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Long-term processes in waste deposits

S. Bozkurt*, L. Moreno, I. Neretnieks

Royal Institute of Technology, Department of Chemical Engineering and Technology, Chemical Engineering, SE-100 44 Stockholm, Sweden

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Abstract

A conceptual model, which is a unitary and continuous description of the overall processes in waste deposits, has been developed. In the model the most important processes governing the long-term fate of organic matter in landfills and the transport and retention of toxic metals are included. With the model as a base, a number of scenarios with different levels of complexity have been defined and studied in order to carry out long-term assessments of the chemical evolution in waste deposits for industrial and municipal solid waste containing much organic matter and the leaching of toxic metals. The focus of the modelling has been to quantify the important processes occurring after the methane production phase has ceased, i.e. during the humic phase. The scenarios include the main mechanisms based on various transport processes as well as different landfill constructions, e.g. binding capacities of sulfides and humic substances. They also include transport mechanisms by which the reactant oxygen can intrude into a deposit, sorption capacities of hydrous ferric oxides, and pH-buffering reactions, etc. Scoping calculations have shown that the binding capacity of humic substances is sufficient to bind all toxic metals (Cd, Cr, Pb, Zn and Hg). In addition, the humics could also bind a smaller part of Ca, Fe and Al, provided much of the organic waste remain as humic substances. Sulfides on the other hand can bind approximately twice the amount of all toxic metals. The binding capacity of hydrous ferric oxides, which can be formed by oxidation reactions during the humic phase, is estimated to be three times the total content of metals that can sorb on hydrous ferric oxides. In the studied landfill the pH-buffering capacity, primarily represented by calcite, is estimated to be 1 mol/kg dry waste. Quantifications indicate that the alkalinity of the wastes is high enough to buffer the acidity produced by the oxidation of sulfides and by the degradation of organic matter, as well as that added by acid precipitation. Therefore, the main conclusion is that higher remobilisation rates of heavy metals due to lowering of pH are not expected for many thousands of years. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Conceptual model; Solid waste; Landfill processes; Metals; Long-term; Transport processes; Oxygen; Contaminant release; pH buffering; Redox; Modelling

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* Corresponding author. Tel.: +46-8-790-8236; fax: +46-810-5228.
E-mail address: sami@ket.kth.se (S. Bozkurt)

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1. Introduction

The long-term hazard potential for landfills is not well quantified. It is known that waste landfills have a high contamination potential in terms of heavy metals and other detrimental substances. The amount and concentration of leachate that reaches an aquifer defines the potential for groundwater contamination and thus pollution of the drinking water supply. Data from the literature indicate that very little of the original heavy metal content of a landfill is leached within the first decades after disposal (Ehrig, 1983; Christensen and Tjell, 1984). In the long-term perspective, the remaining metals will either leach out or be immobilised in the landfill. Knowledge of the long-term fate of contaminants in landfills and its relation to waste processes is, as yet, insufficient and calls for additional research. However, existing information is sufficient to raise concern about the potential effect of organic substances on the mobility of toxic metals. In this paper, the long-term emission of landfill contaminants, in particular heavy metals, is assessed and related to biological, chemical, and physical processes that occur over long periods of time. In this study, the times of interest are of the order of hundreds to thousands of years.

Degradation processes in landfills take place over a very long period of time. Until now, considerable work has been done on the early phases, i.e. the initial aerobic phase and the anaerobic phase (Farquhar and Rovers, 1973; Chian and DeWalle, 1976; Ehrig, 1989; Barlaz et al., 1992; Bozkurt and Neretnieks, 1997). The anaerobic phase in turn consists of two sub-phases: the anaerobic acid phase and the methane production phase. The subsequent phase, which is reached after perhaps one century is called 'the humic phase'. The duration of the humic phase is expected to be very long, from the end of the methane production phase to probably many thousands of years (Bozkurt, 1998). The humic phase is not well described in the literature and quantitative descriptions of processes during this phase are scarce (Bozkurt et al., 1999). Prior to this phase, only a very small portion of the toxic metals deposited in a landfill is leached and thus the waste deposits still have a large potential for contamination. More than 99.9% of the metals are still found in the residual solid at the end of the anaerobic phase (Belevi and Baccini, 1989). Long-term processes that may change the leaching behaviour of the waste will therefore be of great importance. In this paper, we address and quantify what we envisage to be the main processes over the long-term.

Studies of waste deposits in the early degradation stages (up to and including the methane production phase) indicate that the leaching rate of contaminants decreases exponentially over time (Belevi and Baccini, 1989). This is sometimes taken as evidence that this decrease will continue and that there is a relatively small risk of long-term contamination from the leachate. However, extreme caution must be exercised in extrapolating the results from one phase to another. Landfill conditions and the composition of the leachate will change over time. Changing conditions (e.g. the pH) during the humic phase may lead to a substantial change in the mobility of heavy metals. One reason is that oxygen may penetrate into the landfill and generate aerobic conditions, which will fundamentally change how metals are bound in the deposit. Oxidation of organic matter will give carbon dioxide, which could decrease the pH to below neutral. Therefore, the effect of changing landfill conditions must not be neglected and a sudden release of accumulated heavy metals must be taken into consideration. This phenomena is sometimes referred to as a chemical time bomb (CTB) (Stigliani, 1991). These changes can also be accelerated by human activities, such as landfill mining.

The mobility of the heavy metals is strongly influenced by the pH, redox conditions and the presence of substances that can bind the metals by sorption, etc. Therefore, the factors that affect these properties are of major importance for long-term predictions; in particular, processes involved in the organic part of the waste. Despite the importance of landfills, there is relatively little information on the factors that serve to increase or decrease the pH. Most available information focuses on the methanogenic fermentation of municipal solid wastes, since methane is an economically desirable byproduct of waste decomposition. As yet, no systematic understanding exists of waste decomposition processes that allow for reliable predictions of pH evolution in landfills. During the humic phase, the pH and the redox will be determined by infiltrating oxygenated rainwater, by oxygen and carbon dioxide that diffuse into the landfill and by the remaining buffer capacity of the solids. Carbon dioxide is also produced in the landfill as the organics degrade. The deposit can become aerobic and acidic when either the organics are depleted or the reactions become too slow to consume in-diffusing oxygen from the atmosphere. If the reducing capacity is depleted and the pH buffering capacity of mostly inorganic components is exhausted, then the metals can be dissolved in the acid-oxidizing pore waters and can escape from the deposit with the water flowing through it and also by diffusion. As a consequence of the oxygen intrusion into the landfill, the organic matter and the sulfides may degrade and release bound metals.

The difficulties associated with making future assessments to embrace up to thousands of years are very obvious. The processes that take place in landfills continue for a very long time and, at present, there is considerable lack of clarity as to which mechanisms control the chemical develop-

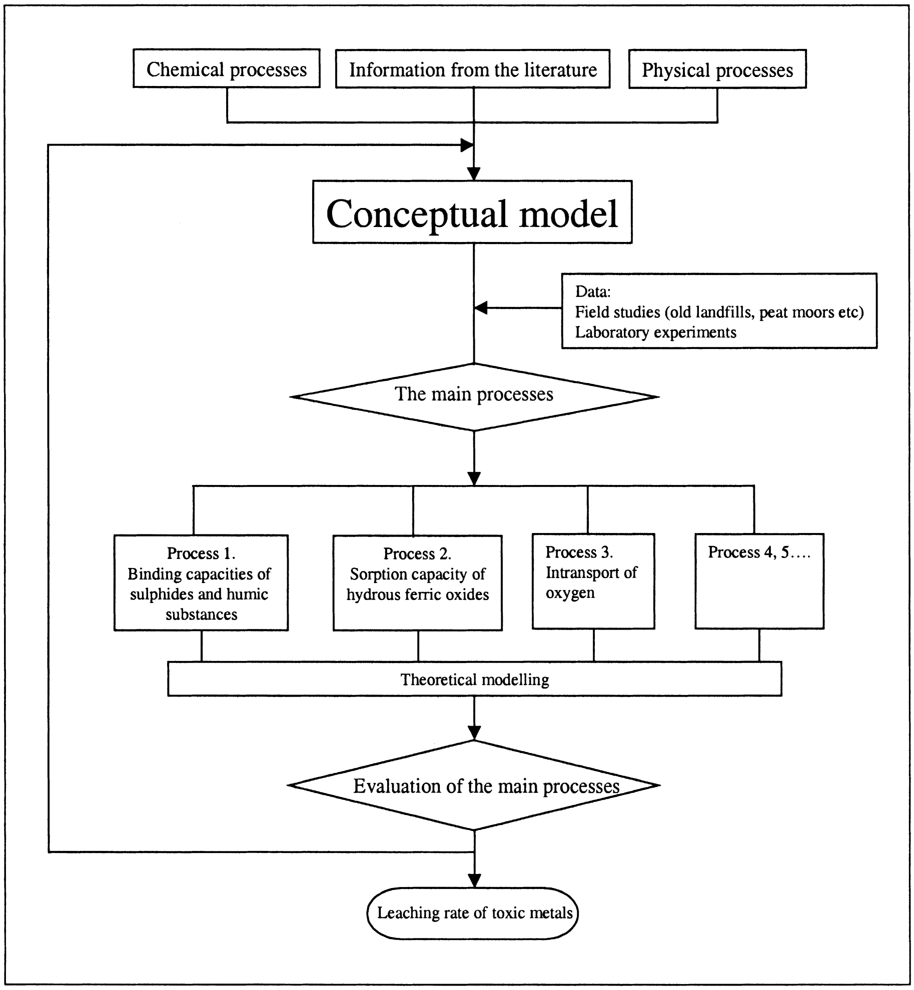

Fig. 1. Methodology to estimate leaching rate.

ment and leaching in a landfill. The general conception of what will happen in a landfill in a long-term perspective is often based on extrapolations and speculations. Obviously, there is a need to systematise, understand and quantify the long-term processes and to develop methods and models that enable us to estimate the long-term risks of pollution.

