

Database

Evaluation of Geochemical and Biochemical
Processes and Release from Landfills

Dutch Sustainable Landfill Foundation

Colophon

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Evaluation of Geochemical and Biochemical Processes and
Release from Landfills

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1. Introduction and background

1.1 Problems of landfilling; current policy and legislation

Landfilling of wastes bears the risk of formation and release of components that can pollute the air, soil, surface or groundwater. The current response to these risks has been containment: the material in the landfill bodies is wrapped in an impermeable shell in a way that emissions can no longer occur. However, due to containment the pollution potential of the landfill remains in place and the containment strategy is only effective as long as the impermeable shell remains in tact. To overcome this, legislators may require eternal aftercare and landfills have been obliged to create financial funds which can be used to restore the impermeable liner in future, whenever needed.

The type of waste determines the specific measures that are prescribed. The European Land Fill Directive (LFD) distinguishes three different types of landfills: inert, non hazardous, and hazardous waste. In the Annex 2 of the LFD a first step is made towards a source term definition controlling emission towards groundwater. However, the current LFD still has serious limitations. Landfilling of hazardous waste under the current acceptance criteria specified in Annex II will require eternal aftercare as leachate quality will not likely meet quality objectives that will come from the Water Framework Directive. The WFD (Water framework Directive) will put requirements on all activities affecting soil and groundwater (primarily groundwater). As such future emission levels from landfills will be derived from the WFD. This implies that tools need to be defined to get assess such impacts as realistically as technically feasible now.

1.2 The integrated research programme on sustainable landfilling

In 1998, the Dutch integrated project on sustainable landfilling was started on initiative of the Dutch association of waste management companies. The overall objective of this project is to find methods to reduce the emissions from landfills in order to meet the criteria of landfills for inert and non-hazardous waste as defined in the EU- LFD by other means than containment alone. The guiding idea of this project is that knowledge of processes responsible for the harmful emissions identifies naturally occurring processes that determine overall emissions. In addition these insights lead to technological and design measures that allow control of processes that cause emissions and reduce emissions to acceptable levels within one generation.

The ultimate aim of the project was to demonstrate that it is possible to reduce aftercare to a minimum or even abstain from additional measures and still maintain safe environmental conditions meeting targets set by regulation.

The composition of the waste that has to be treated in a landfill largely determines the governing landfill processes and its pollution potential. In this study we distinguish three types of landfills each displaying a specific kind of reactive behaviour that require different types of

measures to control or manipulate the occurring bio- and geochemical processes within the landfill body. The three types are:

- landfills containing predominantly organic waste. In these landfills biodegradation is the major mechanism that governs pollution potential.
- landfills containing predominantly inorganic waste. In these landfills solubility control and leaching is the predominant factor that governs the pollution potential
- landfills containing hazardous waste, where immobilization can be an important mechanism to retain hazardous pollutants in the waste matrix.

The hypothesis in this study (see Figure 1) is that (i) through control of processes, emissions from both the predominantly organic waste landfills and the hazardous waste landfills can be transformed into a landfill with the characteristics of an inorganic waste landfill and (ii) through solubility control and flushing emissions from this inorganic waste landfill can be reduced further to a sustainable landfill with negligible emissions.

Leaching is the process by which constituents in a solid material are released to the environment through contact with water. Understanding the rate and extent to which constituents of interest may be released is central to defining:

- 1 potential environmental impacts through water-borne mechanisms including soil, groundwater and surface water contamination,
- 2 human health and ecological risks from beneficial use of commercial materials, and disposal wastes,
- 3 effectiveness of certain treatment processes for wastes,
- 4 designs and acceptance criteria for waste management facilities,

The specific rates and extents of constituent release from materials are a function of:

- 1 the chemical and physical properties of the material under consideration,
- 2 the chemistry of the constituent(s) of interest,
- 3 characteristics of the local environment in which the material is placed, including chemical properties (e.g., pH, oxidation-reduction potential, presence of reacting constituents such as carbon dioxide) and the nature of water interaction (e.g., frequency, amount, interfacial contact area).

Fundamental understanding of leaching processes is achieved through study and research on material testing, geochemistry, constituent mass transfer, and development and verification of mathematical models to estimate long-term behaviour and characterize risks under varied environmental conditions. Extensive research and evolution in understanding fundamental aspects of leaching processes and impact evaluation has been carried out over the past two decades. This research provides a sound foundation for practical applications in leaching characterization and impact assessment.

Recognizing the risks and environmental damage caused by uncontrolled materials use and waste disposal, national and regional regulatory organizations have developed widely variable, and often disparate, test methods and regulatory control frameworks to characterize leaching and make decisions about acceptable and unacceptable use of materials, waste management practices, and contaminated site restoration needs. These regulations, which began evolving in the early 1980's, were based on the best understanding at the time, but are limited in the context of current understanding and needs.

Efforts have been undertaken in the European Union and the United States to develop a more robust and scientifically sound, while practical, framework for characterization of wastes and materials subject to environmental leaching and decision-making based on assessment of potential impacts. Consensus is evolving on an overarching framework and methodological details for implementation (1,2). The framework is a tiered approach, allowing the user to select the level of testing and evaluation required based on the degree of conservativeness required, prior information available, and balancing costs of testing against benefits from more detailed information (e.g., reduced management costs or alternative management options). Use of this approach is starting in both the European Union and the United States. Demand for such a system is also great in other countries (e.g., Japan, Australia, Taiwan).

Such a decision support system should guide choices on test selection, facilitate data management and assessment based on testing results, and provide a comparison with results from others with similar materials and needs. This is coupled with a need for extensive training and technology transfer, as well as consultancy and further research to sort out the problems that are identified by more detailed evaluation of state-of-the-art testing.

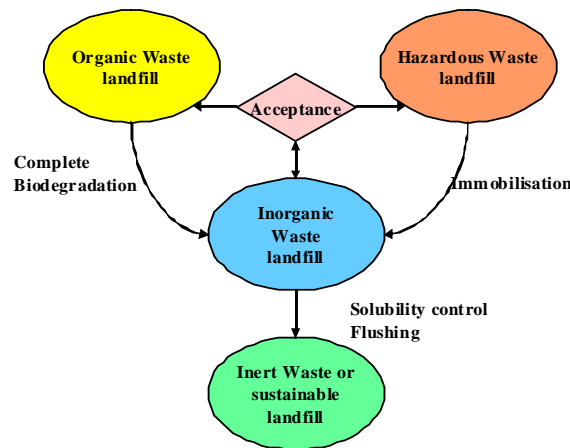


Figure 1 Transformation of landfills containing predominantly organic waste or hazardous waste, to a landfill consisting of largely inorganic waste towards a sustainable landfill (inert).

The approach adopted in the project was to determine the processes that have a major impact on emissions and subsequently monitor their progress. For this purpose experiments were carried out at different scales (lab, lysimeter and field), each reflecting processes that take place on different time-scales. Full-scale demonstrations only give insight in the development of emissions in the first few years. In lab-tests long-term behaviour can be studied, e.g. using high liquid over solid ratios in leach-tests. Lysimeter-tests can be used to confirm whether conclusions can be generalised from lab to field-scale. A graphical representation of the relationship between laboratory, lysimeter and field-scale experiments is given in Figure 2.

For the interpretation of results and extrapolation to longer time scales, different types of waste or altered design or management scenarios a generic framework was made, based on the modelling of the fundamental hydrological, biological and geochemical processes occurring in landfills. This document describes this modelling framework..

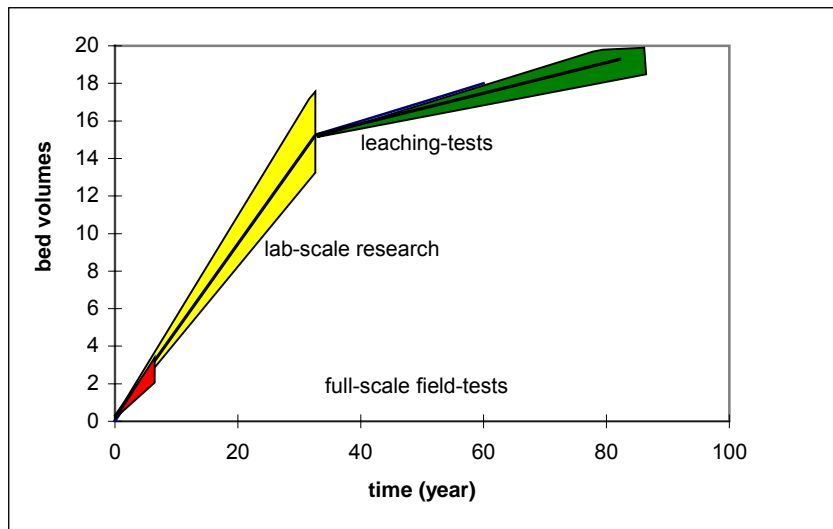


Figure 2 Relationship of laboratory, lysimeter and field-studies. Laboratory leach tests reflect the long-term behaviour of a waste material, lysimeter (lab-scale research) can reflect the short to mid-term behaviour and pilot-studies reflect the actual behaviour of the waste material over a limited time scale.

1.3 Emissions from landfills

Landfilling of wastes gives rise to various emissions. The main processes responsible for transport of contaminants are leaching with infiltrating water and emissions of gasses resulting from the biological degradation of organic matter to CH_4 , CO_2 , water.

Organic macrocomponents as BOD, COD and also landfill gas are being formed and BOD is converted again during biodegradation of fats, sugars, hemi-cellulose and cellulose in the organic fraction in the waste. Since it stems from the same processes, Kjeldahl nitrogen (N_{Kj}) is also considered as one of these organic macrocomponents.

The biochemical processes that result in formation and decay of organic macrocomponents are reasonably well established, and the process is often described in four, five and sometimes even nine phases: hydrolysis, acetogenesis, and various phases of methanogenesis, in some cases ultimately mineralization under aerobic conditions (3). However the cascade of reactions is complicated by the heterogeneity of the waste and in practice different phases will exist simultaneously throughout the landfill. The rate of decay depends on a number of factors, e.g. waste composition, moisture content and temperatures.

Organic microcomponents are generally already in the waste upon deposition, and may end up both in the gas and the leachate. Organic microcomponents can be converted or decomposed under both anaerobic and aerobic conditions, sometimes generating other even more troublesome pollutants, e.g. vinylchloride from hydrodechlorination of trichloroethene.

Metal ions are also present in the waste upon deposition. However by far the largest part of metals stays immobilized and does not end up in the leachate. Mobilization or immobilization of metal ions does occur in a number of processes and is dependent on pH and degradation of organic matrix, as indicated in Figure 3. The top line in brown represents the total amount that is present in a certain waste mix of the considered component. Not all of this is available for leaching, the maximum amount that can be leached is represented by the blue dotted vertical line, marked "potentially leachable". The amount that is actually leached from the pure material in dependence of the pH is indicated by the red drawn line. Through a number of processes the actual leaching in a landfill environment can be different from the behaviour of

the pure material. The actual leached amount can be lower than expected as a result of sorption to organic materials and as a result of the occurrence of reducing conditions. On the other hand the leaching can be increased as a result of chloride-complexation and DOC complexation.

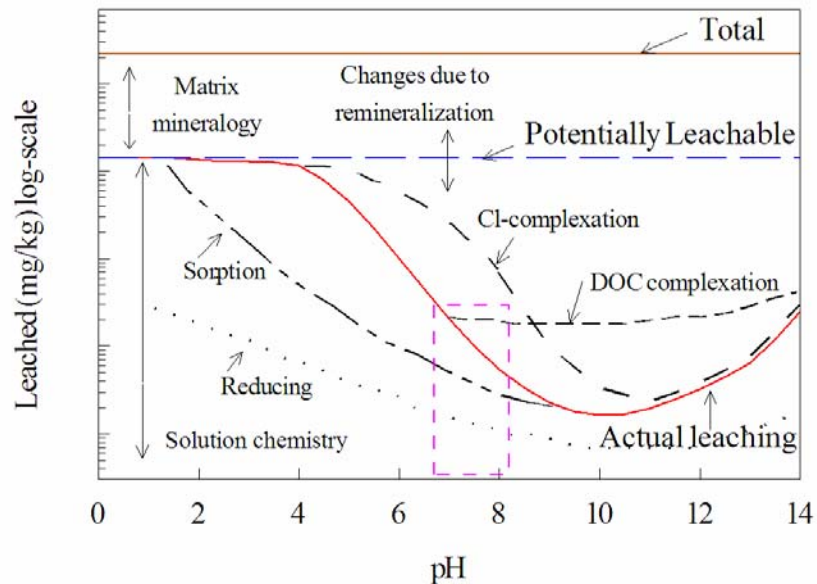


Figure 3 Overview of processes occurring in landfills that have a major influence on the leachability of contaminants to the surroundings.

The frame that has been indicated around neutral pH, indicates the most likely circumstances that can be reached through manipulation of landfill design and operation and specifically through the presence of a sufficient amount of stable organic material.

Oxy anions as SO_4^{2-} , CO_3^{2-} and PO_4^{3-} come from sulphur and phosphorus-precursors, present in the waste upon deposition. The amounts of oxy anions available for pollution is largely determined by the waste composition. The same goes for **salts** as Cl^- .

1.4 Reducing emissions from landfills

Emissions from landfills to the atmosphere (e.g. CH_4 , CO_2) and release from landfills to soil, surface and groundwater (both inorganic as well as organic contaminants) can be reduced in a number of ways:

- **Waste selection** This can be used in three different ways: (i) prevention: not allowing the contaminant to enter the landfill in the first place (ii) adding/preventing additional components to the waste to enable certain processes in the waste, e.g. using permeable shredded tires rather than more impermeable daily covers to enable flushing or (iii) by combining materials in such a way that through their interaction the emission potential for all contaminants is reduced. The interaction may be directly between waste components, but also by creating the right conditions in which other reactions can be stimulated (e.g. adding buffering components to enhance methanogenesis). E.g. organic material has a positive effect on metal ion concentrations are:
 - a the formation of an environment in the landfill with a pH-value of around neutral;
 - b the creation and stabilisation of reducing conditions in the landfill;
 - c the availability of a large number of active sites for the adsorption of soluble components such as heavy metals;

In order to make full use of the positive effects, the negative effects associated with high DOC concentrations (see below under biodegradation) have to be minimised. The production of large quantities of DOC is directly connected with the biological degradation of organic material. In order to limit the effect of high DOC concentrations it is important that the biological degradation is as fast and as complete as possible. Once the active production of DOC has been brought to a low level, the remaining concentration can be reduced by flushing of the liquid phase.

- **Pretreatment** Pretreatment might aim at the removal of specific components prior to landfilling. Examples are mechanical removal metals, paper or plastics, washing to remove salts or biological pretreatment (composting) to convert part of the biodegradable organic material. Pretreatment might also be directed to enable or promote subsequent processes, e.g. shredding to enhance biodegradation or to facilitate flushing;
- **Biodegradation/Conversion** Organic macrocomponents are formed but also largely converted during biodegradation. Conversion can be enhanced through leachate infiltration or creating an aerobic environment in which composting processes occur rather than fermentative. Many organic microcomponents are also converted under anaerobic conditions. Although there is no proof for this, it is likely that measures that enhance biodegradation of organic material, also enhance degradation of organic microcomponents. Biodegradation also affects heavy metal concentrations in the leachate, since dissolved organic carbon concentrations are reduced that tend to mobilise metal ions by complexation.
- **Immobilisation** This can be used as a pretreatment process in order to facilitate the landfilling of materials that would otherwise not be acceptable for landfilling, by binding contaminants in mineral or other phases in the landfill. Matrix retention occurs as less soluble minerals develop in the landfill body, through sorption onto solid organic matter (residual fraction), to mineral oxides and other charged surfaces such as in clay minerals.
- **Solubility control** The release of metal ions is determined by the partitioning between the solid and the liquid phase. This partitioning in turn is mainly determined by the pH, conductivity, redox and DOC concentrations in the liquid phase (see Figure 3). By controlling these circumstances and processes in the right way a minimum level in the liquid concentrations can be achieved. If the release of a certain component is governed by solubility control, the application of flushing is only capable of reducing the concentrations as long as the flushing is continued. As soon as the flushing stops, the system will return to its equilibrium concentrations, at least for as long as there is still enough material left in the solid phase.

Converting the appearance of the component to the right chemical form can be achieved by combining different waste streams in a creative way, or by adding specific chemical or mineral agents to allow the component to precipitate in the most suitable form.

- **Flushing:** Of the processes discussed flushing is probably the most straightforward to understand. The principle applied by flushing is that soluble components are removed from the liquid phase of the landfill by introducing fresh liquid, which does not contain the component in question. From a theoretical point of view it soon becomes clear that a reduction of the concentration by two orders of magnitude will require a throughput of fresh liquid which is in the order of three times the liquid content of the landfill. If this has to be achieved by natural precipitation then the time scale of one generation is not nearly sufficient. In order to reach sufficient dilution in the proposed time period the infiltration rate has to be in the order of 1500 – 3000 mm/year. This puts certain demands on the construction and operation of the landfill:

- * The permeability of the landfill body has to be high enough to allow for a water flow of this magnitude. The permeability of the landfill body is a function of several parameters

including waste composition, from of compaction, height of the landfill and the build-up of the landfill in layers;

- * In order to avoid having to discharge large amounts of leachate on the one hand and to infiltrate comparable amounts of clean water, a recirculation loop including specific treatment of the leachate will be necessary;

Figure 4 describes a typical metal ion concentration in the leachate during the process from an organic waste landfill to an inert waste landfill and subsequently to a sustainable landfill. In the organic waste landfill, biodegradation results in high concentrations of dissolved organic material in the leachate. Since complexation to dissolved organic materials is the governing mechanism for metal ion dissolution, leachate metal ion concentrations are high as well. Upon progress of biodegradation, the amount of dissolved organic material is reduced until complexation is no longer the most important factor that determines metal ion concentrations. At this point, the landfill has become a landfill with the properties of an inorganic waste landfill, where emissions are governed by solubility and flushing. Further flushing ultimately results in concentrations that can be considered sustainable.

