonation disallows the existence of portlandite upstream of calcite in the waste when there is in-transit of gaseous CO₂ or dissolved carbonate. Based upon this observation, we can therefore assume that portlandite will always be depleted before calcite in a waste heap or landfill.

If an organic redox buffer is introduced as a third mineral component in this system, however, the picture becomes slightly more complicated. Given that portlandite and calcite will always leach in a fixed order, there are three principal leaching sequences that are possible (i.e. \( ^3P_2 / 2 = 3 \)). These three sequences (A, B, and C) are illustrated in figure 19 below:
Once we have established that there are only three possible leaching sequences for this system, we can make a mass balance to calculate the correct leaching sequence and the depletion time for each of the buffering minerals. As the quantity of carbonate generated by the redox reaction has such a strong influence upon the depletion rate of the portlandite/calcite pair, the redox model is clearly a good starting point for this mass balance.

In general, the pH of the leachant will not influence the rate of organic oxidation, provided it remains within the bounds in which bacteria thrive. For this reason we can achieve some degree of freedom by making the assumption that the oxidation reactions will influence the rate of pH buffer depletion, but not the reverse. If we consider an organic oxidation reaction that consumes oxygen in accordance with a first order rate law, equations 69 and 70 give the flux of oxygen entering and leaving the control volume bounded by the redox front ($z_R$) and the base of the landfill (L). The difference between the oxygen flux into and out of this control volume is equal to the specific rate of carbonate generation in the waste owing to oxidation processes. If
we assume steady state conditions, the rate of carbonate generation added to the net rate of carbonate transport in the leachant entering and leaving the landfill is equal to the rate of carbonate consumption.

For the case where the portlandite reaction front is somewhere between the redox front and the base of the landfill, the leaching system may appear as shown in figure 20 below:

![Diagram showing mass balance variables of importance for portlandite depletion processes](image)

**Figure 20**  Diagram showing mass balance variables of importance for portlandite depletion processes

When the quasi-stationary state approximation is valid, many pore-volumes of leachant must pass through the landfill until there is a noticeable change in the distribution of buffering minerals in the waste. In the time taken for a small packet of fluid to pass from the redox front to the base of the landfill, the redox front will therefore only have moved a very short distance. If the redox front can be considered as being approximately stationary during this time, the fluid packet will accumulate a quantity of carbonate (resulting from organic oxidation reactions) that can be estimated from steady-state mass balance considerations:

\[
X_c = \frac{b J_{Alk} - J_L C}{V \rho_{H2O}}
\]

As was illustrated in figure 17 and figure 18, there is only a certain amount of carbonate that can be added to water until ebullition occurs. When this happens, the CO\(_2\) gas may be transported out of the landfill and be lost to the atmosphere. In a model such as this, it is not possible to treat the out-transport of CO\(_2\) in any simple
way and it has therefore been neglected. In reality, there may be significant loss of 
CO₂, particularly when the effective diffusivity and oxidation rate are high.

In the model for pH buffering presented in this chapter, it is assumed that any gas 
bubbles are transported out of the landfill together with the leachate. The GSWLM 
will thus tend to overpredict the extent of carbonation. In spite of this inaccuracy, it is 
still thought that the model can provide important insights into the role of organic 
oxidation processes in waste landfills.

As mentioned previously, portlandite is thermodynamically unstable in the presence 
of large amounts of carbonate in the leachate and will be rapidly transformed into 
calcite. If the portlandite reaction front is somewhere short of the base of the landfill, 
the leachate leaving the landfill will be in equilibrium with portlandite and most of the 
carbonate will have been scavenged from the leachate by carbonation reactions 
upstream. As in the simple model of pH buffering, the rate at which portlandite is 
depleted from the waste will be equal to the rate of carbonation added to the rate of 
flushing. By making a mass balance, the time taken (\( t_p \)) to completely deplete 
portlandite from the waste will be given by:

\[
\rho_{\text{bulk}} \ln \frac{n_{\text{Ca(OH)}_2}^0}{n_{\text{Ca(OH)}_2}^\text{initial portlandite}} - \int V_{\text{H}_2\text{O}} \left[ C_T^0 - C_T^p \right] h \, dz \, dt - 0.5 V_{\text{H}_2\text{O}} \, \Delta [\text{Alk}] = 0 \quad (82)
\]

Although the redox front may be approximately stationary in the time taken for an 
individual fluid packet to pass through the landfill, it will probably move some 
distance in the time taken to deplete the waste of portlandite. The variable \( X_c \) is 
therefore likely to vary during this time. From equation 76, however, we have an 
analytical relation between time and the position of the redox front (\( z_R \)). In terms of 
\( z_R \), we can therefore write:

\[
X_c = b Q_R \left[ \frac{D_v \lambda_2}{V_{\text{H}_2\text{O}}} \right] \exp \left( \frac{\alpha_2 - z_R}{b} \right) \quad (83)
\]

Based upon equation 82, we define the following objective function:
\[
F(t) = \rho_{\text{bulk}} L n_{\text{Ca(OH)2}}^0 - V \rho_{\text{H2O}} \int C_T^\circ - C_T^p \ h X_c \ dt + 0.5 \Delta [\text{Alk}] \ j \tag{84}
\]

where \(F(t)\) is the amount of portlandite remaining in the waste at time \(t\). The solution to equation 82 is found when \(F(t) = 0\) (i.e., when the portlandite is exhausted). Using this objective function we can easily test whether the portlandite content of the waste is exhausted before the redox buffer, or vice versa. This can be done by calculating \(F(t)\) at the time corresponding to redox front breakthrough \(t_R\). At this time the organic redox buffer is completely exhausted and the total amount of carbonate generated by oxidation processes will be exactly equal to the initial organic content of the waste. This permits the following simplification of equation 84:

\[
F(t_R) = \rho_{\text{bulk}} L C_{\text{Ca(OH)2}}^\circ - n_{\text{CH2O}}^0 \ h V \rho_{\text{H2O}} t_R C_T^\circ - C_T^p \ h + 0.5 \Delta [\text{Alk}] \ j \tag{85}
\]

The calculated value of \(F(t_R)\) gives us the following information:

\(F(t_R) < 0 \Leftrightarrow \) portlandite depleted before redox buffer \((t_p < t_R)\)

\(F(t_R) > 0 \Leftrightarrow \) portlandite depleted after redox buffer \((t_p > t_R)\)

If the redox buffering capacity is depleted before portlandite, the time for portlandite depletion \(t_p\) is given by:

\[
t_p = \frac{\rho_{\text{bulk}} L C_{\text{Ca(OH)2}}^\circ - n_{\text{CH2O}}^0 \ h}{V \rho_{\text{H2O}} C_T^\circ - C_T^p \ h + 0.5 \Delta [\text{Alk}] \ j} \tag{86}
\]

When there is a very large amount of organic matter in the waste, or the rate of oxidation is very slow, the portlandite may be exhausted before a steady state redox mineral concentration profile has been established. During this time, the redox front is stationary and another simplification is possible. By evaluating \(F(t)\) at \(\tau_0\) (the time required for the formation of a steady state mineral concentration profile) we can test whether the portlandite is exhausted before or after the steady state has become established. Before the redox front has begun to move, we can write:

\[
F(\tau_0) = \rho_{\text{bulk}} L n_{\text{Ca(OH)2}}^0 - V \rho_{\text{H2O}} \tau_0 C_T^\circ - C_T^p \ h + 0.5 \Delta [\text{Alk}] \ j \tag{87}
\]

where
\[ X_c^0 = b Q_0 \left( D_x^{\frac{\lambda_2}{V \rho_{\text{H}_2\text{O}}}} \right) \exp \left( b \lambda_1 \right) \]  

(88)

The calculated value of \( F(\tau_0) \) gives us the following information:

\[
F(\tau_0) < 0 \quad \iff \quad t_p < \tau_0
\]

\[
F(\tau_0) > 0 \quad \iff \quad t_p > \tau_0
\]

If the portlandite is exhausted before the redox front has begun to move, the depletion time \((t_p)\) is given by:

\[
t_p = \frac{\rho_{\text{bulk}} L n_{\text{Ca(OH}_2}}^0}{V \rho_{\text{H}_2\text{O}}} \left[ e_c + C_c^0 - C_T^p \right] \Delta[\text{Alk}]_p j
\]

(89)

If the portlandite is depleted before the redox buffer and after \( \tau_0 \), we must solve the integral equation 84 numerically. The simplest way of performing this calculation is to differentiate equation 84 with respect to time and solve the resultant expression using a suitable ODE solver:

\[
\frac{dF}{dt}(t) = -V \rho_{\text{H}_2\text{O}} e_c + C_c^0 - C_T^p \Delta[\text{Alk}]_p j
\]

(90)

As this equation gives the rate of change of the portlandite content of the waste, the appropriate initial condition is the initial quantity of portlandite in the waste:

\[
F(0) = \rho_{\text{bulk}} L n_{\text{Ca(OH}_2}}^0
\]

(91)

The solution of equation 90 also requires the solution of the non-linear relation (equation 76) that gives the redox front location \((z_R)\) as a function of time in equation 83. The time required to completely deplete the portlandite can then be found by making use of the zero location feature that is common to most ODE solver packages.

Once portlandite has been depleted from the waste, calcite becomes the solubility-controlling mineral for Ca. The correct leaching sequence and the depletion time for calcite may then be calculated by making an overall mass balance. In a similar fashion to the mass balance used to compute the depletion time for portlandite, the time
required to completely leach the acid neutralising capacity ($\text{ANC}_{\text{Ca}}$) of the waste will be given by:

$$\rho_{\text{bulk}} L \cdot \text{ANC}_{\text{Ca}} - V p_{\text{H}_2\text{O}} \int_0^t \Delta[\text{Alk}] \, dt = 0 \quad (92)$$

where,

$$\Delta[\text{Alk}] = f \mathcal{B}_c \zeta \quad (93)$$

As previously, we can define a function $G(t)$ that can be used to test whether the acid neutralising capacity is exhausted before or after the redox buffer:

$$G(t) = \rho_{\text{bulk}} L \cdot \text{ANC}_{\text{Ca}} - V p_{\text{H}_2\text{O}} \int_0^t \Delta[\text{Alk}] \, dt \quad (94)$$

where $G(t)$ is the amount of acid neutralising capacity remaining in the waste at time $t$. As portlandite controls the leaching of Ca for a certain length of time ($t_p$), equation 94 is equivalent to:

$$G(t) = \rho_{\text{bulk}} L \cdot \text{ANC}_{\text{Ca}} - V p_{\text{H}_2\text{O}} \int_0^{t_p} \Delta[\text{Alk}] \, dt + \int_{t_p}^{t_R} \Delta[\text{Alk}] \, dt \quad (95)$$

By evaluating $G(t)$ at the time corresponding to redox front breakthrough ($t_R$), we have:

$$G(t_R) = \rho_{\text{bulk}} L \cdot \text{ANC}_{\text{Ca}} - V p_{\text{H}_2\text{O}} \int_0^{t_R} \Delta[\text{Alk}] \, dt \quad (96)$$

The calculated value of $G(t_R)$ gives us the following information:

$$G(t_R) < 0 \iff \text{ANC}_{\text{Ca}} \text{ depleted before redox buffer } (t_c < t_R)$$

$$G(t_R) > 0 \iff \text{ANC}_{\text{Ca}} \text{ depleted after redox buffer } (t_c > t_R)$$

As $\Delta[\text{Alk}]$ is a non-linear function of $X_c$, equation 96 must be solved numerically. This may be done using the same technique that was used to compute equation 84. By differentiating equation 94 with respect to $t$, we have:

$$\frac{dG}{dt}(t) = -V p_{\text{H}_2\text{O}} \Delta[\text{Alk}] \quad (97)$$

where,
\[ \Delta [\text{Alk}] = \Delta [\text{Alk}]_p = \text{constant} \quad t \leq t_p \quad (98) \]

\[ \Delta [\text{Alk}] = \Delta [\text{Alk}] = f(X_c) \quad t > t_p \quad (99) \]

The initial condition for this ODE is the initial acid neutralising capacity of the waste:

\[ G(0) = \rho_{\text{bulk}} L \cdot \text{ANC}_{ca} \quad (100) \]

The following logical test procedure can then be used to determine the correct leaching sequence, based upon the calculated values of \( F(t_R) \) and \( G(t_R) \):

1. If \( F(t_R) < 0 \) and \( G(t_R) < 0 \), then \( t < t_c < t_R \), which corresponds to leaching sequence A

\[ F(t_R) < 0 \quad G(t_R) < 0 \quad \iff \quad \text{leaching sequence A} \quad (101) \]

2. If \( F(t_R) < 0 \) and \( G(t_R) > 0 \), then \( t_R < t_c \), which corresponds to leaching sequence B

\[ F(t_R) < 0 \quad G(t_R) > 0 \quad \iff \quad \text{leaching sequence B} \quad (102) \]

3. If \( F(t_R) > 0 \) and \( G(t_R) > 0 \), then \( t_p < t_c \), which corresponds to leaching sequence C

\[ F(t_R) > 0 \quad G(t_R) > 0 \quad \iff \quad \text{leaching sequence C} \quad (103) \]

If leaching sequence A is valid, the value of \( t_c \) is found automatically by the zero location function in the solver and we therefore have:

\[ \int \Delta [\text{Alk}] \, dt = t_p \Delta [\text{Alk}]_p + \int_{t_p}^{t_c} \Delta [\text{Alk}] \, dt \quad (104) \]

For leaching sequence B, we have instead:

\[ \int \Delta [\text{Alk}] \, dt = t_p \Delta [\text{Alk}]_p + \int_{t_p}^{t_c} \Delta [\text{Alk}] \, dt + b - t_r \cdot g[\text{Alk}] \quad (105) \]

where,

\[ \Delta [\text{Alk}] = [\text{Alk}] - [\text{Alk}]_0 \quad (X_c = 0) \quad (106) \]

The term \( \Delta [\text{Alk}] \) is the difference in alkalinity between the landfill leachate ([Alk]) and the acid rain leachant ([Alk]) when no extra carbonate is added to the system (i.e. \( X_c = 0 \)). The time required to completely leach the acid neutralising capacity is therefore given by:

\[ -V_p H_{2O} b - t_r g[\text{Alk}] + G(t_R) = 0 \quad (107) \]
Rearranging this equation, we obtain:

\[ t_c = t_R + \frac{G(t_R)}{V \rho_{H_2O} \Delta[Alk]} \]  \hspace{1cm} (108)

For leaching sequence C, the time integral of \( \Delta[Alk] \) is linear:

\[ \int \Delta[Alk] \, dt = t_p \Delta[Alk]_p + d - t_p \Delta[Alk]_j \]  \hspace{1cm} (109)

The time required to completely leach the acid neutralising capacity is therefore given by:

\[ L \rho_{bulk} \cdot ANC_{Ca} - V \rho_{H_2O} \Delta[Alk]_p - t_p \Delta[Alk]_j = 0 \]  \hspace{1cm} (110)

Rearranging this equation gives \( t_c \) explicitly:

\[ t_c = \frac{L \rho_{bulk} \cdot ANC_{Ca} - V \rho_{H_2O} t_p \Delta[Alk]_p - \Delta[Alk]_j}{V \rho_{H_2O} \Delta[Alk]} \]  \hspace{1cm} (111)

The value of \( \Delta[Alk] \) as a function of \( X_c \) can be easily incorporated in the numerical calculation by linear interpolation within a table of equilibrium data (the same data as is contained in figure 17). If the equilibrium data are sufficiently detailed, this will be accurate for most practical purposes.

The concentrations of the various aqueous constituents in the leachate as well as the \( P_{CO_2} \) and \( pH \) can be obtained by interpolation within this table in the same way that the alkalinity of the leachate is determined. This allows us to plot the leachate concentration profiles as a function of time for a waste landfill of given depth (L). By calculating the depletion times and concentration profiles for a range of different values of L, the conditions at any depth within a waste landfill can be obtained as a function of time.

5.3 The Assumption of an Infinitely Fast Redox Reaction

If the rate of redox reaction is sufficiently fast, diffusional resistance in the landfill will control the transport of oxygen. If this occurs, it is possible to simplify the calculation procedure presented in chapter 5.2 by actually assuming that the redox
reaction is infinitely fast. When the redox reaction is infinitely fast, all in-transported oxygen is consumed at the redox front (i.e. \( Q_R = 0 \)) and the distance over which the redox front moves is exactly proportional to the amount of carbonate generated by the organic oxidation reaction. Equation 84 can therefore be simplified to the following expression:

\[
F(t) = \rho_{\text{bulk}} C n_{\text{Ca(OH)2}}^0 - z_R n_{\text{CH2O}}^0 \ h F \rho_{\text{H2O}} t \ \rho_{\text{H2O}} E \ C_T^0 - C_T^p + 0.5 \Delta [\text{Alk}]_p j
\]  

Equation 112 is easier to solve than equation 84, and the value of \( t_p \) (i.e. the solution to \( F(t) = 0 \)) can be computed using a zero-finding algorithm. The time required to completely exhaust the acid neutralising capacity \( t_c \) is then found using the same alkalinity balance as described in chapter 5.2 (equation 92), where the variable \( X_c \) is calculated according to:

\[
X_c = \frac{b J_R^w}{V \rho_{\text{H2O}}} = \frac{-b D_{\text{H2O}} \phi Q_0}{V \rho_{\text{H2O}}}
\]  

The variable \( J_R^w \) is the limiting rate of oxygen transport for an infinitely fast redox reaction (equation 71).

### 5.4 Simulations of Landfill Leaching

The generalised solid waste leaching model has been used to calculate the depletion times of the three buffering minerals and thus the leachate concentration profiles as a function of time. The simulations have only been made for the MSWI ash, as this was the only waste material examined in this project likely to contain organic material. Two different case studies have been investigated to evaluate the role of organic oxidation processes. The first case study simulates leaching with the same pH and redox buffering capacity as determined in chapter 3 (i.e. ANC_{Ca} and \( n_R^0 \)). It has been further assumed that the measured reducing capacity is entirely organic in origin. The second case study considers the same pH buffering capacity, but the organic concentration is assumed to be roughly ten times greater. This second case is an interesting comparison that is particularly relevant for discussions about the
desirability of combustion residue and organic waste co-disposal and whether organic matter can actually improve the leaching qualities of MSWI bottom ash.

Two of the leaching parameters that are most difficult to characterise are the effective diffusivity ($D^e_w$) and the approximated first order reaction rate constant ($k$). For this reason the simulations have considered a wide range of effective diffusivities and reaction rate constants to gain an appreciation of how these parameters influence the leaching processes. Figure 21 and figure 22 below, show the depletion times for portlandite ($t_p$), calcite ($t_c$), and organic matter ($t_R$), where both a slow redox reaction rate ($10^{-2}$ year$^{-1}$) and an infinitely fast redox reaction have been considered for an organic reducing capacity of 1.03 mol O$_2$/kg waste and a range of effective gas diffusivities. The vertical lines in the figure indicate instances where the leaching sequences depicted in figure 21 occur:

![Figure 21](image-url)

**Figure 21**  Actual depletion times for portlandite, calcite, and organic content of MSWI bottom ash as a function of effective diffusivity ratio. Leachant flux assumed constant at 0.5 m/y. Simulations consider a reaction rate constant of $10^{-2}$ year$^{-1}$, waste depth of 5m, and a reducing capacity of 1.03 mol O$_2$/kg waste
Figure 22: Actual depletion times for portlandite, calcite, and organic content of MSWI bottom ash as a function of effective diffusivity ratio. Leachant flux assumed constant at 0.5 m/y. Simulations consider an infinitely fast redox reaction rate, waste depth of 5m, and a reducing capacity of 1.03 mol O₂/kg waste.

The results suggest that the depletion time for portlandite and calcite are relatively independent of the redox reaction rate under the simulated conditions with an organic reducing capacity of 1.03 mol O₂/kg waste. For low effective diffusivities, the rate of organic oxidation is largely transport controlled and the redox reaction rate is of minor importance. As the effective diffusivity increases, a limit is reached where all carbonate generated by the redox reaction is consumed by carbonation processes. After this point, an increased effective diffusivity has no influence upon the depletion rate of portlandite and calcite. It is only at higher effective diffusivities, however, that the redox reaction rate begins to have an influence upon the rate of redox buffer depletion.

All three possible leaching sequences can be distinguished from the depletion time curves in both figure 21 and figure 22. For low effective diffusivities, the reducing capacity is consumed slowly because of the low rate of oxygen transport within the waste. Here, the depletion sequence A can be observed, where the buffering minerals are depleted in the order: portlandite, calcite, organic. For higher effective
diffusivities, a substantial amount of calcite is formed as a result of the increased oxidation rate. The redox buffer depletion front may then be able to overtake the calcite depletion front.

While the calcite depletion front is downstream of the redox front, the CO$_2$ partial pressure is relatively high and calcite is depleted quickly owing to its high solubility under these conditions. Once the redox front overtakes the calcite depletion front, the upstream solubility of calcite decreases by some two orders of magnitude and the depletion time increases. At this point, the rate of portlandite flushing is still greater than the rate of carbonation and the portlandite depletion front is therefore downstream of the redox reaction front. This corresponds to leaching sequence B, where the buffering minerals are depleted in the order: portlandite, organic, calcite.

For very high effective diffusivities, all of the carbonate generated by the redox reaction is used to transform portlandite into calcite. Even if all of the carbonate is used to form calcite, there is not enough to completely transform the portlandite content of the waste. The redox front velocity, however, continues to increase with increasing effective diffusivity and the redox front may, at some point, overtake the portlandite depletion front. Here we have leaching sequence C, where the buffering minerals are depleted in the order: organic, portlandite, calcite.

In figure 23 and figure 24 below, the depletion times are given for the case where the organic reducing capacity of the waste is increased to 10 mol O$_2$/kg waste. As for the previous simulations, both a very slow and an infinitely fast redox reaction rate have been considered for a range of effective gas diffusivities:
Figure 23  Actual depletion times for portlandite, calcite, and organic content of MSWI bottom ash as a function of effective diffusivity ratio. Leachant flux assumed constant at 0.5 m/y. Simulations consider a reaction rate constant of $10^{+2}$ year$^{-1}$, waste depth of 5m, and a reducing capacity of 10 mol O$_2$/kg waste.

Figure 24  Actual depletion times for portlandite, calcite, and organic content of MSWI bottom ash as a function of effective diffusivity ratio. Leachant flux assumed constant at 0.5 m/y. Simulations consider an infinitely fast redox reaction rate, waste depth of 5m, and a reducing capacity of 10 mol O$_2$/kg waste.
The redox buffer reaction rate has a much stronger influence upon the depletion rate of portlandite in this simulation. This is largely due to the fact that there is a surplus of organic matter over that which is required to completely transform the portlandite content of the waste into calcite. This means that leaching scenario C will never occur in this situation as the rate of portlandite depletion increases roughly in proportion to the rate of redox buffer depletion.

Even in this case there is an upper limit for the calcite depletion time. This occurs when all of the portlandite is transformed into calcite. The differences between the calcite depletion times in the each of the case studies are difficult to observe in the figures owing to the logarithmic time scale. Changes in the carbonation efficiency influence the calcite depletion time in a linear fashion. Doubling the amount of calcite formed, for example, doubles the depletion time for calcite. These differences are difficult to see on a logarithmic time scale. As for the simple model of pH buffering presented in chapter 4.1, it is possible to calculate a carbonation efficiency using equation 52. These results are given in figure 25 below, as a function of the effective diffusivity ratio, redox reaction rate constant, and organic reducing capacity:
Figure 25  Efficiency of carbonation as a function of effective diffusivity ratio and organic concentration. Thick lines correspond to a kinetic rate constant of $10^{+2}\text{ year}^{-1}$; broken lines are for an infinitely fast redox reaction.

For the actual waste reducing capacity (1.03 mol O$_2$/kg waste) the maximum attainable efficiency is roughly 55 percent in the absence of diffusional in-transport of CO$_2$. For this reducing capacity, the rate of redox reaction appears to have only a very small influence upon the carbonation efficiency. For the higher reducing capacity (10 mol O$_2$/kg waste), the redox reaction rate has a greater influence upon the carbonation efficiency, particularly for high effective diffusivities.

Leachate concentration profiles have been calculated based upon the leaching sequences identified in figure 21. The calculated concentration profiles correspond to the effective diffusivity ratios $2\times10^{-4}$ (sequence A), $2\times10^{-3}$ (sequence B), and $2\times10^{-2}$ (sequence C). The figures 26-31 below, show the total concentrations, pH, P$_{CO_2}$, and P$_{O_2}$ in the leachate as a function of time for each of these leaching sequences:
Leaching Sequence A

Figure 26  Leachate concentrations as a function of time for leaching sequence A. Thick lines are total Ca concentrations; thin lines are total carbonate concentrations. Arrows indicate depletion times for portlandite, calcite, and organic matter.

Figure 27  pH, $P_{CO_2}$ and $P_{O_2}$ in leachate as a function of time for leaching sequence A
Figure 28  Leachate concentrations as a function of time for leaching sequence B. Thick lines are total Ca concentrations; thin lines are total carbonate concentrations. Arrows indicate depletion times for portlandite, calcite, and organic matter.

Figure 29  pH, $P_{CO_2}$ and $P_{O_2}$ in leachate as a function of time for leaching sequence B
Figure 30 Leachate concentrations as a function of time for leaching sequence C. Thick lines are total Ca concentrations; thin lines are total carbonate concentrations. Arrows indicate depletion times for portlandite, calcite, and organic matter.

Figure 31 pH, $P_{CO_2}$ and $P_{O_2}$ in leachate as a function of time for leaching sequence C
For each of the leaching sequences investigated, the Ca concentrations, pH, and $P_{CO_2}$ are constant during the phase of leaching where portlandite controls Ca solubility. After portlandite has been depleted and calcite becomes the solubility-controlling mineral, the Ca concentration in the leachate varies as a function of the organic depletion rate. The slowly changing organic depletion rate during the calcite controlled leaching period is also reflected in the pH and $P_{CO_2}$ profiles presented in the figures.

Although the redox reaction rate appears to have little effect upon the rate of pH buffer depletion in the first case study ($n^0_R = 1.03 \text{ mol O}_2/\text{kg waste}$), it will have a strong influence upon the leachate $P_{O_2}$. For this slow redox reaction rate ($k = 10^{+2}$ year$^{-1}$) it is unlikely that heavy metal sulphides will form and the heavy metal solubility will thus be largely governed by the leachate pH. For fast redox reaction rates, the leachate $P_{O_2}$ will be significantly lower and the distance over which most of the $P_{O_2}$ variation occurs (i.e. the width of the redox front) will be narrower than for the examples presented in the figures. If the $P_{O_2}$ is sufficiently low, heavy metals may precipitate as insoluble sulphides.

For leaching sequence C, the Ca concentration profile takes the form of a simple step function. In this case, the effective diffusivity is sufficiently high that the redox buffer is exhausted very quickly. In principle, all of the carbonate generated by the redox reaction is consumed by carbonation, which results in roughly 55 percent of the portlandite being converted to calcite. Under these circumstances, the depletion times for both portlandite and Ca can be calculated very simply using equations 86 and 111.
The simulations presented in chapter 5.4 predict no adverse effects due to acid generation for high organic contents and high effective diffusivities. It has already been shown in chapter 2 that both high pH and low pH environments can increase the solubility of heavy metals. Using this as a starting point for assessing ash quality, we can say that a low portlandite and high calcite content is optimal for minimising heavy metal solubility. These conditions can be fulfilled when both the organic content of the waste and the effective diffusivity are high.

It should be remembered that we only consider pure mineral solubilities in making these projections of heavy metal leaching. It is possible that higher concentrations of dissolved organic complexing agents and colloids may increase the mobility of certain heavy metals. In spite of this uncertainty, it is still thought that organic material can improve the quality of waste ash owing to carbonation processes.