The overall aim of this paper is to assess the long-term leaching of toxic substances, such as heavy metals, from waste landfills. We intend to identify the controlling processes involved and, on the basis of these, to devise a model. It needs to be stressed that this paper not only covers the long-term behaviour of a landfill from the point of view of the development of mathematical models, but also pays great attention to the identification and description of the processes.

2. Approach to the problem

Here, one of the main questions we address is: at what rate will the accumulated toxic metals in waste deposits leach from the waste? In order to assess the fate of contaminants in waste deposits over long periods of time it is necessary to identify the governing processes. Studies regarding the long-term evolution of waste deposits are rare and large gaps in the knowledge of quantification of many important long-term processes exist (Bozkurt and Neretnieks, 1997). Obviously there is a need to systematise, understand and quantify the processes which may occur over long periods of time.

In view of the inadequate knowledge and lack of information on long-term behaviour of landfills and quantification of contaminant transport and retention processes in waste deposits, it was necessary to develop a new approach to the problem. This approach, which is schematically illustrated in Fig. 1, is a tool for exploring which processes are important for the *long-term* evolution of a landfill.

We have constructed a conceptual model, which is a unitary and continuous description of the overall processes in waste deposits, by combining the small fragments of information in the literature with basic chemical and physical processes. The intention has been to include only those mechanisms that are considered to be the most important, without at first studying the detailed processes. The model is a simple one on a conceptual and descriptive rather than a strictly mathematical level, in order to facilitate its use. With the conceptual model as a base, the main processes have been evaluated. Some of the processes to quantify are, e.g. binding capacities of sulfides and humic substances, sorption capacities of hydrous ferric oxides, etc. The calculations are simple and are based on mass balances, transport and simple kinetic rate equations. In these specific cases, the quantifications have been made for a landfill for industrial and household waste containing much organic matter, although the approach can also be used for waste that has been incinerated and contains only small amounts of organic material. Since we are interested in the long-term perspectives, the starting point for the studied cases is the humic phase.

In order to assess the evolution of landfills over long times, many different types of data are required. Looking at landfills, the sources of information are field studies, laboratory experiments and theoretical modelling. With experiments it is possible to study specific processes such as degradation of organic material. They can also be used to assess a measure of present leaching rates and for predictions in an intermediate time-scale. However, it is difficult to conduct experiments with complex systems under representative conditions. Furthermore, since many processes in landfills take place over long time scales (many hundreds or even thousands of years) it is not possible to simulate them with experiments. Laboratory experiments and field experiments can provide much more valuable information, but they are not in themselves enough to permit reliable assertions in the long-term, and the slow processes occurring in a waste deposit are difficult to study in a laboratory experiment, e.g. the accumulation of metals at pH fronts.

The assessment must thus be carried out with models that are based on fundamental principles such as mass balances, chemical equilibria between solid phases and the aqueous phase, kinetics of dissolution of phases and contaminant transport. Such models can be used as tools to assess the evolution of waste deposits, and be applied to both short and long periods. They can also be used to evaluate how a landfill behaves under different conditions. We have used the modelling approach, which is based on a set of basic processes containing a number of simplified, well-defined and systemised assumptions. The processes are analysed with the aid of models. Successively, we increase the complexity of the studied cases. Then, one can obtain an indication of what is important and what is not. When it is found that a certain process will not be important under any reasonable circumstances, it need not be of further concern. In addition, sensitivity analyses can often indicate when a process may be important and when not. This can also be used to show where more detailed calculations and measurements must be made as well as to justify the assumptions made. With this in mind, we have also studied combinations of processes in order to ascertain the interactions between them and thus their effect on the leaching rate of toxic metals. The strength of working with such an approach lies in its simplicity. It allows us to gain insights, which may be difficult to observe in the actual system due to its inherent complexity. Models, however, require data that to some extent can be obtained from specifically designed laboratory experiments and to be evaluated against field studies.

Since much pertinent information such as degradation rate coefficients of humic material are lacking in the field of waste management, it has been necessary to study other similar areas such as peat and peat degradation. Observations of old waste landfills and other similar environments, such as peat moors (Lucisano and Bozkurt, 1998), sediments, etc., can probably contribute with valuable information about the long-term behaviour of landfills. It is suggested that peat-accumulating ecosystems could prove to be valuable natural analogues for the study of the long-term evolution of household and industrial wastes. Peatlands can be considered to be waste deposition experiments lasting for several thousands of years.

The structure of the paper is as follows: The succeeding section seeks to lay a foundation for understanding the processes in waste deposits over long times, which is the developed conceptual model. Thereafter, different cases are defined and studied. Finally, the quantitative as well as the qualitative results, which will give important information on which discussions and predictions of sudden release of heavy metals can be based, will be presented.

3. The conceptual model — description of the long-term evolution of the chemistry in waste deposits and its effects on metal release

In this section, the conceptual model, which is a description of the overall processes in waste deposits, is presented. A municipal solid waste is a witch's brew of all the materials our industrial society uses. It may contain plastics, stones, glass, rags, paper, garbage and garden waste, textile, rubber and leather waste, metal waste, wood, etc. The long-term behaviour of a landfill will be strongly influenced by its content of organic material. Therefore, the landfills will be distinguished by their content and as illustration, two cases will be described. The first considers a landfill for industrial and household waste containing a lot of organic matter — *the organic case*, while the second case considers incinerated waste containing inorganic materials with a small amount of organic matter — *the mainly inorganic case*. In both cases the waste is assumed to be placed in landfills of considerable extent and thickness. First, an introduction to the description of the transformation stages is given for the 'organic case'. This is then extended to take into account water transport through the landfill, processes that influence the solubility and mobility/immobility of heavy metals, etc. Finally, the processes in the landfill with a high inorganic content will be described.

3.1. The organic case

Waste deposits contain a complex mixture of different compounds, both organic and inorganic, with variable physical and chemical properties. Over time the waste changes considerably. The composition and structure of the inorganic material changes due to leaching and other mechanisms. The organic material degrades by biologically-mediated anaerobic and/or aerobic processes, which have in common that undissolved, organic matter is first hydrolysed into high-molecular weight dissolved organic matter. This organic matter is further hydrolysed to low-molecular weight compounds. It is primarily the low-molecular dissolved organic material that can be biologically degraded to carbon dioxide and water or to methane. The different biological, chemical and physical transformation stages through which organic matter in a landfill can pass, are briefly described below.

In a landfill, oxygen is initially available in the pores, and this can serve as an oxidizing agent. However, the initial supply of oxygen is limited and it may be used up after a few days. When oxygen is depleted, the anaerobic phase starts, and other substances such as nitrate, sulfate, oxidized manganese compounds and ferric iron compounds act as oxidants. The anaerobic phase is characterised by a rapid polymer hydrolysis and a drop in redox potential (Farquhar and Rovers, 1973; Barlaz et al., 1992) (see Fig. 2) and can be subdivided into an acidic phase and a methane production phase. During the anaerobic acid phase, complex organic material is degraded by hydrolysis to smaller molecules, e.g. alcohols, carboxylic acids and carbon dioxide. The formation of organic acids results in a drop in pH (Farquhar and Rovers, 1973; Barlaz et al., 1992). During the methane production phase, the degradation products act as substrates for methane-producing bacteria yielding a gas consisting of carbon dioxide and methane. As the organic acids are degraded, the pH increases to an almost neutral level, buffered by the bicarbonate system. The organic matter in the waste provides a large redox buffering capacity. The redox capacity can in a simplified fashion be seen as the maximum