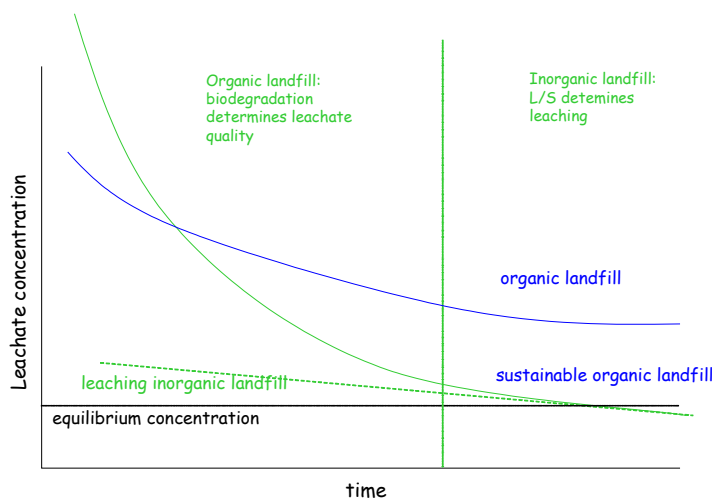


Figure 4 Development of leachate concentrations as a function of time for a conventional organic waste landfill, a sustainable organic waste landfill and a sustainable inorganic waste landfill. A sustainable organic waste landfill will tend to the behaviour of a sustainable inorganic waste landfill.

1.5 Landfills containing predominantly organic waste

The emission behaviour of waste containing high amounts of degradable organic matter is dominated by the degradation of organic matter. Landfill gas is produced during biodegradation and concentrations of BOD, COD and N_{kj} in leachate are high. The high organic content in the leachate results also in high amounts of metals in the leachate. When biodegradation reaches completion, leachate concentrations are significantly reduced. In time the degradable organic matter in the waste is stabilized to non-degradable organic matter, the behaviour of the landfill has evolved towards to that of a landfill containing predominantly inorganic waste.

For organic waste the challenge is to ensure full degradation of the degradable organic waste fraction within one generation so that the more stable end condition of predominantly inorganic waste can be reached. Leachate recirculation or creating conditions for aerobic conversion are the primary control measures we have to achieve the full degradation at full scale.

1.6 Landfills containing Predominantly inorganic waste

For this type of waste, pH can have a large effect on the leaching behaviour, as illustrated in Figure 3. In a predominantly inorganic waste landfill the release of substances is governed by the partitioning of contaminants between solid phase and leachate. Understanding the factors controlling this partitioning during the lifetime of a landfill holds the key to control leachate quality. Since pH, conductivity, redox and DOC are governed by major elements and the nature of the organic matter in the waste, these factors are important for the degree to which contaminants are partitioned between solid and liquid and also between free and complexed forms. The interaction of both inorganic and organic contaminants with dissolved organic matter (DOC) is crucial in this respect, as the complexed forms are more mobile and in some cases less accessible to organisms.

Although wastes are judged on a waste by waste basis upon delivery to the landfill in line with LFD-Annex II, it is of great importance to know how release from a landfill body can be described. The mutual interactions of waste in landfill body have the tendency to develop a mixed waste release behaviour that can be quantified and described (4). Describing behaviour and thus understanding the controlling factors provides management options to deal with undesired release behaviour. Currently, the modelling capabilities have developed to a level that meaningful conclusions on behaviour of mixed waste can be drawn (5).

1.7 Landfills containing Hazardous waste

The leaching behaviour of hazardous waste should be prevented as much as possible. Therefore the emphasis lies in modifying the release behaviour of the widely varying waste qualities in this category by creating a chemically and physically more homogeneous and thus better controlled matrix. A major challenge is to ensure that such target conditions far from equilibrium with the surroundings can contribute to the sustainable character of the landfill. This is ensured by a landfill design that enhances natural sealing and buffering of leachate pH by a soil layer.

There is a wide body of literature supporting the relevance of the processes described above. Generally speaking neutral pH levels, slightly reduced conditions combined with low DOC levels (especially in the form of humic- and fulvic acids) tend to lead to relatively low emissions of metals and organic contaminants from any of the above-mentioned concepts.

Stabilisation of hazardous waste can be operated in various ways. Recipe development and control of a stable and sustainable end product is a main objective. Work by Ludwig et al. (6) and by Fitch and Cheeseman (7) on cement stabilised MSWI fly ash after preparation of large monolithic waste blocks has shown deterioration of the surface. In both studies substantial carbonation was noted. In the study by Baur et al. (8) and Fitch and Cheeseman (7) a very high pH in leachate was observed as would be expected for the highly alkaline matrix.

Carbonation is believed to be an important process resulting in the sealing of pores, this would imply a lower release of contaminants due to the reduced effective diffusion. Once there is a proper understanding of the major processes and their significance for the release of contaminants from such waste materials, the behaviour of a monofill can be predicted by geochemical/transport models.

2. Modelling approach

2.1 General

The aim of modelling is threefold (see also Figure 5):

- to provide a consistent framework that can integrate all relevant insights in physical, chemical and biochemical processes, obtained on a lab-scale, in lysimeter and in the pilots and understand their joint impact on long-term emissions;
- to provide a tool, which can be used to predict long-term concentrations of all pollutants in the leachate as a function of waste composition and method of waste treatment to identify the mechanisms that control emissions and evaluate the effect of control measures waste selection, enhanced biodegradation, immobilization, removal (flushing), solubility control.

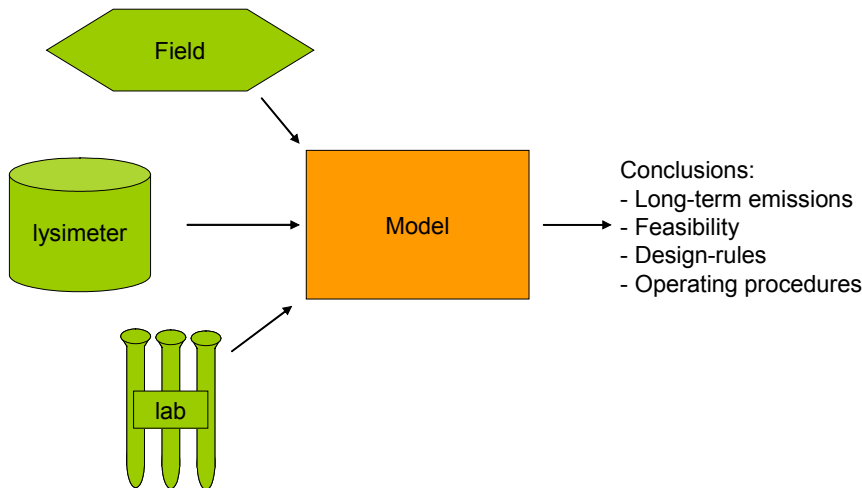


Figure 5 General approach of integration of laboratory, lysimeter and field-studies through modelling of (bio)chemical processes. Modelling allows conclusions to be drawn based on understanding of the processes leading to release.

For practical reasons, two separate models are made:

- one model for landfills in which the organic waste is not yet stabilised, where emissions are largely controlled by the biochemical processes;
- one model for stabilised waste, where emissions are controlled by geochemistry.

The figure below shows the applicability of models in relation to the development of leachate concentrations as depicted before in Figure 6.

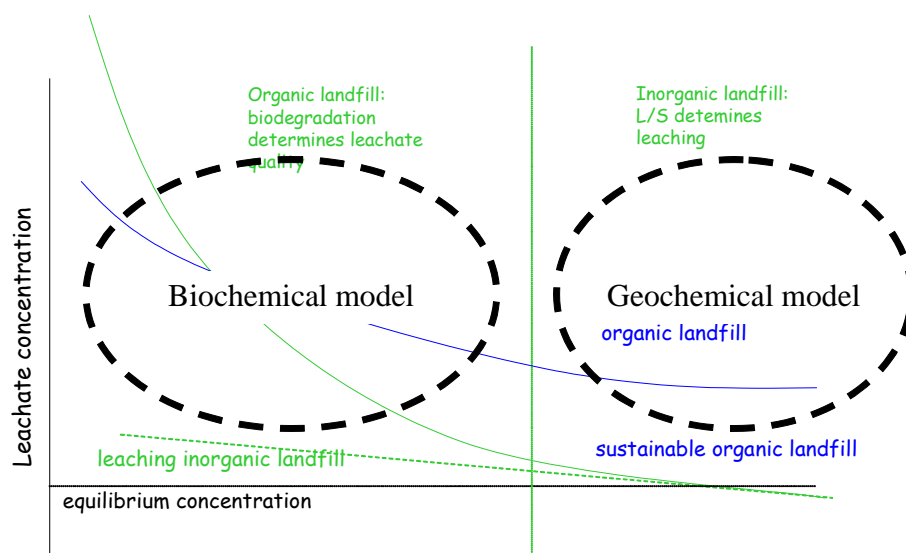


Figure 6 applicability of models to assess (bio)chemical processes in landfills. Both models will be described in this report.

2.2 Approach towards modelling landfill processes in wastes containing unstabilised organic matter

Modelling the processes occurring in landfills that influence the leaching of contaminants requires us to take a large number of chemical, biochemical and transport phenomena in to account:

- 4 *biochemical conversion* of organic materials into dissolved organic materials and the subsequent formation of fatty acids, N_{Kj} and biogas;
- 5 *physical chemical speciation* solution and precipitation of metals, anions and salts; adsorption of components
- 6 *transport of liquids* through pores in the waste
- 7 *transport of gases* that are formed through pores in the waste
- 8 *generation and transport of heat* that is generated as a result of aerobic and anaerobic conversions within the waste;

The objective of the modelling activities within the framework of this study is to predict (i) the pollution potential from the landfill on a long-term to extreme long terms (from decades after deposition of the waste to infinity) and (ii) the effects of measures defined in this study on this pollution potential. This is a very specific objective of modelling, that allows us to significantly simplify processes, compared to landfill models that are developed elsewhere for more general purposes.

The approach used and developed in this project is based on the integration of only the first three sub-models listed above. (1) Biochemical conversion, (2) physical chemical speciation, and (3) transport of liquids are combined to give predictions of the concentrations of organic components, N_{Kj} and all major and minor elements in time. Also sub-models are simplified. E.g. the organic components in the model are divided into three classes: humic acids, fulvic acids, and fatty acids. Of course in reality things are much more complicated, but for the prediction of levels of BOD, COD and trace metals in the leachate on longer terms, more detail is not required. The modelling approach is represented in Figure 7.

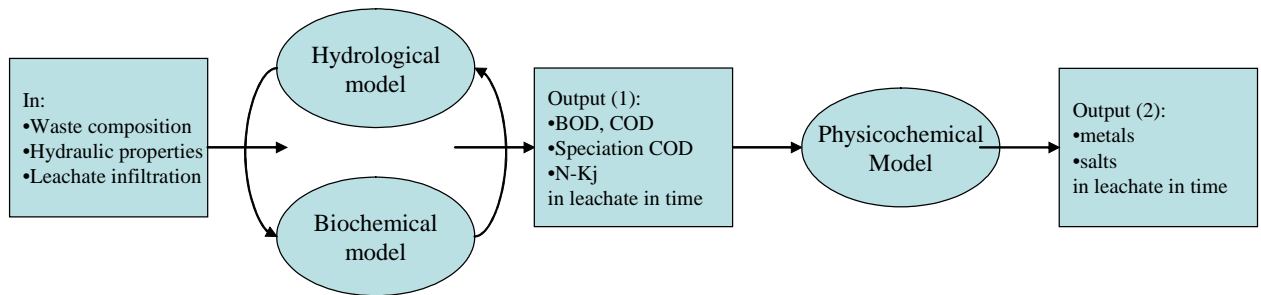


Figure 7 Overview of modelling approach to describe biochemical processes in landfills.

Two of the phenomena listed above are not taken into account, since they are either considered of minor importance, or their effect can be simplified and taken into account in an alternative way:

(4) Gas transport is not taken into consideration. It only occurs in the first years and does not have influence on hydraulics on longer terms. The main effect of gas transport in the initial phases is a reduced hydraulic permeability of the waste, since gas-filled pores are not available for liquid transport and thus reduce the effective porosity. The effect of gas-transport can be taken into account by assuming a reduced hydraulic permeability in the first years after depositing waste. (5) Generation and transport of heat is not modelled as well, since under anaerobic conditions, only little heat is produced, so its effect is small. The only effect it has is on the rate of bioconversions and also this can be neglected for two reasons: (a) its impact is small compared to e.g. the impact of leachate recirculation; (b) the speed of bioconversion (within limits) proves not to be a major governing factor for long-term leaching behaviour of the landfill. The latter assumption is proved further on by the results from the modelling.

2.3 Geochemical release modelling from stabilised waste

The geochemical modelling framework ORCHESTRA (9), which uses an extended MINTEQA2 database with thermodynamic constants for inorganic reactions, was coupled to a database/expert system (LeachXS) (2) containing the pH dependent leach test data, the tank test data, pilot and field leachate data. The database/expert system LeachXS was developed in cooperation with van der Bilt University (USA) and DHI (Denmark) and was used in this study to allow quick data retrieval, processing and presentation.

The generalized two-layer model of Dzombak and Morel (10) was used to take complexation to iron (hydr)oxide surfaces into account. The amount of amorphous iron/aluminium (hydr)oxides in the waste mixture was estimated based on results from comparable cementitious materials. An overview of the procedures to measure Fe/Al(hydr)oxides is given in (11). DOC was used as the input for humic acid in the NICA-Donnan model (12) and might be quantified according to (13). The maximum leachable concentration (i.e. the amount available for leaching) was estimated for each element by taking the maximum concentration leached in the pH-static leach test on crushed waste. This value was used as input for the model, which predicted the leached concentrations as a function of pH and the chemical speciation in both the leachate and the solid waste matrix.

The first step in the model calculations is to identify relevant solubility controlling mineral phases from pH dependent leaching test data from size-reduced samples. With the minerals identified through this process, the reactive organic matter, reactive Fe/al-oxides and the element availability for leaching as input parameters, the release was modelled. The leached

concentrations as a function of pH and the release from a monolithic waste material were predicted.

For the latter, the optimised input data from the pH dependence test were used. In addition, the porosity and the tortuosity of the product were estimated to be 30% and 1.75 respectively. The suitability of these values can be verified by comparing the calculated and measured release of relatively non-reactive components such as K, Na and Cl.

2.4 Estimation of model parameters

The quantities of “reactive” organic carbon in the solid and the solution phase (i.e. HA and FA) were estimated by a batch procedure (13), which is derived from the procedure currently recommended by the International Humic Substances Society (IHHS) for solid samples (14) and liquid samples (15), respectively. In short, the procedure is based on the solubility behaviour of HA (flocculation at $\text{pH} < 1$) and the adsorption of FA to a polymer resin (DAX-8). The amount of amorphous and crystalline iron (hydr)oxides in the waste mixture was estimated by a dithionite extraction described in Kostka and Luther III (16). The amount of amorphous aluminum (hydr)oxides were estimated by an oxalate extraction according to Blakemore (17). The extracted amounts of Fe and Al were summed and used as a surrogate for hydrous ferric oxides (HFO) in the model.

2.5 Geochemical speciation and release modelling

Chemical speciation of the solutions was calculated with the ORCHESTRA modelling framework (9). Aqueous speciation reactions and selected mineral precipitates were taken from the MINTEQA2 database. Ion adsorption onto organic matter was calculated with the NICA-Donnan model (12), with the generic adsorption reactions as published by Milne et al. (18). Adsorption of ions onto iron and aluminium oxides was modelled according to the generalized two layer model of Dzombak and Morel (10).

The database/expert system LeachXS (see chapter 0) was used for data storage, e.g. pH dependent leaching data, percolation test data, lysimeter and field leachate data and for visualization of the calculated and measured results (19,20). The coupled LEACHXS - ORCHESTRA combination allowed for very quick data retrieval, automatic input generation for modelling, processing of calculated results and data presentation.

The input to the model consisting of metal availabilities, selected possible solubility controlling minerals, active Fe- and Al-oxide sites (Fe- and Al-oxides were summed and used as input for HFO as described in (21)), particulate organic matter and a description of the DOC concentration as a function of pH (

Table 3). Basically, the speciation of all elements is calculated in one problem definition in the model with the same parameter settings. This limits the degrees of freedom in selecting parameter settings considerable, as improvement of the model description for one element may deteriorate the outcome for other elements. As a starting point for the model calculations, the maximum value as obtained in the pH dependence leaching test (between pH 3 and 13) was used as the available concentration. This proved not to be adequate for Al, Pb and carbonate, so these values were adjusted to ensure sufficient calcite precipitation to match the measurements, sufficient binding of oxyanions in Pb containing minerals and to ensure a proper balance between the major elements Si, Ca and Al. Earlier work also confirmed that

estimation of the availability at pH 2, 4 or 13 might not be adequate for geochemical modelling purposes (11,22).