The simulations described in chapter 5.4 do not consider the in-diffusion, or out-diffusion of CO\(_2\). For a waste with a high organic content this may lead to an overestimation of the carbonation efficiency, as there will probably be substantial transport of CO\(_2\) out of the waste as a result of diffusion and ebullition. For a waste with a low organic content, the in-diffusion of atmospheric CO\(_2\) may play a more important role and the carbonation efficiency will thus be underestimated. The assumption of portlandite, on the other hand, will give an overestimation of the Ca leachability as it is the most soluble Ca mineral that is likely to be present in the waste. This will tend to give conservative estimates of the time required to deplete the acid neutralising capacity of the waste. The simulation results presented in this thesis therefore should be regarded as a rough guide to how the waste will behave in different leaching environments rather than an exact calculation tool for predicting leaching behaviour.

Waste landfills are generally designed to minimise water infiltration and in-diffusion of gaseous constituents. The leachant flowrate may therefore be considerably less than
the 0.5 m³/m²/year assumed in these calculations. Under the simulated hydraulic conditions, the acid neutralising capacity was found to last between 2000 and 100 000 years for a 5 metre deep waste heap, depending on the carbonation efficiency. Even if the available acid neutralising capacity is only a fraction of that measured in laboratory experiments, it is clearly sufficient to last a very long time.

When the acid neutralising capacity of the waste is exhausted, heavy metal concentrations should be expected to increase as a result of decreased leachate pH levels. The simulations in this thesis assume average values for transport and kinetic parameters describing the properties of waste. Certain of these parameters, such as the effective diffusivity and redox reaction rate, are somewhat uncertain owing to heterogeneities in the waste materials. For this reason, a wide range of possible values have been considered in the simulations. In a real landfill, heterogeneities in the waste will result in a distribution of breakthrough times for the different buffering constituents at various locations in the landfill. Any eventual increase in heavy metal pollution loads will thus occur over a long period of time rather than in a sudden release mode as these simulations may suggest.

Combustion residue and slag type wastes are often aged in heaps for some months before deposition. This is generally done so as to avoid explosion risks associated with hydrogen gas generation once the waste is landfilled. The simulations presented in this thesis, however, indicate that ageing of waste materials in heaps with a high effective gas diffusivity will also have a favourable impact upon the leaching properties of these wastes as a result of carbonation processes. A case could even be argued for the addition of easily degradable organic material (compost, for example) to the waste so as to accelerate the carbonation process during stockpiling. Using the models developed here, simulations can be made to help optimise the ageing of waste in such heaps. Although beyond the scope of the project, such an approach could be used to estimate the optimal heap dimensions, the ideal length of time for stockpiling, and if irrigation or leachate recirculation is desirable.
In principle, it should be possible to adapt the GSWLM to simulate the leaching of wastes containing sources of mineral acidity such as elemental sulphur or pyrite (FeS$_2$). Some preliminary investigations were carried out with the PHREEQC geochemical simulation program to see if this was possible. As has been mentioned previously, the oxidation of these reducing constituents can result in very low pH levels in the leachant. Under these conditions, the activity model used in the PHREEQC program ceases to be valid. A program that may be suitable for calculations where the pH drops to low levels is the PHRPITZ geochemical simulation program (Plummer et al., 1988). This program incorporates a more sophisticated model of aqueous activity that is valid for brines and other highly concentrated solutions.

Although simulations have not been made for sulphidic waste materials, it appears that they will behave very differently to wastes containing a mainly organic reducing capacity. Sulphidic wastes ideally should be stored under fully saturated conditions so as to minimise interaction of the waste with the atmosphere. If this type of waste is stored under partially saturated conditions, oxidation processes will result in acid production and heavy metals will be leached rapidly. Even in the absence of heavy metal contamination, high concentrations of aluminium (Al) mobilised by extremely acidic leachant can have a devastating impact upon aquatic ecosystems.

For a waste that contains mainly organic reducing constituents, it is not possible for the leachate pH to decrease as dramatically as for sulphidic waste materials and the advantages of a fully saturated landfilling environment are less compelling.

If the waste is stored under fully saturated conditions, the diffusional resistance of the water will impair the oxidation of organic material by molecular oxygen. Under these conditions, organic material may be oxidised by sulphate in accordance with the reaction:

$$\text{CH}_2\text{O (s)} + \frac{1}{2}\text{SO}_4^{2-} \leftrightarrow \frac{1}{2}\text{HS}^- + \text{CO}_3^{2-} + \frac{1}{2}\text{H}^+$$

(114)
The reduction of sulphate results in the generation of both $\text{HS}^-$ and dissolved carbonate. Carbonation processes will therefore continue to occur under fully saturated conditions even in the absence of molecular oxygen. As discussed in previous chapters, the oxidation of organics by way of sulphate reduction does not result in a depletion of the reducing capacity, but merely a transfer of reducing equivalents from one form into another. The generation of $\text{HS}^-$ may also result in the formation of insoluble heavy metal sulphides. This is the main advantage of disposal in a fully saturated environment.

If the waste is stored under partially saturated conditions, oxidation of organic material by molecular oxygen is relatively unhindered and will occur via the reaction:

$$\text{CH}_2\text{O (s) + O}_2(\text{g}) \leftrightarrow \text{CO}_3^{2-} + 2\text{H}^+$$  \hspace{1cm} (115)

In this case, there will be no formation of metal sulphides owing to the high partial pressure of oxygen in the waste and the heavy metal solubility will be controlled purely by the buffering pH of calcite.

Owing to the possibility of heavy metal immobilisation by sulphide formation, the fully saturated landfilling environment appears to be a better choice for the final disposal of waste materials that contain organic residues. This presupposes, of course, that there is sufficient sulphate and organic matter present in the waste for sulphide immobilisation to occur. Regardless of whether the waste is landfilled under fully saturated or only partially saturated conditions, it appears that organic material can play a key role in minimising the leachability of heavy metals from these wastes. It is also apparent from these simple analyses that it may be important to consider the geochemistry of sulphate-organic interactions in calculations that predict rates of redox buffer depletion and carbonation.
CONCLUSIONS

The main purpose of this project was to develop simple models of pH and redox buffering that can be used to make approximate estimates of how landfill leachate quality may be expected to evolve over long timescales.

The model, which has been developed, is simple and sufficiently flexible that it can be adapted to different waste types with relative ease. The redox buffering sub-model incorporates advective and diffusive oxygen transport, combined with a kinetic description of oxygen consumption within the waste. The pH buffering sub-model is based upon a local equilibrium assumption with portlandite and calcite as the primary pH buffering minerals. The mass balance is performed using a mixture of analytical and numerical techniques. The equilibrium chemistry is calculated rigorously using a geochemical simulation program (PHREEQC) and incorporated into the mass balance by way of interpolation in a list of tabulated data.

The following secondary conclusions can also be drawn from the experimental and theoretical investigations carried out within the framework of this project:

(1) The acid neutralising capacity (ANC) of a solid waste material as determined by a pH titration cannot be extrapolated directly to landfilling conditions without considering the identities of individual minerals that give rise to the observed pH buffering characteristics.

(2) The experimentally measured acid neutralising capacity of the three waste materials studied is overwhelmingly dominated by weathering processes involving the release of Ca and Mg ions.

(3) The theoretical acid neutralising capacity of the waste materials used in this study can be calculated from the known analytical concentrations of Ca, Mg, and S known to be initially present in the waste. For the three waste materials investigated in this study, the theoretically calculated acid neutralising capacities (ANC<sub>CaMg</sub>) are:
Between 40 and 60 percent of the theoretical acid neutralising capacity of the waste can be leached within 24 hours in a pH static leaching experiment carried out at pH 4. The rapid rate of leaching also appears to be approximately consistent with a transport controlled release mechanism.

An analytical method based upon oxidation of the waste followed by titration of unreacted oxidant was used to measure the reducing capacity of solid waste materials. Using this method, the reducing capacities of the three waste materials investigated were found to be:

- 1.03 mmol O₂/g waste (MSWI bottom ash)
- 0.56 mmol O₂/g waste (AFS bottom ash)
- 0.34 mmol O₂/g waste (BFS bottom ash)

From the known analytical concentrations of various elements in the waste materials and knowledge about the origin of the waste, it is possible to draw conclusions about the nature of the reducing capacity in each of the waste materials investigated. Based upon this information it is suggested that the reducing capacity of MSWI probably originates from residual organic material and reduced Fe compounds. For BFS slag the reducing capacity is most likely to be in the form of CaS and possibly a small quantity of free sulphur. The reducing capacity of AFS most likely results from reduced metal oxides (principally Fe(II)O).

It has been observed in previous studies that redox reactions may not necessarily go to completion in a landfill leaching environment. From theoretical considerations it has been shown that the “operational” reducing capacity can be estimated based upon the different types of redox reactions.
assumed to take place within the waste. For MSWI and AFS wastes it is thought that the operational reducing capacity will be roughly the same as that measured experimentally using the procedure outlined in chapter 3.2.2. For the BFS waste, on the other hand, the operational reducing capacity may be as little as half to one third of that measured experimentally if thiosulphate is produced as a reaction product rather than sulphate.

(6) Ca containing minerals that buffer at lower pH levels are generally less soluble than those that buffer at higher pH levels. The assumption that the soluble Ca content of the waste is initially in the form of portlandite will overestimate the ANC depletion rate. Calculations based upon this assumption will thus tend to give conservative estimates of the time taken to completely deplete the acid neutralising capacity of the waste.

(7) The time required to completely deplete the acid neutralising capacity will increase significantly even if only a small fraction of the highly soluble Ca fraction is transformed into calcite by carbonation processes.

(8) The acid neutralising capacity of the three waste materials is sufficient to buffer infiltrating acid rainwater at circumneutral to alkaline pH levels for very long times after landfill deposition. Depending on the effective gas diffusivity, the acid neutralising capacity can be expected to last somewhere between 2,000 and 100,000 years for a five metre deep waste heap with a rainwater infiltration rate of 0.5 m³/m²y.

(9) The presence of residual organic matter in waste materials does not appear to have a detrimental influence upon leachate pH or the rate of acid neutralising capacity depletion. In addition, the oxidation of organic material promotes the transformation of highly soluble Ca minerals into calcite thereby improving the leaching qualities of the waste. Oxidation of organics will occur under partially saturated conditions using molecular oxygen, or under fully saturated conditions by way of ferric and sulphate reduction. All of these reaction pathways result in the production of dissolved carbonate. A
more sophisticated model of redox buffer depletion will therefore need to consider both the in-transport of molecular oxygen as well as the geochemistry of Fe(III)-organic and sulphate-organic interactions.

(10) The best storage method for most types of solid waste seems to be deposition under fully water saturated conditions. If the waste contains sulphidic reducing material, the low effective diffusivity offered by the saturated environment will hinder oxidation processes that may lead to the generation of strong acids. For wastes that contain organic material, it has been shown that oxidation processes actually improve the leaching properties of the waste. The reduction of sulphate that accompanies anaerobic decomposition of organic matter can also promote the formation of metal sulphides that, being largely insoluble, will immobilise heavy metals. For wastes that contain a reducing capacity in the form of organic matter, sulphide immobilisation of heavy metals is the principal advantage of deposition under fully saturated conditions.
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<td>ANC</td>
<td>acid neutralising capacity of waste material</td>
<td>meq/g (eq/kg)</td>
</tr>
<tr>
<td>$\Delta[\text{ANC}]_{\text{waste}}$</td>
<td>change in waste ANC expressed in terms of aqueous concentration</td>
<td>mol/kg$_{\text{H}_2\text{O}}$</td>
</tr>
<tr>
<td>ANC$_{\text{Ca}}$</td>
<td>theoretical ANC based upon Ca content of waste</td>
<td>meq/g (eq/kg)</td>
</tr>
<tr>
<td>ANC$_{\text{CaMg}}$</td>
<td>theoretical ANC based upon Ca and Mg content of waste</td>
<td>meq/g (eq/kg)</td>
</tr>
<tr>
<td>ANC$_{7.0}$</td>
<td>experimentally measured ANC at pH 7</td>
<td>meq/g (eq/kg)</td>
</tr>
<tr>
<td>ANC$_{4.0}$</td>
<td>experimentally measured ANC at pH 4</td>
<td>meq/g (eq/kg)</td>
</tr>
<tr>
<td>b</td>
<td>stoichiometric coefficient for generalised redox reaction (equation 33)</td>
<td>−</td>
</tr>
<tr>
<td>$c_1$</td>
<td>constant (equation 46)</td>
<td>mol/m$^2$ y</td>
</tr>
<tr>
<td>$c_2$</td>
<td>constant (equation 46)</td>
<td>mol/m$^2$ y</td>
</tr>
<tr>
<td>$C_T$</td>
<td>total carbonate concentration</td>
<td>mol/kg$_{\text{H}_2\text{O}}$</td>
</tr>
<tr>
<td>$C_T^0$</td>
<td>total carbonate concentration (in-flowing leachant)</td>
<td>mol/kg$_{\text{H}_2\text{O}}$</td>
</tr>
<tr>
<td>$C_T^p$</td>
<td>total carbonate concentration (portlandite equilibrium)</td>
<td>mol/kg$_{\text{H}_2\text{O}}$</td>
</tr>
<tr>
<td>$C_w$</td>
<td>aqueous concentration of component</td>
<td>mol/m$^3$</td>
</tr>
<tr>
<td>$D_0^a$</td>
<td>free diffusivity of gaseous component in air</td>
<td>m$^2$/y</td>
</tr>
</tbody>
</table>
\[ D_{0}^{\text{CO2-Air}} \] free diffusivity of \( \text{CO}_2 \) in air \( \text{m}^2/\text{y} \)

\[ D_{0}^{\text{CO2-H2O}} \] free diffusivity of \( \text{CO}_2 \) in water \( \text{m}^2/\text{y} \)

\[ D_{0}^{\text{O2-Air}} \] free diffusivity of \( \text{O}_2 \) in air \( \text{m}^2/\text{y} \)

\[ D_{0}^{\text{O2-H2O}} \] free diffusivity of \( \text{O}_2 \) in water \( \text{m}^2/\text{y} \)

\[ D_{0}^w \] free diffusivity of gaseous component in water \( \text{m}^2/\text{y} \)

\[ D_{e}^a \] effective diffusivity of gaseous component in air \( \text{m}^2/\text{y} \)

\[ D_{e}^{\text{CO2-Air}} \] effective diffusivity of \( \text{CO}_2 \) in air \( \text{m}^2/\text{y} \)

\[ D_{e}^{\text{O2-Air}} \] effective diffusivity of \( \text{O}_2 \) in air \( \text{m}^2/\text{y} \)

\[ D_{e}^w \] effective diffusivity of gaseous component in water \( \text{m}^2/\text{y} \)

\[ E_c \] carbonation efficiency \( \% \)

\[ F \] objective function (equation 84) \( \text{mol/m}^2 \)

\[ G \] objective function (equation 94) \( \text{mol/m}^2 \)

\[ [\text{H}^{-}\text{Acy}] \] proton acidity \( \text{mol/kg}_{\text{H}_2\text{O}} \)

\[ \Delta [\text{H}^{-}\text{Acy}] \] change in leachate proton acidity \( \text{mol/kg}_{\text{H}_2\text{O}} \)

\[ \Delta H_r^0 \] heat of reaction at reference temperature \( (T_0) \) \( \text{kcal/mol} \)

\[ J_c \] net rate of carbonate transport \( \text{mol/m}^2 \text{y} \)

\[ J_L \] \( \text{O}_2 \) flux at depth \( L \) in landfill \( \text{mol/m}^2 \text{y} \)

\[ J_L^\infty \] \( \text{O}_2 \) flux at depth \( L \) in landfill (with infinitely fast redox reaction kinetics) \( \text{mol/m}^2 \text{y} \)

\[ J_R \] \( \text{O}_2 \) flux at redox front \( \text{mol/m}^2 \text{y} \)

\[ J_R^\infty \] \( \text{O}_2 \) flux at redox front (with infinitely fast redox reaction kinetics) \( \text{mol/m}^2 \text{y} \)

\[ J_z \] \( \text{O}_2 \) flux at depth \( z \) in waste \( \text{mol/m}^2 \text{y} \)

\[ k \] first order reaction rate constant for aqueous oxygen consumption \( 1/\text{y} \)

\[ k_c \] first order reaction rate constant for organic consumption \( 1/\text{y} \)

\[ K \] equilibrium constant for aqueous phase reaction

\[ K_0 \] equilibrium constant for aqueous phase reaction at reference temperature

\[ K_g^* \] Henry’s constant for gas absorption \( \text{mol atm/ m}^3_{\text{H}_2\text{O}} \)

\[ K_q \] Henry’s constant for \( \text{O}_2 \) gas absorption \( \text{mol atm/ m}^3_{\text{H}_2\text{O}} \)

\[ L \] landfill depth \( \text{m} \)

\[ n_{\text{Ca}} \] Ca content of waste \( \text{mol/kg (mmol/g)} \)
\[ n_{\text{CaCO}_3}^0 \quad \text{initial calcite content of waste} \quad \text{mol/kg (mmol/g)} \\
\[ n_{\text{Ca(OH)}_2}^0 \quad \text{initial portlandite content of waste} \quad \text{mol/kg (mmol/g)} \\
\[ n_{\text{CaS}} \quad \text{CaS content of waste} \quad \text{mol/kg (mmol/g)} \\
\[ n_{\text{CH}_2\text{O}} \quad \text{organic (CH}_2\text{O) content of waste} \quad \text{mol/kg (mmol/g)} \\
\[ n_{\text{Cl}} \quad \text{chloride content of waste} \quad \text{mol/kg (mmol/g)} \\
\[ n_{\text{Fe}} \quad \text{metallic Fe content of waste} \quad \text{mol/kg (mmol/g)} \\
\[ n_{\text{Fe(II)O}} \quad \text{Fe(II)O content of waste} \quad \text{mol/kg (mmol/g)} \\
\[ n_{\theta}^0 \quad \text{proton generation capacity of waste} \quad \text{mol/kg (mmol/g)} \\
\[ n_{\theta}^e \quad \text{operational proton generation capacity of waste} \quad \text{mol/kg (mmol/g)} \\
\[ n_{\text{K}} \quad \text{K content of waste} \quad \text{mol/kg (mmol/g)} \\
\[ n_{\text{Mg}} \quad \text{Mg content of waste} \quad \text{mol/kg (mmol/g)} \\
\[ n_{\text{N(V)}} \quad \text{nitrates content of waste} \quad \text{mol/kg (mmol/g)} \\
\[ n_{\text{Na}} \quad \text{Na content of waste} \quad \text{mol/kg (mmol/g)} \\
\[ n_{\text{R}} \quad \text{reducing capacity of waste} \quad \text{mol/kg (mmol/g)} \\
\[ n_{\text{R}}^0 \quad \text{total reducing capacity of waste} \quad \text{mol/kg (mmol/g)} \\
\[ \Delta[n_{\text{R}}^0] \quad \text{change in overall waste reducing capacity} \quad \text{mol/kg}_\text{H}_2\text{O} \\
\[ n_{\text{R}}^e \quad \text{operational reducing capacity of waste} \quad \text{mol/kg (mmol/g)} \\
\[ \Delta[n_{\text{R}}^e] \quad \text{change in operational waste reducing capacity} \quad \text{mol/kg}_\text{H}_2\text{O} \\
\[ n_{\text{S(IV)}} \quad \text{sulphate content of waste} \quad \text{mol/kg (mmol/g)} \\
\[ P_{\text{comp}} \quad \text{gaseous component partial pressure} \quad \text{atm} \\
\[ P_{\text{O}_2} \quad \text{O}_2 \text{ partial pressure} \quad \text{atm} \\
\[ P_{\text{O}_2}^0 \quad \text{atmospheric O}_2 \text{ partial pressure} \quad \text{atm} \\
\[ Q \quad \text{aqueous oxygen concentration} \quad \text{mol/m}^3_\text{H}_2\text{O} \\
\[ Q_0 \quad \text{in-transported aqueous oxygen concentration} \quad \text{mol/m}^3_\text{H}_2\text{O} \\
\[ Q_{\text{R}} \quad \text{aqueous oxygen concentration at redox front} \quad \text{mol/m}^3_\text{H}_2\text{O} \\
\[ R \quad \text{universal gas constant} \quad \text{atm m}^3/\text{mol K} \\
\[ S \quad \text{water saturation} \quad \text{m}^3_\text{H}_2\text{O}/\text{mol} \\
\[ t \quad \text{time} \quad \text{y} \\
\[ T \quad \text{temperature} \quad \text{K} \\
\[ T_0 \quad \text{reference temperature} \quad \text{K} \\
\[ t_c \quad \text{time to deplete total Ca content of waste} \quad \text{y} \\
\[ t_p \quad \text{time to deplete portlandite content of waste} \quad \text{y} \\
\[ 93 \]
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>t_R</td>
<td>time to deplete reducing capacity of waste</td>
<td>y</td>
</tr>
<tr>
<td>V</td>
<td>leachant flux</td>
<td>m³/m² y</td>
</tr>
<tr>
<td>x_a</td>
<td>constant in equation 116</td>
<td>–</td>
</tr>
<tr>
<td>X_c</td>
<td>carbonate added irreversibly to leachant</td>
<td>mol/kg H₂O</td>
</tr>
<tr>
<td>X'_c</td>
<td>carbonate added irreversibly to leachant</td>
<td>mol/kg H₂O</td>
</tr>
<tr>
<td>x_w</td>
<td>constant in equation 116</td>
<td>–</td>
</tr>
<tr>
<td>z</td>
<td>depth</td>
<td>m</td>
</tr>
<tr>
<td>z_c</td>
<td>depth of calcite depletion front</td>
<td>m</td>
</tr>
<tr>
<td>z_p</td>
<td>depth of portlandite depletion front</td>
<td>m</td>
</tr>
<tr>
<td>z_R</td>
<td>depth of redox front</td>
<td>m</td>
</tr>
<tr>
<td>α₁, α₂</td>
<td>integration constants (equation 56)</td>
<td>–</td>
</tr>
<tr>
<td>δ</td>
<td>constrictivity</td>
<td>m/m</td>
</tr>
<tr>
<td>ε</td>
<td>porosity</td>
<td>m³/m³</td>
</tr>
<tr>
<td>φ</td>
<td>constant (equation 68)</td>
<td>–</td>
</tr>
<tr>
<td>λ₁, λ₂</td>
<td>Eigen values in equation 56</td>
<td>1/m</td>
</tr>
<tr>
<td>μ</td>
<td>viscosity of water</td>
<td>N/m²s</td>
</tr>
<tr>
<td>μ₀</td>
<td>viscosity of water at reference temperature</td>
<td>N/m²s</td>
</tr>
<tr>
<td>ρ bulk</td>
<td>bulk density of waste</td>
<td>kg/m³</td>
</tr>
<tr>
<td>ρ_H₂O</td>
<td>density of water</td>
<td>kg/m³ H₂O</td>
</tr>
<tr>
<td>τ</td>
<td>tortuosity</td>
<td>m/m</td>
</tr>
<tr>
<td>τ₀</td>
<td>formation time for steady state mineral concentration profile</td>
<td>y</td>
</tr>
</tbody>
</table>
REFERENCES


APPENDICES

APPENDIX 1  Effective Diffusivity in a Porous Medium

PAPERS


IV  Crawford J., Bellander C., and Neretnieks I., 1999. Acid neutralising kinetics of slags and combustion residue waste materials. (submitted for publication)
The effective diffusivity of a gaseous component in a waste landfill is a highly non-linear function of porosity, pore tortuosity, pore constrictivity, particle size distribution, particle aggregation, and the degree of water saturation. A number of methods have been developed for the correlation of effective diffusivity in porous media. One of the more successful models is that of Millington and Shearer (1971). An extended version of this model, developed by Collin (1987) accounts for the diffusion of gaseous components in both the water and air-filled voids of the medium. This model can estimate the effective diffusivity reasonably well for non-aggregated particle beds, but may underestimate the effective diffusivity if there is a high degree of particle aggregation.

Using this estimation method, the effective diffusivity is given by:

\[
\frac{D_e}{D_0} = b \cdot \frac{g^b}{S^g} - S^a + K^*_g R T \cdot b \cdot \frac{g^b}{S^g} - \frac{1}{K^w} \cdot \frac{b^g}{S^g}
\]

where \(D_0\) is the free diffusivity of the component in air, \(D_0^w\) is the free diffusivity of the component in water, \(\varepsilon\) is the total porosity, \(S\) is the fraction of water saturated porosity, \(K^*_g\) is the Henry’s constant for absorption of the gaseous component in water, \(R\) is the universal gas constant, and \(T\) is the temperature. The parameters \(x_a\) and \(x_w\) are found by solving the following non-linear equations:

\[
[\varepsilon b]^{x_a} + [1 - \varepsilon]^{x_a} = 1
\]

\[
[\varepsilon S]^{x_w} + [1 - \varepsilon S]^{x_w} = 1
\]

The Henry’s constant is defined so that:

\[
C_w = K^*_g P_{\text{comp}}
\]

where \(C_w\) is the total concentration of the component in the aqueous phase, and \(P_{\text{comp}}\) is the partial pressure of the component in the gas phase.
A slightly modified version of this model may be used for the estimation of effective
diffusivities in aggregated media. Unfortunately, this more advanced model requires
extra information about the water distribution, which is not possible to predict from
theoretical considerations unless further assumptions are made.

Simpler, but theoretically less rigorous is the direct proportionality model also
described by Collin (1987). The model assumes that the effective diffusivity is
directly proportional to the area available for diffusion, and accounts for diffusion
both in the aqueous and gaseous phases. Although the model overestimates the
effective diffusivity for non-aggregated media, it may give more realistic results for
aggregated heaps of combustion residues and slags. Using this model, the effective
diffusivity of a gaseous component is given by:

\[
\frac{D_e^a}{D_0^a} = \frac{\delta}{\tau^2} \frac{S}{\alpha} K R T S \frac{D_0^w}{D_0^a},
\]

(120)

where \(\delta\) is the pore constrictivity, and \(\tau^2\) is the pore tortuosity. The variable
combination \(\delta \epsilon / \tau^2\) is referred to as the formation factor for diffusion and is entirely
dependent upon the geometrical properties of the porous medium.

These estimation methods give results that are subject to large variation depending
upon the assumed values of different parameters in the models. In spite of these other
uncertainties, it may sometimes be appropriate to account for the variation of free
diffusivity and Henry’s constant as a function of temperature. The gas and liquid
phase diffusivities may be approximately corrected for temperature variations using
the following relationships:

\[
\frac{D_0^a}{D_0^w} = \frac{D_0^a}{D_0^w} \left(\frac{T}{T_0}\right)^{1.823},
\]

(Perry and Green, 1997) \hspace{1cm} (121)

\[
\frac{D_0^w}{D_0^w} = \frac{D_0^w}{D_0^w} \left(\frac{T}{T_0}\right)^{1.823},
\]

(Bird and Lightfoot, 1960) \hspace{1cm} (122)

where \(T\) is the ambient temperature and \(T_0\) is the reference temperature. \(D_0^a\), \(D_0^w\), \(D_0^a\), \(D_0^w\), \(D_0^w\), and \(D_0^w\) are the free diffusivities of the component in air and
water evaluated at the temperatures indicated in parentheses. \( \mu_0 \) is the viscosity of water at the reference temperature and \( \mu \) is the viscosity of water at temperature \( T \).