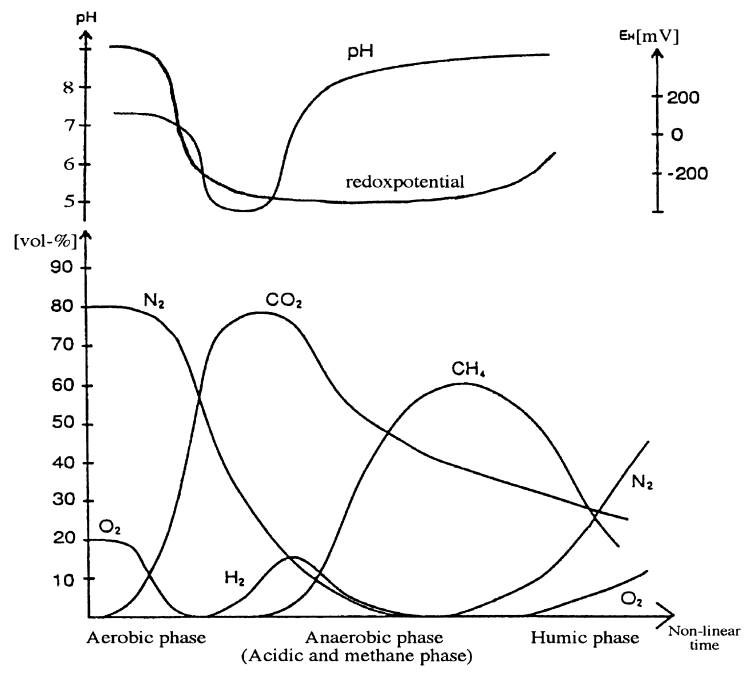

Fig. 2. Schematic illustration of the redox potential, pH (in pore waters) and gas composition during different phases in a landfill.

amount of oxygen with which the waste can react. Thus, reducing conditions will prevail for a long time in the landfill.

3.1.1. The humic phase

As the remaining substrate becomes more and more resistant to degradation, microbial activity slows down and the humic phase is reached. Parts of the organic matter are transformed to compounds, which are much more stable than the original compounds. The more stable compounds are mainly humic substances. Up until the humic phase, any oxygen supplied to the landfill can readily react with simple organic compounds. During the humic phase, the available degradable organic material is either depleted or the reactions are too slow to consume oxygen entering the landfill. The pH and the redox conditions are then determined by infiltrating oxygenated rainwater and oxygen that diffuses into the landfill and by the slow reactions with the remaining buffer capacity of the solids. The deposit may then become aerobic and acidic due to the carbon dioxide formed.

3.1.2. Metal mobility in a landfill

When the solid waste comes into contact with water, such as infiltrating rain water or groundwater, metals will become dissolved and leached out (see Fig. 3). The flowing water transports the leached metals downstream where they may precipitate or participate in further reactions. The substances that dissolve and react influence the chemistry of the leachate. The processes that govern the leaching are complex and as yet it is not possible to describe them in detail. Important mechanisms and processes are complexation, redox reactions, precipitation/dissolution, adsorption, ion exchange, etc. However, the solubility of the metals is strongly influenced by the pH, the redox potential, the presence of complexing agents such as chlorides, sulfates, carbonates, organic

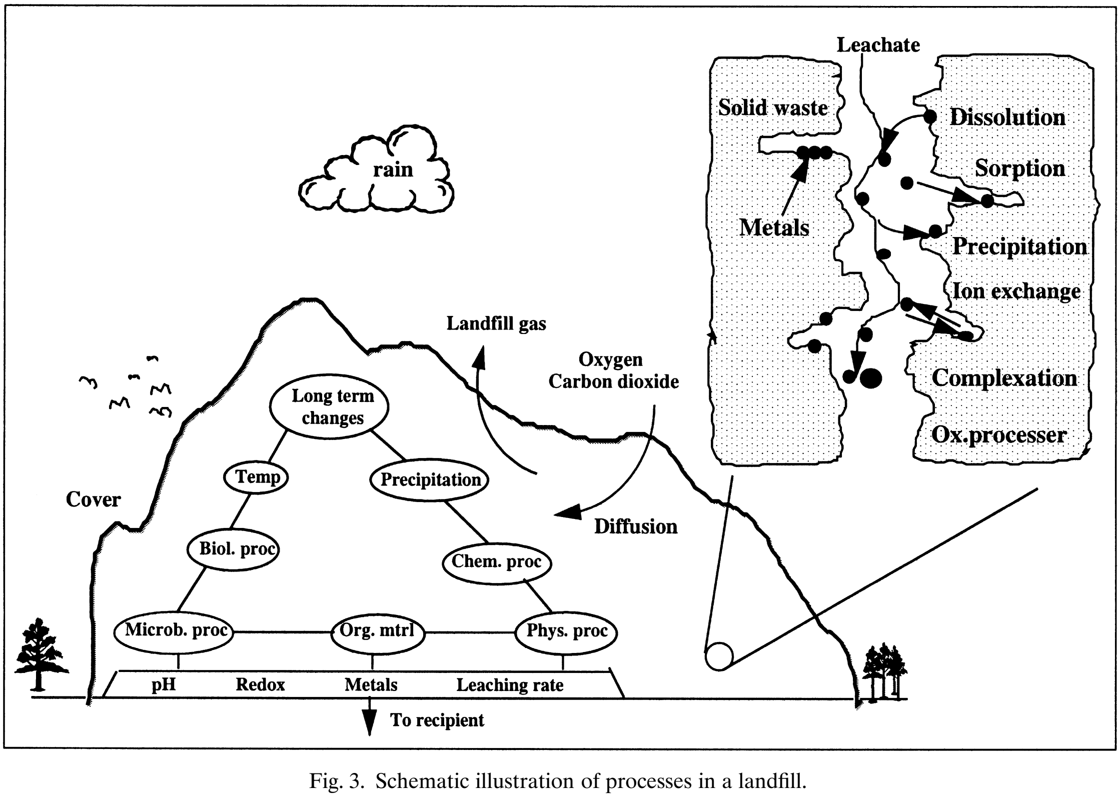

Fig. 3. Schematic illustration of processes in a landfill.

acids, and the properties of the solid waste phases in and on which the metals can be bound. The composition of the flowing water will not be constant but will change with time, depending on how the upstream conditions have changed.

The solubility and release of many of the toxic metals is low under the conditions generally found in today's completed and operating landfills, i.e. during reducing conditions, almost neutral pH.

The organic degradation during the anaerobic methane production phase will, apart from producing methane and carbon dioxide, also produce a large range of organic compounds. These compounds are organic acids, e.g. low-molecular weight organic acids as well as high-molecular weight fulvic and humic acids. The solubility of these compounds in water varies. Generally, increasing molecular weight decreases the solubility. These acids may increase the solubility and the mobility of heavy metals in the waste by acidifying the water and by forming soluble complexes with the metals (Ciavatta et al., 1993). On the other hand, large amounts of solid organic matter are also formed that can be stable over extremely long periods of time in some environments. These solid organics can be very strong sorbents for many of the leached metals and retard their escape from the landfill. Sulfur compounds in the waste can form sulfides under anaerobic conditions and bind many metals as sulfides. Even so, there is a strong competition for the metals by the organic acids and other complexing agents.

The metal release that takes place during the methanogenic phase is probably to a large extent caused either by release of metals complexed to organic matter or by the release of solid particulate forms transported with the water from the deposit as small particles or colloids. It is thus probable that a fraction of the metals is mobile even during the methane-producing phase. This means that metals will be transformed and relocated within the deposit.

After tens to several hundred years, the humic phase starts, i.e. when the methane production has stopped and the easily degradable organic material has been depleted. The intrusion of oxygen may then lead to the development of oxidizing conditions in the landfill. This makes it possible for a new set of reactions to take place. Once acidic conditions are established in the landfill and the pore water has become oxidizing, an increase in metal solubility and leaching can be expected. The flowing water will carry pollutants with it out of the landfill. The metals can also escape from the landfill by diffusion, which in a longer time frame may be an important transport mechanism. Some of the common metals, e.g. iron and aluminium, can, when oxidized, form very strong 'natural' sorbents. Ferric iron hydroxide present in the material or resulting from the corrosion of iron-containing material is a very potent adsorbent for many of the metals of interest. It exhibits a very large surface area, which gives it a high sorption capacity (Dzombak and Morel, 1990). As iron is quite common in waste deposits, it can under the right circumstances contribute with a large sorption capacity and reduce the mobility of the toxic metals. However, during the oxidation phase, sulfur compounds in the waste present as metal sulfides will also be oxidized resulting in the release of metals bound to them. Metals bound to carbonates may dissolve if pH drops or if the partial pressure of carbon dioxide decreases.

In a very long time perspective, it will be the metal-binding properties of the organic phase and the degradability of organic material that determine the metal release. The metal-binding capacity of the organic material may be sufficient to bind most of the metals, provided the materials are homogeneously distributed. Because of the strong heterogeneity of the landfill, different parts of the landfill develop at different rates. There may thus be parts that enter the humic phase early and others that will not reach it for a considerable time.

3.2. *The mainly inorganic case*

For incinerated waste containing mainly inorganic materials with a small amount of organic matter, the description is quite similar to the 'organic case'. However, there are also some differences, which will briefly be highlighted here.