The mineral phases that were allowed to precipitate were selected after calculation of their respective Saturation Indices (SI) in the original pH dependence leaching test eluates. Saturation indices were calculated for all >650 minerals in the thermodynamic database and a selection of the most likely and relevant phases was made based on the degree of fit over a wider pH range and the closeness of the SI value to 0. Generally, minerals were selected if the SI was in the range of -2 to 2 for more than two data points.

Based on the adequate geochemical model descriptions of the pH dependent leaching data, the chemical speciation in both the solid phase and the leachates can be calculated. Detailed insight in the binding processes (solid phase speciation) and leaching processes (leachate speciation) reveal the important mechanisms leading to release of contaminants.

2.6 Modelling hydrology

Transport of pollutants through the waste is modelled as a cascade of ideally stirred tanks. The general system is described in the figure below. It consists of three zones:

- a stagnant bulk in which no convection takes place
- a mobile zone, with only slow convective transport
- sharp preferential channels through which large part of liquid flow takes place.

Mass transfer between phases takes place through diffusion, possibly accelerated e.g. by micro-turbulences as a result of intermitting waster transport.

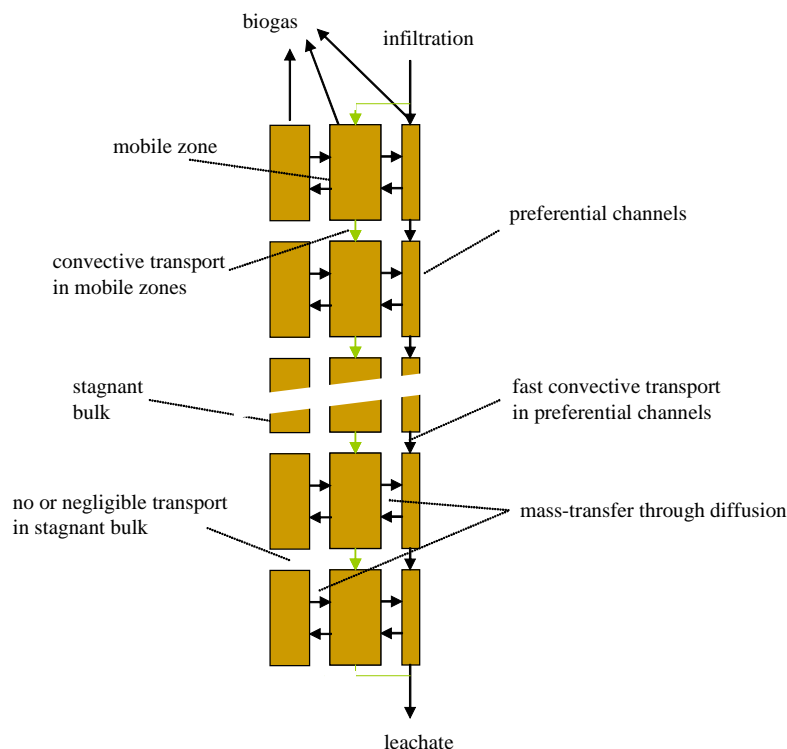


Figure 8 Description of the hydrology in a landfill

With respect to water balance, the landfill is considered to be in a steady state. So for each compartment the amount of water added to the cell equals the amount of water coming out

and accumulation or drainage is zero. This assumption makes calculations much more easy and is justified when the water balance is considered on longer terms (years to decades). This also implies that the model does not accurately describe the effect of large variations in water supply on shorter terms, e.g. weeks or months.

When the water balance is in steady state, the material balance for each component in the n^{th} stirred tank reactor in the stagnant bulk ($C_{s,n}$), the mobile phase ($C_{m,n}$) and the preferential channels ($C_{p,n}$) can be calculated from convection and diffusion:

$$dC_{s,n}/dt = (-k_l A_{s,m} (C_{s,n} - C_{m,n})) / V_s$$

$$dC_{m,n}/dt = (\phi_m (C_{m,n-1} - C_{m,n}) + k_l A_{s,m} (C_{s,n} - C_{m,n}) - k_l A_{m,p} (C_{m,n} - C_{p,n})) / V_m$$

$$dC_{p,n}/dt = (\phi_p (C_{p,n-1} - C_{p,n}) + k_l A_{m,p} (C_{m,n} - C_{p,n})) / V_p$$

The amount of tank-reactors (n) used to model the various phases can be used for retention time distribution determination, describing any situation in between a ideal stirred tank reactor ($n=1$) and plug-flow ($n=\infty$) (23).

2.7 Modelling biochemistry

2.7.1 General

Within landfills with substantial amounts of organic carbon, the amounts of BOD, COD and N_{kj} in the leachate are of major importance. Ultimately BOD and COD in the landfill leachate have to meet certain criteria. Although no leaching limit values are defined for N_{kj} in the EU-landfill directive (24), N_{kj} is a component of importance because of the potential environmental impact and can not be ignored in this project. The second reason is that COD correlates with DOC (dissolved organic carbon). High levels of DOC lead to increased concentrations of heavy metals in leachate due to complexation. In order to meet criterions for heavy metal concentrations in leachate, DOC has to meet certain criteria as well.

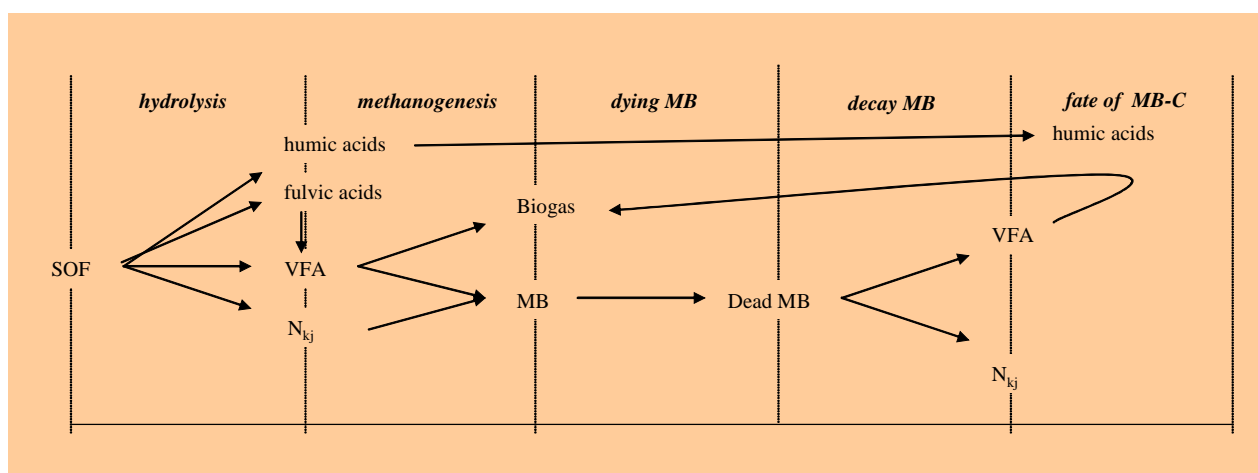


Figure 9 Description of biochemical processes in a landfill.

In order to understand how biochemical degradation influences the leaching of organic components and N_{kj} , a model is developed based on an elaboration of the reaction scheme

proposed by McDougal and Philp (25). In this reaction scheme, several steps are distinguished:

- Hydrolysis: the solid organic fraction (SOF) is broken down to a complex mixture of organic and inorganic components, that on their turn will be converted into other (smaller) dissolved organic components. In this model, the speciation of components will be limited to three classes: fulvic acids, humic acids and volatile fatty acids (VFA), in order to serve as an input in the physicochemical model;
- Methanogenesis: Ultimately VFA will be converted further into biogas. Upon generation of biogas, methanogenic biomass (MB) is being formed: the bacteria responsible for production of biogas;
- Death of methanogenic biomass,
- Decay of dead biomass, releasing N_{kj} again and some amount of organic carbon and conversion of the organic carbon as released by the dying methanogenic biomass.

2.7.2 Hydrolysis

a) Rate of hydrolysis

McDougal and Philp (25) describes the rate of hydrolysis, r_h (consumption of SOF) as:

$$r_h = \theta_E P r_{h,m} \phi$$

in which θ_E describes the influence of moisture content through

$$\theta_E = (\theta - \theta_R) / (\theta_S - \theta_R)$$

and P describes product inhibition through

$$P = \exp(-k_{VFA} C_{VFA})$$

$r_{h,m}$ is the maximum rate of hydrolysis and ϕ describes the slow-down of hydrolysis during its progress:

$$\phi = 1 - ((C_0 - C) / C_0)^n$$

b) Product formation upon hydrolysis

N_{kj} -formation is obtained from the product of the rate of hydrolysis and the N-content of the waste or the C/N-ratio of the waste.

$$r_N = r_h * N_{waste}$$

$$N_{waste} = 0.45 / (C/N)$$

Fulvic acid, humic acid and VFA -formation are calculated as

$$r_{FA} = r_h (B_{FA}) (1 - N_{waste})$$

$$r_{HA} = r_h (B_{HA}) (1 - N_{waste})$$

$$r_{VFA} = r_h (1 - B_{FA} - B_{HA}) (1 - N_{waste})$$

2.7.3 Determining reaction rate constants from landfill gas formation models

Since most of the hydrolysed material is converted landfill gas, and since methanogenesis is fast compared to hydrolysis, the hold-up of organic material in the water phase will be small and the rate of hydrolysis equals the rate of landfill gas production. So existing relations for landfill gas production might also be used to describe hydrolysis, e.g. a first order model (26):

$$A = A_0 \phi; \phi = e^{-kt}$$

Equations 1 and 2 have one thing in common. They both consist of an initial or maximum rate (b and A_0 , resp.) and a term that describes the slow down of the speed of reaction upon progress of decay: ϕ . So it is interesting to compare both approaches. This is done in Figure 10.

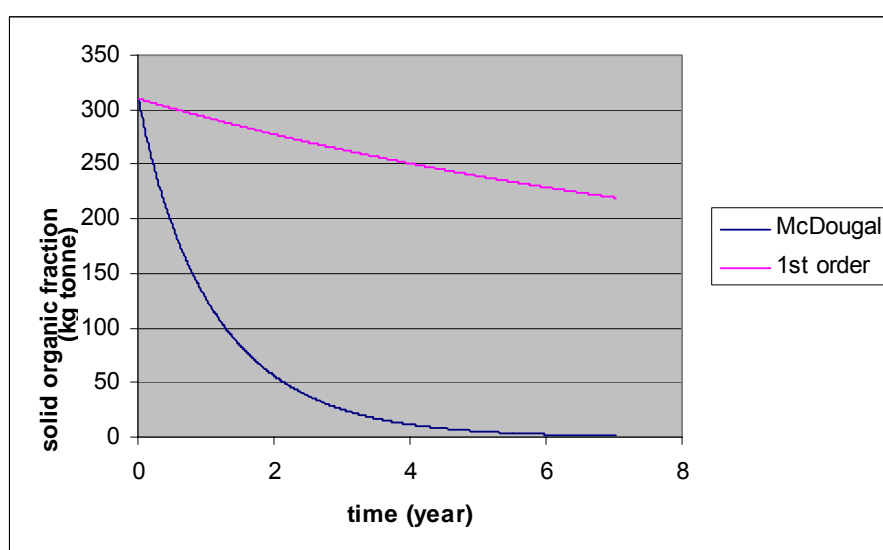


Figure 10 Comparison between the McDougal and Philp model and the multi-phase model

There is quite a difference between the McDougal and Philp model (25) and the first-order decay model. Closer evaluation proves that the differences are caused by:

- the assumption of only 58 % of the organic material is hydrolysed and converted to landfill gas in the first-order model, where McDougal and Philp assume all organic material to be converted;
- a high maximum rate of hydrolysis, which boils down to about 15 times the initial rate of landfill gas production in the first order model;
- the factor n introduces in McDougals equation (25), which introduces a multi-phase character in the model: when $n=1$, the equation boils down to a multi-phase model, with n getting smaller, initial gas production is increased and gas production after some time is retarded (similar to what happens in a multi-phase model).

Also in other literature, high rates for hydrolysis are proposed, comparable to the ones proposed by McDougal and Philp (25), e.g. Reichel et al. (27). These rates of hydrolysis most likely are based on lab-scale experiments where conditions for hydrolysis are much more favourable than in real-scale landfills. There is some discussion on amount and speed of landfill gas formation; however there is agreement on the amount of organic material converted

to landfill gas (dissimilation) being between 50-70% and half-times of biodegradation being about 3-30 years, depending on the nature of the material.

In this model the hydrolysis of McDougals is used; however based on landfill gas models, a dissimilation factor is introduced of about 58% and the maximum rate of hydrolysis is reduced with about a factor 15, thus making the model match existing models for landfill gas formation (see Figure 11).

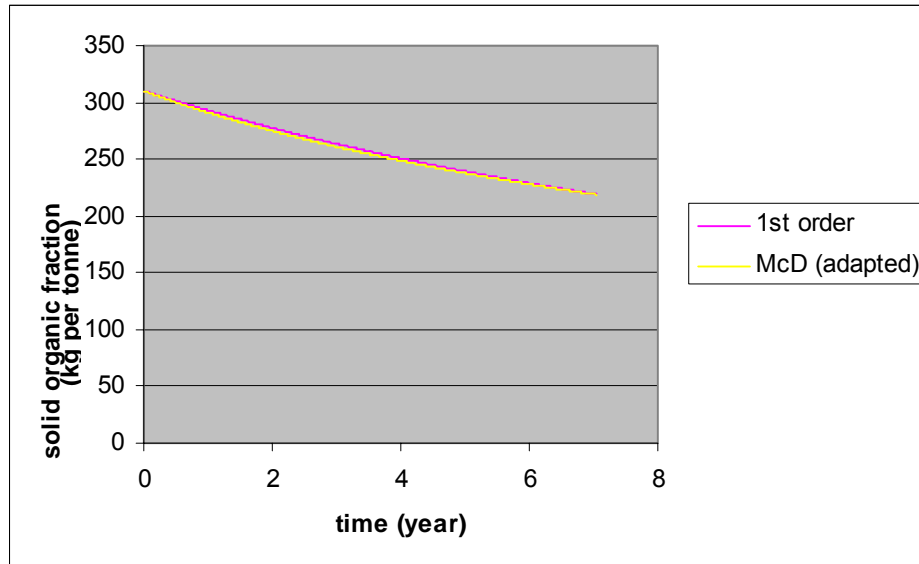


Figure 11 Description of adapted hydrolysis of McDougal and Philp.

McDougals description of hydrolysis, instead of use of the first order decay model, since McDougals model in principle describes two out of three mechanisms for enhancement of hydrolysis through leachate infiltration:

- an increased water content, thus increasing the medium in which bacteria consume the solid organic fraction;
- reduction of the VFA-inhibition;

However, leachate recirculation does also influence hydrolysis through supply of enzymes, bacteria and nutrients. There are two ways of doing this:

- using the current equation for VFA-inhibition, but lowering the threshold value, above which inhibition takes place, this increasing the effect of leachate recirculation;
- (in a multi-cell-model) incorporating a factor that increases maximum rate of hydrolysis, when neighbouring cells are more active and when there is interaction between cells through leachate movement.

At the moment, the first option is chosen. The second option is clearly more realistic and might be introduced in a future improvement of the model.

Conversion of fulvic acids to VFA:

The rate of fulvic acid-conversion to VFA is given by

$$R_{FA} = -k_{FA} * C_{FA}$$

Methanogenesis:

Methanogenesis through Monod kinetics, in which the growth of biomass (r_j) is given by

$$r_j = k_0 C_{VFA} N_{kj} m (k_s + C_{VFA}) * (k_{s,N} + N_{kj})$$

This equation differs from the equation used elsewhere (e.g. (25)) since it also has a term that describes nitrogen limitation. This is important for bioreactor modelling since due to high flushing rates or recirculation of nitrified leachate N_{kj} can reach low values and become rate-limiting

The biogas production (r_h) is given by

$$r_h = r_j / Y$$

Dying of biomass:

Dying of biomass (r_k) during and after methanogenesis is obtained from

$$r_k = k_2 m$$

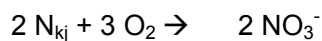
Decay of biomass:

Decay of dead biomass can be described from

$$r_d = k_3 dm$$

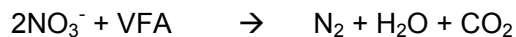
2.7.4 External nitrification of leachate and recirculation of nitrified leachate

Sometimes nitrification of leachate in a separate nitrifying reactor and recirculation of nitrified leachate is proposed as an option to reduce N_{kj} -levels in the bioreactor. External nitrification is described by:



where the performance of the nitrifying reactor is described by the concentration of N_{kj} in the effluent: $N_{kj,e}$.

Denitrification takes place in the waste body itself in a reaction with VFA



Denitrification is assumed to take place instantaneously

2.7.5 Open ends

Effect of leachate recirculation

Leachate recirculation and description of its effect is at the basis of the project sustainable landfilling, so we have to pay attention to the way we model impacts of leachate infiltration. The effect of leachate recirculation in the current model of John McDougall might not suffice. It is based on a relationship of degradation with water content, in combination with VFA-inhibition. According to e.g. Klink and Ham (28), moisture content does not govern the rate of decay, *but moisture movement does*. And moisture movement does not only take away inhibiting components (as VFA) but also brings methanogens and nutrients to parts that are

inactive so far. So we might be forced to come up with a model describing the impact of leachate recirculation on methanogenesis as a function of:

- water content;
- reduction of concentration of inhibitors;
- stimulation of methanogenesis through interaction with neighbouring methanogenic zones.

In this respect the elemental approach of Dach and Jager (29) might be interesting, this describes decay per element by a random chosen lag-time before on-set of hydrolysis, followed by a relative fast degradation of this element. This approach might be used, assuming that the lag-time is shortened in case of (i) neighbouring cells where reactions do take place; (ii) interaction between the cells due to moisture movement.