The value of the Henry’s constant is generally a function of temperature, and in some cases is also dependent upon the leachant chemistry. For carbon dioxide (CO\(_2\)) absorption, the Henry’s constant is strongly dependent upon the pH of the water as the solubility of CO\(_2\) increases with increasing pH. At pH levels higher than about 5.7, the following aqueous phase reactions involving carbonate must be considered:

<table>
<thead>
<tr>
<th>Reaction</th>
<th>( \log_{10} K_0 )</th>
<th>( \Delta H_f^0 ) (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{CO}_2(g) + \text{H}_2\text{O} \Leftrightarrow \text{CO}_3^{2-} + 2\text{H}^+ )</td>
<td>+18.16</td>
<td>-2.22</td>
</tr>
<tr>
<td>( \text{CO}_3^{2-} + \text{H}_2\text{O} \Leftrightarrow \text{HCO}_3^- + \text{H}^+ )</td>
<td>+10.33</td>
<td>-15.13</td>
</tr>
<tr>
<td>( \text{CO}_3^{2-} + 2\text{H}_2\text{O} \Leftrightarrow \text{H}_2\text{CO}_3^- + 2\text{H}^+ )</td>
<td>+16.681</td>
<td>-9.40</td>
</tr>
</tbody>
</table>

Note: \( \text{H}_2\text{CO}_3^- = \text{H}_2\text{CO}_3 + \text{CO}_2^{(aq)} \)

reference temperature \( (T_0) \) is 298 K

The values of \( \log_{10} K_0 \) and \( \Delta H_f^0 \) are the log equilibrium constants and enthalpies of reaction for the given chemical reactions.

The value of Henry’s constant may then be found by combining the mass action equations for CO\(_2\) absorption and carbonate speciation to obtain the total concentration of dissolved carbonate (\( C_T \)) in terms of the \( P_{\text{CO}_2} \) and pH. The total carbonate concentration is:

\[
C_T = [\text{CO}_3^{2-}] + [\text{HCO}_3^-] + [\text{H}_2\text{CO}_3^-]
\]

(123)

At a temperature of 298 K, Henry’s constant for CO\(_2\) absorption is calculated to be:

\[
K^* = \frac{1 + 10^{\frac{b_{33-\text{pH}}}{10}} \cdot 10^{\frac{b_{681-2\text{pH}}}{10}}}{10^{\frac{b_{16-2\text{pH}}}{10}}}
\]

(124)

At temperatures other than 298 K, the log equilibrium constants \( (\log_{10} K) \) for the aqueous phase reactions may be estimated with the aid of the Van’t Hoff equation:
log_{10} K = log_{10} K_0 - \frac{\Delta H_0^0}{R} \left( \frac{1}{T_0} - \frac{1}{T} \right) \tag{125}

(R = 8.314 \times 10^{-3} \text{ kJ/mol K})

Figure A1 below, gives the calculated value of Henry’s constant (K_g^*) for absorption of CO_2 in water as a function of pH and temperature:

![Figure A1](image_url)

**Figure A1** Variation of Henry’s constant (mol/dm^3 atm) for CO_2 absorption in water as a function of pH and temperature (calculated using equations 124 and 125)

Using Millington and Shearer’s model for unaggregated media (equation 116) and the direct proportionality model (equation 120), the effective diffusivity of CO_2 in air may be estimated as a function of both saturation and pH. These results of these calculations are shown in figures A2 and A3, below.
Figure A2  effective diffusivity of \( \text{CO}_2 \), relative to free diffusivity in air as a function of pH and degree of water saturation (calculated using equation 116, assuming a porosity of 30% and a temperature of 298K)

Figure A3  Effective diffusivity of \( \text{CO}_2 \) in air, relative to free diffusivity as a function of pH and degree of water saturation (calculated using equation 120, assuming a formation factor of 0.3 and a temperature of 298K)
From mass balance considerations it is also possible to express the effective diffusivity in terms of aqueous phase concentrations

\[
\frac{D_e^w}{D_0} = \frac{1}{K_g^* \text{ RT}} \cdot \frac{D_0^e}{k_0^e}
\]  

(126)

Or, put more simply

\[
D_e^w = \frac{D_0^e}{K_g^* \text{ RT}}
\]

(127)

where \( D_0^e \) is the effective diffusivity of the component in water. In chapter 4.2, the Henry’s constant for O\(_2\) absorption is given the variable name \( K_q \) so as to distinguish it from the variable \( K_g^* \) that is used for CO\(_2\) absorption.

The solubility of oxygen (O\(_2\)) in water does not vary with pH as is the case for CO\(_2\).

The Henry’s constant for oxygen absorption in water varies from \( 1.27 \times 10^{-3} \) (mol/dm\(^3\)atm) at 273K to \( 2.18 \times 10^{-3} \) (mol/dm\(^3\)atm) at 298K. Figure A4 below, shows the effective diffusivity of O\(_2\) as a function of water saturation, calculated using both Millington and Shearer’s model for unaggregated media (equation 116) and the direct proportionality model (equation 120):
Puura (1998) has reviewed a number of studies of the effective diffusivity in heaps of pyritic mining waste. It was found that the relative effective diffusivity rarely exceeds \( D_e^a / D_0^a \approx 0.05 \) for well-drained heaps. In this thesis it has been assumed that these results are roughly applicable to heaps of ashes and slags.

The free diffusivities of carbon dioxide in air and water are:

\[
D_{0}^{CO2-Air} (0^\circ C) = 1.38 \times 10^{-5} \text{ m}^2/\text{s} \quad \text{(Perry and Green, 1997; table 2-371)}
\]

\[
D_{0}^{CO2-H2O} (0^\circ C) = 1.96 \times 10^{-9} \text{ m}^2/\text{s} \quad \text{(Perry and Green, 1997; table 2-372)}
\]

The free diffusivities of oxygen in air and water are:

\[
D_{0}^{O2-Air} (0^\circ C) = 1.78 \times 10^{-5} \text{ m}^2/\text{s} \quad \text{(Perry and Green, 1997; table 2-371)}
\]

\[
D_{0}^{O2-H2O} (0^\circ C) = 2.5 \times 10^{-9} \text{ m}^2/\text{s} \quad \text{(Perry and Green, 1997; table 2-372)}
\]
Reducing Properties of Slags and Combustion Residue Waste Materials

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Royal Institute of Technology, S-100 44, Stockholm, Sweden
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Abstract

The reducing capacity of solid wastes has a strong influence upon the chemistry in the leachate from landfills or heaps of such wastes. This reducing capacity is slowly depleted over time as in-transported atmospheric oxygen reacts with the waste. Three different wastes have been examined and their reducing capacities determined analytically. The analytical method consisted of reacting the waste with an excess of Ce(IV) oxidant and then potentiometrically titrating the remaining Ce(IV) with an Fe(II) solution. From theoretical considerations, the proton generation capacity of the waste could also be estimated. In addition, it is shown that the reducing capacity of the waste measured analytically will overestimate the reducing capacity that is available within a landfill where oxidation reactions may not go to completion.

In models describing the transport of heavy metals from landfills or waste heaps, the reducing capacity is an important parameter as it will determine how long we can expect reducing conditions to prevail in the leachate. This helps in the prediction of the long-term changes in leachate composition and heavy metal mobility, which may occur over long periods of time in landfills or heaps of these wastes.

Keywords: reducing capacity, redox buffering, leaching, solid waste, titration

* Corresponding author
1. Introduction

A waste landfill may be thought of as a large chemical reactor. Atmospheric gases and water slowly infiltrate the waste and react. Within the landfill, chemical reactions occur which influence the composition of the leachate as it flows through the waste. The pH and redox state of the leachate are the master variables that control the solubility of heavy metal contaminants that may be present in the waste.

Many anthropogenic wastes are reducing. This means that they will consume oxidants that are present in the infiltrating leachant. Although not all of the redox reactions occurring in a waste landfill directly involve oxygen, the major oxidant transported into the landfill is atmospheric oxygen. Redox buffering processes may also lead to the generation of protons. This can have a significant impact upon the rate of pH buffer depletion in the waste, particularly if the waste is only partially saturated with water.

While there is still a pH and redox buffering capacity present in the waste material, the rate of heavy metal leaching may be very low owing to the poor solubility of the heavy metals under basic and reducing conditions. When the pH- and redox buffering capacity becomes exhausted, however, the heavy metal release rate can increase dramatically over a short period of time.

Ashes from municipal solid waste incineration typically contain 1-5 wt% of non-combusted organic material (Zevenbergen, 1994). A certain proportion of this non-combusted organic material may be refractory (i.e. non-reactive under landfilling conditions). Very little appears to be known about this residual organic fraction. Krebs (1988) adopted a rule of thumb that 50 percent of the total organic carbon content (TOC) is refractory in order to make scoping calculations. As the nature of the organic residue is poorly characterised it is often assumed to have the symbolic empirical formula CH$_2$O.

Blast furnace and other, ore-based slags generally contain very small amounts of organic material, and most of the reducing capacity arises from reduced forms of sulphur. Electric arc furnace slags, on the other hand, are unlikely to contain significant quantities of reduced sulphur or organic material as the smelting process is usually scrap metal based. The reducing capacity in these types of slags may instead be due to the presence of free metals and reduced metal oxides. In many situations, the reducing capacity of a waste is the result of a combination of different reducing constituents. Some of the redox reactions, which may be of importance in a waste landfill, are given in table 1 below:
Table 1  Redox reactions that may be important for leaching problems involving ashes and slags

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Oxidant</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{CH}_2\text{O}(s) + \text{O}_2 \leftrightarrow \text{CO}_2^{-} + 2\text{H}^+$</td>
<td>$\text{O}_2$</td>
</tr>
<tr>
<td>$\text{CH}_2\text{O}(s) + \frac{1}{2} \text{O}_2 \leftrightarrow \text{HCOO}^- + \text{H}^+$</td>
<td>$\text{O}_2$</td>
</tr>
<tr>
<td>$\text{CH}_2\text{O}(s) + \frac{1}{2} \text{H}_2\text{O} \leftrightarrow \frac{1}{2} \text{CH}_4(\text{g}) + \frac{1}{2} \text{CO}_2^{-} + \text{H}^+$</td>
<td>$\text{H}_2\text{O}$</td>
</tr>
<tr>
<td>$\text{CH}_2\text{O}(s) + \frac{1}{2} \text{NO}_3^- \leftrightarrow \frac{1}{2} \text{N}_2(\text{g}) + \text{CO}_2^{-} + \frac{3}{2} \text{H}^+ + \frac{3}{2} \text{H}_2\text{O}$</td>
<td>$\text{NO}_3^-$</td>
</tr>
<tr>
<td>$\text{CH}_2\text{O}(s) + \frac{1}{2} \text{NO}_3^- + \frac{1}{2} \text{H}_2\text{O} \leftrightarrow \frac{1}{2} \text{NH}_4^+ + \text{CO}_3^{2-} + \text{H}^+$</td>
<td>$\text{NO}_3^-$</td>
</tr>
<tr>
<td>$\text{CH}_2\text{O}(s) + 2\text{MnO}_2(\text{s}) + 2\text{H}^+ \leftrightarrow \text{CO}_3^{2-} + 2\text{Mn}^{2+} + 2\text{H}_2\text{O}$</td>
<td>$\text{Mn(IV)}$</td>
</tr>
<tr>
<td>$\text{CH}_2\text{O}(s) + 2\text{MnO}_2(\text{s}) + 2\text{H}_2\text{O} \leftrightarrow \text{CO}_3^{2-} + 2\text{Mn(OH)}_2(\text{s}) + 2\text{H}^+$</td>
<td>$\text{Mn(IV)}$</td>
</tr>
<tr>
<td>$\text{CH}_2\text{O}(s) + 2\text{MnO}_2(\text{s}) + \text{CO}_3^{2-} + 2\text{H}^+ \leftrightarrow 2\text{MnCO}_3(\text{s}) + 2\text{H}_2\text{O}$</td>
<td>$\text{Fe(III)}$</td>
</tr>
<tr>
<td>$\text{CH}_2\text{O}(s) + 4\text{Fe(OH)}_3(\text{s}) + 6\text{H}^+ \leftrightarrow \text{CO}_3^{2-} + 4\text{Fe}^{3+} + 10\text{H}_2\text{O}$</td>
<td>$\text{Fe(III)}$</td>
</tr>
<tr>
<td>$\text{CH}_2\text{O}(s) + 4\text{Fe(OH)}_3(\text{s}) \leftrightarrow \text{CO}_3^{2-} + 4\text{Fe(OH)}_2(\text{s}) + 2\text{H}^+ + 2\text{H}_2\text{O}$</td>
<td>$\text{Fe(III)}$</td>
</tr>
<tr>
<td>$\text{CH}_2\text{O}(s) + 4\text{Fe(OH)}_3(\text{s}) + 3\text{CO}_3^{2-} + 6\text{H}^+ \leftrightarrow 4\text{FeCO}_3(\text{s}) + 10\text{H}_2\text{O}$</td>
<td>$\text{Fe(III)}$</td>
</tr>
<tr>
<td>$\text{CH}_2\text{O}(s) + \frac{1}{2} \text{SO}_4^{2-} \leftrightarrow \frac{1}{2} \text{HS}^- + \text{CO}_3^{2-} + \frac{1}{2} \text{H}^+$</td>
<td>$\text{SO}_4^{2-}$</td>
</tr>
<tr>
<td>$\text{CH}_2\text{O}(s) + \frac{3}{2} \text{SO}_4^{2-} \leftrightarrow \frac{1}{2} \text{S}_2(\text{s}) + \text{CO}_3^{2-} + \frac{3}{2} \text{H}^+ + \frac{3}{2} \text{H}_2\text{O}$</td>
<td>$\text{SO}_4^{2-}$</td>
</tr>
<tr>
<td>$\text{CH}_2\text{O}(s) + \frac{1}{2} \text{SO}_4^{2-} \leftrightarrow \frac{1}{2} \text{H}_2\text{S} + \text{CO}_3^{2-} + \text{H}^+$</td>
<td>$\text{SO}_4^{2-}$</td>
</tr>
<tr>
<td>$\text{S}(\text{s}) + \frac{3}{2} \text{O}_2 + \text{H}_2\text{O} \leftrightarrow \text{SO}_4^{2-} + 2\text{H}^+$</td>
<td>$\text{O}_2$</td>
</tr>
<tr>
<td>$\text{S}(\text{s}) + \frac{1}{2} \text{O}_2 + \frac{1}{2} \text{H}_2\text{O} \leftrightarrow \frac{1}{2} \text{S}_2\text{O}_3^{2-} + \text{H}^+$</td>
<td>$\text{O}_2$</td>
</tr>
<tr>
<td>$\text{CaS}(\text{s}) + 2\text{O}_2 \leftrightarrow \text{Ca}^{2+} + \text{SO}_4^{2-}$</td>
<td>$\text{O}_2$</td>
</tr>
<tr>
<td>$\text{CaS}(\text{s}) + \text{O}_2 + \text{H}^+ \leftrightarrow \text{Ca}^{2+} + \frac{1}{2} \text{S}_2\text{O}_3^{2-} + \frac{1}{2} \text{H}_2\text{O}$</td>
<td>$\text{O}_2$</td>
</tr>
<tr>
<td>$\text{Mn(II)}\text{O}(\text{s}) + \frac{1}{2} \text{O}_2 \leftrightarrow \text{MnO}_2$</td>
<td>$\text{O}_2$</td>
</tr>
<tr>
<td>$\text{Mn(OH)}_2(\text{s}) + \frac{1}{2} \text{O}_2 \leftrightarrow \text{MnO}_2 + \text{H}_2\text{O}$</td>
<td>$\text{O}_2$</td>
</tr>
<tr>
<td>$\text{MnCO}_3(\text{s}) + \frac{1}{2} \text{O}_2 + \text{H}_2\text{O} \leftrightarrow \text{MnO}_2 + \text{CO}_3^{2-} + 2\text{H}^+$</td>
<td>$\text{O}_2$</td>
</tr>
<tr>
<td>$\text{Fe}(\text{s}) + \frac{1}{2} \text{O}_2 + 2\text{H}^+ \leftrightarrow \text{Fe}^{2+} + \text{H}_2\text{O}$</td>
<td>$\text{O}_2$</td>
</tr>
<tr>
<td>$\text{Fe}(\text{s}) + \frac{3}{2} \text{O}_2 + \frac{3}{2} \text{H}_2\text{O} \leftrightarrow \text{Fe(OH)}_3$</td>
<td>$\text{O}_2$</td>
</tr>
<tr>
<td>$\text{Fe(II)}\text{O}(\text{s}) + \frac{1}{2} \text{O}_2 + \frac{1}{2} \text{H}_2\text{O} \leftrightarrow \text{Fe(OH)}_3$</td>
<td>$\text{O}_2$</td>
</tr>
<tr>
<td>$\text{Fe(OH)}_2(\text{s}) + \frac{1}{2} \text{O}_2 + \frac{1}{2} \text{H}_2\text{O} \leftrightarrow \text{Fe(OH)}_3$</td>
<td>$\text{O}_2$</td>
</tr>
<tr>
<td>$\text{FeCO}_3(\text{s}) + \frac{1}{2} \text{O}_2 + \frac{1}{2} \text{H}_2\text{O} \leftrightarrow \text{Fe(OH)}_3 + \text{CO}_3^{2-} + 2\text{H}^+$</td>
<td>$\text{O}_2$</td>
</tr>
<tr>
<td>$\text{Al}(\text{s}) + 3\text{H}_2\text{O} \leftrightarrow \text{Al(OH)}_3(\text{s}) + \frac{3}{2} \text{H}_2(\text{s})$</td>
<td>$\text{H}_2\text{O}$</td>
</tr>
</tbody>
</table>

Owing to thermodynamic considerations, the different types of oxidation reactions generally follow in the sequence: oxygen reduction, denitrification, Mn(IV) reduction, nitrate reduction, ferric reduction, sulphate reduction, fermentation (CH}_4 formation), hydrogen formation. Details concerning this are given elsewhere in the literature by,
for example, Stumm and Morgan (1996). In flow through systems, the concentrations of the various oxidants and reaction products given in the above reactions are often seen to vary in step with this reaction sequence.

As many combustion residues contain high amounts of metallic Al, they are often stockpiled for some months before landfilling in order to reduce the explosion risk associated with hydrogen generation. These reactions tend to dissipate quickly, however, once the metallic Al has acquired a surface layer of aluminium oxide.

The carbonate reaction product of organic oxidation is given as free carbonate ($CO_3^{2-}$) in the reaction pathways listed above. Owing to different speciation at different pH levels, free carbonate may not be the dominant species in solution. For this reason, the amount of proton generation will appear to vary depending upon the dominant carbonate species in solution. The overall reaction for the oxidation of organic material with oxygen may therefore be written in three different ways:

\[
CH_2O(s) + O_2(g) \leftrightarrow HCO_3^- + H^+ \quad 6.3 < \text{pH} < 10.3 \quad (1)
\]

\[
CH_2O(s) + O_2(g) \leftrightarrow CO_3^{2-} + 2H^+ \quad \text{pH} > 10.3 \quad (2)
\]

\[
CH_2O(s) + O_2(g) \leftrightarrow H_2CO_3^- \quad \text{pH} < 6.3 \quad (3)
\]

The oxidation of reduced forms of sulphur is complicated by the fact that the oxidation reactions may not necessarily go to completion. It has been found in serial batch leaching experiments, for example, that most of the sulphur leached exists in the form of thiosulphate ($S_2O_3^{2-}$) rather than sulphate ($SO_4^{2-}$) under basic and mildly oxidising conditions (Bäverman, 1997; Goldhaber, 1983). Thiosulphate is not thermodynamically stable under basic conditions in the presence of dissolved oxygen. This suggests a kinetic barrier for the oxidation of thiosulphate.

The incomplete oxidation of elemental sulphur to produce thiosulphate actually produces more protons per mole of oxygen reacted (2 mol H$^+$/mol O$_2$) than the complete oxidation reaction pathway (1.33 mol H$^+$/mol O$_2$). It should be remembered, however, that the overall redox buffering capacity of elemental sulphur is less when it is only partially oxidised to thiosulphate. A greater quantity of protons is therefore generated per mole of elemental sulphur by the complete oxidation pathway than by the incomplete pathway.

Redox conditions in the leachate leaving the landfill may be strongly reducing, particularly if the landfill is fully saturated with water. Under these conditions, reducing equivalents may be flushed from the system in the form of dissolved Fe(II), Mn(II), HS$^-$, H$_2$S, NH$_4^+$, and organic acids. Reducing equivalents may also be lost in the form of partially oxidised sulphidic and organic colloids suspended in the
leachate, or gases formed during nitrate reduction, fermentation, and hydrogen generation reactions.

If the waste initially contains a mixture of reduced and oxidised constituents, the oxidised constituents may function as a source of oxidant in the system. This will be most important for waste materials where organic matter is found in combination with Fe(III) or sulphate containing minerals (MSWI bottom ash is a good example of this). The reduction of Fe(III) or sulphate does not result in the creation or destruction of reducing capacity, but merely a transfer of organic reducing equivalents to a ferrous or sulphide form. In the case of ferric reduction, the dissolved Fe(II) reaction product may precipitate in the form of siderite (FeCO$_3$) or Fe(OH)$_2$. These reduced forms of Fe may be subsequently oxidised by in-transported oxygen from the atmosphere. By examining the stoichiometry of the oxidation reactions it is easy to see that the same amount of oxygen is required to oxidise the waste regardless of whether the oxidation occurs directly, or via a sequence of redox reactions involving transfer of reducing equivalents from one form to another.

In a flow through system, it is possible to make a balance over the amount of reducing capacity depleted from the waste irrespective of whether the reactions occur in the solid phase or in the aqueous phase. If we consider the molal concentrations (i.e. mol/kg) of reducing equivalents transported across the system boundaries, this balance can be written as:

$$\sum \text{oxidising equivalents} - \sum \text{reducing equivalents} = \frac{\rho_{\text{bulk}} L}{\rho_{H_2O} V} \int n_R \, dt$$

(4)

The variable $n_R$ (mol O$_2$/kg waste) in equation 4 is the reducing capacity of the waste, $\rho_{\text{bulk}}$ (kg/m$^3$) is the bulk density of the waste, $\rho_{H_2O}$ (kg/m$^3$) is the density of the leachate, $L$ (m) is the depth of the landfill, and $V$ (m$^3$/m$^2$y) is the leachate flux. By a slight modification of these equations, it is also possible to define a term that we can call the operational reducing capacity ($n_{Re}^c$) of the waste. This is equal to the initial reducing capacity of the waste ($n_{R0}$) less the reducing capacity that is lost through flushing processes:

$$n_{Rc} = n_{R0} - \left( \frac{\rho_{H_2O} V}{\rho_{\text{bulk}} L} \right) \int \sum \text{reducing equivalents} \, dt$$

(5)

In this equation, $t_r$ is the length of time required to completely deplete the reducing capacity of the waste under the influence of in-transported oxidant. The operational reducing capacity is thus the net reducing capacity of the waste that is consumed within the landfill, when we account for the out-transport of reducing equivalents in the form of reduced or partially oxidised constituents. If we assume that the types and
extent of the redox reactions are constant throughout the lifetime of the landfill, it is possible to calculate both the overall reducing capacity \( n_R^0 \) and the operational reducing capacity \( n_R^e \) from theoretical considerations without the need to calculate the integral in equation 5.

It should be noted that the term “operational reducing capacity” used here is not in any way related to the term “operational valence” used in the PHREEQE geochemical simulation program (Parkhurst et al., 1990).

In all the reaction pathways for incomplete oxidation, the total reducing capacity of the waste is less than that for the full oxidation reaction, as products are transported out of the waste in the leachate without being completely oxidised. Although, the amount of proton acidity generated per mole of oxygen consumed may be greater for the incomplete oxidation pathways, the overall quantity of proton acidity generated by the reaction of a given amount of reducing material is generally highest for the complete oxidation pathways.

The principal oxidant transported into the waste landfill is molecular oxygen. If we use the rate of oxygen in-transport as a measure of the reducing capacity depletion rate, it is not necessary (from a mass balance point of view) to examine the detailed geochemistry of the individual redox reactions. For this reason, the individual oxygen consuming reactions may be lumped together into an overall reducing capacity.

If we assume that reaction products leached from the waste are fully oxidised, an overall reducing capacity can be defined for the waste if we also assume that CH₂O, S, CaS, Fe, and Fe(II)O are the only reducing constituents likely to be present in non-negligible quantities. It is difficult to predict how much of the waste reducing capacity will be lost by flushing processes without examining the detailed geochemistry and kinetics of individual redox reactions. For this reason, it is assumed here that the organic, ferrous, and sulphide reducing capacities are relatively immobile and reducing equivalents can only be lost in the form of thiosulphate.

From the stoichiometry of the oxidation reactions we shall define an overall reducing capacity \( n_R^0 \) and proton generation capacity \( n_H^0 \) based upon the equivalent number of moles of \( O_2 \) that can be consumed per mole of each reducing species in the waste:

\[
n_R^0 = n_{CH_2O} + \frac{1}{2} n_S + 2 n_{CaS} + \frac{1}{4} n_{Fe} + \frac{1}{4} n_{Fe(II)O}
\]

\[
n_H^0 = 2n_{CH_2O} + 2n_S
\]

The terms \( n_i \) in the equation above, refer to the molal concentrations of each reducing constituent \( i \) in the waste expressed in moles per gram of waste.
If we were to assume that thiosulphate is the main reaction product resulting from the oxidation of reduced forms of sulphur, equation 6 and equation 7 would need to be defined as:

\[ n_R^e = n_{\text{CH}_2\text{O}} + \frac{1}{2} n_S + n_{\text{CaS}} + \frac{1}{2} n_{\text{Fe(II)O}} \] (8)

\[ n_H^e = 2n_{\text{CH}_2\text{O}} + n_S - n_{\text{CaS}} \] (9)

If we combine the different redox reactions together to make a generalised, symbolic reaction equation, we can write:

\[ R(s) + O_2(g) \Leftrightarrow a H^+ + b CO_3^{2-} + R_{\text{diss}}^{(2b-a)} \] (10)

In this reaction equation, R represents the overall reducing capacity of the solid and \( R_{\text{diss}}^{(2b-a)} \) represents a dissolved reaction product resulting from the oxidation of one mole of R. The superscript \((2b-a)\) refers to the charge on this dissolved species and is included only to ensure that the reaction is electrostatically balanced. It is important to include the carbonate ion \((CO_3^{2-})\) in the generalised redox reaction as it can participate in other processes which may have a significant bearing upon the depletion of the pH buffering capacity of the waste (i.e. carbonation reactions, gas exchange, and solution pH buffering reactions).

For the complete oxidation pathways, the following relations give the stoichiometric coefficients in equation 10 (a and b):

\[ a = \frac{n_H^0}{n_R^0} ; \quad b = \frac{n_{\text{CH}_2\text{O}}}{n_R^0} \] (11)

If the oxidation reactions involving reduced sulphur do not go to completion, the stoichiometric coefficients are given instead by:

\[ a = \frac{n_H^e}{n_R^e} ; \quad b = \frac{n_{\text{CH}_2\text{O}}}{n_R^e} \] (12)

The relative quantities of each of the reducing species in the waste must be known in order to calculate these variables. It is difficult to know these quantities in the absence of an extensive mineralogical investigation. In spite of this apparent difficulty, there is often indirect evidence to support certain simplifying assumptions about the reducing capacity of the waste.

Some information about the organic content of the waste may be obtained by the mass loss on ignition (LOI) obtained at 550°C. Depending upon how much of the organic
fraction is assumed to be non-refractory, this data can be used to specify the amount of organic material which comprises the total reducing capacity of the waste.

The amount of reduced sulphur in the waste is difficult to specify a priori. It does seem, however, that wastes that are likely to contain appreciable quantities of reduced sulphur often have relatively low metallic Fe, Fe(II)O, and organic contents.