The inorganic matter in incinerated municipal wastes (ash) consists mainly of aluminium silicates, calcium and iron compounds in crystalline or amorphous form (Yan, 1998). The accumulated metals occur primarily as sulfides, oxides, hydroxides and carbonates. Compared to the organic case, the concentration of most metals is much higher per mass of waste. Their concentration are often tens to hundreds of times higher in ash than in natural geological materials (Yan, 1998).

When incinerator residues are deposited in a landfill, some of the toxic metals are subjected to leaching as water percolates through the deposit. The water composition changes through the deposit and the main controlling factors determining the changes are pH, redox potential, presence of complexing agents and the properties and composition of the solid waste. Most of the toxic metals present in combustion residues are concentrated in the glass phases or adsorbed on crystal surfaces. The glass phases react very slowly and their dissolution rate is determined by reaction kinetics (Yan, 1998). Metals are released either by desorption from the surfaces of the particles or by dissolution of the solid phases. Other release processes that may be important are diffusion from inner parts of particles and corrosion of metal surfaces. Important entities that influence the leaching rate of metals are reaction rates, diffusion properties, etc. However, metals may not only be released from minerals, but also sorbed onto new mineral surfaces when these form as the waters become oversaturated with respect to some minerals or they may take part in additional reactions. When new minerals precipitate out of the saturated leachant they are often referred to as 'secondary' minerals if they are not present initially.

3.2.1. Reaction fronts

As long as the landfill is near neutral pH and is strongly reducing, the evolution of the chemistry in the waste will not change much with time. Under such conditions, many of the toxic metals have low solubilities. Reducing and near neutral conditions will prevail as long as there are buffering materials present. The redox capacity is made up mostly of metals, pyrite, ferrous iron, and residual organic compounds. The pH buffering capacity is due mostly to the presence of calcium oxide, hydroxide and carbonate compounds and to some extent to aluminium silicates. Oxygen and carbon dioxide diffusing into the waste deposit will eventually deplete the buffering capacities. Infiltrating acidic rainwater will also consume the buffering capacities. Carbon dioxide generated by the oxidation of organics can also act as an acid and exhaust the pH buffering capacity. The dissolution of solids under the influence of these in-transporting reactants is referred to as hydrolysis.

As the pH and redox buffering capacities at a location are used up, the pH will drop and the redox potential will increase, making the metals more mobile. The mobilised metals may then be transported downstream to parts of the landfill where the pH is still high and the redox potential is low. This may result in a reprecipitation of metals at the new location. Thus, reaction fronts may develop that will propagate in the deposit. At these fronts, metal solubilities may change by several orders of magnitude. These types of fronts have been observed in similar situations in nature (Cross et al., 1991). Eventually these fronts may move through the landfill, in an ongoing process as the buffering capacity of the waste is used up, and release the metals carried by them. This process is illustrated in Fig. 4.

4. Evaluation of the main processes

4.1. Binding capacities

For decades, heavy metals have been disposed of in dumps and landfills. The mobility of heavy metals, and hence their potential risk to the surroundings, depends partly on the complexing capacity of the organic matter in the landfilled waste. In order to assess the binding capacity for metals, the binding capacity of sulfides and humic substances has been studied in detail. The conditions in many closed landfills, as well as in landfills that are in operation, are still anaerobic and the sulfur is in the reduced state and is present as

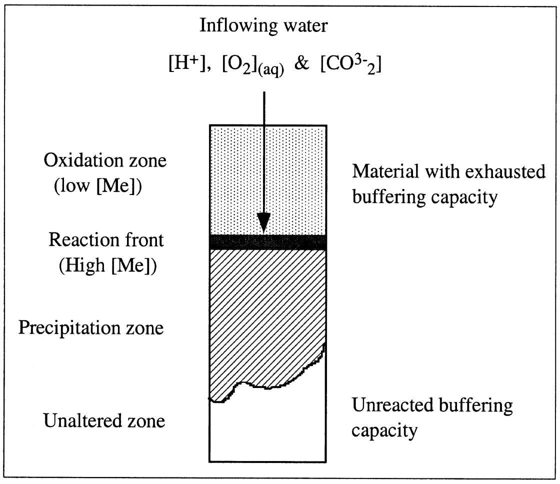

Fig. 4. Schematic illustration of a reaction front (Me is taken symbolically as a metal).

sulfides. The metals may be present as minerals, included in amorphous phases, bound to organic material or sorbed onto mineral phases. In a first step, only the humic substances are considered. The sulfides are discussed later. Data and information used in the different scenarios are presented in Table 1.

Our starting point is the humic phase and it is assumed that only a fraction, one-third, of the originally present organic matter (3 000 000 t) remains and is in the form of humic substances, HS. This means that the amount of humics that will be produced is approximately 1 000 000 t. In soils and sediments, humic acids tend to be mostly present in the solid organic matter. The overall complexation reaction between humic substances and metals can be symbolically written:

$$n\mathrm{Hum}^- + \mathrm{Me}^{n+} \rightarrow \mathrm{Hum}_n - \mathrm{Me} \qquad (1)$$

Where Hum is a humic substance and Me is taken symbolically as a metal.

The organic matter, especially the humic substances, forms complexes with heavy metals that may either increase or decrease their concentration in the pore waters, depending on whether they bind to the mobile or to the immobile part of the humic substances. The amount of the latter part is probably several order of magnitudes higher than the former part and, in this case, it is assumed that the metals are bound only to the immobile fraction of the organic matter. In a long-term perspective, humic substances play a dominant role in the behaviour of heavy metals in soil.

The binding capacity of humic acids for metals has been assumed to be 1 meq./g HS and that

Table 1
Data used for the different scenarios (Bozkurt, 1998)

Metals and binding substances	Molecular weight	Amount[a] in tonnes	Humic-binding metals (Mequivalents)	Sulfide-binding metals (Mequivalents)
Cd^{2+}	112	30	0.54	0.54
Cr^{3+}	52	450	26	
Pb^{2+}	207	10 000	97	97
Zn^{2+}	65	10 000	310	310
Hg^{+}	200	13	0.065	0.065
Fe^{2+}	56	200 000	7140	7140
Ca^{2+}	40	150 000	7500	
Al^{3+}	27	50 000	5555	
Sum metals		**420 493**	**20 630**	**7550**
Binding substances			Mequivalents	Mequivalents
Organic matter as humic substances	1000[b]	1 000 000	**1000**	
Sulfur	32	15 000		**940**

[a] Large variations are observed in different locations in the landfill.
[b] Equivalent weight.

the maximum amount of any metal ion that can be bound is equal to this capacity. In practice, this maximum capacity can probably seldom be used because of competition among the metals and competition with the proton. The binding capacity can thus be expected to be strongly influenced by pH and by the presence of other ligands. The binding capacity has been reported to vary from 0.2 to 40 meq./g HS (Bozkurt and Neretnieks, 1997), although the higher value may depend on other processes than complexation, i.e. secondary precipitation. Although the binding capacity of humics may be different for different metals, the used binding capacity has not been varied in this scenario. Instead a representative and conservative value has been chosen, with respect to among other things, the competition. This figure falls within the reported values in the literature. For waste-containing organics, the tentative conclusion is that the humic substances (while they exist) should have a capacity sufficient to bind all toxic metals (Cd, Cr, Pb, Hg, Zn) in a deposit, even if the humic matter also binds a portion of Ca, Fe and Al, provided that all matter is evenly distributed and that the affinity for these metals is higher than for the others (such as Fe, Al, Ca, etc.). However, it cannot be ruled out and it is even probable that the large amount of other metals may hinder some part of the toxic metals of being bound.

Regarding sulfide formation, sulfur compounds in the waste can form sulfides under anaerobic conditions and bind many metals as sulfides. The calculations are based on the equation:

$$\mathrm{Me}^{n+} + \mathrm{S}^{2-} \rightarrow \mathrm{Me}_2\mathrm{S}_n \quad (2)$$

In Table 1 it is seen that there is enough sulfide to bind the toxic metals if there were no competition with the iron. As it is likely that iron is a strong competitor for sulfide, it must be concluded that the sulfides cannot be safely assumed to bind all the toxic metals.

During anaerobic conditions sulfides have a driving force to form sparingly soluble precipitates with many metals. As it has been shown, there is not enough sulfur to bind all the metals. The question is whether the sulfur will be able to bind the metals Pb, Zn, Cd, Hg in competition with Fe. Simulations using the computer code PHREEQC (Parkhurst, 1995) were conducted to indicate if this may be the case as well as to deduce which of the metals will precipitate as sulfides. The calculations show that when the amount of sulfur is insufficient to bind all the metals the first metals that will form sulfide minerals are: $\mathrm{Hg} > \mathrm{Pb} > \mathrm{Cd} > \mathrm{Zn}$. 'A' > 'B' means that A tends to precipitate before B. A fraction of the iron will also precipitate as sulfide (either FeS or FeS_2).