N_{kj} and inorganic NH₃-salts

Inorganic sources might be a buffer for N_{kj}, delaying its release. We have to find an answer to the question whether this might be important. According to Beaven and Walker (30), formation and dissolution of MgNH₄PO₄ does not take place. He doesn't find a decrease in dissolved Mg in the leachate, where N_{kj} does reduce significantly due to the formation of methanogenic biomass.

2.8 Nomenclature and suggested values

	Kinetics	Selectivity
hydrolysis	McDougall and Philp (25) propose overall kinetics; Dach and Jager (29) propose an interesting approach to decay, based on finite elements and stochastic change of start of hydrolysis. Overall rate of hydrolysis equals rate of gas formation and is described by Oonk et al. (26).	Selectivity as amount of BOD, nBOD and N _{kj} formed, throughout stabilisation process might be obtained from column experiments of Beaven and Walker (30) under acetogenic and methanogenic conditions.
methanogenesis	By McDougall and Philp (25); from experiences in anaerobic digestion.	Amount of MB formed by McDougall and Philp (25); N _{kj} -uptake from Beaven and Walker (30).
dying MB Fate of MB-C	From McDougall and Philp (25)	N _{kj} -release from Beaven et al. (1997) Most likely being metabolised (according to Beaven and Walker, (30))

Parameter	Description	Dimension ¹⁾	Suggested value ²⁾	Reference
B _{fulvic}	Fraction of SOF converted to fulvic acids	-/-	0,02	
B _{humic}	Fraction of SOF converted to humic acids	-/-	0,02	
C _{s,n}	Concentration of a component in the nth element of the stagnant phase	g/m ³	result of model calculations	
C _{m,n}	Concentration of a component in the nth element of the mobile phase	g/m ³	result of model calculations	

Parameter	Description	Dimension ¹⁾	Suggested value ²⁾	Reference
$C_{p,n}$	Concentration of a component in the nth element of the preferential channel	g/m^3	result of model calculations	
C_{FA}	Liquid phase concentration of fulvic acids	g/m^3	result of model calculations	
C_{HA}	Liquid phase concentration of humic acids	g/m^3	result of model calculations	
$C_{N_{kj}}$	Liquid phase concentration of N_{kj}	g/m^3	result of model calculations	
C_{VFA}	Liquid phase concentration of VFA	g/m^3	result of model calculations	
C_0	Initial content of biodegradable organic dry material in waste	kg/tonne	~70	
C	Actual content of biodegradable organic dry material in the waste	kg/tonne	result of model calculations	
dm	Dead methanogenic biomass	kg/tonne	result of model calculations	
k_0	Maximum growth rate of methanogenesis	y^{-1}	10	McDougal, 2001
k_2	Rate constant of biomass dying	y^{-1}	0.2	McDougal, 2001
k_3	Rate constant of dead biomass decay	y^{-1}	$\ll 0.1$	
k_s	Half saturation constant of methanogenesis	$g\ m^{-3}$	20.000	McDougal, 2001
$k_l A_{s,m}$	Mass transfer coefficient between stagnant and mobile phase	m^3/jr	10-100	Beaven, 2005
$k_l A_{m,p}$	Mass transfer coefficient between mobile phase and preferential channel	m^3/jr	10-100	Beaven, 2005
m	Methanogenic biomass	g/m^3	result of model calculations	
n	Structural transformation parameter	-/-	0.7	McDougal, 2001
N_{mb}	N-content of the methanogenic biomass	-/-	0.1	
N_{waste}	N-content of the dry organic matter	-/-	0.05	
P	Product inhibition of hydrolysis		result of model calculations	
r_{FA}	Rate of fulvic acid-production or removal	$g\ m^{-3}\ y^{-1}$	result of model calculations	
r_{HA}	Rate of humic acid-production or consumption	$g\ m^{-3}\ y^{-1}$	result of model calculations	
r_N	Rate of N_{kj} -production or consumption	$g\ m^{-3}\ y^{-1}$	result of model calculations	

Parameter	Description	Dimension ¹⁾	Suggested value ²⁾	Reference
r_{VFA}	Rate of VFA-production or consumption	$g\ m^{-3}\ y^{-1}$	result of model calculations	
r_d	decay rate of methanogenic biomass	$g\ m^{-3}\ y^{-1}$	result of model calculations	
r_h	Rate of hydrolysis	$g\ m^{-3}\ y^{-1}$	result of model calculations	
$r_{h,m}$	Maximum rate of hydrolysis	$g\ m^{-3}\ y^{-1}$	35.000	See above
r_j	Growth of Methanogenic biomass	$g\ m^{-3}\ y^{-1}$	result of model calculations	
r_h	Rate of methanogenesis production	$g\ m^{-3}\ y^{-1}$	result of model calculations	
r_k	Dying rate of methanogenic biomass	$g\ m^{-3}\ y^{-1}$	result of model calculations	
rN	Rate of N_{kj} production or consumption	$g\ m^{-3}\ y^{-1}$	result of model calculations	
t	time	year		
Y	Cell/substrate yieldcoefficient	-/-	0,2	
V_s	Liquid volume in the stagnant phase	m^3/m^3 bulk volume		
V_m	Liquid volume in the mobile phase	m^3/m^3 bulk volume		
V_p	Liquid volume in the preferential channel	m^3/m^3 bulk volume		
θ	Volumetric moisture content	-/-	not yet used	
θ_E	Moisture enhancement	-/-	result of model calculations	
θ_R	Residual moisture content (field capacity)	-/-		
θ_S	Saturated moisture content	-/-		
ϕ	Relative digestability	-/-	result of model calculations	
ϕ_m	Liquid flow through the mobile phase	$m^{-3}\ y^{-1}$		
ϕ_p	Liquid flow through the preferential channel	$m^{-3}\ y^{-1}$		

1) m^3 refers to m^3 of liquid phase

2) for parameters that are intermediate or final results of calculations, no value is suggested.

3. Development of database/expert system

3.1 Introduction

The expert system serves as a tool for research, environmental assessment, regulatory decision-making, material treatment evaluation and quality control based on understanding of the leaching behaviour of materials in the environment. The system was developed by researchers at The Energy research Center of the Netherlands, Vanderbilt University and DHI Water & Environment. During the sustainable landfill project, the database/expert system played a major role in comparison of data at different scales of testing and for geochemical modelling of chemical processes in landfills.

The global set-up of the expert system is given in Figure 12. It can be seen that the LeachXS program plays a central role in the system. The program can access several databases with information. The leach test data, lysimeter data and field data are stored in the materials leaching database. The re-use and disposal scenarios for waste materials are defined in the scenario database. This database contains information on dimensions of a landfill, infiltration regimes and liner performance. Finally, the regulatory database contains the limit values for national and European legislation on the re-use and disposal of waste materials.

LeachXS is also coupled to the chemical speciation and transport-modelling environment Orchestra. This allows leaching data to be transferred automatically to Orchestra for geochemical speciation calculations. Orchestra returns the results to LeachXS, where the data can be graphically represented and interpreted. The output of all actions in LeachXS can be exported to Excel spreadsheets for further processing in reports and publications.

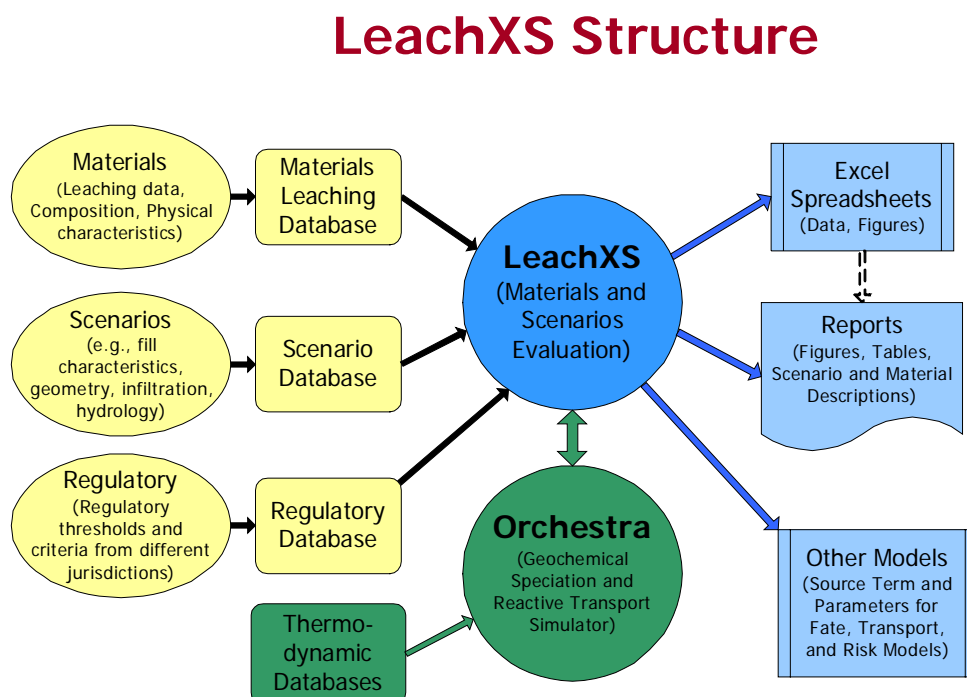


Figure 12 Schematic representation of Database/Expert system

The actual software currently consists of the following elements:

- Access database in unified data format with examples from public domain leaching tests and field studies for all relevant components of the data evaluation system.
- Database management tool for (leaching) data import in Access database
- Expert system LeachXS for data retrieval, processing, and graphical presentation and tabular presentation in Word or Excel format
- Granular material test data
- Monolithic material test data
- Field leachate
- Total composition
- Other (such as degradation or radioactive decay)
- Orchestra: Java based code for chemical speciation/transport modeling

Materials considered as part of the system include but are not limited to wastes, secondary materials, construction materials, contaminated soils, water treatment sludges, and sediments. The expert system can be used to evaluate waste management options, site-specific contaminant release scenarios, environmental impact of construction materials, land-application of sludges, waste treatment processes, and to define quality control criteria. The expert system includes selection and definition of testing protocols, integrated data management, quality control procedures, geochemical speciation evaluation, source term models to estimate potential future constituent release under various environmental conditions and management scenarios, environmental risk characterization, uncertainty analysis, and a reference database of leaching characteristics for previously evaluated materials. The expert system will be able to integrate laboratory and field data of various types and origins. The expert system is intended to make best-practices decision-making widely accessible.

3.1.1 Functionality of database/expert system

The expert system will be comprised of software components (Figure 12) that provide facilities, testing protocols and guidance in the following areas:

- 1 **Problem Definition and Test Selection** - Guidance on problem definition; selection of characterization needs and methods, detailed methodologies; existing information on characteristics and behaviour of similar materials; citations.
- 2 **Data Collection and Management** - Guidance on laboratory, lysimeter and field data collection (including experimental design and quality control considerations); data management, formatting and graphical presentation, (including consistency and quality control checking); existing information from similar pilot and field evaluations; citations.
- 3 **Management Scenario Description** – Development of detailed description of potential management scenarios or beneficial materials use scenarios; site-specific information (including material configuration, site geometry and topography, infiltration rates, climate); design specifications.
- 4 **Material Properties**– Guidance on test methods for obtaining material-specific properties; data management facilities.
- 5 **Direct data evaluation, parameter derivation and comparative data sets for**
 - a **pH and L/S Ratio Dependence** – evaluation of aqueous concentrations from batch testing (including cations, anions, reduction/oxidation potential, EC, DOC, ionic strength); geochemical speciation; acid/base neutralization capacity (ANC/BNC); leaching potential (availability).

- b **Release With Time – Percolation Release** – granular materials and monolithic materials from sequential data sets (including L/S ratio or time from column testing or lysimeter testing); associated geochemical speciation; mass transfer parameter estimation. This mode of release differs from surface related release.
- c **Release With Time – Surface Related Release** - granular materials and monolithic materials from sequential data sets (including tank leach testing of monolithic and compacted granular materials); associated geochemical speciation; mass transfer parameter estimation.
- 6 **Source Term Description** - Development of a source term description that would estimate constituent release as a function of time for default or user defined use or management scenarios. This would include selection of appropriate source term models, evaluation of the effects of potential external stresses (e.g., waste mixtures, carbonation, oxidation, reduction, acidification) and uncertainty analysis.
- 7 **Impact Evaluation** – Assessment of potential impacts to sub-soils or groundwater; risk characterization.
- 8 **Judgment and Decision-Making** - Algorithms for comparing evaluation results and decision-making based on regulatory criteria from different jurisdictions; recommendations on reduced-testing quality control programs, approaches to reduce constituent release, development of remediation end-points, and long-term stewardship requirements.

Inherent in the system would be components that would be distributed to system users (e.g., problem definition and methods guidance) and components that would be resident in centralized servers (e.g., database of related physical, chemical and leaching characterization information from other materials).

3.1.2 Materials included in the leaching database

Data from landfill percolate water and groundwater was converted and stored in the database for the sustainable landfill project. Currently, information from about 70 different waste compartments from European landfills is stored. Groundwater data from about 300 monitoring wells is available in the database. Moreover, the data generated in this project from laboratory, lysimeter and field studies was converted and imported in the database. The total database with leaching data also contains information on: soil, contaminated soil, sediment, sludge, compost, waste, mining waste, stabilized waste, industrial slag, metals, construction products, asphalt, road construction materials, preserved wood, aggregates, alternative materials used in road construction.

ANNEX A provides a list of materials for which this system would be applicable and for which database information is already available.

3.1.3 Chemical elements and compounds in leaching database

Inorganic - all elements of the periodic system - major , minor and trace constituents

Organic - all organic contaminants - VOC, water soluble compounds, hydrophobic compounds.

Radionuclides - all natural occurring radionuclides as a result of concentrating in a process

For modelling geochemical speciation it is of great relevance to have major and minor element composition data, as these elements dictate the behaviour of trace constituents.

3.1.4 Test types

The system has been designed to take any type of leaching test data ranging from pH dependence leaching test, percolation and tank test to TCLP, SCE, CaCl₂ extraction, etc.. In addition it can take leachate data from lysimeter studies, field leachate data, data from large-scale pilot studies. Total composition data, physical properties of material, etc.

3.1.5 Management scenarios

Table 1 provides a list of waste management scenarios for which the system would be applicable. Moreover, scenarios for the beneficial use of materials can be implemented in the system. This enables a uniform way of environmental risk assessment based on understanding of chemical processes in materials.

Table 1 *List of Potential Management Scenarios in LeachXS*

Management Scenarios
Landfill (with/without leachate control)
Stabilised waste monofill
Bioreactor landfill
Contaminated site evaluation
Mining waste landfill (acid mine drainage)
Dredge spoil disposal
Biodegradation of organic waste
Treatment of waste evaluation
Evaluation of mixed waste behaviour

3.2 Characterisation, quality control and judging treatment methods

Figure 13 shows the central role of waste material characterisation in facilitating regulatory criteria development, and its link to quality control of materials through compliance testing and to verification of product improvement. Characterisation tests provide a basis of reference for a material or material class, as materials produced to a certain specification generally have similar mechanical, physical and chemical properties. Once the properties of a material or material class have been established, only limited testing is required to demonstrate that the material being tested falls within the expected range for that material type. For easy reference, such information should be readily accessible through a database capable of handling all relevant data. With this type of database available, well-characterised materials will not require repeated characterisation in each of the EU member States.

Waste acceptance criteria such as specified in the EU landfill directive ((24)) are based on test results from individual waste materials. However, it is unclear whether these results have any significance with regard to the final behaviour and emissions of a complete landfill. In earlier work (20) laboratory tests were performed with relatively small additions (up to 10%) of contaminated (or alkaline) waste materials to a stable (neutral pH, low organic carbon content) waste material (mix of sludge, soil remediation sludge and construction and demolition waste). We have shown that relatively small additions (up to 10%) of contaminated waste materials do not significantly disturb the leaching behaviour of the total waste mix. This approach provides a means of gaining more understanding and subsequently more control over the long-term

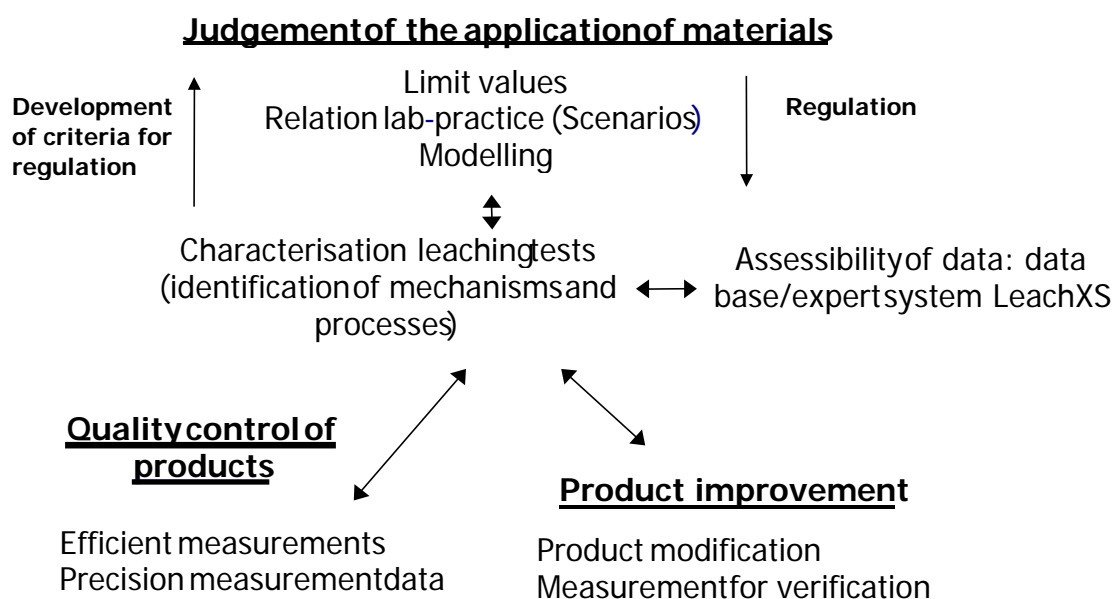


Figure 13 Role of characterisation leaching tests in environmental judgement of materials.

release of inorganic contaminants and identification of possible long-term processes that can disturb the biogeochemical equilibrium of the sustainable landfill.