The overall reducing capacity of the waste upon complete oxidation ($n_R^0$) may be determined by a redox titration. The difference between the measured overall reducing capacity and that given by the estimated amount of non-refractory organic carbon and reduced sulphur may be assumed to be either Fe or Fe(II)O in the above scheme.

Although there are many assumptions implicit in this representation of the reducing properties of the waste, different case studies can be defined to explore the possible theoretical ranges of redox buffering behaviour. In this way it is possible to approximately describe the reducing properties of the waste, even in the absence of detailed analytical data.

2 Experimental Methods for determining Waste Reducing Properties

Experiments have been carried out upon three different waste materials in order to determine their reducing capacity. These materials were a municipal solid waste incineration residue (MSWI), and two different types of steel slag. The MSWI is a non-magnetic fraction of a municipal solid waste bottom ash produced at an incinerator located in Linköping, Sweden. One steel slag (AFS) is a non-magnetic fraction from a scrap based electric arc furnace (Fundia Steel AB, Smedjebacken, Sweden). The other slag is an unsorted blast furnace slag (BFS) originating from an ore based steel production process (SSAB Oxelösund, Sweden).

It is tedious to determine the reducing capacity of a largely inorganic waste material using molecular oxygen as a reactant. The kinetics of oxidation reactions involving oxygen are often slow in a laboratory time frame and it may take many days or even months to fully oxidise the waste. There is also the additional problem of measuring the extent of the redox reaction. In a waste that consists mainly of organic material, the rate of organic mass depletion may be used as a direct measure of the extent of the redox reaction. This is not possible when the mass fraction of reducing material in the waste is small in comparison to the mass of inert material. For this reason, it is often not practical to carry out a redox titration of an inorganic solid waste material using oxygen, owing to the problem of quantifying the amount of oxygen that reacts with the waste in a reliable way.
A modified version of a method suggested by van der Sloot (1993) has been adopted in order to measure the reducing capacity of the waste materials examined in this project. In this method, finely ground waste material is oxidised with an excess quantity of Ce(IV). Cerium is used as its reaction kinetic is much faster than that for molecular oxygen. In addition, the oxidising intensity of Ce(IV) is relatively independent of pH (unlike permanganate ion (MnO$_4^-$), for example).

Ce is not likely to be present in most waste materials in any significant quantity. This allows a simple analytical procedure to be used to measure the extent of reaction. This procedure consists of performing a potentiometric titration on the filtered supernatant fluid using Fe(II) as a reductant. The amount of Fe(II) added to the titrate at the equivalence point is equal to the amount of unreacted Ce(IV) remaining after the waste oxidation step. The balanced redox reaction equation for the reduction of Ce(IV) to Ce(III) using Fe(II) is:

$$\text{Ce}^{4+} + \text{Fe}^{2+} \leftrightarrow \text{Ce}^{3+} + \text{Fe}^{3+}$$ \hspace{1cm} (13)

The difference between the initial amount of Ce(IV) added to the waste and the amount of Fe(II) required to reduce the remaining Ce(IV) gives the reducing capacity of the waste in terms of electron equivalents. This may be converted to a reducing capacity in terms of oxygen consumption, using the half electrode reaction for water:

$$\text{O}_2(g) + 4\text{H}^+ + 4\epsilon \leftrightarrow 2\text{H}_2\text{O}$$ \hspace{1cm} (14)

Dividing the molar reducing capacity in terms of electron equivalents by four gives the reducing capacity in moles of O$_2$ that can be consumed by the waste.

As an excess of oxidant is used in these measurements, it is reasonable to expect that all the redox reactions go to completion.

3 Experimental Procedure

The three waste materials studied in this investigation were identical to those used by Bäverman (1997), and Fällman et al. (1994). The waste was ground until all of the material passed a 0.16mm sieve and most of the material passed the 0.125mm sieve. The waste was dried for a period of time in an oven at 105°C in order to remove most of the free moisture.

The oxidising reagent was prepared as a 0.1M solution of Ce(SO$_4$)$_2$ in 1M H$_2$SO$_4$. The reducing solution for the potentiometric titration was prepared as a 0.1M solution of FeSO$_4$ in 0.1M H$_2$SO$_4$. A 0.1M solution of oxalic acid (C$_2$H$_2$O$_4$) was also prepared as a primary standard in order to calibrate the Ce(IV) oxidant solution. By performing a
titration using the calibrated Ce(IV) solution, the Fe(II) solution could be calibrated indirectly.

In order to determine the optimal oxidant/waste ratio for these experiments, some preliminary tests were carried out on the three waste materials. The optimal mass of waste was deemed to be that which would reduce roughly half of the oxidant solution. An optimal oxidant/waste ratio is necessary to obtain accurate results during the Fe(II) titration procedure.

In the actual experiments, 50ml of the acidified Ce(IV) oxidising solution was added to the optimal mass of waste as determined in the preliminary tests. The reacting suspensions were kept in airtight, glass Erlenmeyer bottles. The reaction suspensions were left to stand for nine days after which the solutions were filtered through a glass fibre filter. 20ml samples of the filtered fluid were titrated with the 0.1M Fe(II) reducing solution. The titration was carried out using a manually operated burette and a Metrohm redox electrode with voltmeter. The electrode was a combined standard electrode in platinum (Pt) with the couple Ag/AgCl as the reference electrode. The initial oxidising capacity of the Ce(IV) reaction solution was measured by titration with the Fe(II) solution. The difference between the initial and the final oxidising capacity of the Ce(IV) solution was taken to be the reducing capacity of the waste material with which it had reacted. As only 20ml samples of the initially 50ml reaction solutions were titrated, the results had to be multiplied by a factor of 2.5 to obtain the correct reducing capacity for the waste. The results reported are the average of duplicate titrations

4 Experimental Results

In order to determine the optimal reaction time, preliminary tests were carried out on MSWI. It was found that there was very little change in the measured reducing capacity of the waste for reaction times longer than seven days. On the basis of the results obtained in the reaction time optimisation tests, the reducing capacity measurements were carried out with a reaction time of 9 days.

The reducing capacity of MSWI was found to be 1.03 mol O₂/kg of waste. In the case of BFS, the measured reducing capacity was 0.34 mol O₂/kg of waste. For AFS, the measured reducing capacity was 0.56 mol O₂/kg of waste.

It is not practical to experimentally measure the amount of proton acidity generated by the redox reactions when the waste is oxidised using Ce(IV). This is because the acidified reagents mask the effect of any protons generated in the redox reactions. In spite of this, it is possible to make certain assumptions about the type of reducing
material that may be present in the waste and define scenarios for proton generation according to equations 6-9.

5 Discussion

In order to draw conclusions about the type of reducing constituents, which may be active in a waste material, it is useful to consider both the origin and the elemental composition of the waste. The major reducing element composition and LOI of the three different waste materials used in these experiments are listed in table 2 (Fällman et al., 1994).

<table>
<thead>
<tr>
<th></th>
<th>MSWI (mol/g)</th>
<th>AFS (mol/g)</th>
<th>BFS (mol/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>1.93×10^{-3}</td>
<td>4.33×10^{-3}</td>
<td>3.04×10^{-5}</td>
</tr>
<tr>
<td>S</td>
<td>2.67×10^{-4}</td>
<td>3.93×10^{-5}</td>
<td>5.33×10^{-4}</td>
</tr>
<tr>
<td>LOI [wt%]</td>
<td>4.3</td>
<td>&lt; 0.1</td>
<td>&lt; 0.1</td>
</tr>
<tr>
<td>CH₂O [mol/g]</td>
<td>1.43×10^{-3}</td>
<td>&lt; 3×10^{-5}</td>
<td>&lt; 3×10^{-5}</td>
</tr>
</tbody>
</table>

In the case of MSWI, the measured reducing capacity correlates well with the estimated organic content of the waste based upon the LOI at 550°C. It is likely, however, that a fraction of measured reducing capacity is in the form of metallic Fe or reduced Fe(II) oxides. The MSWI waste has been observed to become a brownish, rust colour over time in batch experiments where the leaching vessels have been exposed to the atmosphere. This is a good circumstantial indicator for the presence of Fe or Fe(II)O that has been oxidised to a ferric oxide or hydroxide form. It is thought that the sulphur content of this waste is probably oxidised in the form of anhydrite (CaSO₄) or gypsum (CaSO₄·2H₂O) and is unlikely to be initially present in a reduced state.

For BFS, the amount of organic material based upon the LOI is negligible. The Fe content of the waste is also known to be low. The observed reducing capacity is therefore most likely to be due to the presence of reduced sulphur compounds. If the reducing capacity were to be in the form of elemental sulphur, this would require about 20 percent more sulphur than is known to be present in the waste. If the main reducing component of the BFS is assumed to be CaS, on the other hand, about 97 percent of the sulphur content would need to be in this form in order to account for the measured reducing capacity. The bottles used for the oxidation of the BFS slag had a distinct odour of H₂S. This is a good circumstantial indicator for the presence of
reduced sulphur compounds in the waste. For this waste it is assumed that the main reducing constituent is most likely to be CaS with perhaps a small amount of elemental sulphur.

For AFS, the amount of organic material based upon the LOI was also found to be negligible. The amount of sulphur in the waste is also low and the reaction bottles had no odour of H$_2$S as was the case for BFS. For this reason it is probably safe to assume that the observed buffering capacity of the waste originates almost entirely from metallic Fe or reduced Fe oxides (Fe(II)O).

In the reducing capacity measurements, a large excess of Ce(IV) oxidant is used. It is probably reasonable to assume, therefore, that the aqueous reaction products are completely oxidised (i.e. Fe$^{+3}$ and SO$_4^{2-}$ reaction products are formed). As discussed previously, these redox reactions may not necessarily go to completion in a landfill environment. It follows that the reducing capacity measurements may overpredict the available reducing capacity in a landfill environment.

Based upon the assumptions about the composition of the reducing material in the waste, it is possible to estimate the both the minimum effective reducing capacity ($n_R$) and the parameters in the generalised redox reaction given by equations 11 and 12. Drawing upon equations 6-9, we can calculate the stoichiometric parameters in the generalised redox reaction equation. These data are given in table 3 below:

**Table 3**  Ratio of measured and operational reducing capacities as well as generalised stoichiometric coefficients for the three waste materials investigated

<table>
<thead>
<tr>
<th></th>
<th>MSWI</th>
<th>AFS</th>
<th>BFS</th>
</tr>
</thead>
<tbody>
<tr>
<td>$n_R^e/n_R^0$</td>
<td>$n_R^e/n_R^0 \approx 1$</td>
<td>$n_R^e/n_R^0 \approx 1$</td>
<td>$\frac{1}{3} \leq n_R^e/n_R^0 \leq \frac{1}{2}$</td>
</tr>
<tr>
<td>$a$</td>
<td>$0 \leq a \leq 2$</td>
<td>$a = 0$</td>
<td>$-1 \leq a \leq 2$</td>
</tr>
<tr>
<td>$b$</td>
<td>$0 \leq b \leq 1$</td>
<td>$b = 0$</td>
<td>$b = 0$</td>
</tr>
</tbody>
</table>

From this analysis it appears that the MSWI waste has the largest reducing capacity and the highest potential for proton generation. If the reducing constituents are assumed to be organic, then the operational reducing capacity in a landfill should be the same as that measured analytically. Under fully saturated conditions, however, there is the possibility that organic reducing equivalents are transformed into a reduced sulphur form by way of sulphate reduction reactions. Under these conditions, reducing equivalents may be lost in the form of soluble reduced sulphur compounds. Similarly, fermentation reactions may lead to the loss of reducing equivalents in the form of methane gas that can diffuse to the atmosphere. If part of the reducing capacity is in the form of metallic Fe or Fe(II)O, the operational reducing capacity
may also be less than that measured analytically depending upon how much Fe(II) is transported out of the waste during leaching. Subject to the waste composition, the proton generation capacity may be as much as +2 mol H⁺/mol of oxygen consumed if the reducing capacity is entirely organic in origin.

The operational reducing capacity for BFS should be roughly half that measured analytically if the oxidation of the CaS redox buffer results in the formation of thiosulphate rather than sulphate. If thiosulphate is formed as a reaction product, the oxidation of CaS will actually lead to a net consumption of protons in the system. If sulphate is a reaction product of CaS oxidation, then there should be no net production or consumption of protons in the waste and the reducing capacity will be the same as that determined analytically. Oxidation of free sulphur leads to the production of protons for both the complete and incomplete oxidation pathways. BFS has the lowest reducing capacity of the waste materials tested in these experiments.

For AFS waste, the operational reducing capacity is dependent largely upon the ratio of metallic Fe and Fe(II)O in the waste and how much soluble Fe(II) is transported out of the waste during leaching. If the oxidation results in the formation of Fe³⁺ (precipitating as Fe(OH)₃ under basic conditions), there will be no net production or consumption of protons. If Fe²⁺ is formed as a reaction product, there should be a net consumption of protons (-4 mol H⁺/mol of oxygen consumed). In this paper, however, we assume that Fe(II) is relatively immobile and consider that only Fe(III) species can be transported out in the leachate.

6 Conclusions

Experiments conducted upon three different waste types indicate a redox buffering capacity lying somewhere between about 0.3 and 1.0 moles of reducing capacity (based upon oxygen consumption) per kilogram of waste material. Municipal solid waste incineration residue (MSWI) was found to have the highest reducing capacity of the waste materials tested. The measured reducing capacity of 1.03 mol O₂/kg corresponds well with the speculated organic content of the MSWI based upon the loss of mass upon ignition (LOI) at 550°C. In spite of this close correlation it is thought that a proportion of the measured reducing capacity is actually in the form of Fe or Fe(II)O.

Blast furnace slag (BFS) was found to have the lowest reducing capacity of the three waste materials with a value of 0.34 mol O₂/kg. From the known sulphur and iron content of the waste and the strong odour of H₂S in the containers used to store the waste, the reducing capacity of BFS is assumed to be most likely in the form of CaS with perhaps a small amount of free sulphur.
Arc furnace steel slag (AFS) was found to have a reducing capacity of roughly 0.5 mol O₂/kg. Owing to the high iron content and low sulphur content of this waste, the reducing capacity is assumed to be in the form of Fe or Fe(II)O. The organic content of both BFS and AFS is below the level of detection by the LOI test and is not likely to contribute to the measured reducing capacity significantly.

It is speculated that the experimentally measured reducing capacities overpredict the actual reducing capacity that may be available under landfilling conditions. From theoretical considerations, however, it is possible to explore a range of redox buffering behaviour, which should encompass most of the possibilities encountered in a landfilling environment. Based upon previous observations of the incomplete oxidation of aqueous sulphur species in leachate, it is suggested that the measured reducing capacity of BFS is roughly twice that which would be available in a landfill leaching environment. For MSWI and AFS, the available reducing capacity may be less than that measured in the experiments. Whether, or not, this is the case in a landfill leaching environment, however, is open to speculation.

From theoretical considerations it is also possible to predict the proton generating capacity of the reducing material by considering the actual measured reducing capacity, the origin of the waste, and the known elemental composition of the waste. Using this approach, a range of possible values for the proton generation properties of the waste may be estimated. Under certain circumstances, proton acidity may even be consumed by the redox buffering processes occurring in a landfill environment.

**Acknowledgement**

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References


van der Sloot, H., Determination of the reducing properties and the reducing capacity of construction materials and waste materials, Draft Proposal; NVN 7348; 1993, Netherlands Energy Research Foundation (ECN), Petten, Holland


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Abstract

Simulation of leaching processes occurring in landfills of waste materials is a valuable tool as it is often not practical to conduct realistic laboratory experiments over sufficiently long time scales that long-term changes in the leachate composition can be observed. Simulation tools can be used to ascertain under which circumstances the leaching of toxic substances may occur and how the observed concentrations of these substances can be expected to change over time. One of the major variables influencing the mobility of heavy metals is the redox state of leachant following a flowpath through the landfill. Using mass balance models, it is possible to simulate the depletion of the redox buffering capacity of a waste material under the influence of in-transported oxygen. Central to this type of modelling is a kinetic description of the reaction of reducing substances with oxygen. This paper concentrates upon the reducing properties of the organic fraction of a municipal solid waste incineration residue (MSWI) and details a procedure through which kinetic data from literature may be converted into a form that is appropriate for coupled transport and reaction simulation models. In addition, the influence of physical heterogeneity is examined and a theoretical analysis is carried out to determine the effect that particle size has upon the effective redox reaction rate in a landfill of this type of waste.

Keywords: reducing capacity, redox buffering, leaching, solid waste, kinetics, oxidation, MSW, incineration, bottom ash

* Corresponding author
1 Introduction

Most anthropogenic waste materials are reducing and will tend to react with in-transported oxidising agents when disposed of in a waste landfill. The primary oxidant of importance in waste leaching problems is atmospheric oxygen. Oxygen may be transported into the waste material either dissolved in the infiltrating rainwater or by gaseous diffusion if the landfill is only partially saturated. Under certain conditions, oxygen may even be transported into the landfill by convective flow.

The rate of oxygen consumption in waste materials depends largely upon a combination of transport resistance and chemical kinetics. In a waste landfill, there are generally three different types of transport resistance, which operate in series to limit the rate of oxidation. These are: heap-, film-, and particle resistance. If we neglect the role of convective airflow, heap resistance may occur where oxygen must diffuse some distance through the bulk waste material in order to reach the reaction zone. Film resistance results from the diffusion of oxygen through the laminar film of fluid that surrounds reacting waste particles. Film mass transfer is a relatively fast process and is unlikely to control observed reaction rates for low temperature redox processes (i.e. at ambient temperatures). Particle resistance relates to the resistance for oxygen diffusion from the bulk fluid into the internal porosity of particles in the waste landfill. This may play an important role depending upon the rate of chemical reaction within individual particles.

The rate of chemical reaction is usually proportional to the concentration of oxygen, as well as the concentration and the specific surface of reducing material exposed to the leachate. If the specific surface of reducing material in contact with water is low, the redox reaction may be very slow. This will occur if there is very little reducing material, if the reactive particles are very large, or if the waste is dry as it is usually only wet material that will react. The reactive substance may also have a high activation energy for reaction. The reaction rate is related to the activation energy through the Arrhenius equation; the higher the activation energy, the slower the reaction. Microbes possess enzymes that lower the activation energy for specific redox reactions very efficiently. This is why the microbially mediated degradation of organic matter and the oxidation of pyrite are usually many orders of magnitude faster than the corresponding abiotic oxidation rates.

If the reaction kinetics are fast, then diffusional resistance may control the rate of oxygen consumption as it is this which limits the rate of oxygen transport in the waste. If, on the other hand, the reaction kinetics are slow, diffusional resistance may play only a very minor role in limiting the rate of oxygen consumption.
In this paper, the reaction kinetics of the organic fraction in municipal solid waste incineration residue (MSWI) are studied. The particular waste examined is a non-magnetic fraction of an MSWI bottom ash from an incinerator located in Linköping, Sweden.

2 Organic Oxidation Rates in Municipal Solid Waste Incineration Residues (MSWI)

Most municipal solid waste incineration residues (MSWI) contain 1-5wt% of uncombusted organic material (Zevenbergen, 1994). The quantity of organic material is often estimated through the loss on ignition (LOI) at 550°C. In this test, it is generally assumed that the loss of mass is due to oxidation of residual organic material in the waste. A certain proportion of the organic content as determined by the LOI test may be non-reactive with oxygen (refractory) under ambient conditions. This refractory material may consist of recalcitrant organic compounds and possibly carbon cinders. There is no easy way of quantifying the fraction of easily oxidisable organic material in the waste and many researchers adopt a rule of thumb approach. Krebs (1988), for example, has assumed that about 50% of the LOI is easily oxidisable organic matter in order to make scoping calculations.

There is a considerable body of literature describing the bio-degradation of organic materials (Moreno, 1982; Westrich and Berner, 1984; Boni and Musmeci, 1998). The degradation rate of organic materials is highly dependent upon the type of organic material, temperature, moisture content, and oxygen availability in the waste.

As very little is known about the nature of the organic fraction in MSWI, it is difficult to extrapolate data in the literature without making considerable assumptions. One way of approaching the problem in the absence of reliable data for a particular waste material is to examine a whole range of organic oxidation rates to explore the possible limits of leaching behaviour.

In the literature, the rate of disappearance of organic matter is almost exclusively described as a first order process with respect to a fixed partial pressure of oxygen (P\textsubscript{O}\textsubscript{2}). If neither the P\textsubscript{O}\textsubscript{2} nor the organic concentration is constant, then the reaction rate is approximately proportional to both the P\textsubscript{O}\textsubscript{2} and the concentration of organic material in the waste. The redox reaction rate is thus an essentially second order process. The specific surface of the reactive organic fraction is very difficult to specify, as it has no well-defined surface structure, unlike most minerals. For this reason, measured rate constants generally incorporate the specific surface of organic material implicitly.
In a coupled transport and reaction model for landfill leaching it may be appropriate to describe the redox processes in terms of the consumption rate of oxygen transported into the landfill. If we want to use a formulation that describes the rate of disappearance of oxygen in the waste, the kinetic constant based upon the rate of organic consumption must be first converted to a useable form.

If we symbolically define organic material as having the empirical formula CH₂O, the oxidation reaction can be given as:

\[
\text{CH}_2\text{O}^{(s)} + \text{O}_2^{(g)} \Leftrightarrow \text{HCO}_3^- + \text{H}^+
\]

Assuming that the consumption of organic material may be described as an approximately second order process, one way of writing the reaction rate expression is:

\[
-\frac{dC}{dt} = k_r Q_s C = k_c C
\]

where,

\( k_r \) = second order rate constant with respect to aqueous oxygen concentration and organic concentration (\( \text{m}^3_{\text{water}} / \text{mol year} \))

\( k_c \) = first order rate constant with respect to organic concentration and fixed aqueous oxygen concentration (1/year)

\( Q_s \) = aqueous concentration of oxygen (\( \text{mol} / \text{m}^3_{\text{water}} \))

\( C \) = concentration of oxidisable matter (\( \text{mol} / \text{m}^3_{\text{solid}} \))

In an experiment where the system is open to the atmosphere, equation 2 becomes a first order rate expression with a kinetic constant (\( k_c \)) incorporating the fixed partial pressure of atmospheric oxygen (\( P_{\text{O}_2}^{0} \)). The constant \( k_c \) given in equation 2 is the rate constant most often reported in the literature. If we assume equilibrium between the gas and liquid phases, the dissolved oxygen concentration is related to the partial pressure of oxygen through an equilibrium constant, \( (K_q) \) so that:

\[
Q_s = K_q P_{\text{O}_2}
\]

If we now consider a closed system in which both the organic and oxygen concentration are depleted, there is a mass balance relationship between the molar rate of organic oxidation and oxygen consumption:

\[
\text{n}_{\text{CH}_2\text{O}} = \text{n}_{\text{O}_2}
\]

\[
\text{n}_{\text{CH}_2\text{O}} = V_t b \varepsilon \int dt
\]
\[ n_{O_2} = \frac{V_a}{RT} \frac{dP_{O_2}}{dt} + V_{wt} \frac{dQ_s}{dt} = V_T \left( \frac{S g}{RT} \right) S \frac{Q_s}{dt} \quad (6) \]

where,

- \( V_a \) = volume of air in the system (m^3)
- \( V_{wt} \) = volume of water in the system (m^3)
- \( V_T \) = total volume of system (m^3)
- \( \varepsilon \) = total porosity (m^3/void / m^3_total)
- \( K_q \) = equilibrium constant for the dissolution of gaseous oxygen in water (mol / Pa m^3)
- \( n_{CH,O} \) = overall molar rate of organic consumption (mol/y)
- \( n_{O_2} \) = overall molar rate of oxygen (O_2) consumption (mol/y)
- \( P_{O_2} \) = partial pressure of oxygen in gas phase (Pa)
- \( R \) = universal gas constant (Pa m^3/mol K)
- \( S \) = degree of saturation (m^3_water / m^3_void)
- \( T \) = temperature (K)

The value of the dimensionless term \( K_qRT \) is calculated to be approximately \( 3.1 \times 10^{-2} \) at 298 K.

Under partially saturated conditions, oxygen is contained both in the gas phase and the liquid phase. If we assume that equilibrium exists between the gas and liquid phases, the rate of change of organic concentration (C) may be related to the rate of change of the aqueous oxygen concentration (Q_s) through equation 4:

\[ \frac{dC}{dt} = \frac{S g}{RT} S \frac{Q_s}{dt} \quad (7) \]

By integrating equation 7, the organic concentration may be expressed in terms of the oxygen concentration:

\[ C = C_0 - \frac{F_{HG}}{1 - \varepsilon} \left( \frac{S g}{RT} S \frac{Q_{s0}}{1 - \varepsilon} - Q_s \right) \quad (8) \]

where,

- \( Q_{s0} \) = initial aqueous concentration of oxygen (mol / m^3_water)
- \( C_0 \) = initial concentration of oxidisable organic matter (mol / m^3_solid)
If the organic content of the waste is somewhat larger than the amount of oxygen contained in the closed system (this is usually true of wastes with an organic content higher than about 0.1wt%), the organic concentration may be assumed to be approximately constant \( C_0 \) without introducing significant errors. Making the appropriate substitutions, we obtain for the rate of oxygen consumption:

\[
\frac{dQ_s}{dt} = \epsilon k Q_s C_0
\]  

(9)

The first order rate expression for the disappearance of dissolved oxygen in a closed system is:

\[
\frac{dQ_s}{dt} = -k_q Q_s
\]

(10)

where,

\[ k_q = \text{first order rate constant with respect to aqueous oxygen concentration and fixed organic concentration (1/year)} \]

The rate constant for consumption of dissolved oxygen in a closed system \( (k_q) \) may now be calculated in terms of the rate constant determined for the disappearance of organic matter in the open system:

\[
k_q = \frac{k C_0}{\beta K q P_{O2}^0}
\]

(11)

where,

\[
\beta = \frac{L \epsilon S g S}{RT}
\]

(12)

Using the measured reducing capacity of the waste instead, we can write:

\[
k_q = \frac{k \rho_{\text{bulk}} n_R^0}{\epsilon \beta K q P_{O2}^0}
\]

(13)

where,

\[ \rho_{\text{bulk}} = \text{bulk density of waste material (kg/m}^3\text{)} \]

\[ n_R^0 = \text{reducing capacity of waste material (mol O}_2/\text{kg)} \]

Using equation 11 or 13 it is possible to convert rate constant data given in the literature to values that may be used in conjunction with a coupled transport and reaction model for oxygen consumption in a waste landfill.
Table 1 below, summarises some data taken from the literature for the first order organic rate constant ($k_e$) as well as half lives ($t_{1/2}$) for various organic materials under conditions of roughly constant oxygen partial pressure:

<table>
<thead>
<tr>
<th>Waste type</th>
<th>$k_e$ (1/year)</th>
<th>$t_{1/2}$</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>marine sediment</td>
<td>18</td>
<td>14 days</td>
<td>Westrich et al., 1984</td>
</tr>
<tr>
<td>composted MSW</td>
<td>17</td>
<td>15 days</td>
<td>Moreno, 1982</td>
</tr>
<tr>
<td>biodegradable polyethylene</td>
<td>0.15</td>
<td>4.62 years</td>
<td>Boni et al., 1998</td>
</tr>
<tr>
<td>Kraft paper</td>
<td>20</td>
<td>13 days</td>
<td>Boni et al., 1998</td>
</tr>
<tr>
<td>cardboard</td>
<td>17</td>
<td>15 days</td>
<td>Boni et al., 1998</td>
</tr>
</tbody>
</table>

It should be noted that the temperature term used in this derivation is used to account for the molar volume of oxygen in the gas phase and does not reflect a true temperature dependency for the reaction rate constant $k_q$. The temperature dependency of the redox reaction is contained implicitly in the value of $k_e$ as this reflects the measured rate of organic degradation under the particular experimental conditions used (i.e. temperature, humidity, etc.).