As a consequence of chemical and physical heterogeneities it is very unlikely that the different materials are so evenly distributed that they always can find each other and form complexes or sulfides. However, if the system were well mixed and homogeneous, the sulfides and the humics could bind a considerable fraction, if not all, of the toxic metals. If the humics and sulfides were oxidized by oxygen the bound metals could be released. If at the same time, the pH of the pore water becomes low due to the formation of sulfuric acid from the oxidation of the sulfides and carbonic acid from the CO_2 (from the degradation of organic matter), the solubility of the toxic metals increases and they can be mobilised.

4.2. Oxygen intrusion and reaction rate

As mentioned previously, the most important factor in the construction of a time-scale for deposits is probably the effects of intrusion of oxygen. Under reducing conditions the toxic metals can to a large extent be bound to humics and sulfides. The apprehension is that the mobility of the metals may increase as conditions change, e.g. oxygen may penetrate into the landfill and cause aerobic conditions. If oxygen or other oxidants intrudes, sulfide and humic oxidation would occur. Here, the most important reactant is oxygen entering the landfill. When this occurs their binding capacity is lost and the metals are released. Therefore, the release of metals from a landfill will be strongly correlated to the rate by which oxygen enters the landfill. This, we have considered in the modelling efforts (Bozkurt et al., 1999). We have studied the long-term fate of organics in waste deposits by considering the oxidation rate in a deposit to be determined by the rate of inward transport of oxygen. The intrusion rate of oxygen is different for different construction types of deposits, i.e. an uncovered or a covered deposit, made in the form of a hill, where the cover is intact or broken, or a deposit under the water table. In addition, there are different processes by which oxygen may enter a landfill. The different cases studied were various transport processes such as, diffusion, self convection and advection (forced flow) for oxygen into a partially saturated landfill and a saturated landfill. In the studied cases, the only reaction considered was the oxidation of organic matter since the amount of organics is more than two orders of magnitude larger than the sulfides. It is common practice to write the subsequent reactions of the organic matter as if it consists of a multiple of CH_2O. The overall reaction can then be written:

$$CH_2O + O_2 \rightarrow CO_2 + H_2O \tag{3}$$

In the calculations the landfill was modelled as a column reactor for transport in one dimension at steady state. The model is based on the law of mass conservation that in a mathematical form can, in general, be written as:

$$\varepsilon_p \frac{\partial c}{\partial t} + q\frac{\partial c}{\partial x} = D\frac{\partial^2 c}{\partial x^2} + R \tag{4}$$

This is the well known advection–diffusion equation with reaction. Here ε_p is the porosity, c is the oxygen concentration (which varies with t and x) (mol/m^3), t is time (s), q is water or air flux [m^3/(m^2 s)], x is distance in the direction of transfer (m), D is the effective diffusion coefficient (m^2/s), and R is taken symbolically as the mass produced/depleted per unit volume per unit time [moles/(m^3 s)]. A more profound mathematical description of the different cases can be found in Bozkurt (1998) and Bozkurt et al. (1999).

In the humic phase the reaction rate of the humic substances is expected to be low. It is assumed in these calculations that it is comparable to that of peat which consists of a large amount of humic substances (Bozkurt et al., 1998). The kinetic constant with respect to humic matter depletion is then taken to be 10/year. This is a value that is within the range observed in peat bogs. The landfill considered is 10 m deep and the amount of humic substances and sulfides is taken to be 100 kg/(m^3 landfill) and 2.8 kg/(m^3 landfill), respectively. With the oxygen intrusion rates calculated for the different scenarios, the reaction would be completed within the times presented in Table 2. The most rapid degradation was identified in a partially water saturated landfill without a cover. The rate of degradation is entirely governed by the rate of intrusion of oxygen. The (bio)-chemical reaction rate is found not to be limiting.

Table 2
Oxygen intrusion rate and estimated time to deplete all organic matter for the different scenarios, in a 10-m thick landfill

Case	Influx of O_2/m^2/year	Time to deplete organic material (years)
Diffusion-partially saturated		
With a cover	35×10^{-3} kg	30 000
With a cover (10% function)	0.29 kg	3000
Without a cover	1.5 kg	600
Fully saturated	$< 2 \times 10^{-3}$ kg	> 500 000
Forced convection	0.06 kg	20 000
Natural convection	3×10^{-3} kg	300 000

If there is oxygen in the landfill, the sulfides may be oxidized before the oxygen is scavanged by the humics since sulfides are highly redox sensitive (Langmuir, 1997). The oxidation of sulfides under atmospheric conditions is inevitable. The oxidation of iron sulfide leads to the production of acidity and formation of ferric oxy-hydroxide (see Eqs. (5) and (6)).

$$FeS + 2.25O_2 + 1.5H_2O \rightarrow FeOOH + 2H^+ + SO_4^{2-} \tag{5}$$

$$FeS_2 + 3.75O_2 + 3.5H_2O \rightarrow Fe(OH)_3(s) + 4H^+ + 2SO_4^{2-} \tag{6}$$

In the remainder of this article we will consider the sulfides to be only FeS_2 for the purpose of scoping calculations. The ferric oxy-hydroxide has a high sorption capacity for the heavy metals and thus, it is possible that even if the sulfides are oxidized, the humic substances and ferric oxy-hydroxide provide sufficient binding capacity for the heavy metals. Unfortunately, there are no data available on the competition of heavy metals between the organic matter and ferric oxy-hydroxide binding sites. It has to be pointed out that we do not only consider the amount of ferric oxy-hydroxide produced by the oxidation of pyrite. The remaining part of the iron in the landfill that is not in the form of sulfides is also assumed, when oxidized, to form ferric hydroxides.

Under the influence of intransported oxygen waste below the cover will be depleted of its reducing capacity. As a result of this depletion, a redox reaction front will develop and recedes into the waste as the buffering capacity of the waste is used up. In general, the rate of sulfide and organic depletion in the waste will be equal to the rate at which oxygen is transported into the landfill. From mass balance considerations, the rate at which the depletion front recedes into the waste is:

$$\frac{\mathrm{d}z}{\mathrm{d}t} = \frac{J_{O_2}}{M_{O_2}} \sum_{i=1}^{N} \frac{M_i}{\eta^i_{O_2}\rho_i} \tag{7}$$

where z is the depth to which the front has advanced in the waste (m), J_{O_2} is the oxygen flux into a landfill [kg O_2/(m^2 year)], t is time (year), ρ is the density (kg/m^3 landfill), M is the molecular weight (kg/kmol), the subscript i denotes organic matter and the different sulfides (here represented by FeS_2), $\eta^i_{O_2}$ is the stoichiometric coefficient for oxygen in the oxidation reaction (kmol O_2/kmol i). Note that the oxidation of sulfides and the degradation of organic matter have been considered to occur simultaneously, which is a scientifically sound approach. How these processes affect the pH will be discussed in a subsequent section.

Rearranging Eq. (7) and integrating the resulting expression gives the time required for the redox front to proceed to the depth z_R.

$$t - t_0 = \frac{\rho_i \eta^i_{O_2} M_{O_2}}{M_i} \int_0^{z_R} \frac{\mathrm{d}z}{J_{O_2}} \tag{8}$$

where t_0 (year) is the time required for the formation of a steady state concentration profile before the redox front begins to move. In the following case the reducing capacity of the waste is considered to consist of only organic matter and that the depletion occurs according to Eq. (3) and since the quasi-stationary state approximation (Lichtner, 1988) can be applied here t_0 approaches zero. On the landfill a cover that offers all the resistance to flow is considered. We also assume, for the sake of simplicity and as an illustrative example, that the oxygen flux through the cover is given only by diffusional transport:

$$J_{O_2} = -M_{O_2} D^e_1 \frac{\mathrm{d}c}{\mathrm{d}z} \tag{9}$$

where D^e_1 is the effective diffusivity of oxygen (m^2/s) in the cover material and the concentration gradient is taken to be the maximum driving force, i.e. $\mathrm{d}c = c^{\mathrm{atm}}_{O_2}$ where $c^{\mathrm{atm}}_{O_2}$ is the oxygen concentration in the atmosphere (kmol/m^3). As the reducing capacity degrades, settlement in the landfill will take place. From landfill data reported at the International Landfill Symposium in Sardinia (e.g. Konstantinos et al., 1997) it can be concluded that the total settlement can be more than 40–45%. This mechanism depends on, among other things, the fraction of degradable matter in the deposit. In the calculations, a settlement of 20% of the landfill height is taken into account and that it takes place during the entire depletion time. The remaining material with exhausted buffer capacity will also contribute to the resistance to oxygen flow into the landfill. Although this resistance will probably not be as high as the final top cover offers we assume that both materials have the same effective diffusivity of oxygen, which means that the numerator in Eq. (8) can be substituted with $(H_0 + 0.8Z)$. This is schematically illustrated in Fig. 5. The solution of