Better understanding of interactions between contaminants and reactive surfaces in waste materials (e.g. natural organic matter, clay and iron/aluminium oxides) is of crucial importance for environmental risk assessment. Over recent years this understanding has significantly improved, resulting in multi-component interaction models for ion adsorption onto iron/aluminium oxides and natural organic matter (humic- and fulvic acid). These models have been successfully applied to describe the speciation of metals in soils (11,31) and waste materials (32). These models were implemented within the modelling framework ORCHESTRA (9).

The long-term leaching behaviour of a landfill is strongly affected by the macro-chemistry, which is currently largely ignored in monitoring of leachate. At the start of the project additional parameters have been identified that needed to be measured to enable chemical speciation modelling in order to understand the chemical processes in the landfill leading to a release of contaminants. A major challenge is to develop means to predict the long-term leachate quality based on geochemical reaction transport modelling, taking into account the geochemistry as well as preferential flow aspects which are occurring in landfills.

Understanding the physical/chemical processes in a landfill allows one to predict the long-term emissions. Moreover, geochemical modelling can point out important contaminant sequestration processes. Once these are identified, it is feasible that landfill managers can control the amount of reactive surfaces (iron/aluminium oxides and stabilised solid organic matter) and the potential leachable amount of contaminants in order to ensure good environmental behaviour of the waste body. The anticipated outcome is a disposal practice through new waste acceptance strategies that will reduce the contaminant emissions to acceptable levels on the long-term. Prediction of the long-term leaching behaviour of a landfill is particularly relevant for judging the need for aftercare.

In this paper, geochemical speciation modelling is used to determine important chemical processes that determine the release of contaminants from waste materials in short and long term. Moreover, model calculations are performed to show the sensitivity of the waste mixture to changes in the contaminant availability and binding capacity by changing the amounts of HFO and organic matter. It will be shown that in spite of the heterogeneity in waste going to landfill there is a scientific basis for more focused waste selection/acceptance criteria in order to reduce the environmental impact of landfills, thereby creating a landfill with minimal impact which in that way can be regarded as sustainable.

3.3 Test methods

In CEN/TC 292 (Characterisation of waste) test methods are in development for characterisation the leaching behaviour of granular and monolithic materials. For granular materials the characterisation methods consist of a pH dependence leaching test and a percolation test to assess respectively the sensitivity to chemical changes with time and the long term behaviour as the L/S can be related to a time scale through the infiltration rate. For monolithic materials the standardisation process is still ongoing. In recent studies, the combination of a pH dependent leaching test and a dynamic monolith leach test (type of tank test) has been identified as a suitable combination to derive the needed parameters for impact modelling. The pH dependent leaching test provides the necessary insight in the chemical speciation aspects, whereas the percolation test and the dynamic monolith leach test provide the time dependent release characteristics. The developed test methods are outlined in Figure 14. This approach has also been followed in the sustainable landfill pilot studies.

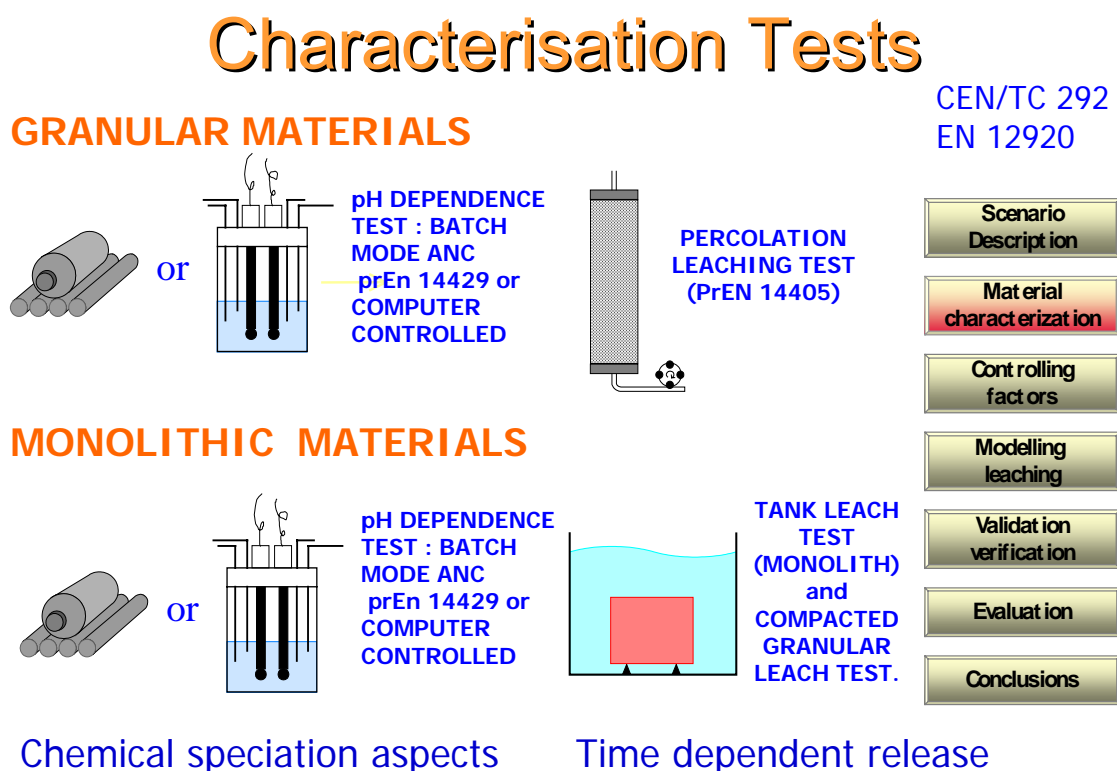


Figure 14 Outline of proposed test methods for material characterization of granular and monolithic materials

The main question to be answered is not providing a test result, but how the test result(s) can be used to answer the question. This implies an evaluation that requires more than just the leaching test. Kosson et al. (1) have designed an integrated framework to determine intrinsic waste leaching parameters in order to provide a sound basis for estimating contaminant release in a range of different waste management scenarios. This approach is an alternative to the simpler yet less appropriate approach of using too simple or inadequate tests that simulate contaminant release under specific environmental conditions, and then apply the outcomes to a diverse range of scenarios. The work in this study is consistent with the integrated framework as described by Kosson et al. (1) and with the methodology described in EN 12920 (2004). The integrated approach (EN 12920) takes the following aspects into account:

- Problem Definition and Management Scenario Description
- Test Selection, data collection and material properties
- Direct data evaluation, parameter derivation and comparative data sets for
 - * pH and L/S Ratio Dependence
 - * Release With Time – Percolation Release
 - * Release With Time – Surface Related Release
- Source Term Description and modelling Impact Evaluation
- Verification in field
- Judgment and Decision-Making

This shows how the different aspects are related and are all needed to come to a final judgement. A database/expert system forms the core of such a system. Such a system will provide a good reference base for already well-characterised materials, for which only limited testing of a limited set of parameters (defined through characterisation testing) against the reference information is generally sufficient.

The Toxicity Characterisation Leaching Protocol (TCLP) is an example of a too simple leaching test designed to simulate one specific environmental scenario (co-disposal of industrial waste with municipal solid waste), and thus has no relation to the conditions of a stabilised waste monofill. This leaching procedure is currently the test protocol for judgement of hazardous and non-hazardous waste in the United States despite the fact that it cannot be used for estimating the long-term behaviour of monolithic waste materials. Several studies have addressed the limitations of the TCLP (1,33-35).

The fundamental approach used to understand the complex system of cement-stabilised waste under environmental conditions starts with determining the intrinsic material characteristics by measuring contaminant release from the crushed material as a function of pH. In this work, the pH dependence leaching test was performed in accordance with TS 14429 (2005).

Depending on the material characteristics (granular or monolithic), the following leach tests were performed:

- The mass transfer rate is estimated by performing a tank-leach test according to the Dutch standard NEN 7375 on the intact monolithic material.
- The up-flow percolation test (PrEN 14405 (2003) was used for the judgement of the long-term release of granular waste materials.

Contaminant release is then evaluated for the appropriate field scenario, which also incorporates relevant external factors (such as carbonation, oxidation, hydrology and mineralogical changes). Once there is a proper understanding of the major processes controlling contaminant release from such waste materials, the behaviour of a landfill can be

predicted by geochemical and transport models. This gives more reliable estimates of the environmental impact in both the short- and long-term, which then allows regulatory criteria for stabilised waste to be established.

In view of the confusion resulting from the use of many different leach tests, and the observation that many tests compare well with a pH dependent leach test, a percolation test or a tank leach test, the need to harmonise leach tests and data presentation emerges (36). These three characterisation tests have been or are in the process of being standardised in CEN TC 292 (Characterisation of waste). Although developed for waste, the applicability of these methods to a wider range of materials (e.g. construction materials, treated wood, soil, sediment and sludge) has been demonstrated in several studies (36-38).

4. Results and discussion

4.1 Functionality of database/expert system

4.1.1 Data comparison of laboratory leaching tests

3.1 Laboratory leaching tests

Stabilised waste products, prepared according to each of the currently available recipes, have been characterised at least once by the pH dependent leach test and the tank leach test. The results for a few typical elements, namely Mo, Cd and Zn, are plotted in Figure 15 as examples. It can be seen that the concentration leached from waste stabilised using different recipes can vary by up to 2 orders of magnitude in both the pH dependent leaching test (in $\mu\text{g/L}$) and the tank leaching test (cumulative emission in mg/m^2). However, despite the variability between wastes stabilised using different recipes, which is dictated by the nature of the waste, the pH dependent leaching behaviour is rather systematic, which indicates that the factors controlling contaminant release from these residues is similar. Very similar release patterns of elements are also observed in the tank test for the different waste types. The differences in the extent of leaching in both the pH dependent leach test and the tank leach test are mainly due to differences in the amount of a contaminant that is available for leaching (i.e. the availability). In the tank leach test, product porosity and tortuosity also affects contaminant release, but these factors appear to be minimal compared to the chemical and hydrological aspects.

The shape of the emission curve characterises the release controlling mechanism. The upper grey line in Figure 15 has a slope of 0.5. When the emission curve follows this line diffusion is probably the mechanism controlling leaching; this can be seen for Mo and Zn. In the later stages of the tank leach test Zn emissions start to deviate from this line, which indicates either Zn depletion or a change in the conditions controlling release (e.g. pH change, redox change). Cd emissions behave similarly to Zn emissions, implying that Cd, too, becomes depleted in the later stages of the leach test. A few waste samples have an increased release of contaminants at the end of the tank leach test. The pH of these specific samples increased from 10.7 to 11.3 in the last two stages of the test; this could explain the increased Cd emissions in these fractions. The increase in pH is difficult to explain since the pH generally decreases during the test due to atmospheric carbonation. Possibly, cracking or deterioration of the sample has occurred in these leach tests.

Considering the variability in the extent of leaching between samples, the leaching patterns as a function of pH and time are remarkably consistent. This indicates that the processes controlling leaching in these materials are similar. Therefore, characterisation leach tests, in combination with geochemical speciation modelling, form the basis of evaluating release from landfill for various field scenarios.

This form of data representation and comparison of leach test results is greatly enhanced by data storage in a uniform data format. The subsequently developed expert system LeachXS enables the user to choose samples for data comparison and graphical representation as outlined in Figure 15.

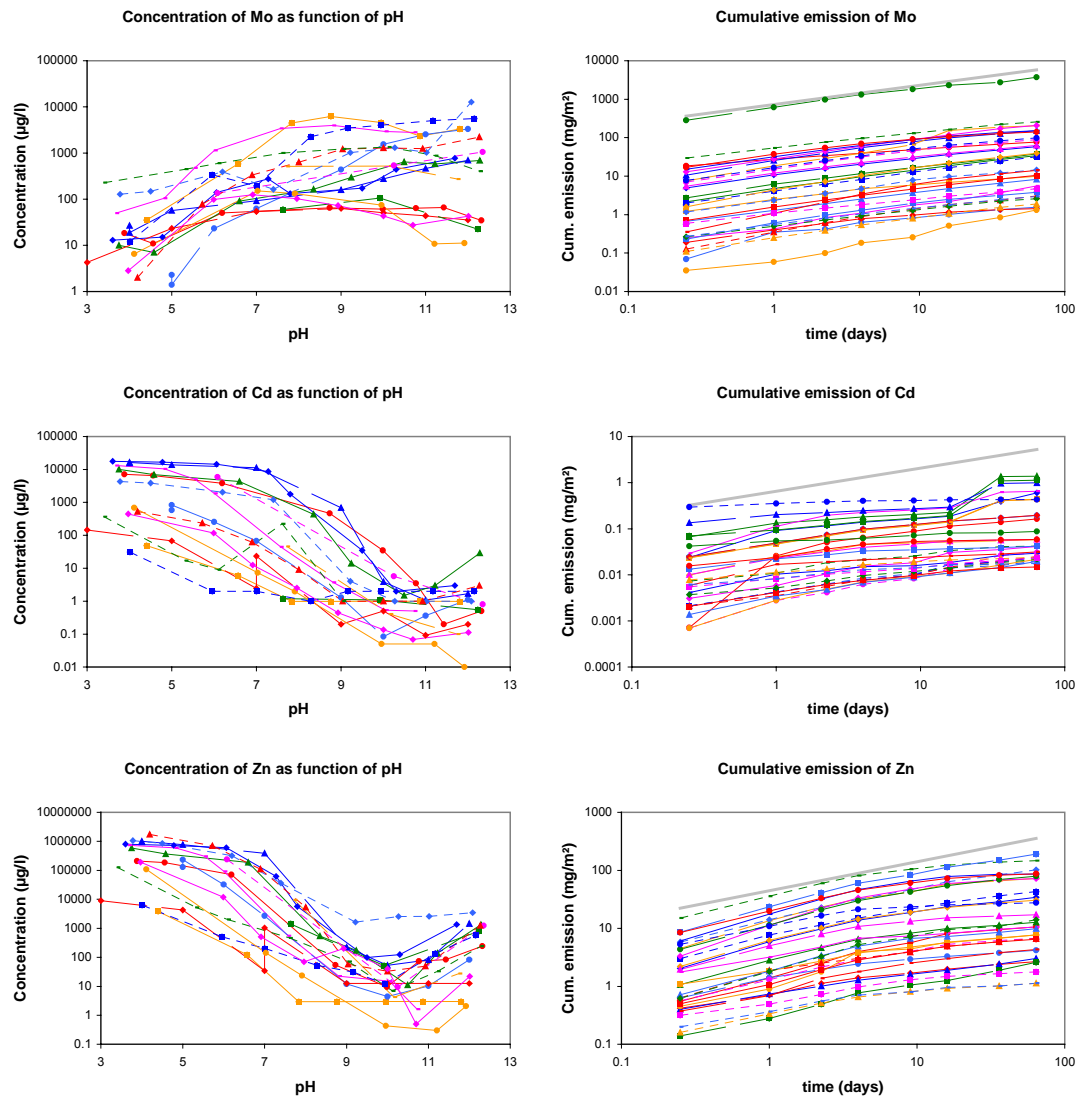


Figure 15 Results of the pH dependent and tank leach test on crushed stabilised waste and the intact material respectively.

4.1.2 Comparison of laboratory and field data

Increased Fe- concentrations in landfill leachates are commonly related to complexation with dissolved organic matter. At the same time, it is widely recognised that presumed reducing conditions in the system might increase the concentrations in solution as well. Low redox potential increases the solubility of Fe(hydr)oxides due to decreased mineral stability. Both processes of DOC- complexation and increased solubility due to redox conditions lead to the same effect, and therefore when only measured Fe- and DOC concentrations are available, conclusions are not easily made about the governing process of Fe- solubility. In this example we will show results from laboratory and field measurements and the capability of geochemical modelling to make the distinction between the importance of DOC complexation and reducing conditions on Fe solubility. We will illustrate this with an example for landfill leachates below.

Figure 16 shows an example of Fe- data as a function of pH, from landfills with very different compositions. A common factor of many data-points that are included, is the high to very high DOC concentrations (over 10.000 mg C/L). The Fe- data are more or less grouped together

between the upper left of the figure to neutral pH, suggesting that the processes governing Fe solubility are similar for most situations.

Because predominantly inorganic waste produces the lowest Fe- concentrations in solution, the suggestion is raised that the high Fe- concentrations in solution are directly caused by high TOC concentrations in solution, but as mentioned before, the (combined) effect of redox conditions should not be ruled out beforehand.