The variation of the ratio $\varepsilon_k \frac{k_q}{k_c}$ is plotted as a function of both saturation ($S$) and volumetric reducing capacity ($\rho_{\text{bulk}} n^0_R$) in figure 1:

![Conversion Factor for Organic Oxidation Rate Constant](image)

**Figure 1.** Conversion factor for the organic oxidation rate constant in terms of reducing capacity of waste and degree of saturation
In these calculations it is implicitly assumed that all of the redox buffering capacity in the waste is available for oxidation. This may not be entirely true for low levels of saturation as the redox reaction generally will only occur in the water filled porosity of the waste material. If the waste is relatively dry, a proportion of the reducing capacity may not be in contact with the liquid phase and thus be unavailable for reaction. The actual reaction rate constant may, therefore, be substantially lower than the predicted values under these circumstances. For this reason, the broken line in figure 1 corresponding to zero saturation \( (S = 0) \) is physically unrealistic. It is included in the figure purely to indicate the possible theoretical range of \( k_q \) given that all of the reducing capacity is available for reaction.

The MSWI used in this project has a loss on ignition (LOI) of approximately 4.3wt\%. If this is assumed to be readily oxidisable organic material, the reducing capacity would be 1.43 mol \( \text{O}_2 \)/kg. The analytically determined reducing capacity of this waste, however, is 1.03 mol \( \text{O}_2 \)/kg. This was measured by oxidising the waste with an excess of a Ce(IV) oxidising solution. By titrating the unreacted Ce(IV) with an Fe(II) reducing solution, the reducing capacity of the waste could be determined.

The measured reducing capacity is remarkably close (72\%) to the value predicted from LOI measurements. This doesn’t necessarily mean that the reducing capacity is entirely organic. Indeed, a substantial fraction of the measured reducing capacity is likely to be in the form of metallic Fe or reduced Fe(II) oxides. In spite of this uncertainty, we shall assume for these simple calculations that the measured analytical reducing capacity is entirely organic in origin.

If we take the value for the reducing capacity and use it in conjunction with equation 13 (or the data in figure 1), the value of \( k_q \) and \( t_{1/2} \) may be estimated. These results are summarised in table 2a and 2b, below, where a total porosity of 30\% (\( \varepsilon = 0.3 \)) has been assumed:
Table 2a. First order reaction rate constant ($k_q$) calculated for various values of $k_c$ and saturation ($S$) with an assumed total porosity of 0.3

<table>
<thead>
<tr>
<th>$k_c$ [year$^{-1}$]</th>
<th>0.1</th>
<th>1.0</th>
<th>20</th>
</tr>
</thead>
<tbody>
<tr>
<td>$S = 0$</td>
<td>5.2×10$^{-1}$</td>
<td>5.2×10$^{-2}$</td>
<td>1.0×10$^{-4}$</td>
</tr>
<tr>
<td>$S = 0.25$</td>
<td>6.8×10$^{-1}$</td>
<td>6.8×10$^{-2}$</td>
<td>1.4×10$^{-4}$</td>
</tr>
<tr>
<td>$S = 0.5$</td>
<td>1.0×10$^{-2}$</td>
<td>1.0×10$^{-3}$</td>
<td>2×10$^{-4}$</td>
</tr>
<tr>
<td>$S = 0.75$</td>
<td>1.9×10$^{-2}$</td>
<td>1.9×10$^{-3}$</td>
<td>3.8×10$^{-4}$</td>
</tr>
<tr>
<td>$S = 1$</td>
<td>1.7×10$^{-3}$</td>
<td>1.7×10$^{-4}$</td>
<td>3.4×10$^{-5}$</td>
</tr>
</tbody>
</table>

Table 2b. Half life of oxygen ($t_{1/2}$) calculated for various values of $k_c$ and saturation ($S$) with an assumed total porosity of 0.3

<table>
<thead>
<tr>
<th>$k_c$ [year$^{-1}$]</th>
<th>0.1</th>
<th>1.0</th>
<th>20</th>
</tr>
</thead>
<tbody>
<tr>
<td>$S = 0$</td>
<td>4.9 days</td>
<td>12 h</td>
<td>35 min</td>
</tr>
<tr>
<td>$S = 0.25$</td>
<td>3.7 days</td>
<td>8.9 h</td>
<td>27 min</td>
</tr>
<tr>
<td>$S = 0.5$</td>
<td>2.5 days</td>
<td>6.1 h</td>
<td>18 min</td>
</tr>
<tr>
<td>$S = 0.75$</td>
<td>1.3 days</td>
<td>3.2 h</td>
<td>10 min</td>
</tr>
<tr>
<td>$S = 1$</td>
<td>3.6 h</td>
<td>22 min</td>
<td>1.1 min</td>
</tr>
</tbody>
</table>

In a flow system, where in- and out-transport transport of oxygen occurs through a combination of advective and diffusive processes, the 1-dimensional mass balance for oxygen may be written as:

$$-\frac{D^x}{\beta} \frac{\partial^2 Q^x}{\partial z^2} + \frac{V}{\beta} \frac{\partial Q^x}{\partial z} + k_q Q^x \xi = -\xi \frac{\partial Q^x}{\partial t}$$

(14)

When the quantity of reducing material in a waste is large in relation to the dissolved concentrations of oxygen, many volumes of leachant need to be transported through the system until there is a noticeable change in the mass distribution of unreacted reducing material. If the time taken to establish a steady state concentration profile in the leachant (with respect to the length variable, $z$) is significantly less than the time required to completely react a constituent in the solid phase, the quasi-stationary state approximation may be valid. Lichtner (1988) discusses criteria for when this approximation may be valid.

The assumption of a quasi-stationary state permits setting the accumulation term on the right hand side of equation 14 to zero. Under these conditions, it is not necessary to include the parameter $\beta$ in the derivation of the first order reaction constant for oxygen consumption. Equation 14 can then be simplified to:
\[-D_e \frac{\partial^2 Q}{\partial z^2} + V \frac{\partial Q}{\partial z} + k Q_s = 0\] 

(15)

where,

\[k = b \frac{e \sigma P_{O_2} c \rho_{bulk} K^0_{O_2}}{K^0_{O_2}}\] 

(16)

The first order reaction rate constant \(k\) given in equation 16 is appropriate for a coupled transport and reaction calculation incorporating the quasi-stationary state approximation. If one wishes to solve the transient problem given by equation 14, however, both the porosity and saturation in the system will have an effect upon the rate of oxygen consumption.

It should be remembered that the value of the first order rate constant given by equation 11, 13, or 16 considers only the maximum reaction rate that would be encountered in a flow through system. Over time, the amount of organic material remaining in the waste will decrease and the observed rate of oxygen consumption will also tend to decrease. As depletion of the organic matter occurs gradually along a fluid flowpath, there will be a variation in organic concentration along the hypothetical column of waste. At the leading edge of the redox front, there will only be a very small amount of organic material and the reaction rate will be low. Further downstream, however, the organic concentration will increase until it is equal to that contained in the unreacted waste and at this point the reaction rate will be at a maximum. The assumption of a first order reaction rate constant (for oxygen consumption) doesn’t consider the variation of organic concentration along a flowpath. The predicted oxygen concentration profiles will therefore be somewhat narrower than what would be predicted from a second order rate expression. Although this may give results that are not entirely physically realistic, the assumption should be sufficiently accurate for the purposes of making scoping calculations.

3 The Influence of Physical Heterogeneity on the Observed Redox Reaction Rate

In the analysis thus far, it has been assumed that the redox reaction rate constant is uninfluenced by the transport properties of individual particles in the waste material and equal to the homogeneous reaction rate. In reality, transport effects may have a large influence upon the observed reaction rate, particularly when the calculated homogeneous reaction rate is fast.

If we make the assumption that individual particles (or particle agglomerates) in the waste material may be roughly approximated as being spherical with a water saturated and porous internal structure, we can set up a mass balance for the transport and
reaction of oxygen within the interior of such a particle. Figure 2 below, shows conceptually how the oxygen concentration profile may appear within the spherical particle, where the redox reaction is assumed to occur throughout the particle in a similar fashion to models of heterogeneous catalysis (Bird et al., 1960):

Figure 2. Oxygen concentration profile within a spherical particle

If we assume approximately steady state conditions, the mass balance describing this system is (in spherical co-ordinates):

\[
\frac{D_w}{r^2} \frac{d}{dr} \left( r^2 \frac{dQ}{dr} \right) + k_p Q = -k_p Q \quad (17)
\]

The constant, \(k_p\), in equation 17 is a first order rate constant for the reaction of dissolved oxygen in a porous waste particle. Within the waste particle, the relationship between the rate of oxygen consumption and the rate of organic oxidation at any point in space is given by equation 4. We can therefore write:

\[
\frac{dC}{dt} = -k_p Q C = -k_p Q C \quad (18)
\]

where,

- \(Q\) = aqueous oxygen concentration within particle (mol/m\(^3\)_solid)
- \(\varepsilon_p\) = porosity of waste particle (m\(^3\)_pore-water/m\(^3\)_particle)
- \(R_p\) = specific rate of oxygen consumption within particle (mol/m\(^3\)_pore-water/yr)

The relations between the different kinds of porosity in the system are:
\[ \varepsilon = \frac{V_a}{V_T} + \frac{V_w}{V_T} + \frac{V_p}{V_T} \]  

(19)

\[ \frac{V_a}{V_T} = \varepsilon S \]  

(20)

\[ \frac{V_p}{V_T} = \frac{\varepsilon_p}{d - \varepsilon_p} \]  

(21)

\[ \frac{V_w}{V_T} = S\varepsilon - \frac{\varepsilon_p}{d - \varepsilon_p} \]  

(22)

where,

\[ V_p = \text{volume of pore water contained in waste particle (m}^3_{\text{pore-water}}) \]

\[ V_a = \text{volume of air in the system (m}^3_{\text{air}}) \]

\[ V_w = \text{volume of water in the inter-particle porosity (m}^3_{\text{ext. water}}) \]

\[ V_T = \text{total volume of system (m}^3_{\text{total}}) \]

If we assume that the quantity of organic matter in the waste particle is somewhat higher than the quantity of dissolved oxygen in the pore water, equation 18 may be modified to give:

\[ R_p = \frac{k_p C_0}{K_p p_{O2}^0} = - \frac{k_p Q}{\varepsilon_p} \]  

(23)

The particle reaction rate constant, \( k_p \), is therefore equal to:

\[ k_p = \frac{k_c}{d - \varepsilon_p} \frac{C_0}{K_p p_{O2}^0} \]  

(24)

In terms of the measured reducing capacity of the waste, \( k_p \) may be written as:

\[ k_p = \frac{k_p_{\text{bulk}} n_i^0}{K_p p_{O2}^0} \]  

(25)

Equation 17 is subject to the following boundary conditions:

\[ Q = Q_s \quad r = r_0 \]  

(26)

\[ \frac{dQ}{dr} = 0 \quad r = 0 \]  

(27)

By solving equation 17, the surface flux of oxygen (relative to the radial axis \( r \)) may be shown to be (Bird et al., 1960):
\[ J_{\theta_0} = \frac{D^w_c Q_s \theta_0}{r_0} \quad (28) \]

where,

\[ \theta_0 = 1 - r_0 \sqrt{\frac{k_p}{D^w_c}}} \coth \left( \frac{k_p}{D^w_c} \right) \quad (29) \]

The external area of the waste particle is:

\[ A_p = 4\pi r_0^2 \quad (30) \]

The number of particles per unit volume in the system is given by:

\[ n_p = \frac{b^d e_j q^3}{d^e_p 4\pi r^3} \quad (31) \]

Thus, the total specific rate of oxygen consumption in the system \((\text{mol} / \text{m}^3 \text{total} \ \text{y})\) is:

\[ N_{r\theta_0} = n_p A_p J_{r\theta_0} = \frac{3 b^d e_j q^3 D^w_c Q_s \theta_0}{d^e_p 4\pi r_0^3} \quad (32) \]

Furthermore, it can be shown that:

\[ \lim_{r_0 \to 0} N_{r\theta_0} = -\frac{b^d e_j q^3}{d^e_p} k_p Q_s = -\frac{b^d e_j q^3}{d^e_p} k_p \frac{C_0}{Q_{O2}} Q_s \quad (33) \]

Equation 33 gives the limiting rate of oxygen consumption in the system for infinitely small waste particles.

The concentration profile of oxygen within individual particles is given by the expression (Bird et al., 1960):

\[ \frac{Q}{Q_s} = \frac{b^d e_j q^3}{d^e_p} k_p \frac{\sinh \left( \frac{e_j}{k_p / D^w_c} \right)}{\sinh \left( \frac{e_j}{k_p / D^w_c} \right)} \quad 0 \leq r \leq r_0 \quad (34) \]

By integrating the oxygen concentration profile over the volume of the waste particle, the average concentration of oxygen in the particle may be shown to be:

\[ Q_{\text{average}} = Q_s \varphi = Q_s \frac{\frac{b^d e_j q^3}{d^e_p} k_p C_0}{\frac{\sinh \left( \frac{e_j}{k_p / D^w_c} \right)}{\sinh \left( \frac{e_j}{k_p / D^w_c} \right)}} \quad Z r^2 \text{dr} \]

The integral in equation 35 can be solved analytically to obtain:

\[ \varphi = -\frac{3 D^w_c \theta_0}{r_0^2 k_p} \quad (36) \]
The rate of change of the total quantity of oxygen within the particles is:

$$\frac{d}{dt} Q_s = V_p \phi \frac{dQ_s}{dt} \quad (37)$$

In a closed, partially saturated system, the overall rate of oxygen consumption is given by:

$$V_a + V_w + \phi V_p \frac{dQ}{dt} = V_t N_{e0} \quad (38)$$

Using the definitions for the various types of porosity, we obtain:

$$\varepsilon \frac{dQ}{dt} = \frac{3D^\varepsilon \theta_0}{r_0^2 \kappa_p} \cdot \frac{dQ_s}{dt} = N_{e0} \quad (39)$$

Combining equations 32 and 39 gives:

$$\varepsilon \beta_p \frac{dQ_s}{dt} = \frac{3D^\varepsilon \theta_0}{r_0^2 \kappa_p} \cdot \frac{dQ_s}{dt} \quad (40)$$

where,

$$\beta_p = \frac{0 - S}{RT} - \frac{- 3D^\varepsilon \theta_0}{r_0^2 \kappa_p} \quad (41)$$

By rearranging equation 40, an effective first order rate constant may be defined:

$$k_{eff} = \frac{-3D^\varepsilon \theta_0}{r_0^2 \kappa_p \beta_p} \quad (42)$$

where,

$$\frac{dQ_s}{dt} = -k_{eff} Q_s \quad (43)$$

The assumption of a fully saturated internal particle porosity also requires the following inequality to be fulfilled:

$$S \geq \frac{-3D^\varepsilon \theta_0}{r_0^2 \kappa_p \beta_p} \quad (44)$$

As the particle radius approaches zero, equation 42 simplifies to:

$$\lim_{r_0 \to 0} k_{eff} = \frac{-3D^\varepsilon \theta_0}{r_0^2 \kappa_p \beta_p} \quad (45)$$

Or, in terms of the measured reducing capacity of the waste:
This is the same result as was found previously where it is assumed that there is no diffusional resistance (equation 11 and 13).

Using equation 42, it is possible to investigate the influence that particle size has upon the observed redox reaction rate in a waste landfill. In order to perform these calculations, however, it is necessary to determine the effective diffusivity ($D_e^w$) for oxygen in the waste particles as well as their porosity ($\varepsilon_p$).

Bäverman (1994) has experimentally determined the effective diffusivity of slabs of blast furnace slag using a method developed by Skagius (1986). In this technique, the rate of aqueous diffusion of a non-sorbing tracer (uranine) is measured across a slab of solid material between a high concentration and a low concentration chamber. If it is assumed that oxygen is also non-sorbing, the value for the effective diffusivity of oxygen may be calculated from the effective diffusivity for uranine, given the free solution diffusivities of both oxygen and uranine.

Based upon the experimental measurements, the effective diffusivity of oxygen is calculated to be roughly $1.2\times10^{-11}$ m$^2$/s or $3.8\times10^{-4}$ m$^2$/year. In the same experiments, the porosity of the waste was determined to be 20% ($\varepsilon_p = 0.2$). If we assume that the data for blast furnace slag is approximately valid for MSWI, the value of $k_{eff}$ may be estimated as a function of particle size and saturation for a given total porosity. The data used for these calculations is summarised in table 3:

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>$D_e^w$ (m$^2$/y)</td>
<td>$3.8\times10^{-4}$</td>
<td>Bäverman, 1994</td>
</tr>
<tr>
<td>$D_e^w / D_0^w$</td>
<td>$\approx 5\times10^{-3}$</td>
<td></td>
</tr>
<tr>
<td>$n_R^0$ (mol O$_2$ / kg)</td>
<td>1.03</td>
<td></td>
</tr>
<tr>
<td>$\rho_{bulk}$ (kg / m$^3_{total}$)</td>
<td>1296</td>
<td>Fällman et al., 1994</td>
</tr>
<tr>
<td>$\varepsilon$ (m$^3_{void}$ / m$^3_{total}$)</td>
<td>0.3</td>
<td>assumed</td>
</tr>
<tr>
<td>$\varepsilon_p$ (m$^3_{pore water}$ / m$^3_{particle}$)</td>
<td>0.2</td>
<td>Bäverman, 1994</td>
</tr>
<tr>
<td>S (m$^3_{water}$ / m$^3_{void}$)</td>
<td>S $\geq 0.583$</td>
<td>assumed</td>
</tr>
</tbody>
</table>

The influence that particle size has upon the calculated value of $k_{eff}$ is shown in figures 3 and 4 below for two different levels of saturation, using the data from table 3:
Figure 3. Effective rate ratio \( (k_{\text{eff}}/k_q) \) as a function of particle diameter for different values of \( k_c \) and \( S = 1 \)

Figure 4. Effective rate ratio \( (k_{\text{eff}}/k_q) \) as a function of particle diameter for different values of \( k_c \) and \( S = 0.6 \)

The results shown in figure 3 and 4 indicate that the transport properties of the waste particles start to have an observable influence upon \( k_{\text{eff}} \) for fast homogeneous reaction
rates even when the particles are only a few tenths of a millimetre in diameter. For the fastest reaction rate \((k_c = 20 \text{ year}^{-1})\), the value of \(k_{\text{eff}}\) is less than 10 percent of the homogeneous reaction rate constant \((k_q)\) when the particles are one centimetre in diameter. Generally speaking, the slower the redox reaction, the less that particle diffusion will influence the effective reaction rate. Even for relatively slow redox reactions, the value of \(k_{\text{eff}}\) is measurably less than that of the homogeneous reaction rate constant when the particle diameter is one centimetre. For very small particle sizes (less than \(10^{-4} \text{ m}\)), the calculated value of \(k_{\text{eff}}\) is indistinguishable from the homogeneous reaction rate constant for all values of \(k_c\) under 20 year\(^{-1}\).

From these calculations it appears that particle size is an important factor when assigning a reaction rate constant for the simulation of redox processes in waste landfills. This depends, of course, upon the homogeneous redox reaction rate. The particle size is particularly critical for fast redox reactions, but will have less importance in systems where the redox reactions are very slow.

The calculations presented in this paper consider only the initial reaction rate, which would be observed in a closed system containing organic material. In a flow-through system, where the waste reacts continuously with in-transported oxygen, the reducing capacity is steadily depleted and we can no longer make the assumption that the concentration of organic material is roughly constant. Owing to the depletion of the reducing capacity, the value of the first order rate constant \((k\) or \(k_q)\) at later times should be considerably less than the initially predicted value.

In a heterogeneous system, redox reaction fronts may even begin to appear in individual particles after a period of time. If the homogeneous reaction rate is low, the buffering capacity may be depleted, more or less, simultaneously throughout the particle. In this case there will be no redox front formation. If the homogeneous reaction rate is relatively fast, however, a redox front may form. In this case, the reducing capacity near the surface of the particle will be depleted first. When the outer layers of the particle have been depleted of reducing constituents, oxygen must diffuse from the surface of the particle to the redox front in order to react. When the redox front has retreated sufficiently far into the particle, the diffusional resistance between the surface of the particle and the redox front may become the rate-limiting process.

Similarly to the previous analysis, the 1-dimensional, advective-diffusive mass balance for oxygen can be shown to be:

\[
-\frac{D^*}{\beta_p} \frac{\partial^2 Q_s}{\partial z^2} + \frac{V}{\beta_p} \frac{\partial Q_s}{\partial z} + k_{\text{eff}} Q_s \epsilon = -\epsilon \frac{\partial Q_s}{\partial t} \tag{47}
\]
If the quasi-stationary state approximation is valid, equation 47 reduces to:

\[-D_e \frac{\partial^2 Q_s}{\partial z^2} + V \frac{\partial Q_s}{\partial z} + \frac{30}{\varepsilon_0} \frac{\partial}{\partial z} \left( \frac{\varepsilon_s \varepsilon_p}{\varepsilon_p} \right) \theta_0 Q_s = 0\]  

(48)

It should be remembered that although no kinetic constant appears to be contained in the equation above, the variable θ₀ incorporates the equivalent particle reaction rate constant (kₚ) calculated using equation 24 or 25.

As in the previous analysis, the effective rate constant given by equation 42 corresponds to the maximum that would be observed in the heterogeneous particle system. In this case, however, there will be a distribution of organic concentrations both along the direction of fluid flow and within individual particles along the fluid flowpath. As was the case for the estimated homogeneous rate constant (k or \(k_q\)), the effective first order rate constant predicted by equation 42 may not be entirely physically realistic, but will be sufficiently accurate for the purposes of making scoping calculations.

4 Conclusions

It has been shown that when the redox reactions are fast, particle size may have a certain relevance for the choice of rate constant used in simulations of reducing capacity depletion. If the waste particles are small, then chemical reaction kinetics will dominate and the rate constant will be quite close to that for a homogeneous redox reaction. If the waste particles are large, transport processes within the waste particles may determine the reaction rate constant to be used in simulations.

The calculation procedure developed in this paper allows kinetic data (for organic oxidation) taken from the literature to be converted into a form which is appropriate for coupled transport and reaction programs describing the rate of oxygen consumption within a waste heap or landfill.

Based upon the theoretical analysis, the waste material used in this project is predicted to have a first order reaction rate constant for oxygen consumption (k or \(k_q\)), somewhere in the range of \(10^{+2} - 10^{+5}\) year⁻¹. If the waste material consists of large particles or lumps, the reaction rate constant should also be modified in order to reflect approximately the effects of particle diffusion.

It should be remembered that these calculations make the assumption that the waste particles are perfect spheres and that the concentration of organic matter is approximately constant. Notwithstanding this, however, the calculations are useful as a rough guide to the influence of particle size on the effective redox reaction rate. The results should be approximately applicable to anthropogenic wastes such as ashes and
slags as these are frequently granular and are likely to have a similar effective diffusivity as that used in these calculations.

Acknowledgement

The financial support of this project by the Swedish Waste Research Council and the Swedish Environmental Protection Agency is gratefully acknowledged.
Notation

\( A_p \)  
external surface area of waste particle (m²)

\( C \)  
concentration of oxidisable matter (mol / m³_{solid})

\( C_0 \)  
initial concentration of oxidisable organic matter (mol / m³_{solid})

\( D_0^w \)  
free aqueous diffusivity of oxygen (m²/ y)

\( D_e^w \)  
effective aqueous diffusivity of oxygen in waste particle (m²/ y)

\( J_{r0} \)  
flux of oxygen into an individual particle (mol/m² year)

\( k_c \)  
first order rate constant with respect to organic concentration and fixed aqueous oxygen concentration (1/year)

\( k_{eff} \)  
effective first order rate constant with respect to organic concentration and fixed aqueous oxygen concentration (1/year)

\( k_p \)  
first order rate constant for a particle with respect to aqueous oxygen concentration and fixed organic concentration (1/ year)

\( K_q \)  
equilibrium constant for the dissolution of gaseous oxygen in water (mol / Pa m³)

\( k_q \)  
first order rate constant with respect to aqueous oxygen concentration and fixed organic concentration (1/ year)

\( k_r \)  
second order rate constant with respect to aqueous oxygen concentration and organic concentration (m³_{water} / mol year)

\( n_{_{CH_2O}} \)  
overall molar rate of organic consumption (mol/ y)

\( n_{O_2} \)  
overall molar rate of oxygen (O₂) consumption (mol/ y)

\( n_p \)  
number of particles per unit volume of waste material (number / m³_{total})

\( n^0_R \)  
reducing capacity of waste material (mol O₂ / kg)

\( N_{R0} \)  
total specific rate of oxygen consumption (mol O₂ / m³_{total})

\( P_{O_2} \)  
partial pressure of oxygen in gas phase (Pa)

\( P^0_{O_2} \)  
atmospheric partial pressure of oxygen (Pa)

\( Q_s \)  
aqueous concentration of oxygen (mol / m³_{water})

\( Q_{s0} \)  
initial aqueous concentration of oxygen (mol / m³_{water})
$r_0$  external particle radius (m)
$r$  radial distance from particle centre (m)
$R$  universal gas constant (Pa m$^3$/mol K)
$R_p$  specific rate of oxygen consumption within particle (mol / m$^3_{\text{pore-water}}$)
$S$  saturation (m$^3_{\text{water}}$ / m$^3_{\text{void}}$)
$T$  temperature (K)
$V_a$  total volume of air in the system (m$^3_{\text{air}}$)
$V_p$  volume of pore water contained in waste particle (m$^3_{\text{pore water}}$)
$V_T$  total volume of system (m$^3_{\text{total}}$)
$V_w$  volume of water in the inter-particle porosity (m$^3_{\text{ext. water}}$)
$V_{wt}$  total volume of water in the system (m$^3_{\text{water}}$)

$\varepsilon$  total porosity (m$^3_{\text{void}}$ / m$^3_{\text{total}}$)
$\varepsilon_p$  porosity of waste particle (m$^3_{\text{pore water}}$ / m$^3_{\text{particle}}$)
$\rho_{\text{bulk}}$  bulk density of waste material (kg / m$^3_{\text{total}}$)
$\phi$  dimensionless constant (equation 36)
$\theta_0$  dimensionless constant (equation 29)
References


Simulation of the Redox Buffer Depletion Rate in Landfills of Combustion Residue Waste Materials

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Abstract

Simulations have been made of the redox buffer depletion rate in landfills of combustion residue wastes. The model is based upon a one-dimensional mass balance where oxygen transport results from a combination of advective and diffusive processes. A simple, generalised representation of redox buffering properties is used where dissolved oxygen reacts in accordance with a first order rate law. Using certain simplifying assumptions, it is possible to obtain an analytical solution for the time required for complete depletion of the redox buffering capacity of landfilled solid wastes. The results indicate the overwhelming importance that the effective diffusivity of oxygen in the landfill has upon the rate of redox buffer depletion. The results also show under which conditions transport effects may be expected to dominate the leaching processes and determine an upper limit for the depletion rate.

Keywords: simulation, reducing capacity, redox buffering, leaching, solid waste, landfill, quasi-stationary state

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1 Introduction

Modelling of the leaching processes that take place within a waste landfill is a valuable tool as it is often not possible to conduct experiments over sufficiently long time scales to observe the long term leaching behaviour of wastes. Leaching processes can be accelerated in the laboratory, but this may give results that cannot be directly extrapolated to landfill situations as the wastes have been exposed to more aggressive conditions than would exist in natural systems.

If the major constituents in the waste which control the chemistry of the leachant can be determined, then geochemical modelling may be a viable alternative to experimental determination of the waste leaching properties. By modelling the chemical reactions and transport of these constituents, then changes in the landfill effluent composition over time may be predicted with the aid of mass balance simulation tools.