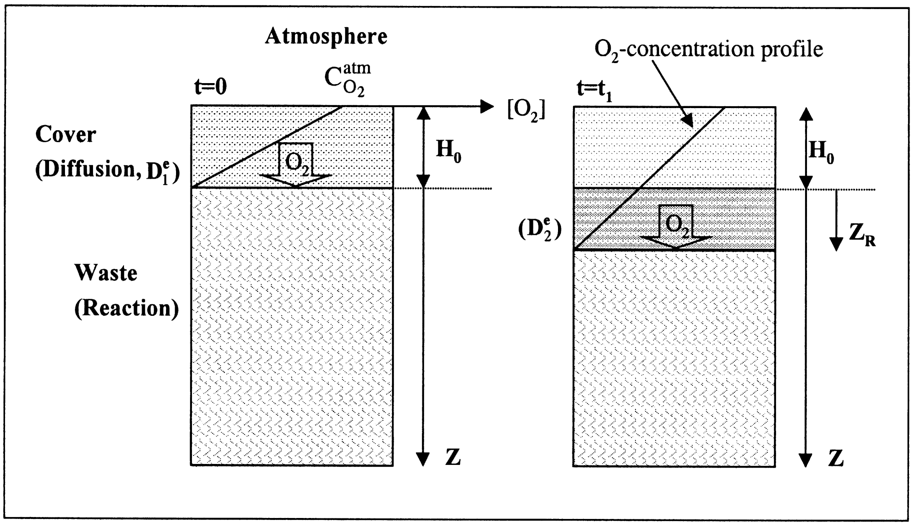

Fig. 5. Conceptual figure of remaining waste, with exhausted reducing material, acting as a cover material.

considering different effective diffusivities is quite straightforward but will not be presented here.

With the following restrictions:

$$z(t=0)=0 \tag{10}$$

$$z(t=t)=z_R \tag{11}$$

the integral in Eq. (8) can be solved analytically to obtain:

$$t=\frac{\rho_{CH_2O}\eta_{O_2}^{CH_2O}}{D_1^e M_{CH_2O} C_{O_2}^{atm}}\left(H_0 z_R+0.4(z_R)^2\right) \tag{12}$$

The appropriate simplifications made in this case allow us to reach an analytical but still powerful and useful solution, which gives a more enhanced insight into the main processes than the use of a sophisticated numerical solution. In Fig. 6 the depletion time is plotted against the redox front depth in the waste material for an infinitely fast reaction. The profile is for a 10-m deep landfill with a 1-m deep soil cover that has an effective diffusivity of 2×10^{-8} m^2/s (Bozkurt et al., 1999).

It is obvious that the redox buffer capacity will last for a considerably long time. In Fig. 6 we have also accounted for the sulfides as reducing capacity and it can be deduced that their contribution to the depletion time is negligible which justifies the assumption about the composition of the reducing capacity. It should be noted that this simulated case is based on the same conditions and to a certain degree comparable with the first case presented in Table 2 (diffusion — partially saturated, with a cover). In the latter case we circumvented the problem with a moving boundary as we assumed a constant oxygen flux into the landfill, which was calculated for a 5-m thick landfill and was taken as an average value for the whole deposit. Comparing both of the cases investigated it can be concluded that the assumption made in the previous case was permissible.

As an illustrative example, the amount of oxygen intruding into a partially saturated landfill without a cover is able to oxidize 1.5 kg organic matter/year/m^2. This means that the maximum amount of released heavy metals could be of the order of 100 g/year/m^2 with respect to the binding capacity of humic materials for metals used. The release of heavy metals from a landfill with a cover is of the order of 2 g/year/m^2. Even though the organic material is degraded it is possible that there will be no immediate and continuous release of toxic metals from the landfill. There is a

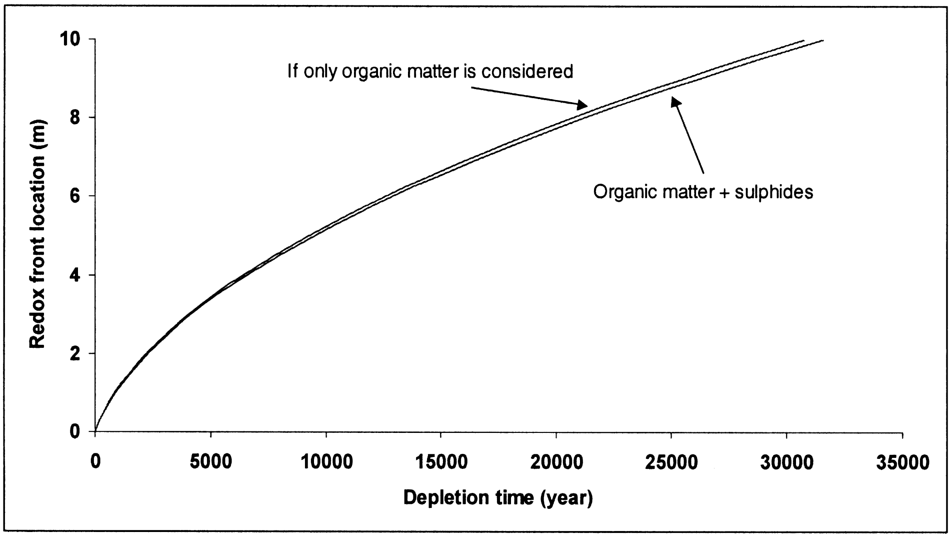

Fig. 6. Reducing capacity depletion time as a function of redox front depth.

surplus of organics in the landfill. If toxic metals were complexed with the oxidized organic matter and are locally released it is most likely that they may be transported further down to parts of the landfill where the binding capacity is not used up. There the metals can temporarily be re-adsorbed which will result in a moving front where the toxic metals accumulate increasingly. The front will move through the landfill as the organics are used up and release the metals carried by them.

4.3. Hydrous ferric oxides

If and when the conditions have become oxidizing in the landfill the sulfides and the humics are assumed to have disappeared or at least lost their binding properties. On the other hand, some of the common metals, e.g. iron and aluminium, can, when oxidized, form very strong ‘natural’ sorbents. Metallic and ferrous iron will become oxidized and have formed amorphous ferric-oxy-hydroxides. This is a very strong sorbent and can bind a part of the toxic metals, which is illustrated in Eqs. (13) and (14):

$$\mathrm{FeOOH} + \mathrm{Me}^{n+} \rightarrow \mathrm{FeOOH{:}Mn}^{n+} \quad (13)$$

$$\mathrm{Fe(OH)_3} + \mathrm{Me}^{n+} \rightarrow \mathrm{Fe(OH)_3{:}Me}^{n+} \quad (14)$$

In the landfill there is approximately 3570 mmol of Fe (see Table 1) and assuming a site density of 0.2 mol/mol Fe (Dzombak and Morel, 1990; Langmuir, 1997) and that all of the available sites can be occupied give 714 mmol of metals that can be sorbed. It corresponds to more than three times the total content (203 mmol) of metals that we assume can be sorbed to hydrous ferric oxides. Here, the influence of dissolved organic matter which may bind the metal to the inorganic surface by forming ternary surface complexes and competition effects such as between the adsorbing surface and the dissolved organic ligand for the metals have not been taken into account. The adsorption is also largely pH-dependent. Typical curves for the adsorption of metals onto inorganic substances, such as iron oxyhydroxides, increases from almost nothing to near 100% as pH increases though a critical range 1–2 units wide (Förstner, 1995). However, this tentative calculation highlights the possible sorptive effects that the hydrous oxides have and as there might be high concentrations of iron in a landfill, hydrous ferric oxide can play a major role in sorbing the toxic metals and thus retard their mobility. Furthermore, the bulk of the inorganic matter consisting mainly of alumino silicates (Yan, 1998) may form clays due to hydrolysis. The formed clays have sorbing and ion exchange properties and can aid in retaining the metals. However, with time the ferrous iron hydroxides will crystallise and form haematite, which is illustrated in Eq. (15), and the metals can be released again.

$$\mathrm{FeOOH{:}Me}^{n+} \rightarrow \mathrm{Fe_2O_3} + \mathrm{Me}^{n+} \qquad (15)$$

4.4. The evolution of the pH

In discussing the effect of pH it is necessary that factors which have an influence on pH must also be considered. Many studies have been performed on soil buffer capacity with respect to forestry and agricultural practices, but in the field of land disposal of solid wastes, little use has been made of the concept of buffer capacity when seeking to explain the retention/mobility of toxic metals in landfills. There are several different sets of heterogeneous reactions that either can produce hydrogen ions or consume protons and efficiently buffer the pH. Table 3 shows the processes, which can modify the proton balance. Under conditions of high pH, heavy metals in well-buffered waste deposit are generally retained, and the concentrations in the leachate are low. As the pH of the waste declines, so does its capacity to immobilise heavy metals. Acidification of landfills leads to mobilisation of heavy metals. All acid generating processes will contribute to the acid production capacity of the system. To what extent a landfill is acidified and whether heavy metals are dissolved depends on the acid neutralisation capacity.