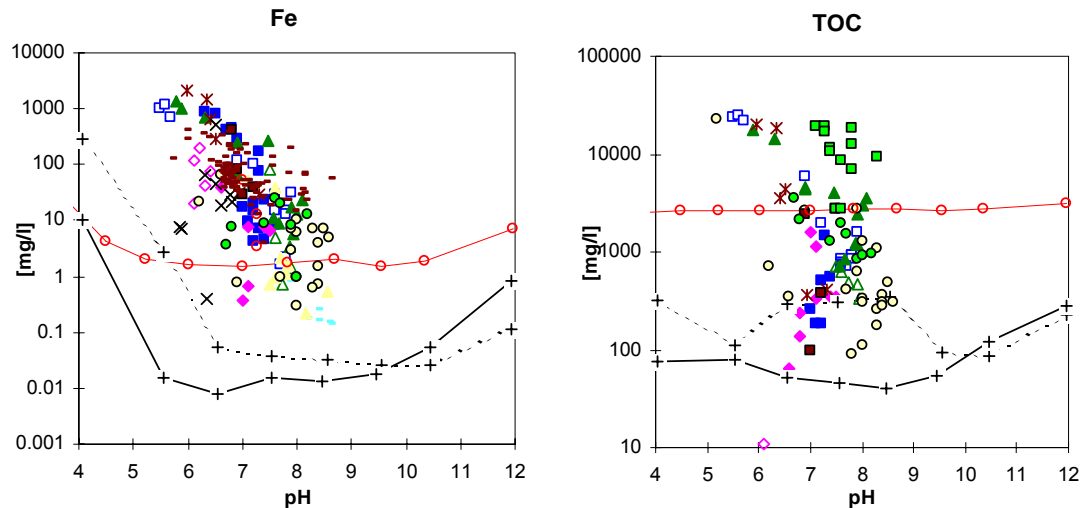


Figure 16 Fe and dissolved organic carbon (here TOC) in landfill leachates of different composition and origin (legend given in Figure 17). The lines with +- marks are pH stat data from leachates produced by predominantly inorganic waste such as MSWI bottom ash. The red line with the o- mark is organic wet fraction of MSW.

Figure 17 shows the output of model calculations together with the data from Figure 16. The black line in the left corner (at bottom of figure) indicates the solubility of Fe caused by dissolution of Ferrihydrite under oxidised conditions when DOC does not play a role (DOC = 0 mg/L). It can be seen that even when Fe is controlled by a relatively soluble Fe- (hydr) oxide, this leads to extremely low concentrations in solution. In practice, such systems are rarely found, and redox conditions or DOC complexation often influences Fe concentrations. The effect of redox is immediately seen when comparing the “oxidised” system to the “transition zone” system (the blue line). Here, Ferrihydrite is still thermodynamically stable and Fe concentrations are still governed by its dissolution, but Fe^{2+} is dominant over Fe^{3+} in solution which causes the increased Fe- concentrations. This effect becomes stronger when the redox potential is lower (see the “mildly reducing” black line).

The slope of the line is virtually very similar to the trend in measured Fe- concentrations. It would however be too easy to conclude that the Fe- concentrations are caused purely by redox effects, because complexation with organic matter is very strong and therefore may mask the redox effect.

From the “mildly reducing” line, we included the model results of DOC complexation in the figure. It can be seen that under these conditions, concentrations of Fe in solution are strongly increased due to complexation with DOC. At lower pH, the concentration-enhancing effect of DOC becomes less important, because the activity of Fe^{2+} is already very high due to the low redox potential. However, under oxidising conditions, the concentration enhancing effect would still exist at this pH (see background information). The model results show that a

concentration enhancing effect of DOC is extremely important at neutral to basic pH values both in oxidising and reducing environments.

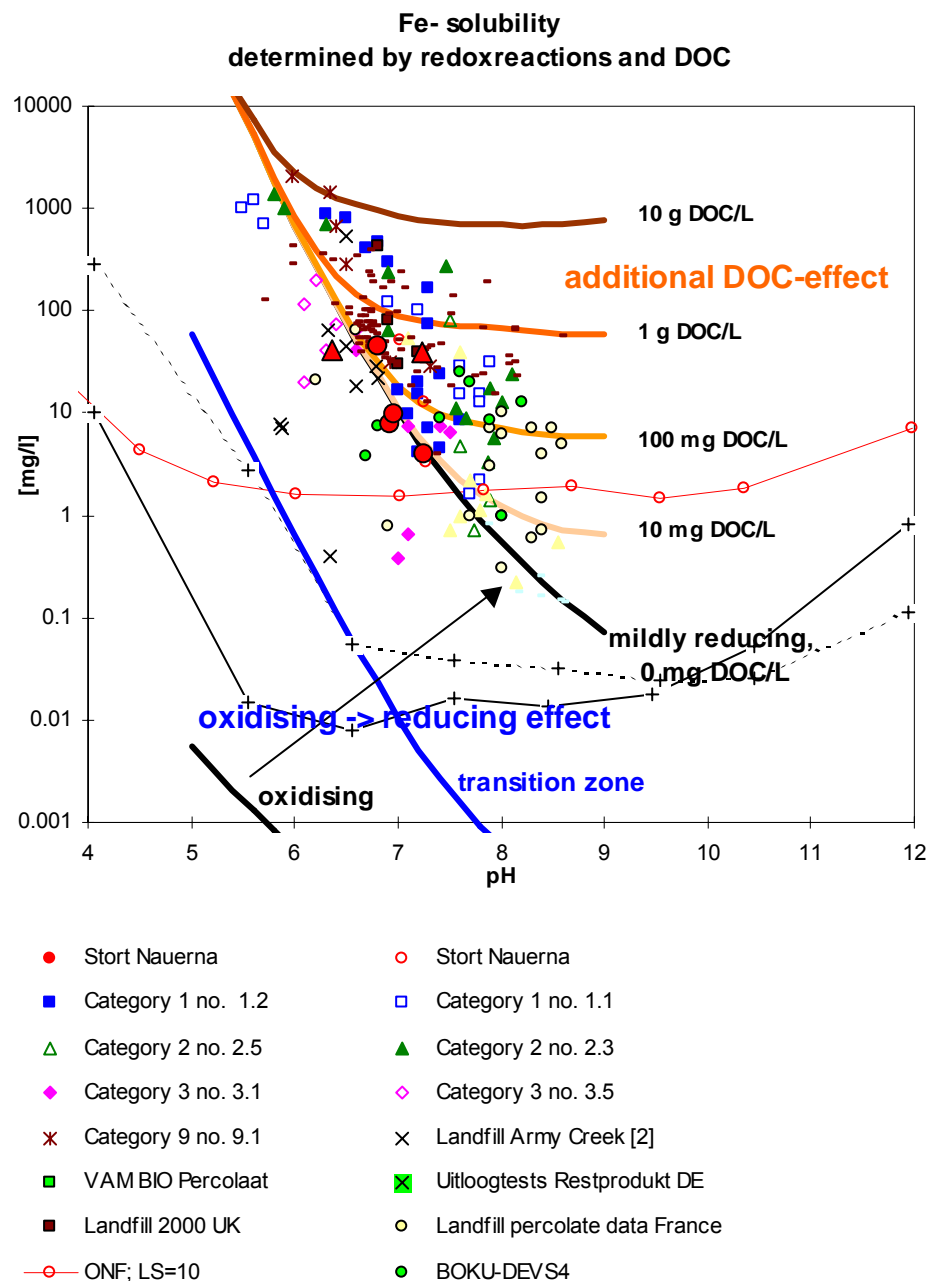


Figure 17 Results of the model output with ECOSAT. Solid lines are model output. The arrow under in the Figure indicates the effect of *only* redox conditions (DOC = 0 mg/L) when going from an oxidised system to a reduced system. The big red dots in the middle of the picture are data from the pilot Nauerna. The triangles are from the corresponding laboratory tests.

It should be stressed that the data plotted in Figure 17 are not meant as a validation of the model, or as a model description of the data; therefore we would also need information on redox potential. The model results are not specifically calculated for each data point, which

may be a source for differences between the model and the data. For example, concentrations of competing ions may very well be different from the system that we have chosen; also, other competing cations may play a role (such as Cu^{++}). Therefore, the data itself should be interpreted with some care. Colloidal Fe can also cause the extremely high Fe-concentrations. It should be realised that dissolved organic matter may already contain some low amount of Fe. At extremely high DOC levels, this may explain (some part of) the measured Fe-concentration in solution.

In general, modelling metal-DOC interaction of macro components such as Fe is possible, because it can be rather safely assumed that in many systems the dissolution of (hydr) oxide minerals control Fe^{3+} activity. However, trace contaminant concentrations are in most systems more likely controlled by sorption. In that case, more information is necessary as input in ECOSAT such as available concentration (estimated at extreme pH values), and amount of solid organic matter and of other reactive surfaces (Fe/Al minerals, clay content).

4.1.3 Integration of laboratory, lysimeter and field data

a) Predominantly inorganic waste

In this paragraph, an example is given for the integration of laboratory, lysimeter and field data for predominantly inorganic waste. Figure 18 shows the cumulative emission (left) and the measured concentration (right) of Cr and Pb as a function of the L/S ratio. The cumulative Cr release shows a very consistent pattern amongst the different scales of testing. Cr leaching is solubility controlled, the emission follows the line with slope=1. It can be seen that the individual concentrations are within a relatively small range, dictated by geochemical

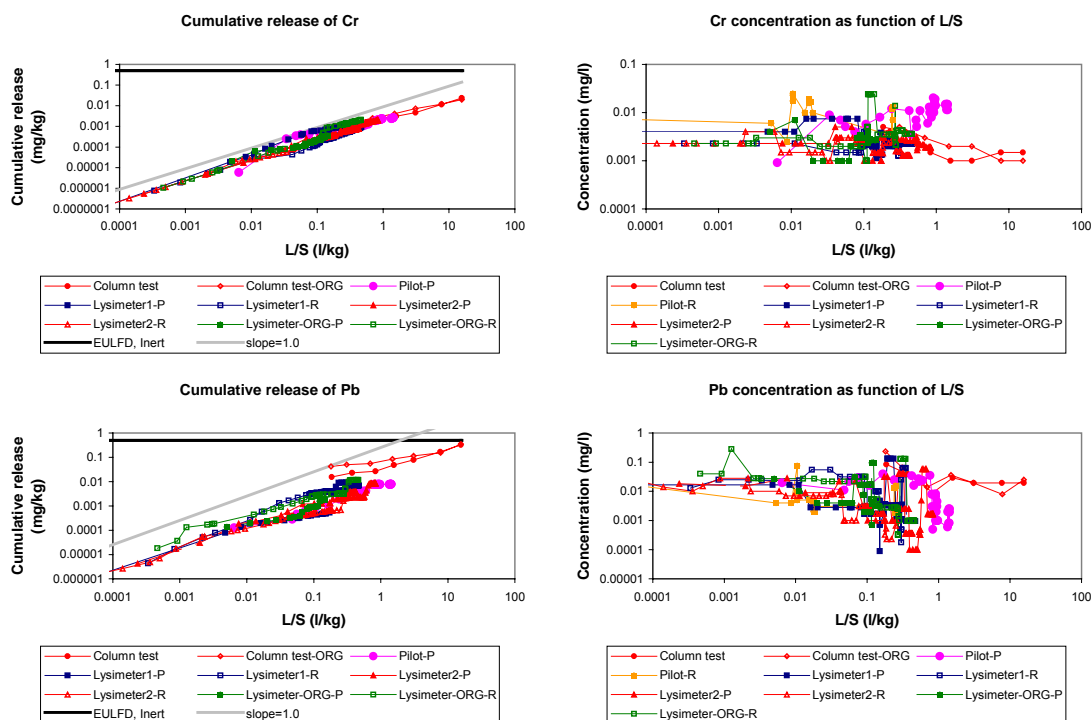


Figure 18 Example of data comparison at different scales of testing. This example shows the results from the predominantly inorganic waste concept at laboratory, lysimeter and pilot scale.

processes in the waste mixture. The horizontal solid line in the left graph shows the regulatory criterion for the acceptance of waste (LFD-inert). Cr emissions from the predominantly inorganic waste landfill are not critical with respect to the inert waste limit.

The measured Pb concentrations in the first three fractions of the column leach test are relatively high compared to the other experiments. This leads to an increased emission at L/S 0.1-0.2 and a subsequent shift in the cumulative Pb emission. The Pb emissions are also solubility controlled in all experiments. However, the pilot experiment seems to show some depletion since the Pb concentrations are decreasing. The emission in the laboratory leaching test at L/S=10 is about a factor 2 lower than the acceptance criteria for inert waste. Based on these results, it is expected that Pb emissions will not reach critical values on the long-term. This approach enables the comparison of data from different scales of testing. Results from laboratory, lysimeter and field studies might seem different at first sight. However, the results are comparable when shown as a function of the L/S ratio. The obtained L/S ratios in these experiments are partly overlapping. Agreement of the data from different scales of testing enables long-term prediction of the leaching behaviour.

b) Stabilised waste

Cu, Mo, Pb and Zn concentrations in stabilised waste leachates (specifically laboratory data, landfill leachate and core leachates, pilot experiment percolate and run-off, and lysimeter samples) are shown as a function of pH in Figure 19. The solid lines represent the leaching behaviour predicted using ORCHESTRA. The modelling describes the observed leaching behaviour in pH-static experiments very well for Cu, Pb and Zn, and is adequate for Mo at high pH. At neutral to low pH, the model prediction for Mo leaching deviates significantly from the measured leaching behaviour. In general, the data from landfill core leachates, lysimeter experiments, landfill leachate water and the pilot experiment percolate and run-off water (Figure 19) show a pH dependent leaching behaviour that is consistent with the laboratory data and the model description. The consistency of the leaching data between tests does suggest that the same chemical processes control contaminant leaching, e.g. solubility control by mineral phases, sorption to HFO and complexation with organic matter. This conclusion is not contradicted by the observation that relatively large differences between percolate and run-off water EC are seen, as soluble salts are released independent of pH. This implies that estimating contaminant release under field conditions requires data from both the pH-static leach test and the tank leach test. The low volume to area ratio in the stabilised waste landfill scenario as well as the intermittent dry periods leads to significant reduction in projected release compared with the assumption of continuous release by diffusion that is implicit in a tank leach test (where the experimental conditions aim at a maximum concentration gradient. In general, the leachate concentrations of Mo are high whereas Pb, Cu and Zn concentrations are relatively low (Figure 19). This implies that release of oxyanions is more relevant than that of heavy metals in this type of disposal scenario. The monitoring will continue to validate these initial results and to check whether the contaminant concentration range in the leachates will change.

The balance between surface neutralisation (and possibly pore sealing) through carbonation and alkalinity release by diffusion on the buffering capacity of the soil layer is crucial for maintaining a moderate leachate pH, and hence for this landfill concept remaining sustainable.

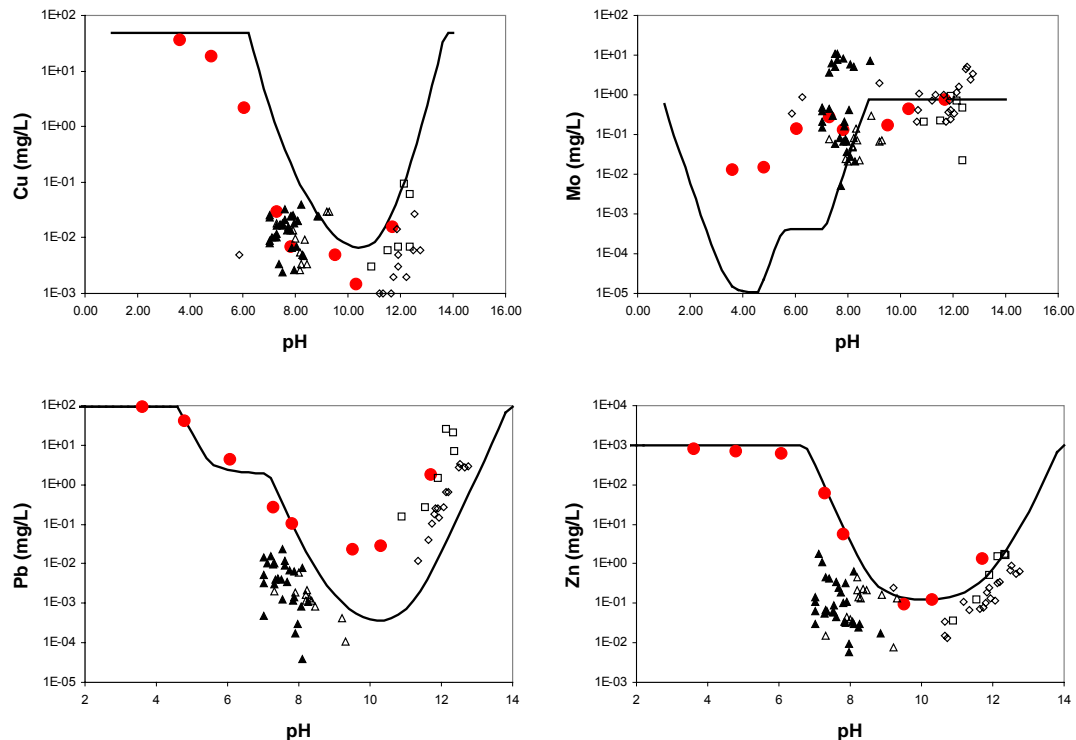


Figure 19 pH dependent leaching of Cu, Mo, Pb and Zn from laboratory tests on stabilised waste (●solid circles) compared with landfill and pilot experiment percolate data (▲), pilot experiment run-off data (Δ), landfill core leachates (□) and lysimeter data (◇, taken from (39)). The solid line represents the leaching behaviour predicted by geochemical equilibrium modelling.