In this paper, a method is presented which may be used to predict landfill leaching processes over long periods of time. The model is based upon a generalised representation of redox buffering processes with combined advective and diffusive in-transport of oxygen. The model is intended to be simple and flexible enough that it may be adapted to different waste types with relative ease.

A waste landfill may be thought of as a large chemical reactor. Atmospheric gases and rainwater may slowly infiltrate the landfill and react with the waste. Within the landfill, a multitude of chemical reactions occur which influence the composition of the water (leachant) as it follows a flowpath through the waste. The pH and redox state of the leachant, as well as the presence of aqueous complexing agents have a strong influence upon the solubility of heavy metal contaminants that may be present in the waste.

Many anthropogenic wastes are reducing. This means that they will consume oxidants, which may be present in the leachant. Although not all of the redox reactions occurring in a waste landfill directly involve oxygen, the major oxidant transported into the landfill is atmospheric oxygen. It is often convenient therefore, to describe the redox state of the leachant in terms of oxygen fugacity (or oxygen partial pressure). Redox buffering processes may also lead to the generation of acidity. This may have an effect upon the rate of pH buffer depletion in the waste, particularly if the landfill is only partially water saturated.

After a period of time, under the influence of in-transported oxygen, waste near the surface of a landfill will be depleted of its reducing capacity. As a result of this, a
redox reaction front will develop along the leachant flowpath. This reaction front slowly recedes into the waste as the buffering capacity of the waste is used up.

At the redox front, the composition of the leachant may change quite suddenly. Upstream of the redox front, the redox buffering capacity of the waste is exhausted, whilst downstream there remains unreacted buffering capacity. The sharpness of the leachant composition change depends upon kinetic factors, dispersion, and diffusion. The composition changes may appear to occur very abruptly in a system where diffusion and dispersion are negligible and the residence time of the leachant is sufficiently high relative to the reaction rate. The effects of reaction kinetics, diffusion, and dispersion operate to smooth out these compositional changes. The rate of reaction front movement depends upon the rate of mass transport and the initial quantities of the reacting constituents present in the waste.

While there is still a redox buffering capacity present in the waste material, the rate of heavy metal leaching may be very low owing to the poor solubility of redox sensitive heavy metals under reducing conditions. When the redox buffering capacity of the waste is completely exhausted, however, the heavy metal release rate can increase dramatically over a relatively short period of time.

2 The Simulation of Redox Front Movement in Waste Landfills

In this section, an analytical representation of gaseous diffusional processes within a landfill will be made. It is inevitable with analyses of this type that assumptions and simplifications need to be made in order to make the problem mathematically tractable. It is possible, however, to make a reasonably robust model, which may be used for scoping calculations.

The depletion of the reducing capacity in a waste material with the formation of a redox front is an example of a moving boundary problem. Moving boundary problems involving advective and diffusive flow are quite well documented in the literature; see, for example, Crank (1984). Other physical examples where moving boundary type problems may arise are the freezing of liquids and electrochemical machining.

The transport of oxygen into a landfill will lead to a depletion of the reducing capacity of the waste. After a period of time, the redox front formed as a result of this depletion will have receded to a certain depth \( z_R \) in the waste. The oxygen concentration profile may thus appear as shown conceptually in figure 1:
In the proposed model for redox buffering, it is assumed that a number of basic redox reactions may be lumped together in the form of a single, generalised oxygen consuming reaction. One way of writing the generalised redox reaction is:

$$R_{(s)} + O_2(g) \rightleftharpoons aH^+ + bCO_3^{2-} + R_{diss}^{(2b-a)}$$

In this reaction, $R$ represents the overall reducing capacity of the solid and $R_{diss}^{(2b-a)}$ represents a dissolved reaction product resulting from the oxidation of one mole of $R$. The superscript $(2b-a)$ refers to the charge on this dissolved species and is included only to ensure that the reaction is electrostatically balanced. It is important to include carbonate ion ($CO_3^{2-}$) in the generalised redox reaction as it can participate in other processes that may affect the pH buffering capacity depletion rate.

It is difficult to assign a meaningful equilibrium constant to this generalised redox reaction as the system is likely to contain a number of redox couples, which may not necessarily be in equilibrium. In spite of this, the equilibrium partial pressure of oxygen ($P_{O2}$) is often extremely low in reducing systems and it is not uncommon for the $P_{O2}$ to be as low as $10^{-30} - 10^{-70}$ atmospheres. The actual $P_{O2}$ may influence the solubility of toxic metals, but from a mass balance viewpoint the equilibrium $P_{O2}$ is of minor importance. It makes little difference to the mass balance of oxygen whether the equilibrium $P_{O2}$ is $10^{-30}$ or $10^{-70}$ atmospheres as, in both cases, the partial pressure is for all practical purposes zero. To simulate the depletion of the redox buffering capacity, an arbitrarily low equilibrium $P_{O2}$ may therefore be assumed.
As the rate of oxygen consumption is often the result of many different redox reactions, the kinetics of the oxygen consumption are actually quite complex. In this analysis, the rate of oxygen consumption is assumed to be a first order rate process. Upon first glance, this may seem to be an unrealistic assumption. In fact, the assumption of a first order reaction rate constant is probably about as complex as the nature of the problem allows. The kinetics of oxygen consumption may depend upon surface reaction rates, homogeneous reaction rates, bio-catalysis, particle and film diffusional resistances, or combinations thereof. The amount of physical and chemical heterogeneity in the system, which is difficult to characterise to any degree of certainty, will strongly influence these rate-limiting processes.

A first order reaction rate, although a much simplified representation of the actual behaviour, does exhibit many of the same characteristics as a more complex description of the kinetics (i.e. a maximum rate that decreases roughly in proportion to the oxygen availability).

### 2.1 Combined Advective and Diffusive Transport

If we consider a generalised redox reaction that consumes oxygen in accordance with a homogeneous first order rate law, we may write a one-dimensional mass balance for oxygen where transport results from a combination of diffusive and advective processes. This mass balance is subject to the following assumptions:

1) sorption of oxygen on pore surfaces is neglected
2) the leachate flux is sufficiently low that dispersion is small and molecular diffusion dominates
3) there is no capillary barrier over the landfill that may act as a diffusive resistance
4) there is diffusive transport of gaseous components and advective transport of aqueous components only
5) the material properties of the waste are spatially and temporally invariant, and the reactive medium is infinitely deep
6) absorption drift is neglected (see explanation following)
7) equilibrium exists between gaseous and aqueous phases

As the concentration of oxygen in air is relatively high, there is a small enhancement of mass transfer that arises due to the consumption of oxygen at the redox front. This is also known as the “absorption drift factor”. The drift factor is neglected in order to simplify the mathematical treatment of the coupled reaction and transport equations.
By neglecting the drift factor, the oxygen flux to the redox front may be underestimated by up to a maximum of 12 percent (Collin, 1987). In view of the magnitude of other uncertainties in the calculation, such as the effective diffusivity and counter-diffusion effects (which reduce the importance of the drift factor), this may not be a bad assumption.

In terms of dissolved oxygen concentration \((Q)\), the one-dimensional, unsteady-state mass balance is:

\[-D_e \frac{\partial^2 Q}{\partial z^2} + V \frac{\partial Q}{\partial z} + k Q = -\varepsilon \left( \frac{S}{RT} + S \right) \]  

(2)

where

\(D_e\) = effective diffusivity of oxygen based upon aqueous concentrations  
\(\text{m}^2 \text{ year}^{-1}\)

\(k\) = first order kinetic constant for oxygen consumption \((1/\text{ year})\)

\(K_q\) = equilibrium constant for dissolution of oxygen in water

\(Q\) = aqueous oxygen \((\text{O}_2)\) concentration \((\text{mol} / \text{m}^3_{\text{water}})\)

\(R\) = universal gas constant \((\text{Pa} \cdot \text{m}^3 / \text{mol K})\)

\(S\) = degree of saturation \((\text{m}^3 / \text{m}^3)\)

\(t\) = time (year)

\(T\) = temperature (K)

\(V\) = advective flux of leachant \((\text{m}^3 / \text{m}^2 \text{ year})\)

\(z\) = waste depth (m)

\(\varepsilon\) = total porosity \((\text{m}^3 / \text{m}^3)\)

When the quantity of reducing material in the waste is large in relation to the dissolved concentrations of oxygen, many volumes of leachant need to be transported through the system until there is a noticeable change in the mass distribution of unreacted reducing material. If the time taken to establish a steady state concentration profile in the leachant is significantly less than the length of time required to completely react a constituent in the solid phase, the quasi-stationary state approximation may be applicable. Lichtner (1988) discusses criteria for when this approximation may be valid. The quasi-stationary state approximation has been shown to be valid for advective, diffusive, and combined advective-diffusive systems. It can also be shown that the approximation is valid for the cases studied in this paper (see appendix). The assumption of a quasi-stationary state permits setting the
accumulation term on the right hand side of equation 2 to zero. Equation 2 can then be written as:

\[
\frac{d^2Q}{dz^2} - \frac{V}{D_e^a} \frac{dQ}{dz} - \frac{k}{D_e^w} Q = 0
\]

(3)

From mass balance considerations, we may also define the following relation between the overall effective diffusivity based upon gaseous partial pressures \(D_e^a\) and the overall effective diffusivity based upon aqueous oxygen concentrations \(D_e^w\):

\[
D_e^w = \frac{D_e^a}{K_q RT}
\]

(4)

The dimensionless conversion factor, \(K_q RT\) is calculated to be \(3.1 \times 10^{-2}\) at 298 K. Equation 4 is a useful conversion formula as effective diffusivities are often reported in terms of the free diffusivity of oxygen in air.

Equation 3 has the standard solution:

\[
Q = \alpha_1 \exp \left( \frac{b}{2} z \right) + \alpha_2 \exp \left( -\frac{b}{2} z \right)
\]

(5)

where

\[
\lambda_1 = \frac{V}{2 D_e^a} + \sqrt{\frac{V^2}{4 D_e^a^2} + \frac{k}{D_e^w}}
\]

(6)

\[
\lambda_2 = \frac{V}{2 D_e^w} - \sqrt{\frac{V^2}{4 D_e^w^2} + \frac{k}{D_e^w}}
\]

(7)

(\(\alpha_1\) and \(\alpha_2\) are integration constants)

We note that after some time, all reducing matter will have been depleted at the inlet and over time this depletion zone will advance further into the hypothetical column of waste. The boundary between where there is, and where there is not any reducing material \(z = z_R\) is referred to as the redox front.

In general, the reducing capacity of the waste at any position downstream of the redox front is depleted at a rate that is proportional to the oxygen concentration at that position. At some location downstream, the oxygen concentration will be so low that the rate of redox buffer consumption can be assumed to be approximately zero. The redox buffer depletion rate never actually decreases to zero, however, as the reaction rate is an exponentially decaying function of distance.

As the redox reaction is absent upstream of the redox front, equation 5 is subject to the following restrictions:

\[
k = 0 \quad 0 < z < z_R
\]

(8)
\( k > 0 \quad z_R < z < \infty \) (9)

\[ J_z \big|_{z_R} = J_z \big|_{z_R} \quad \text{(continuity of oxygen flux)} \] (10)

\[ Q \big|_{z_R} = Q \big|_{z_R} = Q_R \quad \text{(continuity of oxygen concentration)} \] (11)

In addition, we have the boundary conditions:

\[ z = 0 \quad Q = Q_0 \] (12)

\[ z = \infty \quad \frac{dQ}{dz} = 0 \] (13)

Applying these conditions gives the following expressions for the aqueous oxygen concentration profile in the waste:

\[ Q = Q_0 - Q_0 \frac{\exp \left( -c_e z \right)}{1 + \phi} - Q_R \frac{\exp \left( -c_e z_R \right)}{1 + \phi} \quad 0 < z < z_R \] (14)

\[ Q = Q_R \exp \left( -c_e z_R \right) \phi \quad z_R < z < \infty \] (15)

The flux of oxygen anywhere in the system is equal to the sum of advective and diffusive fluxes:

\[ J_z = VQ - D_e \frac{dQ}{dz} \] (16)

The mass balance requires that the spatial derivatives of both equation 14 and 15 be equal at the redox front. This means that there is equal flux of oxygen at both sides of the redox front (equation 10). Equating these derivatives, both evaluated at \( z = z_R \), gives the following expression for \( Q_R \):

\[ Q_R = \frac{Q_0 \phi}{b + \phi} \] (17)

where

\[ \phi = \frac{1 - \exp \left( -c_e z_R \right)}{1 - \exp \left( -c_e z_R \right)} \] (18)

As the redox front recedes into the landfill, the concentration of oxygen at the redox front decreases owing to the diffusive resistance for mass transport in the depleted zone upstream of the redox front.
By combining equation 15 and 16, the expression for the flux of oxygen at the redox front becomes:

\[ J_V = C - D_e \lambda_2 h_R \]  

(19)

The flux of oxygen at a depth \( L \), downstream of the redox front is:

\[ J_L = C - D_e \lambda_2 h_R \exp \left( -z_R \right) \]  

(20)

The total amount of depleted reducing capacity in the semi-infinite landfill at any given time will be equal to:

\[ N_R^d = \rho_{\text{bulk}} S_A \int_{0}^{\infty} C_R^d h_R \, dz \]  

(21)

where,

\[ N_R^d = \text{total amount of depleted reducing capacity (mol O}_2\text{)} \]

\[ n_R^0 = \text{initial reducing capacity of the waste (mol O}_2\text{/kg)} \]

\[ n_R = \text{reducing capacity (mol O}_2\text{/kg)} \]

\[ \rho_{\text{bulk}} = \text{bulk density of waste (kg/m}^3\text{)} \]

\[ S_A = \text{cross sectional area of waste (m}^2\text{)} \]

If we consider the location of the redox front when it has receded to a depth \( z_R \) in the waste material, equation 21 is equivalent to:

\[ N_R^d = \rho_{\text{bulk}} S_A n_R^0 z_R + \rho_{\text{bulk}} S_A \int_{0}^{z_R} C_R^d h_R \, dz \]  

(22)

The rate of depletion of the reducing capacity is therefore:

\[ \frac{dN_R^d}{dt} = \rho_{\text{bulk}} S_A n_R^0 \frac{dz_R}{dt} + \rho_{\text{bulk}} S_A \frac{d}{dt} \int_{0}^{z_R} C_R^d h_R \, dz \]  

(23)

After a stationary state is established, the concentration profile of dissolved oxygen downstream from the redox front is proportional to the oxygen concentration at the redox front. If the oxygen concentration at the redox front were to remain constant, the concentration profile of oxygen (and the reducing agent) downstream would have a constant pattern and move without changing shape. Although this is not strictly true in our case owing to the fact that the oxygen concentration at the redox front \( (Q_R) \) changes slowly with time, we use this simplification later to allow for the use of simple analytical solutions. This gives a better insight into the main processes than the use of numerical solutions.
If the reaction rate profile for the redox buffering mineral is of constant shape, the integral for the mass of depleted redox buffer downstream of the redox front will also be constant. This leads to the following simplification:

\[
\frac{d}{dt} \left( n_R^0 - n_R \right) = 0
\]  

(24)

\[
\frac{dN_{R}^0}{dt} = \rho_{\text{bulk}} S \frac{n_R^0}{n_R} \frac{dz}{dt}
\]

(25)

The rate of redox buffer depletion is equal to the rate of oxygen transport into the landfill. By equating the expression for oxygen flux at the redox front (equation 19) with that for the rate of redox buffer depletion (equation 25), the instantaneous velocity of the redox front may be obtained:

\[
\frac{dz}{dt} = \frac{J_R}{\rho_{\text{bulk}} n_R^0}
\]

(26)

This is a variables separable, ordinary differential equation. Rearranging this equation and integrating the resultant expression gives the time required for a redox front to recede from the surface of the landfill to the depth \( z_R \):

\[
t - \tau_0 = \rho_{\text{bulk}} n_R^0 \int dz \frac{J_R}{z_R}
\]

(27)

The parameter \( \tau_0 \) is the time initially required for the formation of a steady state mineral concentration profile before the redox front begins to move. The time required to establish this steady state is given by (see appendix):

\[
\tau_0 = \frac{\rho_{\text{bulk}} n_R^0}{kQ_0}
\]

(28)

The integral in equation 27 may be solved analytically to obtain:

\[
\frac{t - \tau_0}{\rho_{\text{bulk}} n_R^0} = \frac{D_e^w}{V^2 Q_0} \frac{\lambda_2}{\lambda_1} \exp \left( \frac{V}{D_e^w} z_R \right) \frac{z_R}{VQ_0}
\]

(29)

It may be shown that there is a maximum rate of redox buffer depletion when the redox reaction is very fast. In this case, \( \lambda_2 / \lambda_1 \approx -1 \) and the resultant equation for redox buffer depletion time is:

\[
\frac{t}{\rho_{\text{bulk}} n_R^0} = - \frac{D_e^w}{V^2 Q_0} \exp \left( \frac{V}{D_e^w} z_R \right) \frac{z_R}{VQ_0}
\]

(30)

When the redox reaction is very fast, the time required for the formation of a steady state mineral concentration profile becomes very small. For this reason, the term \( \tau_0 \)
may be neglected in equation 30. If the advective flowrate decreases to zero and there is only diffusive flux of oxygen, equation 30 reduces to:

\[
\frac{t}{\rho_{\text{bulk}} n^0_R} = \frac{z_R^2}{2 D^R Q_0} \tag{31}
\]

This result is identical to that given by a shrinking core model with an instantaneous reaction at the redox front (Romero, 1995). If, on the other hand, the oxygen transport is purely advective, as may be the case in a saturated landfill, equation 29 reduces to:

\[
\frac{t - \tau_0}{\rho_{\text{bulk}} n^0_R} = \frac{z_R}{V Q_0} \tag{32}
\]

It should be noted that under purely advective flow conditions, the rate of movement of the redox front (after the formation of a steady state mineral concentration profile) is independent of the redox reaction rate and is dependent only upon the reducing capacity of the waste and the rate of advective oxygen transport into the landfill. This is the same conclusion reported by Lichtner (1988, 1993). Furthermore, in the absence of diffusional transport, the oxygen concentration at the redox front will be constant and equal to that in the leachant flowing into the landfill.

### 2.2 Purely Advective Transport

If the waste is fully saturated (\(S = 1\)) and the transport of oxygen is considered to be purely advective, equation 3 may be written as a variables separable ordinary differential equation:

\[
\frac{dQ}{dz} - \frac{k}{V} Q = 0 \tag{33}
\]

If we solve this equation subject to the same conditions as given in equations 8-11, the system can be shown to have the following solution:

\[
Q = Q_0 \quad 0 < z < z_R \tag{34}
\]

\[
Q = Q_0 \exp \left( \frac{k}{V} \left( -z_R + z \right) \right) \quad z_R < z < \infty \tag{35}
\]

It can also be shown that the fluxes of oxygen at the redox front and at depth \(L\) (downstream of the redox front) in the landfill are:

\[
J_{R}^{\text{adv}} = Q_0 V \tag{36}
\]

\[
J_{L}^{\text{adv}} = Q_0 V \exp \left( \frac{k}{V} - z_R \right) \tag{37}
\]

If equation 36 and 27 are combined and integrated, the result for the redox buffer depletion time is identical to that given in equation 32.
2.3 Purely Diffusional Transport

If the advective transport term in the oxygen mass balance is neglected, equation 3 may be written as:

$$\frac{d^2 Q}{dz^2} - \frac{k}{D_e} Q = 0$$

(38)

Solving this equation subject to the same conditions as used previously, the system will have the following solution:

$$Q = Q_0 - Q_R \begin{cases} 0 < z < z_R \\ z_R < z < \infty \end{cases}$$

(39)

$$Q = Q_R \exp \left( -z_R \sqrt{\frac{k}{D_e}} \right)$$

(40)

According to the requirement of flux continuity (equation 10), the derivatives of equation 39 and 40 must be equal at the redox front. By equating these derivatives (both evaluated at \( z = z_R \)), \( Q_R \) is found explicitly:

$$Q_R = \frac{Q_0}{z_R \sqrt{\frac{k}{D_e}}}$$

(41)

In the case where there is only diffusional transport, the oxygen flux is given by:

$$J_z = -D_e \frac{dQ}{dz}$$

(42)

The fluxes of oxygen at the redox front and at depth \( L \) (downstream of the redox front) in the landfill therefore are:

$$J_R = D_e Q_R \sqrt{\frac{k}{D_e}}$$

(43)

$$J_L = D_e Q_R \exp \left( -z_R \sqrt{\frac{k}{D_e}} \right)$$

(44)

If equation 26 and 43 are combined and integrated, the time for redox buffer depletion is found to be:

$$\frac{t - \tau_0}{\rho_{\text{bulk}} n_R^{0}} = \frac{z_R}{D_e Q_0} \sqrt{\frac{k}{D_e}} + \frac{1}{\sqrt{\frac{k}{D_e}}}$$

(45)

When the redox reaction is very fast, the redox buffer depletion time given by equation 45 reduces to that given by equation 31.
3 Estimation of Transport Parameters and Reaction Rate Constants

3.1 Effective Diffusivity

The effective diffusivity of oxygen in a landfill is a complicated function of porosity, pore tortuosity and constrictivity, particle size distribution, and water saturation. Puura (1998) has reviewed a number of studies of the effective diffusivity in heaps of pyritic mining waste. In these studies, the effective diffusivity ratio is rarely reported to be higher than $D_e^a/D_0^a \approx 0.05$ for well-drained heaps ($D_0^a$ is the free diffusivity of oxygen in air). If we assume that these results are roughly applicable to heaps of ash or slag, this would give an approximate upper limit for the effective diffusivity of $D_e^a = 28 \text{ m}^2/\text{year}$. Using equation 4, the equivalent $D_e^w$ is calculated to be $900 \text{ m}^2/\text{year}$.

3.2 Leachant Flux

The leachant flux in the landfill depends on the local rainfall, the amount of surface runoff, and the water retention characteristics of the particular medium. These parameters are highly variable and are influenced by geographic location, topography, and the physical properties of the waste material itself. In order to make a conservative estimate of the relative depletion times for the different waste materials, it is assumed that there is no surface runoff, no capillary barrier against water infiltration, and that the water can drain freely.

In the middle part of Sweden, the average rainfall over a 30-year period was estimated to be roughly $0.3 \text{ m/year}$ by Lindgren and Rasmuson (1994). In the calculations presented in this paper, however, the leachant flux will be assumed to be a conservative $0.5 \text{ m/year}$.

3.3 Redox Reaction Rate

There is a considerable body of literature describing the bio-degradation of organic materials (Moreno, 1982; Westrich and Berner, 1984; Boni and Musmeci, 1998). In the literature, the rate of disappearance of organic matter is often described as a first order process with respect to a fixed partial pressure of oxygen (usually the atmospheric partial pressure of oxygen, $P_{O_2}^0$). If neither the $P_{O_2}$ nor the organic concentration are constant, then the oxidation of organic matter is essentially a second order process where the rate of oxidation is roughly proportional to both the organic- and oxygen concentration. If the organic concentration is assumed to be roughly constant (a necessary assumption to simplify the mathematical treatment of the system), the oxidation rate will be a first order process that is proportional to the
Using literature values for the oxidation rate in terms of organic concentrations, the rate for aqueous oxygen consumption may be estimated from mass balance considerations:

$$k = \frac{k_c P_{O_2}^0 n_R^0}{Q_0 K_p}$$

where

- \(k_c\) = first order rate constant with respect to organic concentration and fixed aqueous oxygen concentration (1/year)
- \(P_{O_2}^0\) = ambient oxygen (O\(_2\)) partial pressure (Pa)

The variable, \(k_c\), is the rate constant for organic depletion that is most often reported in the literature and usually lies between about 0.01 year\(^{-1}\) and 20 year\(^{-1}\) for non-refractory organic materials. As the actual reaction rate is quite uncertain, a range of first order aqueous rate constants (k) varying between \(10^{+2}\) and \(10^{+5}\) year\(^{-1}\) have been examined in the simulations presented in this paper.

### 3.4 Reducing Capacity of Municipal Solid Waste Bottom Ash

Ashes from municipal solid waste incineration (MSWI) typically contain 1-5% of non-combusted organic material (Zevenbergen, 1994). A certain proportion of this non-combusted organic material may be refractory (i.e. non-reactive under landfilling conditions). The redox buffer depletion times reported in this paper are based upon an assumed organic content of 3% (by weight). This corresponds to a reducing capacity of roughly 1.0 mol O\(_2\)/kg of waste.

### 4 Case Studies of Redox Front Movement in a Hypothetical Waste Landfill

Using the estimated reducing capacity of the waste and the equations developed in the previous sections, it is possible to calculate the length of time required for total depletion of the redox buffering capacity if a waste is landfilled. In order to do so, however, the transport properties of the landfill and the leachant flux need to be determined as well as the kinetic constant for the lumped redox reaction. As the current analysis centres upon a hypothetical landfill, these parameters are chosen to reflect what are considered to be conservative scenarios for leaching based upon the discussions in the previous sections. Table 1 summarises the input data used for these calculations:
Table 1  Parameters used for redox buffer depletion calculations

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$n^0_R$ (MSWI)</td>
<td>1.0 mol O$_2$/kg</td>
</tr>
<tr>
<td>$\rho_{bulk}$</td>
<td>1296 kg/m$^3$</td>
</tr>
<tr>
<td>$Q_0$</td>
<td>2.65×10$^{-4}$ mol/l</td>
</tr>
<tr>
<td>$D_e/D_0$</td>
<td>0.05</td>
</tr>
<tr>
<td>$V$</td>
<td>0.5 m/year</td>
</tr>
</tbody>
</table>

By normalising the time for the reducing capacity depletion with respect to the volumetric reducing capacity (as in equation 29), the value of $(t - \tau_0)\rho_{bulk}n^0_R$ is general for all reducing capacities, provided that the quasi-stationary state approximation is valid. Figure 2 below, shows the value of the generalised depletion time $(t\rho_{bulk}n^0_R)$ plotted against the redox front depth in the waste material for a range of different kinetic constants ($k$) as well as for purely advective flow conditions:

![Graph showing generalised reducing capacity depletion time as a function of redox front depth (corrected for initial transient period)](image)

**Figure 2**  Generalised reducing capacity depletion time as a function of redox front depth (corrected for initial transient period)

The results in figure 2 have been corrected for the time required to form the initial steady state mineral concentration profile $(\tau_0\rho_{bulk}n^0_R)$ and therefore represent the total leaching time.

The depletion time under purely advective flow conditions is generally much longer than that for combined advection-diffusion. The results also indicate that for shallow
landfill depths, the depletion time is strongly dependent upon the redox reaction rate when there is significant diffusive transport of oxygen. The depletion time asymptotically approaches that for an infinitely fast redox reaction with increasing depth. This indicates that the rate of redox buffer depletion becomes predominantly transport controlled with increasing depth. For purely advective flow, the depletion rate is entirely transport controlled.

As the effective diffusivity assumed in these calculations is high, the results obtained by neglecting advective transport of dissolved oxygen (equation 45) are almost identical to those calculated for combined advection-diffusion (equation 29). For very low effective diffusivities, however, advective transport of oxygen plays a more important role and should not be neglected.