A brief description can help to clarify the acidification/buffering processes, following the changes from relatively high to low pH. Addition of acids, i.e. protons, in landfills causes an initial decrease in pH. This is followed by dissolution of the buffering substances and a new equilibrium is established, which reduces the pH shift which would take place in the absence of the buffering substances. Carbonate solids are efficient buffers in the neutral to basic pH range ($\mathrm{pH} > 6.2$) (Stigilani, 1996) and they will provide pH buffering as long as carbonate solids are present and available for dissolution. When a buffer substance is depleted, added protons decrease the pH until dissolution of a new solid phase starts to consume the protons added. This will prevent a further drop of the pH. When solid carbonate is de-

Table 3
Important acid producing oxidation and acid buffering reactions in waste deposits

Type	Reactions	Range
Acid producing:		
Sulfides	$\mathrm{FeS} + 2.25\mathrm{O_2} + 1.5\mathrm{H_2O} \rightarrow \mathrm{FeOOH} + 2\mathrm{H^+} + \mathrm{SO_4^{2-}}$	(16)
	$\mathrm{FeS_2} + 3.75\mathrm{O_2} + 3.5\mathrm{H_2O} \rightarrow \mathrm{Fe(OH)_3(s)} + 4\mathrm{H^+} + 2\mathrm{SO_4^{2-}}$	(17)
Organic	$\mathrm{CH_2O} + \mathrm{O_2} \rightarrow \mathrm{CO_2} + \mathrm{H_2O} \rightarrow \mathrm{CO_3^{2-}} + 2\mathrm{H^+}$	(18)
Acid consuming:		
Carbonate minerals	$\mathrm{CaCO_3} + 2\mathrm{H^+} \rightarrow \mathrm{Ca^{2+}} + \mathrm{CO_2} + \mathrm{H_2O}\ \mathrm{pH} \geq 6.2$	(19)
Silicate minerals	Primary rock mineral + $2\mathrm{H^+}$ $+ \mathrm{H_2O} \rightarrow$ cations + $\mathrm{H_4SiO_4}$ + secondary minerals	(20)
Cation exchange	$\mathrm{SO{:}\ Me} + 2\mathrm{H^+} \rightarrow \mathrm{SO{:}\ H_2} + \mathrm{Me^{2+}}\, 4.2 \leq \mathrm{pH} < 6.2$	(21)
Aluminium	$\mathrm{Al_2O_3} + 6\mathrm{H^+} \rightarrow 2\mathrm{Al^{3+}} + 3\mathrm{H_2O}\ 3.8 \leq \mathrm{pH} < 4.2$	(22)
	$\mathrm{Al(OH)_3} + 3\mathrm{H^+} \rightarrow \mathrm{Al^{3+}} + 3\mathrm{H_2O}$	(23)
Iron	$\mathrm{Fe_2O_3} + 6\mathrm{H^+} \rightarrow 2\mathrm{Fe^{3+}} + 3\mathrm{H_2O}\ \mathrm{pH} < 3.8$	(24)

pleted, the buffering processes are controlled by aluminosilicate clay. Aluminum silicate minerals can provide a considerable resistance to pH changes (Stumm and Morgan, 1996). Dissolved hydrogen ions can also be removed from the solution by ion exchange reactions. These changes are in general non-linear, and the buffering regime operating at a particular time may later switch to another regime with a lower pH range. These changes could in turn trigger the release of stored toxic heavy metals.

The most important oxidation reactions leading to a decrease of pH in landfills will now be evaluated. The major process affecting the lowering of pH values is probably the exposure of pyrite (FeS_2) to atmospheric oxygen and moisture, whereby the sulfidic component is oxidized to sulfate and acidity is generated [Eq. (17)]. The oxidation of, for example, 10 g of pyrite in a 300-l solution would decrease the pH from 7 to 3. Another important reaction is the oxidation of organic matter resulting in a release of carbon dioxide, which will provide a driving force for the pH to decrease in a landfill that is not in equilibrium with the atmosphere [Eq. (18)]. 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 oxidized, but this may not always be the case. Since the main oxidant transported into landfills is considered to be oxygen, we can use the rate of oxygen in-transport as a measure of the capacity depletion rate. Thus it is not necessary, from a mass balance point of view, to examine the detailed chemistry of the individual reactions.

During oxidation, each mole of sulfide mineral will produce 4 moles of acidity (H^+). With respect to the amount of iron sulfide in the landfill and, as a worst case considering that this entire amount is depleted, 940 Mmol of protons are produced. However, as long as $CaCO_3$ is present, added protons will be consumed by dissolution reactions, and the pH of the system will remain constant. In the studied landfill the amount of calcite is estimated to be 1 mol/(kg dry waste) which is equivalent to the consumption 2 mol H^+/(kg dry waste). This figure is approximately one order of magnitude higher than reported in Flyhammar (1997). He estimated the content of carbonates in degraded waste to be at least 0.15 mol/(kg dry waste). On the other hand, our figure is three times less than the one measured by Belevi and Baccini (1989). They found that a partly stabilised MSW could neutralise 6 mol H^+/(kg dry waste) when the pH of the leachate was above 7. The supply of protons by acid rain (pH 4) is 0.02 mol/year/m^2 in our scenario. In our studied landfill, the total acid neutralising capacity is 8000 Mmol which, implies that there are sufficient carbonates in the waste to neutralise the oxidation of all sulfides in the waste.

The effect of solely carbon dioxide evolved from the oxidation of organic matter will be discussed without considering the multitude of possible reactions. Note that the in-diffusion of CO_2 from the atmosphere has been neglected. Scoping calculations have been made with the geochemical simulation program PHREEQC (Parkhurst, 1995) and the WATEQ4F database (Ball and Nordstrom, 1991) in order to calculate the pH, alkalinity and P_{CO_2} of leachate. The database was modified to include thermodynamic data of simplified organic matter — CH_2O (Stumm and Morgan, 1996). In this simple case we assume that the landfill contains calcite that initially is in equilibrium with acidic rainwater (pH 4). A constant infiltration rate of 200 l/(m^2 year), which corresponds to an infiltration–precipitation ratio of 0.4, and a 10-m thick waste deposit has been used. When the organic matter is oxidized in an aqueous environment, dissolved carbonate is generated. If the organics continue to oxidize, the carbonate concentration and the P_{CO_2} in the leachate will increase. The partial pressure of carbon dioxide in air is $10^{-3.5}$ while the maximum P_{CO_2} in waste deposits and soils can be several orders of magnitude higher. In these calculations the assumed hydrostatic pressure is 1 atm. It can be seen in Eq. (18) that the molar quantity of carbonate added to the leachate is equal to the molar quantity of oxidized organics. In a simplified fashion, adding carbonate (mol CO_3^{2-}/(kg H_2O) as an independent variable to the leachate can simulate the organic oxidation reaction. Figs.

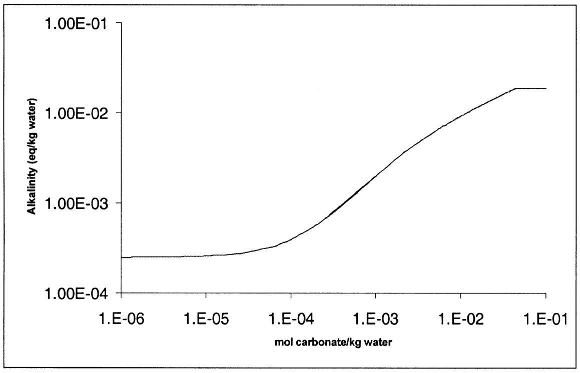

Fig. 7. The evolution of leachate alkalinity with carbonate addition.

7 and 8 show the progression of pH and alkalinity where fixed quantities of carbonate have been added to the leachate.

The results indicate that the solubility of calcite decreases with increasing amounts of carbonate added to the solution and that the alkalinity reaches maximum when $\log_{10}(P_{CO_2}) \approx 0$. When the partial pressure of carbon dioxide reaches and exceeds the hydrostatic pressure in the leachate, the solubility of calcite is at a minimum. If additional CO_3^{2-} is added, carbon dioxide gas forms and excess CO_2 is degassed from the system. Following this the chemistry of the leachate will not change which also means that the pH will remain above 6. However, this will last as long as the reducing capacity is only due to organics and calcite is present. In an open system such as a landfill, the acid consuming component will be displaced and thus the pH will be changed irreversibly. By making a mass balance and using the data in Fig. 4 it is possible to calculate the pH buffer depletion rate and thus the time to completely deplete calcite from the waste. It is possible to carry out this quantification since we can estimate how much carbonate, emanating from the organic oxidation reaction, is added to the leachate. The degradation rate of organics is, in turn, estimated with the oxygen intrusion rate presented previously (see e.g. Table 2). Tentative quantifications indicate that it will take many thousands of years (> 3000 years) before the buffering capacity of a partly stabilised waste deposit is exhausted. Therefore, higher remobilisation rates of heavy metals due to lower pH are not expected for many thousands of years. However, due to spatially variable distribution of buffering material and the effects of channel flow the buffering capacity may become exhausted locally, in the channels and their surroundings. When and if this occurs in these so-called preferential pathways there will not be enough alkalinity in the percolating water to buffer the acid and the pH decreases to between 3 and 4.