4.2 Geochemical modelling of release as a function of pH

4.2.1 Interpretation of modelling results

To facilitate the interpretation of the Figures regarding the measured and predicted leaching behaviour, an example is given in Figure 20. The leaching data from a laboratory pH-static leaching test is represented as a function of pH by the red datapoints. The black solid line represents the predicted total concentration of the considered element in solution, which should ideally meet the data points for good understanding of the chemical processes that determine the leaching behaviour. Moreover, Figure 20 shows the calculated chemical speciation of the element in both the solid matrix and the sample solution. The predicted leaching behaviour is therefore the intersection between the calculated speciation in the solid matrix (minerals, sorption to Fe-Oxides and binding to solid organic matter) and in the solution (free+inorganic and complexed by dissolved organic carbon). This type of data presentation integrates the predicted total leached concentration as well as the different species that determine the leached concentrations.

The upper line in Figure 20 gives the total available concentration (input in model). The white area shows the amount of the element bound as minerals in the solid phase. Sorption to Fe-Oxides is represented by the gray area while complexation to solid organic matter is dark green. These areas represent the total amount in the solid matrix as a function of pH. In the leachate solution, the light blue area is the total amount of the free ion and the inorganically

complexed form. The light green area represents the amount of the element that is organically complexed.

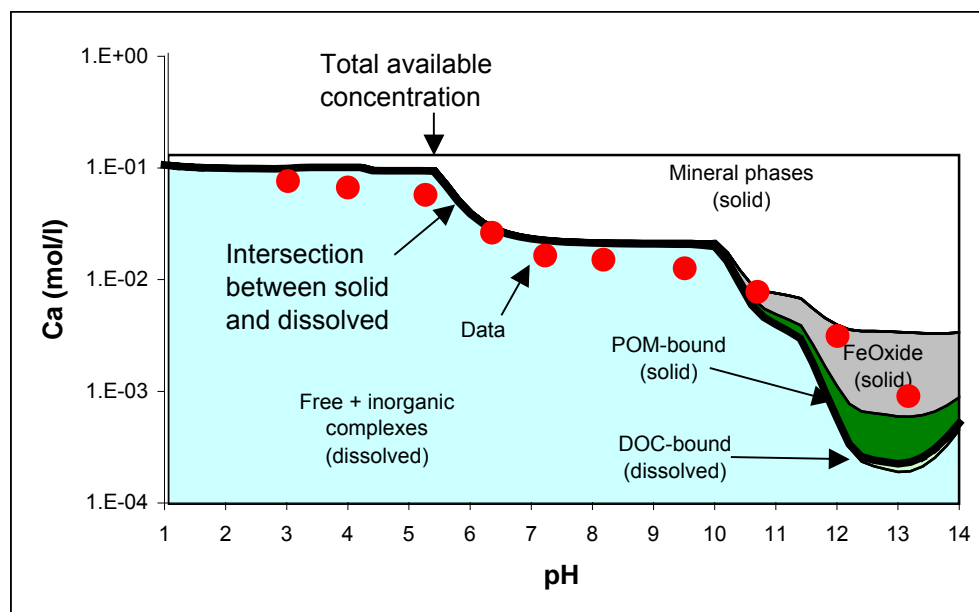


Figure 20 Example of integrated data presentation for pH-static leaching test results and geochemical speciation modelling. Red data points represent leaching data, black solid line is the predicted leached concentration. Areas represent the element speciation: White=minerals, Gray=FeOxide sorption, Dark green=complexation to solid organic carbon, Light green=complexation to dissolved organic carbon and Light blue=free+inorganically complexed form.

4.2.2 Geochemical modelling predominantly inorganic waste

The availability of all elements used as input for geochemical speciation modelling are given in Table 2. It should be noted that the availability was determined as the maximum concentration in the waste of the Equifill pilot that was obtained in the pH-static leaching test. The availability of Al and Pb was changed in the initial speciation calculations. The leached concentrations as measured in the pH dependence test (lowest pH around 4) were not sufficient to properly account for the availability.

DOC plays an important role in the mobilisation of various contaminants. However, DOC is a sum parameter for all organic carbon species. The NICA-Donnan model (12) was used to account for complexation of contaminants to solid and dissolved humic acid. It was assumed that 20% of DOC consists of humic acid over the whole pH range. ORCHESTRA calculates the geochemical speciation from pH 1 to 13 with intervals of 0.2 pH values. We therefore fitted our DOC data to a polynomial function in order to describe the pH dependent leaching of DOC. The calculated DOC concentrations at pH intervals of 0.5 are given in Table 3.

Initial speciation calculations have indicated several possible solubility controlling minerals. The selected set of minerals used for the model prediction calculations are given in Table 4. In some cases, more than one mineral was selected based on possible solubility control in different pH ranges.

Table 2 *Available concentrations of elements used in geochemical modeling of predominantly inorganic waste used in the equifill pilot experiment. Additional parameters to describe binding to the solid phase were: HFO ($4.3\text{E-}3$ kg/kg), total humic acid content ($1.03\text{E-}3$ kg/L) and clay (0 kg/kg).*

Element	Availability (mg/kg)	Element	Availability (mg/kg)	Element	Availability (mg/kg)	Element	Availability (mg/kg)
Al	3000.00	Mg	3002.13	CO3-2	55000.00	SO4-2	12715.33
As	2.57	Mn	573.68	Cr	19.19	Sb	0.39
B	18.65	Mo	2.87	Cu	39.77	Se	0.32
Ba	7.54	Na	1400.00	F	50.00	Si	3014.79
Br	34.52	NH4	609.57	Fe	16360.59	Sr	176.10
Ca	50151.07	Ni	23.23	K	1158.57	V	5.22
Cd	2.76	PO4-3	81.57	Li	3.02	Zn	2400.83
Cl	5267.82	Pb	251.00				

Table 3 *Calculated DOC concentrations as a function of pH based on measurement in pH-static leaching tests*

pH	DOC (kg/l)	pH	DOC (kg/l)	pH	DOC (kg/l)
1	1.96E-05	5.5	1.06E-06	10	7.47E-06
1.5	1.75E-05	6	1.62E-06	10.5	1.01E-05
2	1.44E-05	6.5	2.44E-06	11	1.5E-05
2.5	1.09E-05	7	3.31E-06	11.5	2.32E-05
3	7.54E-06	7.5	4.1E-06	12	3.63E-05
3.5	4.76E-06	8	4.71E-06	12.5	5.6E-05
4	2.71E-06	8.5	5.15E-06	13	8.44E-05
4.5	1.46E-06	9	5.55E-06	13.5	0.000124
5	9.49E-07	9.5	6.17E-06	14	0.000178

Table 4 Possible solubility controlling minerals in predominantly inorganic waste selected from initial speciation calculations. These minerals were subsequently used as input for the model predictions.

Mineral name	Mineral name	Mineral name	Mineral name
Albite[low]	Gypsum	Ferrihydrite	Otavite
AlOHSO4	OCP	Brucite	Hydromagnesite
Boehmite	alpha-TCP	MnHPO4[C]	Strontianite
Leucite	Ca2Cd[PO4]2	PbMoO4[c]	Cr[OH]3[A]
BaSrSO4[50%Ba]	Cd[OH]2[C]	Bunsenite	Manganite
Ba[SCr]O4[96%SO4]	PbCrO4	Pb2V2O7	Ba3[AsO4]2
Anhydrite	Cu[OH]2[s]	Willemite	Sb[OH]3[s]
CSH_ECN	Fluorite	Zincite	
Ca2Pb[PO4]2	FCO3Apatite	Calcite	

The geochemical model results for all elements in comparison with the measurements in the pH-static leaching test are given in Figure 21 to Figure 23. In general, the model describes the leaching behaviour of the waste mixture quite well, especially when it is realised that changes in input parameters may affect the predicted behaviour of several other elements. This implies that the degrees of freedom to vary input parameters are limited dramatically by taking all

elements into account simultaneously. As the model assumes equilibrium and it is known that equilibrium is not reached within 48 hours contact time, kinetics of dissolution and precipitation will be a factor to recon with in judging the results. These effects will result in an apparent

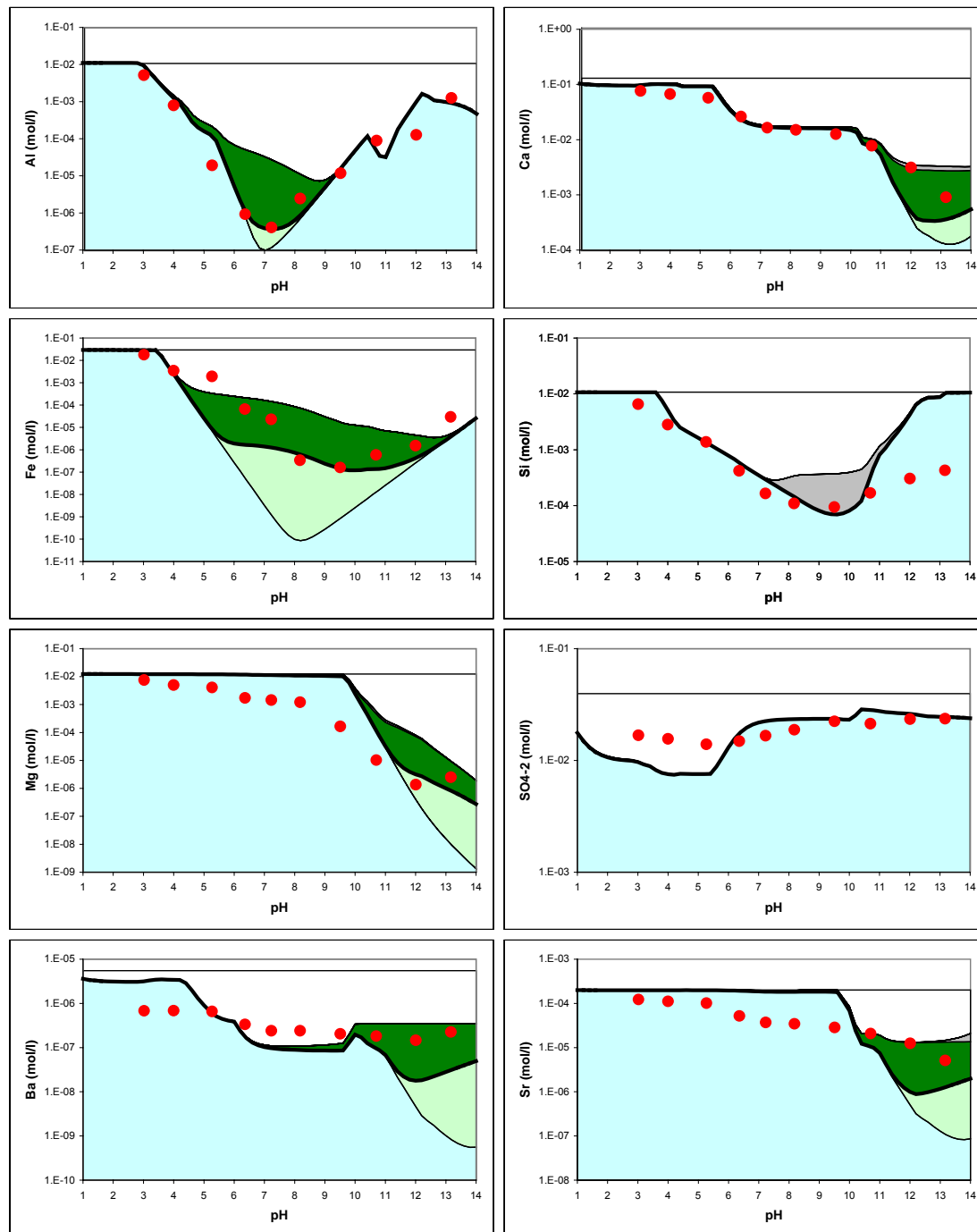


Figure 21 pH-static results and geochemical modelling for the major elements in predominantly inorganic waste. The thick solid line indicates the predicted concentrations in solution. The areas below this line indicate the element speciation in solution (light blue are the free and inorganically complexed species, light green is the organically complexed species). Areas above the thick solid line indicate the element speciation in the solid matrix (dark green indicates binding to solid organic matter, gray is the amount sorbed to hydrous ferric oxide (HFO) and the white area represents the amount present in minerals).

deviation of the model prediction, whereas the leached concentrations might still increase or decrease due to equilibrium and/or kinetic processes. Recent work (40) has shown these effects in relation to the own pH of the material, where the system is closest to equilibrium. This implies that there is sufficient understanding of the chemical processes that determine the leaching behaviour in this waste mixture.

The pH-static leaching data and geochemical model results for Al, Ba, Ca, Fe, Mg, Si, SO_4^{2-} and Sr are presented in Figure 21. There can be significant deviations in the model description compared to the actual leaching data, such as a deviation of more than one order of magnitude for Si at $\text{pH} > 11$. Apparently, the chemistry in this pH range is not fully understood yet. The leaching of Fe is underestimated for about one to two orders of magnitude in the pH range 5 to 7. The deviations of Mg, Sr, SO_4 and Ba are expected to be largely related to kinetics.

Despite the model deviations in the leaching of the described elements, the overall prediction of the major element chemistry is an important finding and provides a good basis for the understanding of chemical processes in these apparently very heterogeneous materials.

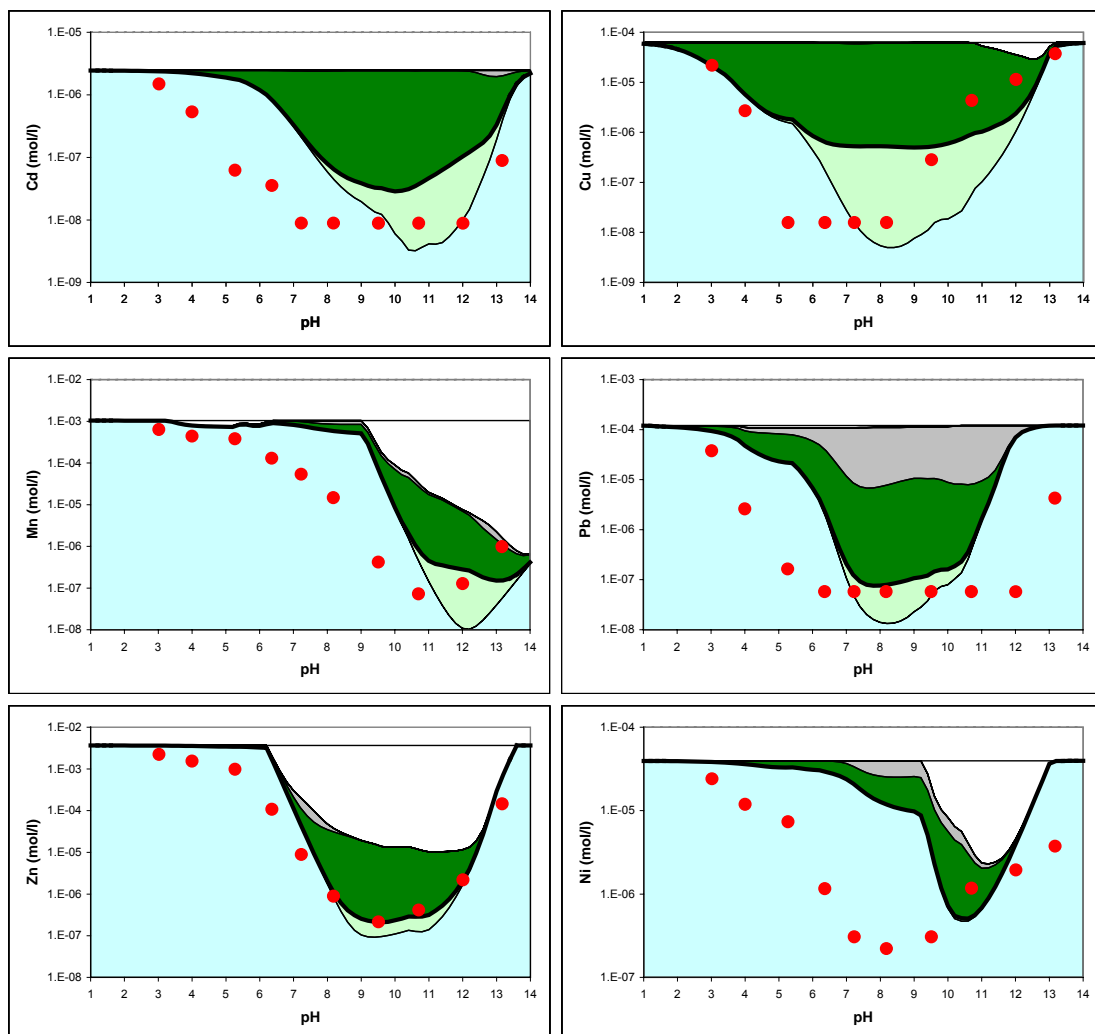


Figure 22 pH-static results and geochemical modelling for heavy metals and salts in predominantly inorganic waste.

Figure 22 shows the pH dependent leaching behaviour and results from geochemical modelling for Cd, Cu, Mn, Ni, Pb, Zn, Cl, K and Na. It can be seen that Cd leaching is generally over-predicted over the whole pH range for up to one order of magnitude. Cu leaching is described adequately at both low and high pH, there is a relatively large overestimation in the pH range from 5 to 9. Leaching of Cu is predominantly controlled by complexation to humic- and fulvic acids in this pH range. However, our modelling results are based on the assumption that 20% of DOC consists of humic acid over the whole pH range. Earlier measurements of humic- and fulvic acid concentrations as a function of pH in leachates of a compost sample have shown that especially the leaching of humic acids is strongly pH dependent (13). This might explain the general overestimation (pH range 5 to 9) of the heavy metals that have a high affinity for complexation to humic- and fulvic acids (Cu, Ni, Cd and Pb). The leaching behaviour of Mn and Zn are reasonably well described. Pb is well described in the neutral pH range, but dissolution kinetics may be the cause for the discrepancy between model and measurement in the mild acidic and mild alkaline range. For Ni the description is not very adequate yet in the pH range 4 to 9, apparently, a relevant chemical process is not well described.