If we consider the reducing capacity of the waste material, it is possible to calculate the actual redox buffer depletion time directly from the generalised curves shown in figure 2. The actual redox buffer depletion times for MSWI bottom ash under conditions of combined advection-diffusion are given below in table 2 where a reducing capacity of 1.0 mol O$_2$/kg of waste is assumed:

<table>
<thead>
<tr>
<th>$k$ [year$^{-1}$]</th>
<th>$\infty$</th>
<th>$10^5$</th>
<th>$10^4$</th>
<th>$10^3$</th>
<th>$10^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\tau_0$ [year]</td>
<td>0</td>
<td>0.05</td>
<td>0.5</td>
<td>5.0</td>
<td>50</td>
</tr>
<tr>
<td>$t_{1m}$ [year]</td>
<td>2.5</td>
<td>3.1</td>
<td>4.6</td>
<td>13</td>
<td>69</td>
</tr>
<tr>
<td>$t_{2m}$ [year]</td>
<td>10</td>
<td>11</td>
<td>14</td>
<td>25</td>
<td>92</td>
</tr>
<tr>
<td>$t_{5m}$ [year]</td>
<td>63</td>
<td>66</td>
<td>71</td>
<td>93</td>
<td>190</td>
</tr>
<tr>
<td>$t_{10m}$ [year]</td>
<td>250</td>
<td>260</td>
<td>270</td>
<td>310</td>
<td>460</td>
</tr>
</tbody>
</table>

The redox buffer depletion times for MSWI bottom ash where oxygen transport results from aqueous advection only are given below in table 3:

| $t_{1m}$ [year]   | 10 100 |
| $t_{2m}$ [year]   | 20 100 |
| $t_{5m}$ [year]   | 50 200 |
| $t_{10m}$ [year]  | 100 000 |

The results show that when the effective diffusivity is high, the redox buffering capacity is consumed very fast in comparison to when only aqueous advective
transport of oxygen is considered. The advective flow case corresponds to the situation where the landfill is completely water saturated (perhaps below the water table) and the effective diffusivity is thus very low. If the landfill is designed in order to minimise the flowrate of leachant, then the redox buffer depletion time may be even longer than these results suggest.

Figure 3 and 4 below, show the oxygen partial pressure variation over time at two different depths in the simulated waste landfill for the combined advection-diffusion case:

![Graph](image)

**Figure 3** Oxygen partial pressure ($P_{O2}$) at a depth of 1 metre as a function of generalised depletion time (y m$^{-3}$/mol) for various redox reaction rates (corrected for initial transient period)
Figure 4  Oxygen partial pressure ($P_{O2}$) at a depth of 10 metres as a function of generalised depletion time ($y \cdot m^3/mol$) for various redox reaction rates (corrected for initial transient period)

The results show that, for example, when a reaction rate constant of $10^{+3}$ year$^{-1}$ is simulated, the initial steady state $P_{O2}$ at a depth of 1m is roughly 0.08 atm (40% of the $P_{O2}$ at the surface of the landfill). At a depth of 10m, however, the oxygen has had more chance to react with the waste and the $P_{O2}$ is $10^{-5}$ atm. When purely advective flow is simulated, the initial steady state $P_{O2}$ at a depth of 1m (and 10m) is, for all practical purposes, zero for the same redox reaction rate.

5 Conclusions

The simulation results clearly illustrate the importance that gaseous phase diffusion has upon the rate of redox buffer depletion in landfills of reducing wastes. It is also shown that there is an upper limit to the rate of redox buffer depletion when an infinitely fast redox reaction rate is assumed. For fast reaction rates, the rate of redox buffer depletion is transport controlled and largely independent of the chemical reaction rate for waste depths of more than a couple of metres.

The results also show, not surprisingly, that the rate of redox buffer depletion under purely advective flow conditions is generally much slower than under partially saturated conditions. In addition, it appears that for the leachate fluxes generally
encountered under landfilling conditions, the advective transport of oxygen may be neglected without introducing a large error when the effective diffusivity for oxygen is high. In view of other uncertainties in the calculation, the impact of this assumption will be insignificant.

Owing to the high degree of heterogeneity in large, open systems such as a waste landfill, it is very difficult to make absolutely reliable predictions about long term leaching behaviour. Quantities such as the redox reaction rate, effective diffusivity, and leachate flux cannot be estimated with anything but a marginal degree of confidence, particularly when they are subject to large seasonal variations. For this reason, it is often not justifiable to attempt to create a detailed geochemical model of leaching processes, which may take place in a landfill leaching environment. Notwithstanding this, however, it is desirable to be able to predict if the landfill is likely to become a heavy metal pollution problem and how the behaviour that we observe today is likely to change in the future. This may influence decisions that are made concerning how certain waste materials should be handled in order to minimise future environmental impact.

The generalised model for redox buffer depletion which has been presented in this paper provides a basis for predicting certain aspects of the long term leaching behaviour of solid wastes. The model is sufficiently simple that calculations can be made where there is insufficient data available for more detailed geochemical models. The model attempts to strip some of the complexity from the description of leaching processes in order that the principal controlling processes may be investigated. The model is flexible and can be adapted to various waste types with reasonable ease, the input parameters being obtainable from simple laboratory experiments and literature data.

Acknowledgement

The financial support of this project by the Swedish waste Research Council and the Swedish Environmental Protection Agency is gratefully acknowledged.
Notation

a  stoichiometric proton generation parameter in generalised redox reaction (equation 1)
b  stoichiometric carbonate generation parameter in generalised redox reaction (equation 1)
$D_e^w$  overall effective diffusivity of oxygen based upon aqueous concentrations (m$^2$/year)
$D_0^a$  free diffusivity of oxygen in air (m$^2$/year)
$J_L$  oxygen flux at depth L in waste landfill (mol/m$^2$/year)
$J_R$  oxygen flux at redox front ($z_R$) in waste landfill (mol/m$^2$/year)
$J_z$  oxygen flux at depth z in waste landfill (mol/m$^2$/year)
$k$  first order rate constant with respect to aqueous oxygen concentration and fixed organic concentration (1/year)
$k_c$  first order rate constant with respect to organic concentration and fixed aqueous oxygen concentration (1/year)
$K_d$  equilibrium constant for dissolution of oxygen in water (mol/Pa m$^3$)
$N_R^d$  total amount of depleted reducing capacity (mol O$_2$)
$n_R$  reducing capacity (mol O$_2$/kg)
$n_R^0$  initial reducing capacity of the waste (mol O$_2$/kg)
$P_{O_2}$  oxygen (O$_2$) partial pressure (Pa)
$P_{O_2}^0$  ambient oxygen (O$_2$) partial pressure (Pa)
$Q$  aqueous oxygen (O$_2$) concentration (mol/m$^3$)
$R$  universal gas constant (Pa m$^3$/mol K)
$S$  degree of saturation (m$^3$ / m$^3$)
$S_A$  cross sectional area of waste (m$^2$)
$T$  temperature (K)
t  time (1/year)
$V$  advective flux of leachant (m$^3$/m$^2$/year)
$z$  waste depth (m)
$z_R$  redox front location (m)
$\varepsilon$  total porosity of medium (m$^3$/m$^3$)
\( \phi \) variable in equation 18

\( \lambda_1, \lambda_2 \) Eigen values of 2nd order ODE equation 3

\( \alpha_1, \alpha_2 \) integration constants (equation 5)

\( \tau \) time for formation of initial steady state aqueous concentration profile (year)

\( \tau_0 \) time for formation of initial steady state mineral concentration profile (year)
Appendix: Validity of the Quasi-Stationary State Approximation

The expressions developed previously for the oxygen concentration profile and the rate of redox front movement in a landfill have assumed the validity of the quasi-stationary state approximation. Lichtner (1988) has shown that the quasi-stationary state approximation may be used if the time required to deplete a mineral is significantly longer than the time taken to establish a steady state concentration profile along a fluid flowpath. Furthermore, if $\tau_0$ is the time required to dissolve a redox mineral at the inlet to a hypothetical column of waste and $\tau$ is the time taken to establish a steady state fluid concentration profile, the following inequality must hold in order for the quasi stationary state to be valid:

$$\frac{\tau_0}{\tau} = \frac{\rho_{\text{bulk}} N_0^R}{16 \epsilon^2 D_k^w k Q_0} \left( \frac{4 \epsilon D_k^w k}{V^2} \right)^2 > 1$$  \hspace{1cm} (47)$$

Additionally,

$$\frac{\tau_0}{\tau} \approx \frac{\rho_{\text{bulk}} n_R^0}{4 \epsilon Q_0} \quad \text{when} \quad \frac{4 \epsilon D_k^w k}{V^2} \gg 1$$ \hspace{1cm} (48)$$

The time required ($\tau_0$) to deplete the redox mineral from the inlet to the hypothetical column of waste is given by:

$$\tau_0 = \frac{\rho_{\text{bulk}} n_R^0}{k Q_0}$$ \hspace{1cm} (49)$$

Using values taken from the previous discussions for the parameters in equation 47 (see table 1), the value of $\tau_0/\tau$ is found to be in the range of 1000-5000. This means that a steady state oxygen concentration profile is established roughly 1000-5000 times faster than the steady state mineral concentration profile. If the concentration of dissolved oxygen at the redox front decreases (as is the case in our system), the value of $\tau_0/\tau$ increases. It follows from this that the quasi-stationary state approximation is valid for the leaching systems being studied in this work.
References


Collin M.: 1987, Mathematical modelling of water and oxygen transport in layered soil covers for deposits of pyritic mine tailings, Licentiate Treatise, Department of Chemical Engineering, Royal Institute of Technology, Stockholm, Sweden

Crank J.: 1984, Free and moving boundary problems, Oxford University Press


Acid Neutralising Kinetics of Slags and Combustion Residue Waste Materials

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Abstract

Leaching experiments have been carried out upon three different waste materials under pH static conditions over a 24-hour period. The waste materials were leached at pH 4 for 24 hours and the results compared with experiments where the waste materials were first leached at pH 7 for 24 hours before being filtered and leached for an additional 24 hours at pH 4. The leachate was sampled during the experiments and analysed for different components that were thought to play an important role in pH-buffering processes. The experimental results were also modelled by assuming transport limited dissolution kinetics with shrinking particle sizes. The simulation results agree well with the experimentally measured pH-buffering behaviour and indicate parameters, which need to be characterised in greater detail in order to draw more specific conclusions about the waste dissolution kinetics. It is also shown theoretically that basic pH values at the surface of a dissolving particle may substantially enhance mass transfer owing to hydrolysis of water in the surrounding laminar boundary layer.

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1 Introduction

Toxic trace elements such as heavy metals are often present in anthropogenic wastes at concentration levels that are significantly higher than those levels found naturally in soils. These heavy metals may be mobilised if the chemistry of infiltrating water (leachant) promotes their dissolution. In order to assess the potential for contamination around a waste landfill it is important to know how much of these heavy metals will be leached out of the waste and over which timescales.

One of the major parameters influencing heavy metal solubility is the pH of the leachant. Most slag and combustion residue type wastes are basic and have a certain capacity for reaction with proton acidity. The pH buffering capacity is slowly depleted as acidic rainwater and carbon dioxide are transported into the waste.

The kinetics of pH buffering may be important in systems where oxidation of reducing material generates a large amount of proton acidity. If there is a high rate of oxygen transport into the waste material, the pH buffering capacity may be depleted very quickly. If the rate of proton generation due to oxidation is faster than the rate of pH buffering, the pH of the leachant may drop locally to a low level and facilitate the rapid leaching of heavy metals.

2 Experimental Materials and Methods

Solid wastes such as slags and combustion residues generally consist of a number of fast reacting and also more slowly reacting constituents. In previous batch experiments it has been suspected that very fast dissolving minerals such as portlandite (Ca(OH)$_2$) and calcite (CaCO$_3$) may mask the influence that more slowly dissolving phases such as Ca-Al-Si-O glasses have upon the concentrations of buffering constituents in the leachate.

The idea behind the two step titration procedure was to attempt to wash out the fast reacting pH buffering constituents, so that the slow pH buffering processes could be observed in more detail. The washing procedure was carried out at pH 7 to ensure that fast dissolving phases such as portlandite and calcite, which generally buffer at pH levels above 7, would be removed from the waste.

The experiments were carried out using three different types of waste material. These materials were a municipal solid waste incineration residue (MSWI), and two different types of steel slag. The MSWI is a non-magnetic fraction of a municipal solid waste bottom ash produced at an incinerator located in Linköping, Sweden. One steel slag (AFS) is a non-magnetic fraction from a scrap based electric arc furnace.
(Fundia Steel AB, Smedjebacken, Sweden). The other slag is an unsorted blast furnace slag (BFS) originating from an ore based steel production process (SSAB Oxelösund, Sweden).

The waste materials were dried and then prepared by crushing until all of the material passed a 0.16mm sieve and most of the material passed a 0.125mm sieve. The crushed materials were the same as those used in previous studies by Fällman (1994) and Bäverman (1997). The major elemental composition of these wastes has been determined by Fällman (1994) using ICP-AES. Table 1 below gives the concentrations of the major components in these waste materials:

Table 1. Major component composition of waste materials used in the experiments given as mol/g waste (Fällman, 1994)

<table>
<thead>
<tr>
<th></th>
<th>AFS</th>
<th>BFS</th>
<th>MSWI</th>
</tr>
</thead>
<tbody>
<tr>
<td>K</td>
<td>1.18×10^-5</td>
<td>1.25×10^-4</td>
<td>3.66×10^-4</td>
</tr>
<tr>
<td>Na</td>
<td>1.61×10^-5</td>
<td>1.87×10^-4</td>
<td>1.15×10^-3</td>
</tr>
<tr>
<td>Mg</td>
<td>1.86×10^-3</td>
<td>4.85×10^-3</td>
<td>4.65×10^-4</td>
</tr>
<tr>
<td>Ca</td>
<td>5.51×10^-3</td>
<td>5.59×10^-3</td>
<td>2.19×10^-3</td>
</tr>
<tr>
<td>Al</td>
<td>8.12×10^-4</td>
<td>2.40×10^-3</td>
<td>2.11×10^-3</td>
</tr>
<tr>
<td>Fe</td>
<td>4.33×10^-3</td>
<td>3.04×10^-5</td>
<td>1.93×10^-3</td>
</tr>
<tr>
<td>Si</td>
<td>2.05×10^-3</td>
<td>5.20×10^-3</td>
<td>7.43×10^-3</td>
</tr>
<tr>
<td>S</td>
<td>3.93×10^-5</td>
<td>5.33×10^-4</td>
<td>2.67×10^-4</td>
</tr>
</tbody>
</table>

Half of the experiments consisted of pH-static titrations carried out at pH 4 for a period of 24 hours. In the other half of the experiments, pH-static titrations were first carried out at pH 7 for 24 hours. Following the pH 7 titrations, the leached solid material was removed by filtration and then titrated for an additional 24 hours at pH 4. The experiments were all carried out at an L/S ratio of approximately 100 (liquid to solid mass ratio). A Metrohm 719 S Titrino device with automatic data logging was used for performing the pH-static titrations.

10 ml samples of the leachate were taken at different times (4, 19, and 24 hours) during the titration procedure so that ion-chromatographic analyses could be made. The leachate samples were filtered with a 0.2µm syringe membrane filter to remove fines and possible colloidal material.

The analyses were carried out with a Dionex DX300 ion chromatograph. An ion exchange suppressor and methanesulphonic acid eluent with conductivity based peak detection was used for the analysis of the base cations (Ca^{2+}, Mg^{2+}, Na^+, and K^+).
Calibration of the system was based upon serial dilutions of external standards. A linear calibration curve forced through the origin was found to give the most reliable results.

The small volume of fluid required for each analysis (20 µl) meant that the leachate samples could be analysed multiple times to obtain more reliable results. The results reported in this paper are therefore the mean of duplicate analyses of the same leachate samples.

3 Experimental Results and Charge Balance Analysis

In all of the leaching experiments it was found that both Ca$^{+2}$ and Mg$^{+2}$ were responsible for the bulk of the measured acid neutralising capacity (ANC) owing to the high concentrations of these species found in the leachate. The measured acid neutralising capacity, the acid neutralisation rate, and the sum of the Ca$^{+2}$ and Mg$^{+2}$ concentrations are given in the following diagrams for the three different waste materials investigated in each of the leaching experiments:
Figure 1. Time dependent acid neutralising capacity [ANC, mmol H⁺/g], sum of major cation concentrations [mol/l], and rate of acid neutralisation [mmol H⁺/g h] for untreated waste materials in pH 4 static experiments
Figure 2. Time dependent acid neutralising capacity [ANC, mmol H⁺/g], sum of major cation concentrations [mol/l], and rate of acid neutralisation [mmol H⁺/g h] for pre-treated waste materials in pH 4 static experiments.
It is possible to see how much the $\text{Ca}^{2+}$ and $\text{Mg}^{2+}$ concentrations influence the acid neutralisation properties of the waste by making use of the electroneutrality principle. According to the electroneutrality principle, the net sum of all cationic and anionic charges in the leachate should be equal to zero. If we assume that the base cations $\text{Mg}^{2+}$ and $\text{Ca}^{2+}$ are primarily responsible for the observed pH buffering, the deficit in the charge balance is given by:

$$\varepsilon = \text{ANC} - \left[ \text{H}^+ \right] - \left[ \text{OH}^- \right] - 2\left[ \text{Mg}^{2+} \right] - 2\left[ \text{Ca}^{2+} \right]$$

(1)

Here, we also assume that the base cations, which have been determined by ion chromatography, are non-complexed and that their activity coefficients are close to
unity. The deficit in the charge balance and the ratio of Ca$^{+2}$/Mg$^{+2}$ in the leachate are given in tables 2-4 for the three different waste materials:

Table 2. Experimentally determined acid neutralising capacities (ANC) [mmol H$^+/g$ waste], leachate Ca$^{+2}$/Mg$^{+2}$ ratios, and charge balance deficits [meq/g waste] for pH static experiments with AFS slag

<table>
<thead>
<tr>
<th></th>
<th>ANC</th>
<th>Ca$^{+2}$/Mg$^{+2}$</th>
<th>ε</th>
</tr>
</thead>
<tbody>
<tr>
<td>4h (pH4, untreated)</td>
<td>6.79</td>
<td>39.3</td>
<td>-0.43</td>
</tr>
<tr>
<td>19h (pH4, untreated)</td>
<td>8.23</td>
<td>32.5</td>
<td>-0.36</td>
</tr>
<tr>
<td>24h (pH4, untreated)</td>
<td>8.38</td>
<td>32.0</td>
<td>-0.56</td>
</tr>
<tr>
<td>4h (pH7, untreated)</td>
<td>4.40</td>
<td>88.1</td>
<td>-0.71</td>
</tr>
<tr>
<td>19h (pH7, untreated)</td>
<td>5.29</td>
<td>56.3</td>
<td>-0.63</td>
</tr>
<tr>
<td>24h (pH7, untreated)</td>
<td>5.43</td>
<td>56.9</td>
<td>-0.74</td>
</tr>
<tr>
<td>4h (pH4, washed)</td>
<td>1.45</td>
<td>9.1</td>
<td>-0.34</td>
</tr>
<tr>
<td>19h (pH4, washed)</td>
<td>2.34</td>
<td>9.5</td>
<td>-0.28</td>
</tr>
<tr>
<td>24h (pH4, washed)</td>
<td>2.46</td>
<td>9.7</td>
<td>-0.35</td>
</tr>
</tbody>
</table>

Table 3. Experimentally determined acid neutralising capacities (ANC) [mmol H$^+/g$ waste], leachate Ca$^{+2}$/Mg$^{+2}$ ratios, and charge balance deficits [meq/g waste] for pH static experiments with BFS slag

<table>
<thead>
<tr>
<th></th>
<th>ANC</th>
<th>Ca$^{+2}$/Mg$^{+2}$</th>
<th>ε</th>
</tr>
</thead>
<tbody>
<tr>
<td>4h (pH4, untreated)</td>
<td>5.15</td>
<td>1.9</td>
<td>-0.27</td>
</tr>
<tr>
<td>19h (pH4, untreated)</td>
<td>9.03</td>
<td>1.9</td>
<td>-0.41</td>
</tr>
<tr>
<td>24h (pH4, untreated)</td>
<td>9.61</td>
<td>2.0</td>
<td>-0.45</td>
</tr>
<tr>
<td>4h (pH7, untreated)</td>
<td>0.58</td>
<td>9.3</td>
<td>-0.34</td>
</tr>
<tr>
<td>19h (pH7, untreated)</td>
<td>0.81</td>
<td>6.9</td>
<td>-0.40</td>
</tr>
<tr>
<td>24h (pH7, untreated)</td>
<td>0.86</td>
<td>6.9</td>
<td>-0.43</td>
</tr>
<tr>
<td>4h (pH4, washed)</td>
<td>2.44</td>
<td>1.7</td>
<td>-0.11</td>
</tr>
<tr>
<td>19h (pH4, washed)</td>
<td>5.76</td>
<td>1.7</td>
<td>-0.69</td>
</tr>
<tr>
<td>24h (pH4, washed)</td>
<td>6.32</td>
<td>1.7</td>
<td>-0.75</td>
</tr>
</tbody>
</table>
Table 4. Experimentally determined acid neutralising capacities (ANC) [mmol H⁺/g waste], leachate Ca²⁺/Mg²⁺ ratios, and charge balance deficits [meq/g waste] for pH static experiments with MSWI BA

<table>
<thead>
<tr>
<th></th>
<th>ANC</th>
<th>Ca²⁺/Mg²⁺</th>
<th>ε</th>
</tr>
</thead>
<tbody>
<tr>
<td>4h (pH4, untreated)</td>
<td>1.49</td>
<td>10.8</td>
<td>-0.28</td>
</tr>
<tr>
<td>19h (pH4, untreated)</td>
<td>1.79</td>
<td>9.8</td>
<td>-0.20</td>
</tr>
<tr>
<td>24h (pH4, untreated)</td>
<td>1.84</td>
<td>9.8</td>
<td>-0.12</td>
</tr>
<tr>
<td>4h (pH7, untreated)</td>
<td>0.35</td>
<td>32.6</td>
<td>-0.44</td>
</tr>
<tr>
<td>19h (pH7, untreated)</td>
<td>0.67</td>
<td>27.6</td>
<td>-0.48</td>
</tr>
<tr>
<td>24h (pH7, untreated)</td>
<td>0.70</td>
<td>28.6</td>
<td>-0.55</td>
</tr>
<tr>
<td>4h (pH4, washed)</td>
<td>0.58</td>
<td>5.4</td>
<td>0.00</td>
</tr>
<tr>
<td>19h (pH4, washed)</td>
<td>0.84</td>
<td>4.9</td>
<td>0.08</td>
</tr>
<tr>
<td>24h (pH4, washed)</td>
<td>0.87</td>
<td>4.9</td>
<td>0.08</td>
</tr>
</tbody>
</table>

The Ca²⁺/Mg²⁺ ratio in the leachate was found to be significantly higher in the experiments involving AFS slag and MSWI than those experiments involving BFS slag. It appears that Mg plays a more important role in the pH buffering processes for BFS slag than for the other waste types examined. For all the waste materials examined, the Ca²⁺/Mg²⁺ ratio was higher at pH 7 than at pH 4. This agrees well with what we would guess from the known solubilities of Ca and Mg oxides.

The calculated charge balance deficit (ε) was found to be a negative number in all of the pH static experiments except for the pre-treated MSWI at pH 4. A negative value for ε indicates that there is a deficit of anionic components in the charge balance. The charge deficit is most likely to be in the form of anions such as sulphate (SO₄²⁻), thiosulphate (S₂O₃²⁻), and possibly chloride (Cl⁻) or forms of dissolved carbonate (principally HCO₃⁻).

It has been found in previous investigations that the sulphur content of leachate is not always in the form of sulphate under basic, mildly alkaline conditions and a large proportion may actually exist in a partially reduced form such as thiosulphate (Goldhaber, 1983; Bäverman, 1997). If it is assumed that that the sulphur content of the waste is fully leached and present in the form of sulphate, however, it could contribute up to 0.08 meq/g of anionic charge in the case of AFS slag. For BFS slag and MSWI ash, the corresponding figures are 1.07 meq/g and 0.53 meq/g.

The waste compositions determined by Fällman (1994) do not include chloride, so the amount of anionic charge that chloride ion can contribute to the charge balance is...
uncertain. In a previous study carried out by Bäverman (unpublished data), the chloride concentration in L/S 20 batch leaching experiments (shake tests) was determined using ion-chromatography. For these waste materials, the leached chloride concentration is roughly constant as a function of time which suggests that the chloride is most likely present in the form of soluble salts such as NaCl and KCl.

If we assume availability controlled leaching, taking the mean of the measured chloride concentrations in these batch tests allows an estimation to be made of the influence that dissolved chloride ion may have upon the charge balance deficit. It is found that chloride ions can contribute up to 0.0024 meq/g of anionic charge in the case of AFS slag. For BFS slag and MSWI ash, the corresponding figures are 0.067 meq/g and 0.041 meq/g. It appears from these results that chloride ions can only play a very minor role in the charge balance and may be neglected without introducing significant errors.

If there are carbonate bearing minerals such as calcite in the waste material, carbon dioxide ebullition may occur if the partial pressure of carbon dioxide ($P_{CO_2}$) in the leachate reaches atmospheric pressure. This happens if the rate of dissolution of carbonate mineral exceeds the rate of diffusion of carbon dioxide to the atmosphere through the surface boundary layer. From the known solubility of carbonate at pH 7 (roughly 0.22 mol/l when $P_{CO_2} = 1$ atm) ebullition of carbon dioxide should not occur at ambient temperatures with an L/S ratio of 100 in a pH-static experiment. From the known Ca content of these wastes, an L/S ratio of less than 30 is required in order for CO$_2$ ebullition to occur at pH 7.

Both the solubility and speciation of dissolved carbonate is a function of pH. At pH 7, roughly 0.82 meq of anionic charge is available per mmol of dissolved carbonate, as most of the carbonate is present in the form of HCO$_3^-$ ion. This may be a significant factor for the charge balance at pH 7 if there are appreciable quantities of carbonate present in the waste material. At pH 4, however, most of the dissolved carbonate is in the form of H$_2$CO$_3$ and will not contribute towards the anionic charge deficit. This is true regardless of how much carbonate mineral is present in the waste material, and whether ebullition of carbon dioxide occurs or not.

In the case of AFS slag, the charge deficit is difficult to explain as the waste contains very little sulphur or chloride. A proportion of the anionic charge deficit at pH 7 may possibly be explained in terms of dissolved carbonate, but this should not be the case in the pH 4 experiments. In view of this, it seems most likely in the case of AFS slag that the discrepancy arises because of inaccuracies in the measured analytical concentrations of Mg$^{2+}$ and Ca$^{2+}$. 

10
The same may be true of the other waste types although it is probable that the sulphur content of BFS slag is responsible for at least some of the observed anionic charge deficit. As much of the sulphur content of the BFS slag is in a reduced form, a large proportion of the sulphur should remain after the washing procedure as this will only remove soluble oxidation products. The measured anionic charge imbalance at pH 4 after washing may be related to the continued slow oxidation of the reduced sulphur content of the BFS slag.

In the case of the MSWI ash, it is thought that there is very little reduced sulphur present and most of the sulphur is present in the form of easily soluble gypsum (CaSO₄·2H₂O) or anhydrite (CaSO₄). This may explain why the closure of the charge balance at pH 4 improves after the washing procedure. For MSWI, there is a very close correspondence between the speculated amount of sulphate in the waste and the observed charge deficit.

In all of the waste leaching experiments carried out with waste that had not been pre-treated, it is likely that gypsum is very close to being saturated owing to the high Ca²⁺ concentrations in the leachate.

If it is assumed that Mg²⁺ and Ca²⁺ are responsible for most of the observed pH buffering processes, a theoretical value for the total ANC of the waste may be calculated from the analytical concentrations of these constituents in the waste materials. Based upon the analysis data given in table 1, the theoretical ANC is calculated to be:

\[ \text{ANC}_{CaMg} \approx 2 \left( C_{Ca} + n_{Mg} - n_{S} \right) \]  \hspace{1cm} (2)

In equation 2, a correction is made for the influence that sulphate ion will have upon the ANC if the sulphur content of the waste is present in the form of CaSO₄ (assumed to be true for AFS slag and MSWI ash), or CaS in the case of BFS slag.