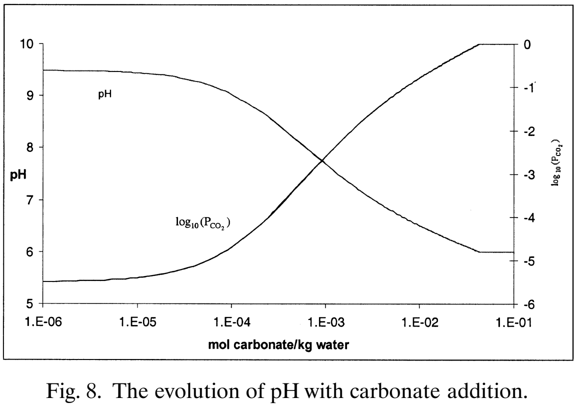

Fig. 8. The evolution of pH with carbonate addition.

5. Discussion and conclusions

Emissions from a landfill arise both in a short-term and a long-term perspective. The composition of the emissions will change with the different phases through which a landfill passes. In the short-term, the emissions of main interest are organic compounds (e.g. dichloromethane, tetrachloroethene, benzonitrile). However, the release of metals is low during the initial anaerobic phases. This implies that metals accumulate in the deposits and thus have a high future contamination potential.

This study focuses on events occurring in the long-term perspective, when the conditions in the landfill may change as a result of natural or human activities. The large amounts of heavy metals accumulated in the landfill may then become more mobile and may be released to the environment. The mobility of the heavy metals is strongly influenced by pH, redox conditions and the presence of substances that can form complexes with the metals.

A conceptual model has been developed to describe the long-term chemical evolution of waste deposits. The model takes into account landfills with different contents, i.e. deposits containing much organic matter as well as landfills containing inorganic materials with a small amount of organic matter. Following the approach developed, scoping calculations of the main processes during the humic phase have been made. The presented quantifications have been made for a landfill for industrial and household waste containing much organic matter, although the approach can also be used for waste that has been incinerated and contains only small amount of organic material. It may be emphasised that the quantifications are based on the main chemical and physical processes and that the landfill is not treated as a 'black box'. The model has been used to assess the long-term chemical evolution in a landfill to assess if, and when, it may release toxic metals. It has also been used to identify areas that must be further studied. The used approach has been successful in the sense that it has increased the understanding of the basic interaction mechanisms and processes that govern the transport and fate of contaminants in waste deposits over long times. The target groups and potential users are those responsible for locating and designing waste deposits, waste handling companies, authorities, etc. The information and methods can be used to assess the *long-term* chemical risks of old as well as new deposits and for landfill construction purposes.

Under reducing conditions the toxic metals can to a large extent be bound to humics and sulfides. We have quantified the binding capacities of humic substances and sulfur compounds in waste deposits with a high content of organic matter. The calculations indicate that the capacity of the humics is sufficient to bind the metals of interest (Cd, Pb, Cr, Hg, Zn) in the deposit, even if the humic matter also binds a fraction of Ca, Fe and Al, provided all matter is evenly distributed and that the affinity for these metals is much higher than for the other potentially competing metals (such as Ca, Fe, etc.). The variability in the complexing capacity of humic substances is very large, and this leads to large uncertainties in the simulations. Practically nothing was found regarding the long-term stability of the 'stable' humic substances in the 1000-year perspective, and this means that for wastes that contain large amounts of organic matter there are at present large uncertainties in predicting the long-term evolution and leaching of toxic metals. Sulfides on the other hand can bind approximately twice the amount of all toxic metals. However, if all the metals are considered then the capacity is only enough to bind one-tenth of the sulfide-binding metals. Simulations showed that when there is not enough sulfur to bind all metals and when competition between the metals for the sulfur was taken into account, the metals will form sulfide minerals in the following order: $Hg > Pb > Cd > Zn$.

Large changes in the metal mobility may occur as the landfill enters the humic phase. When oxygen concentrations will build up in the deposit the humics and sulfides will oxidize and thus lose their binding capacity. The transport properties of gas and water into and in the landfill are key entities and must be well understood. One main focus of the modelling has thus been to assess oxygen transport rates into landfills and how the design and structure of the deposits affect the leaching of toxic metals. With the modelled oxygen intrusion rates, the most rapid organic matter degradation was identified in a partially water saturated landfill without a cover. For this case the amount of oxygen intruding into the system is able to oxidize approximately 1.5 kg organic matter/year/m^2. This means that the time to deplete all the organic matter that remains after the anaerobic phase in a 10-m thick landfill is in round numbers 600 years. The maximum amount of released heavy metals could be of the order of 100 g/(m^2 year) (or 0.5 g/l expressed as leachate concentration) with respect to the binding capacity. This figure is only due to organic depletion but there is an additional transport mechanism by which metals can be transported from the landfill; colloid transport. Assuming that the leachate contains approximately 250 mg organic carbon (OC) per litre of leachate corresponds to an annual metal release of 5 g/m^2 which is equivalent to 25 mg/l. This potential release is two orders of magnitude lower than the metal release during the anaerobic acid phase.

Several studies have explored various alternative long-term migration barrier cover technologies for short-term stabilisation and 'final' closure of waste landfills. The barriers are designed to control and prevent precipitation into the landfill, and to prevent contaminants from flowing out of the deposit. These methods have, however, only been in practice for a relatively short time (maximum 30 years) and it is not known how the results can be used to predict processes in the far future. No top cover can prevent infiltration into the landfilled waste forever and, in the long term, the covers will deteriorate and, consequently, will not prevent contaminant transport out of the landfill. However, if the landfill is placed in a depression — either natural or artificial — and kept fully saturated the time to deplete all organic material would increase by three orders of magnitude and as a result the metal release would decrease by the same magnitude.

As the humics and sulfides have lost, if not all, a part of their binding properties due to oxidizing conditions, the hydrous ferric oxides formed can aid in retaining the metals. The binding capacity of ferric-oxy-hydroxides has been estimated to be three times the total content of metals that are assumed to be sorbed on hydrous ferric oxides. However, sorbed metals can be released during the crystallisation of ferric iron hydroxides.

Acidification, acid rain precipitation and resulting from the oxidation of sulfides represented by pyrite (FeS_2) as a worst case with respect to the amount of protons produced and of organic matter resulting in a release of carbon dioxide, of landfills leads to mobilisation of heavy metals. Applications of the model to pH modelling in landfills have also been made. The long-term development of the leachate pH will depend on the ability of the waste to produce acidity and to neutralise acid constituents. The buffering capacity of solids in landfills is exhausted when the solids are depleted, i.e. not available for dissolution, but also can be limited by reaction kinetics and by faster transport of one of the components of the acid–base pair away from the reaction zone. The pH-buffering scenario has been based on the local equilibrium assumption with calcite as the only buffering mineral. The amount of calcite has been estimated to be 1 mol/(kg dry waste). The equilibrium chemistry has been calculated using the geochemical simulation programme PHREEQC. In the quantifications, it has been assumed that the Ca content of the waste is initially in the form of calcite. This assumption will overestimate the acid neutralising capacity depletion rate; i.e. calculation based upon this assumption will thus give conservative estimates of the time taken to completely deplete the acid neutralising capacity of the waste. Although there are many assumptions implicit in this representation of the pH buffering capacity of the waste, different cases can be defined and studied in order to explore the possible theoretical ranges of redox buffering behaviour, even in the absence of detailed analytical data.

Based on the different cases studied, it can be concluded that the acid neutralising capacity of the waste material is sufficient to buffer infiltrating acid rainwater (pH 4) at circumneutral to alkaline pH levels for long times. The pH buffer, as well as the redox buffer capacity, depletion rate has been found to be strongly dependent on the rate of inflow of oxygen into the deposit. Depending on the oxygen intrusion rate into the landfill, the acid neutralising capacity can be expected to last from 3000 years and upward for a 10-m deep landfill with a rainwater infiltration rate of 0.2 $m^3/(m^2$ year). Considering the landfill to be porous and heterogeneous higher remobilisation rates of deposited heavy metals due to lower pH should not be expected over long periods of time.

Prediction of the pH buffering capacity over time is associated with large uncertainties. Large-scale chemical and physical heterogeneities can cause preferential pathways for leaching or immobilisation. In these flow paths the buffering capacity depletion rate may occur much faster and due to spatially non-uniform distribution of the buffering material the capacity may become exhausted locally. This will cause the pH to decrease to somewhere between 3 and 4.

We have found that there are many uncertainties and that we have been forced to make several assumptions. This points to several areas where further research is needed. One main area is long-term impact of heterogeneities.

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