The total theoretical ANC based upon equation 2 and the percentage ANC reacted after 24 hours are summarised in table 5 for the three different waste materials:
Table 5. Theoretical total acid neutralising capacities (ANC) [mmol H⁺/g waste] and percentage ANC reacted after 24 hours

<table>
<thead>
<tr>
<th>ANC CaMg [mmol/g]</th>
<th>AFS</th>
<th>BFS</th>
<th>MSWI</th>
</tr>
</thead>
<tbody>
<tr>
<td>24h (pH4, untreated)</td>
<td>57%</td>
<td>49%</td>
<td>39%</td>
</tr>
<tr>
<td>24h (pH7, untreated)</td>
<td>37%</td>
<td>4.3%</td>
<td>15%</td>
</tr>
<tr>
<td>24h (pH4, washed)</td>
<td>17%</td>
<td>32%</td>
<td>18%</td>
</tr>
</tbody>
</table>

The three waste materials appear to have very different pH buffering properties. For AFS slag, 60 percent of the total ANC has reacted within 24 hours at pH 4. Approximately two thirds of the reacted ANC is available above pH 7 and slightly less than one third is available between pH 4 and pH 7. In the case of BFS slag, nearly 50 percent of the total ANC has reacted after 24 hours at pH 4. Only a very small proportion of this is available above pH 7 and the bulk of the ANC seems to lie between pH 4 and pH 7. For MSWI ash, 40 percent of the total ANC has reacted after 24 hours at pH 4. In this case the ANC is distributed more evenly, and roughly equal proportions of the ANC are available above pH 7 and between pH 4 and pH 7.

A consistent trend in these results is that the measured ANC in the single-step pH 4 experiments is higher than the combined ANC measured in the two-step leaching experiments. This may have arisen because of heterogeneity in the waste materials, but the consistency of the measured ANC discrepancy suggests that there is some other effect which has not been accounted for. This effect may arise because of the removal of colloidal aluminium hydroxide precipitates during the filtration step after leaching at pH 7. It is possible that these secondary aluminium minerals formed during the congruent dissolution of glass phases may play a minor role in the pH buffering properties at pH 4, thereby giving rise to the observed discrepancy.

4 Modelling of Waste Dissolution Processes

If it is assumed that the dissolution of pH buffering constituents in the waste materials is very fast, the kinetics of pH buffering will be controlled largely by transport processes. If it is further assumed that the fast reacting particles in the waste can be approximated as being roughly spherical, a mass balance may be set up for the diffusion of pH buffering constituents through a laminar boundary layer surrounding individual particles. In spherical co-ordinates, the unsteady state mass balance for transport of protons to the reacting surface is:
where,
\( c_{H^+} \) = proton concentration (mol/m\(^3\))

\( D_v^{H^+} \) = free diffusivity of protons in water (m\(^2\)/s)

\( r \) = radius (m)

\( R_{H^+} \) = rate of proton production due to water dissociation (mol/m\(^3\)s)

The reaction term, \( R_{H^+} \), accounts for the pH buffering effect of water dissociation, which occurs within the laminar boundary layer. A similar mass balance may be written for the diffusion of hydroxyl ions within the laminar boundary layer:

\[
\frac{\partial c_{OH^-}}{\partial t} = D_v^{OH^-} \frac{\partial}{\partial r} \left( r \frac{\partial c_{OH^-}}{\partial r} \right) + R_{OH^-}\]

where,
\( c_{OH^-} \) = hydroxyl ion concentration (mol/m\(^3\))

\( D_v^{OH^-} \) = free diffusivity of hydroxyl ions in water (m\(^2\)/s)

\( R_{OH^-} \) = rate of hydroxyl ion production due to water dissociation (mol/m\(^3\)s)

Note here that the dissociation of a water molecule results in the production of one proton and one hydroxyl ion, and the variables \( R_{H^+} \) and \( R_{OH^-} \) are thereby equal. By making use of the stability constant for water dissociation, equation 3 and 4 may be combined to give:

\[
\frac{\partial}{\partial t} \left( r^2 \frac{D_v^{H^+}}{D_v^{H^+} c_{H^+}^2} \right) = -\frac{D_v^{OH^-}}{D_v^{H^+} c_{H^+}} \left( \frac{K_w}{c_{H^+}} \right) - \frac{D_v^{H^+}}{D_v^{H^+} c_{H^+}^2} \left( \frac{K_w}{c_{H^+}} \right)
\]

If it is assumed that steady state conditions are reached quickly (this is a reasonable assumption over the time scales being considered), equation 5 becomes a variables separable, ordinary differential equation (ODE):

\[
D_v^{H^+} \frac{d}{dr} \left( r^2 \frac{D_v^{H^+}}{D_v^{H^+} c_{H^+}^2} \right) - \frac{D_v^{OH^-}}{D_v^{H^+} c_{H^+}} \left( \frac{K_w}{c_{H^+}} \right) = 0
\]

Integrating equation 6 gives:

\[
\int r^2 \frac{D_v^{OH^-}}{D_v^{H^+} c_{H^+}^2} \frac{dc_{H^+}}{dr} dr = -\frac{r^2 N_n}{D_v^{H^+}}
\]
where,
\[ r_i = \text{radius of dissolving particle (m)} \]
\[ N_{ri} = \text{inward flux of protons at particle surface (mol/m}^2\text{s)} \]

Separating variables and integrating across the thickness of the boundary layer gives:
\[
Z_{r=0}^{r=\infty} \frac{D_{v}^{\text{OH}^{-}}}{D_{v}^{H^{+}}} \frac{K_w}{c_{H^{+}}} \text{dc}_{H^{+}} = -\frac{r^2 N_{ri}}{D_{v}^{H^{+}}} \int_{r_i}^{r} \frac{Z}{r^2} dr
\]  
(8)

where,
\[ c_{H^{+}(0)} = \text{bulk proton concentration in leachate (mol/m}^3\text{)} \]
\[ c_{H^{+}(S)} = \text{proton concentration at dissolving particle surface (mol/m}^3\text{)} \]
\[ \delta_i = \text{boundary layer thickness (m)} \]

This expression may be rearranged to obtain \( N_{ri} \) explicitly:
\[
N_{ri} = \frac{D_{v}^{H^{+}}}{K_w} \frac{1}{\delta_i} \left[ c_{H^{+}(0)} - c_{H^{+}(S)} \right] + \frac{D_{v}^{\text{OH}^{-}}}{D_{v}^{H^{+}}} \frac{K_w}{c_{H^{+}(S)}} - \frac{K_w}{c_{H^{+}(0)}}
\]  
(9)

In terms of a mass transfer coefficient, equation 9 may be written as:
\[
N_{ri} = k_i \Delta c_{\text{TOTH}}
\]  
(10)

where,
\[
k_i = \frac{D_{v}^{H^{+}}}{K_w} \left[ 1 + \frac{1}{\delta_i} \right]
\]  
(11)

\[
\Delta c_{\text{TOTH}} = c_{H^{+}(0)} - c_{H^{+}(S)} + \frac{D_{v}^{\text{OH}^{-}}}{D_{v}^{H^{+}}} \frac{K_w}{c_{H^{+}(S)}} - \frac{K_w}{c_{H^{+}(0)}}
\]  
(12)

In these equations, \( k_i \) is a mass transfer coefficient (m/s) and \( \Delta c_{\text{TOTH}} \) is the total proton concentration driving force (mol/m\(^3\)) based upon the proton and hydroxyl ion concentration, and corrected for differences in species diffusivity. The diffusivity ratio \( D_{v}^{\text{OH}^{-}}/D_{v}^{H^{+}} \) is calculated to be 0.566 at 298 K.

The buffering effect of water in the laminar boundary layer enhances mass transfer considerably if the pH at the dissolving particle surface (pH\(_s\)) is above 7. In order to illustrate this effect, we can define a mass transfer enhancement factor \( f \) such that:
\[
f = \frac{\Delta c_{\text{TOTH}}}{c_{H^{+}(0)} - c_{H^{+}(S)}}
\]  
(13)
The value of the enhancement factor $f$ is plotted as a function of the pH at the dissolving surface ($\text{pH}_s$) for three different values of solution pH ($\text{pH}_0$) in figure 4 below:

![Graph showing the mass transfer enhancement factor ($f$) as a function of solution pH ($\text{pH}_0$) and pH at dissolving surface ($\text{pH}_s$).](image)

**Figure 4.** Mass transfer enhancement factor ($f$) as a function of solution pH ($\text{pH}_0$) and pH at dissolving surface ($\text{pH}_s$)

It is interesting to note that for solution pH levels above 7, the enhancement factor can be substantial even if the surface pH ($\text{pH}_s$) differs only fractionally from that in the solution ($\text{pH}_0$). In the limit as $\text{pH}_s$ approaches $\text{pH}_0$ it can be shown that:

$$\lim_{\text{pH}_s \to \text{pH}_0} f = 1 + \left( \frac{[\text{OH}^-]}{[\text{H}^+]} \right) 10^{\frac{b_{\text{pl}_{\text{H}^+}}}{\text{pH}_0}}$$

In principle, it is possible to include additional pH buffering species ($\text{CO}_3^{2-} / \text{HCO}_3^- / \text{H}_2\text{CO}_3$, for example) in the diffusional mass balance if the surface and bulk concentrations of these species can be determined. In the present analysis, however, it is assumed that the influence of these other minor species is negligible.

It may be shown that for very small particles, or for particles suspended in a stagnant fluid, equation 11 approaches a limiting value:

$$\lim_{r_i \to 0} k_i = \frac{D_{ii}^{\text{H}^+}}{r_i}$$  \hspace{1cm} \text{(small particles)}
Semi-empirical expressions for mass transfer coefficients in multiphase systems are abundant in the chemical engineering literature. One such expression found in Perry’s Chemical Engineers’ Handbook (1997) is:

$$N_{Sh} = k_d \frac{d_i}{D_v} = 2 + 0.31 \frac{\left[\left|\rho_p - \rho_w\right|\right]^{\frac{1}{3}}}{\mu_w D_v^H}$$

where,

- $N_{Sh}$ = Sherwood number (dimensionless)
- $d_i$ = particle diameter (m)
- $\rho_p$ = particle density (kg/m$^3$)
- $\rho_w$ = leachate density (kg/m$^3$)
- $\mu_w$ = leachate viscosity (Pa s)

This correlation is valid for small particles (radius < 1.25 mm) where Stoke’s law may be used to describe the settling velocity of the particle relative to the leachate. In terms of the particle radius, the mass transfer coefficient is:

$$k_i = \frac{D_v^H}{r_i} + \theta$$

where,

$$\theta = 0.31 \frac{\left|\rho_p - \rho_w\right|^{\frac{1}{3}}}{\mu_w D_v^H}$$

If we consider a system containing $m$ discrete particle size fractions, the rate of pH buffering is equal to the surface normalised proton flux ($N_a$) multiplied by the total surface area of dissolving particles in the leachate. If the pH of the leachant is to be maintained at a constant level in a pH-static experiment, the rate of acid addition must be equal to the rate of pH buffering. The expression for the rate of acid addition in a pH static experiment is therefore given by:

$$\frac{dN}{dt} = \sum_{i=1}^{m} \xi_i n_i A_i k_i \Delta c_{TOT} + w_0 R_{final}$$

where,

- $N$ = quantity of strong acid added to the system (mol H$^+$)
\( n_i = \) number of particles of size fraction \( i \)
\( A_i = \) individual surface area of particle size fraction \( i \) (\( m^2 \))
\( \xi_i = \) logical constant
\( \xi_i = 1 \) if size fraction exists
\( \xi_i = 0 \) if size fraction has completely dissolved
\( w_0 = \) total mass of waste (kg)
\( R_{\text{final}} = \) rate of pH buffering for slowly dissolving waste fraction (mol \( H^+ \)/kg s)

The parameter, \( R_{\text{final}} \) in equation 20 accounts for the final rate of pH buffering which is observed to occur after the fast pH buffering phases have completely dissolved. The final rate of pH buffering results from slow surface reactions, diffusion of buffering constituents through surface alteration layers (slow weathering of glass phases), and the recrystallisation of secondary mineral phases. These additional processes have not been accounted for explicitly in the model and it is assumed that a zero order, lumped rate constant is a sufficiently accurate approximation in the absence of sufficient data for a detailed model of slow pH buffering. The logical constant \( \xi_i \) is a parameter that is equal to unity when the dissolving particles are of finite size. When the particle size fraction \( i \) has completely dissolved, the parameter \( \xi_i \) is equal to zero.

In this model of a pH-static experiment it is also assumed that the response time of the process control software is sufficiently fast that it does not need to be accounted for in the differential equation describing the rate of acid addition.

If the fast pH buffering phases may be described as being roughly spherical particles, the rate of acid addition is given by:

\[
\frac{dN}{dt} = 4 \pi D_v^H \Delta c_{\text{TOTH}}^* \xi_i n_i A_i \xi_i r_i^2 + \beta \frac{w_0}{\rho_p} R_{\text{final}} \tag{21}
\]

From mass balance considerations, the initial number of particles in each size fraction may be shown to be:

\[
n_i = \frac{X_i}{r_{i0}^3} \frac{\beta w_0}{\rho_p} \tag{22}
\]

where,
\( \beta = \) mass fraction of readily soluble waste particles (kg/kg)
\( r_{i0} = \) initial radius of particles in size fraction \( i \) (m)
\( X_i = \) mass fraction of particles with initial radius \( r_{i0} \) (kg/kg)
\( \rho_p = \) density of waste particles (kg/m\(^3\))
The rate of change of particle radius is:

\[
\frac{dr}{dt} = \frac{-\xi_i k_i}{\rho_p \text{ANC}_{CaMg}} \Delta c^+_{\text{TOTH}} = \frac{-\xi_i D_v^{ii} \Delta c^+_{\text{TOTH}}}{\rho_p \text{ANC}_{CaMg}} k_i + \theta k
\]  

(23)

Equation 23 is a variables separable ODE and may be solved to obtain \( r_i \) implicitly as a function of time:

\[
\frac{\xi_i D_v^{ii} \Delta c^+_{\text{TOTH}}}{\rho_p \text{ANC}_{CaMg}} k^+ b^{r_i - \log e} \frac{\log e}{\theta^2} + \frac{-\xi_i r_0 \theta}{\theta^2} = 0
\]

(24)

The time required \( (t_{ci}) \) for a given particle size fraction to completely disappear is found by setting the particle radius \( (r_i) \) to zero in equation 24. This gives:

\[
t_{ci} = \frac{\rho_p \text{ANC}_{CaMg}}{D_v^{ii} \Delta c^+_{\text{TOTH}}} \frac{\theta - \log e}{\theta^2} b^{r_i \theta} \]

(25)

The logical constant \( \xi_i \) for each size fraction \( i \) changes from a value of unity to zero for values of \( t \) greater than \( t_{ci} \).

In order to simulate the time dependence of the observed acid neutralising capacity, it is necessary to solve the coupled problem involving the ODE in equation 21 and the \( m \), non-linear algebraic equations describing the particle radii (equation 24). This was implemented using the commercially available MATLAB program. The in-built ODE solver ODE15s was used for the solution of equation 21, and the optimisation routine FMIN was used to find the roots of equation 24 (i.e. the particle radius as a function of time).

The particle size distribution is difficult to determine for very fine particles using dry sieving techniques. This problem has been described previously by Sverdrup (1985) and arises because small particles tend to agglomerate with larger particles giving results that substantially underestimate the fraction of fine particles in the sample. Owing to the fact that the ground waste material has a particle size less than about 0.16mm in diameter, no attempt has been made to determine the particle size distribution.

Calculations made according to the scheme outlined above have shown that it is necessary to have some information about the particle size distribution to interpret the results of the pH-static experiments. As there was no useful data available about the distribution of particle sizes in these waste materials, some different assumptions were made about the nature of the particle size distribution. Two different particle size distributions (PSD) were assumed in the model to observe the effect that particle size had upon the simulated results:
a) a single particle size fraction
b) equal mass fractions of (10) different particle sizes

The computing time increases rapidly in proportion to the number of particle size fractions included in the model. It was found, however, that increasing the number of particle size fractions above 10 had no observable influence upon the results obtained. For this reason, only 10 size fractions were included in the model for the simulations belonging to case b.

The value of $R_{\text{final}}$ (in equation 21) was determined from the experimentally measured rate of acid addition during the final four hours of the pH-static experiments. This may overestimate the slow rate of pH buffering, as it is possible that not all of the fast reacting phases have had a chance to dissolve within 24 hours. The mass fraction of readily soluble waste particles ($\beta$ in equation 22) was chosen to give roughly the same acid neutralising capacity after 24 hours as was observed in the experiments. In the absence of more detailed information about the composition and density of the different phases in the waste, it was also assumed that the acid neutralising capacity and density were the same for both the fast and slow dissolving waste particles. The particle density was estimated from the known bulk density of the waste material and an assumed porosity of 30%.

The numerical model was used to simulate the pH 4 leaching experiments with the untreated waste materials. Examples of typical simulation results are presented in the following figures for AFS slag:
Figure 5. Typical simulation results for AFS steel slag using a single particle size fraction (pH 4 static experiment with untreated waste). Particle diameters are given in micrometers (µm).

In figure 5, the results are presented for the simulations where a single particle size fraction was assumed. In these simulations, the concentration driving force was based
upon a pH\textsubscript{s} of 10 at the dissolving surface and only the particle size (given as the particle diameter in the diagrams) was varied. The circular markers in the figures indicate the time required for the single particle size fraction to be completely dissolved. The results obtained from the simulations indicate that the 24 hour experimental measurements are approximately consistent with transport limited dissolution kinetics for all three waste materials. The experimental data curve does, however, appear somewhat smoother and more rounded than the single particle size fraction model can explain.

Decreasing the initial particle size increases the dissolution rate of the particles in a roughly parabolic fashion owing to the increased surface area of the particles. It is easiest to appreciate the reasons for this by neglecting the sedimentation term ($\theta$) in equation 18 and integrating the resultant equation (this is only strictly true for stagnant systems or very small particles). Using this simplification, the time required for a given particle size fraction to completely disappear ($t_{ci}$) is found to be:

$$t_{ci} = \frac{C_{p_{\text{ANC}}} C_{CaMg} \rho}{2 D_{v} \Delta c_{TOTH}^{*} k_{ci}^{2}}$$

(26)

Halving the initial particle size, therefore, reduces the dissolution time ($t_{ci}$) by a factor of four according to equation 26. When we consider the sedimentation term, the relationship is only approximately parabolic, owing to the non-linear nature of equation 23.

A similar effect may be obtained by adjusting (lowering) the particle density, or the acid neutralising capacity of the waste in the model. This is because there is a linear correspondence between the scale of the time axis and the value of the product $\rho_{p} \text{ANC}_{CaMg}$ for a given particle size. This is true for both the simple and the non-linear models of particle shrinkage.

In the single size fraction simulations, a constant pH\textsubscript{s} was assumed for the dissolving particles. Adjusting the concentration driving force parameter ($\Delta c_{\text{TOTH}}$) by varying the pH\textsubscript{s}, however, will also alter the time scale of the dissolution profile in an inverse fashion according to equation 26. In some studies (Sverdrup, 1985, for example) it is assumed that the surface pH for strongly alkaline minerals undergoing dissolution is significantly higher than the pH in the bulk leachant and therefore may be neglected. As may be seen from equation 13, it is important to include the buffering effect of water at pH levels above about pH 9. For materials that buffer at pH values higher than 9, the pH at the dissolving mineral or glass surface becomes a non-trivial consideration. This is also an explanation for why materials such as sodium hydroxide (NaOH), which buffer at very high pH values, dissolve much faster than materials that
buffer at lower pH values. Most alkaline wastes buffer at high pH values (above pH 6-7). Low surface pH values (i.e. close to that of the bulk leachate for pH 4 static titrations) may therefore be an indication of a slow surface reaction.

Figure 6 shows the results from the simulations where multiple particle sizes were assumed in the model. As previously, the symbols along the curves mark the points where individual particle size fractions completely dissolve.

The dissolution curves predicted by the multiple particle size model are much smoother, more rounded, and have similar appearance to the experimental data. Similarly to the single size fraction model, the dissolution curves may be fitted to the experimental data by tweaking the particle size distribution, particle density, or concentration driving force. In these simulations, however, it was assumed that the estimated particle density and particle size distribution are approximately correct and the concentration driving force has been adjusted in order to obtain a best fit with the data.

It is known that the AFS slag initially buffers pH at high values (pH 11-12) and that the bulk of the pH buffering capacity lies above pH 7 (see table 5). It is therefore likely that the value of pH_s is an important parameter for this type of waste. In figure 6, a pH_s value of 10 was found to fit the experimental data most satisfactorily. It is possible that there is a distribution of different pH_s values for different particles depending upon small variations in waste composition. This may explain why a higher pH_s fits the data well initially, while a lower pH_s may fit the data better at later times. This explanation is rather speculative, however, as it is possible to obtain the same fit by assuming a distribution of particle densities or by adjusting the particle size distribution. These parameters influence the results in such a way that it is impossible to say with any certainty given the available data, which parameter has the most influence or whether it is a combination of these effects that gives rise to the experimentally observed behaviour.

If we assume the validity of the various assumptions in the model, it appears that the pH buffering rate of BFS slag and MSWI bottom ash result from a combination of transport and surface reaction kinetics. This is suspected because pH_s values in the range 4.25-4.50 gave the best agreement with the experimental results. As both BFS and MSWI wastes are reasonably alkaline, pH_s values in this range should only occur as a result of (moderately) slow surface reactions. As discussed previously in the case of AFS slag, this is a purely speculative explanation owing to uncertainties in other parameters, which can be adjusted in order to obtain the same fit with the experimental data.
From the shape of the experimental curves for leaching of the pre-treated waste materials (figure 2) it is thought that even in these experiments, the acid neutralising kinetics are largely transport controlled over the 24-hour timescale of the experiments. If slow surface reaction kinetics were primarily responsible for pH buffering effects, we should expect the rate of acid addition to be significantly slower than what is observed experimentally.

5 Conclusions

From the pH-static experiments it was found that Mg and Ca were overwhelmingly responsible for the bulk of the observed pH buffering properties of the three different waste materials examined. In the case of BFS slag, however, Mg appears to play a more significant role in pH buffering than for the other waste materials studied.

Charge balance calculations for the different constituents analysed for in the leachate indicated that there was a deficit of negative charge. It is speculated that there is some inaccuracy in the experimental measurements for Mg and Ca that gives rise to this calculated charge deficit. It is thought, however, that at least some of the charge balance deficit may due to anionic sulphur species in the leachate that were not determined analytically.

The distribution of the acid neutralising capacity was very different for each waste. In the case of AFS slag, most of the buffering capacity was found to be available over pH 7. In the case of BFS slag, most of the buffering capacity was available under pH 7. MSWI bottom ash, however, had a more even buffering capacity distribution with roughly equal amounts available above and below pH 7.

The theoretical acid neutralising capacity of the waste was calculated based upon the quantities of Mg, Ca, and S known to be in the materials. From this data, the percentage of acid neutralising capacity reacted within a 24 hour leaching experiment could be calculated. It was found that roughly 60 percent of the theoretical buffering capacity of AFS slag had reacted within 24 hours at pH 4. The corresponding figures for BFS slag and MSWI bottom ash were 50 percent and 40 percent, respectively.

The simulations used to model the acid neutralisation behaviour of the waste material indicate that the kinetics of pH buffering over a 24-hour timescale are most likely to be transport limited in the case of AFS slag. For the MSWI and BFS wastes, it appears that a combination of transport and surface reaction kinetics control the rate of acid neutralisation. Although simulations were only carried out for the experiments at pH 4 where untreated material was used, it is thought that the dissolution kinetics of
the pre-leached waste materials are similar to the untreated samples owing to the timescales over which the bulk of the pH buffering occurs.

The results suggest that there is a large amount of fast dissolving material that cannot be removed by the simple washing procedure adopted in these experiments.

The surface pH of buffering materials in the dissolving waste may have a strong influence upon the rate of acid neutralisation. This enhancement of mass transfer has often been neglected in studies of transport controlled dissolution where the pH buffering effect of water is not included in the equations describing transport of protons to the reacting surface.

It is difficult to draw more detailed conclusions about the pH buffering processes based upon the simulation results presented in this paper. This is because a number of parameters were found to influence the simulated acid neutralisation curves in such a way that their effects could not be separated in the absence of more accurate information about the particle size distribution, particle shape, and particle density.

**Acknowledgement**

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Notation

\( A_i \) individual particle surface area of size fraction i (m\(^2\))

\( \text{ANC}_{\text{CaMg}} \) total acid neutralising capacity of waste (mmol/g)

\( c_{H^+} \) proton concentration (mol/m\(^3\))

\( c_{H^+}^{(0)} \) bulk proton concentration in leachate (mol/m\(^3\))

\( c_{H^+}^{(S)} \) proton concentration at dissolving particle surface (mol/m\(^3\))

\( c_{OH^-} \) hydroxyl ion concentration (mol/m\(^3\))

\( d_i \) diameter of particle size fraction i (m)

\( D_{vH^+} \) free diffusivity of protons in water (m\(^2\)/s)

\( D_{vOH^-} \) free diffusivity of hydroxyl ions in water (m\(^2\)/s)

\( k_i \) mass transfer coefficient for particle size fraction i (m/s)

\( K_w \) stability constant for water (mol\(^2\)/m\(^6\))

\( m \) number of particle size fractions

\( N \) quantity of strong acid added to the system (mol H\(^+\))

\( N_{ri} \) inward flux of protons at particle surface for particle size fraction i (mol/m\(^2\)/s)

\( N_{Sh} \) Sherwood number (dimensionless)

\( n_{Ca} \) Ca content of waste (mmol/g)

\( n_i \) number of particles of size fraction i

\( n_{Mg} \) Mg content of waste (mmol/g)

\( n_S \) S content of waste (mmol/g)

\( r \) radius (m)

\( R_{\text{final}} \) rate of pH buffering for slowly dissolving waste fraction (mol H\(^+\)/kg s)

\( r_i \) radius of dissolving particle from size fraction i (m)

\( r_{i0} \) initial radius of particles in size fraction i (m)

\( R_{H^+} \) rate of proton production due to water dissociation (mol/m\(^3\)/s)

\( R_{OH^-} \) rate of hydroxyl ion production due to water dissociation (mol/m\(^3\)/s)

\( t_{ci} \) time required to completely dissolve mineral size fraction i (s)
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$w_0$</td>
<td>total mass of waste (kg)</td>
</tr>
<tr>
<td>$X_i$</td>
<td>mass fraction of particles with initial radius $r_0$ (kg/kg)</td>
</tr>
<tr>
<td>$\beta$</td>
<td>mass fraction of readily soluble waste particles (kg/kg)</td>
</tr>
<tr>
<td>$\Delta c_{\text{TOTH}}$</td>
<td>modified total proton concentration driving force (mol/m$^3$)</td>
</tr>
<tr>
<td>$\delta_i$</td>
<td>boundary layer thickness for particle size fraction i (m)</td>
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<tr>
<td>$\varepsilon$</td>
<td>deficit in charge balance (meq/g)</td>
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<tr>
<td>$\mu_w$</td>
<td>leachate viscosity (Pa s)</td>
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<tr>
<td>$\theta$</td>
<td>Sedimentation parameter (dimensionless)</td>
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<tr>
<td>$\rho_p$</td>
<td>particle density (kg/m$^3$)</td>
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<td>$\rho_w$</td>
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</tr>
<tr>
<td>$\xi_i$</td>
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References