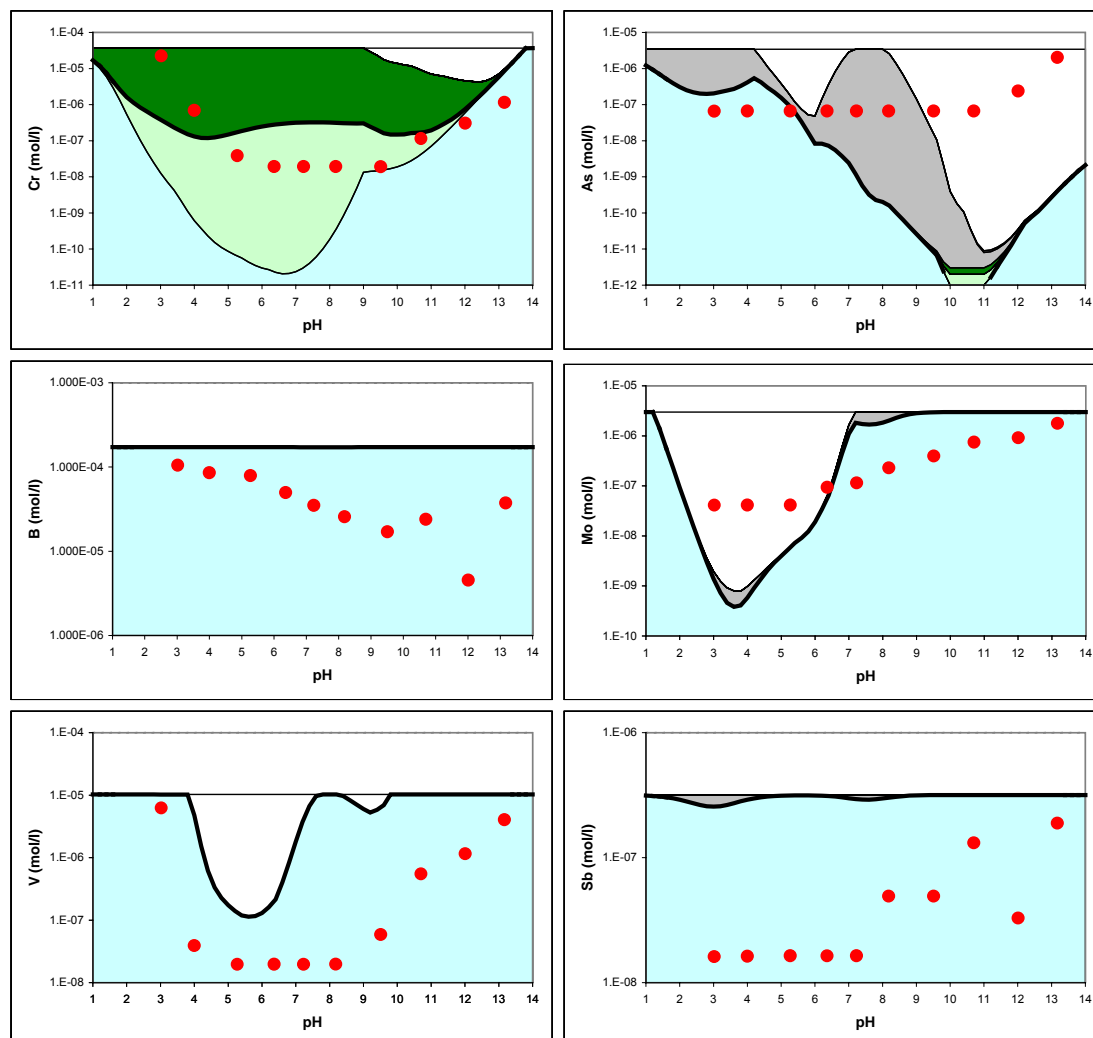


Figure 23 pH-static results and geochemical modelling for oxyanions in predominantly inorganic waste.

The pH-static leaching data and geochemical model results for As, B, CO_3^{2-} , Cr, Mo, Sb, PO_4^{3-} , Se and V is presented in Figure 23. The degree to which the model describes the leaching data of these oxyanions is variable. The leaching behaviour of Cr is quite well described, whereas both Mo and V are reasonable well described. The latter are both controlled by Pb and thus any change in Pb partitioning will affect Mo and V leachability. For B, Sb and Se there is very limited thermodynamic data, which hampers a proper description by this type of modeling. In case of As, a mineral phase assumed to be present at high pH is apparently not formed in the system (underestimation). Sorption to Fe-oxide is predicted as would be expected for As. The prediction of carbonate is overestimated at low pH, but this is due to the fact that CO_2 is not allowed to escape. The underprediction at mild alkaline pH may require some further work. Phosphate requires more work. The thermodynamic database is adequately stocked, but the selection of relevant mineral- or sorptive phases to be included in the predictive modelling requires further work. The partitioning between dissolved and particulate phases as obtained from the present modelling provides a significantly increased insight in mutual relationships between elements, which allows to predict release behaviour under other conditions than those tested in the laboratory.

4.2.3 Geochemical modelling stabilised waste

It is important to realise that modelling the behaviour of a single element in isolation is bound to fail as the constituent behaviour cannot be separated from its chemical environment, which dictates key factors such as pH, redox and EC. Element leaching is also affected by interaction with other constituents (e.g. through precipitation). Mutual competition of elements for sorption sites also implies that failure to take along crucial competing elements will lead to a poor prediction. The challenge has therefore been to input all major, minor and trace elements and all relevant sorption processes into the geochemical model description of a material. Ignoring minerals or the description of sorption processes leads to an insufficient description of the system. The latest developments in modelling (9) attempt to integrate all relevant solubility controlling aspects. This type of approach is highly relevant for waste treatment such as stabilisation, as modifying a recipe for stabilised waste is likely to affect different elements in different ways.

Table 5 *Available concentrations of elements used in geochemical modeling of stabilized waste. Additional parameters used to describe binding to the solid phase were: HFO (1E-4 kg/kg), total humic acid content (5E-5 kg/L) and clay (0 kg/kg).*

Element	Availability (mg/kg)	Element	Availability (mg/kg)	Element	Availability (mg/kg)
Al	6565	Cu	485	Pb	955
As	0.145	F	1904	PO_4^{3-}	4.74
B	59.47	Fe	73.93	Sb	4.92
Ba	19.33	K	33810	Se	0.46
Br	833.8	Li	24.52	Si	3556
Ca	83620	Mg	3903	SO_4^{2-}	19660
Cd	202.2	Mn	175	Sr	206
Cl	53500	Mo	7.7	V	0.58
CO_3^{2-}	30000	Na	25625	Zn	10020
Cr	9.69	Ni	11.29		

The pH dependent leach test data for a specific stabilised waste containing MSWI fly ash has been modelled using LeachXS (with ORCHESTRA embedded). The input parameters and the selected mineral phases are given in Table 5 and Table 6. The mineral phases were selected by means of calculated saturation indices obtained from preliminary speciation calculations of the leachates.

Table 6 *Possible solubility controlling minerals in stabilized waste selected from speciation calculations. These minerals were subsequently used as input for the model predictions.*

Mineral name	Mineral name
Analcime	Fluorite
BaSrSO ₄ [50%Ba]	Gypsum
Boehmite	Manganite
Brucite	Ni[OH] ₂ [s]
Calcite	Pb[OH] ₂ [C]
Cd[OH] ₂ [C]	Pb ₃ [VO ₄] ₂
Cerrusite	PbMoO ₄ [c]
CSH_ECN	PbV ₂ O ₇
Cu(OH) ₂	Portlandite
Ferrihydrite	Zincite

The results, given in Figure 24 through to Figure 26, show that a reasonably good prediction of the pH dependent leaching behaviour can be achieved based on Fe-oxide sorption, selected mineral precipitation and interaction with organic matter (both dissolved and particulate). In the optimisation process undertaken to reach a solution that provides a good description for all elements simultaneously it is obvious that the freedom to vary parameters (reactive Fe/Al content, reactive fraction of DOC or POM or relevant minerals) decreases steadily.

For some elements, discrepancies between the predicted and measured concentrations can be observed (Figure 24 to Figure 26). In judging the agreement between model and data, it should be realised that all constituents are used for the modelling. In addition, the prediction at very low concentration levels may be off by an order of magnitude, while the full trend of the release curve as a function of pH is matched. In such cases, the prediction may be reasonably accurate. It is important to realise that the shape of the leaching curve represents a so-called geochemical fingerprint of the material. If the data and the modelled leaching curve are qualitatively consistent, this implies that the chemistry is understood reasonably well. Differences between predicted and actual leaching might then be attributed to discrepancies in the description of sorption processes and/or complexation to organic matter. In a number of cases, discrepancies within specific pH ranges (particularly at sharp edges) may be attributed to kinetics as shown by Dijkstra et al. (40). This type of modelling will highlight any lack of mineral or other phases controlling the release (e.g. Cd in pH range 7 - 10).

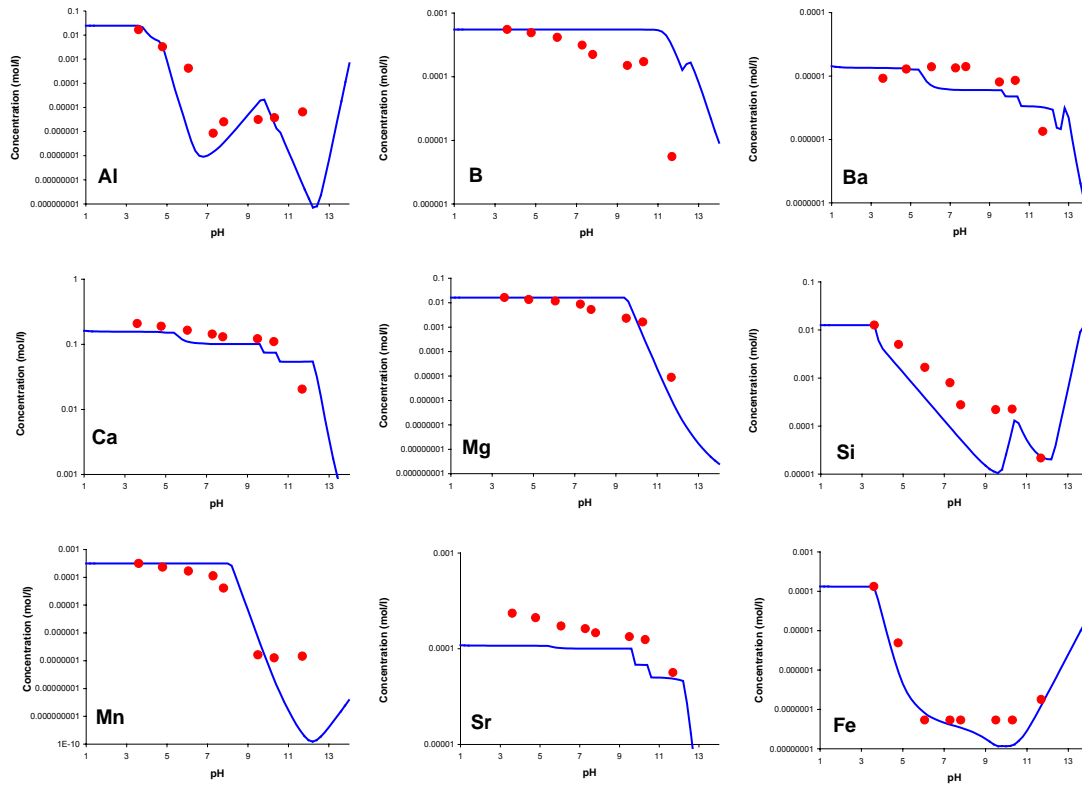


Figure 24 Measured and predicted leaching behaviour of major elements as a function of pH in a stabilised MSWI fly ash recipe.

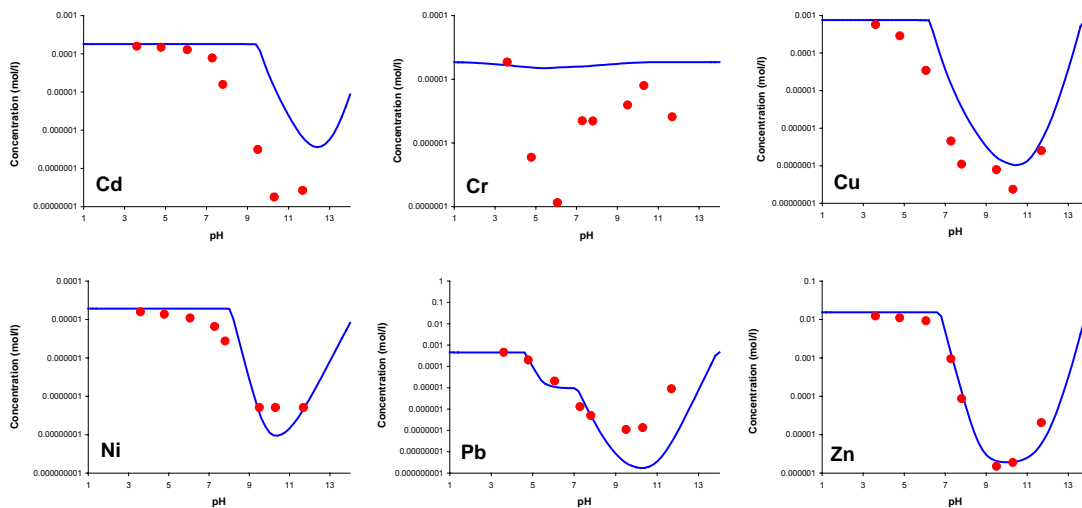


Figure 25 Measured and predicted leaching behaviour of heavy metals as a function of pH in a stabilised MSWI fly ash recipe.

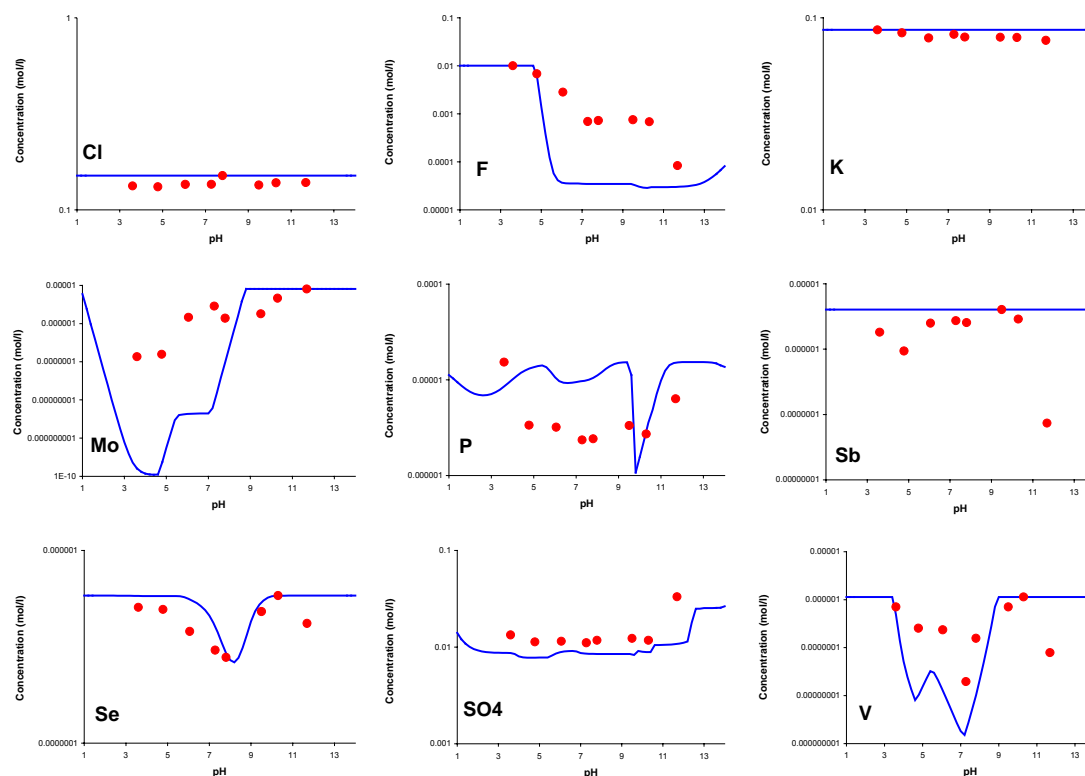


Figure 26 Measured and predicted leaching behaviour of salts and oxyanions as a function of pH in a stabilised MSWI fly ash recipe.

The leaching curves as described earlier are the product of complex chemical processes in both the leachate solution and the solid phase of the waste material. In Figure 27, the calculated Pb speciation in the leachate solution (A), its partitioning in liquid and solid phase (B), its fractionation in solution (C) and its fractionation in the solid phase (D) is presented as a function of pH. This figure illustrates that different processes control Pb leaching at different pHs. The leached Pb exists mainly as the free ion or in an inorganic complex. Between pH 8 and 10, up to 20% of the Pb is complexed with DOC (humic acid).

Pb speciation in the solid phase (Figure 27B) is controlled predominantly by mineral solubility and sorption to HFO (between pH 3 to 7). In the pH range from 1 to 7, a significant proportion of Pb is found in the minerals PbMoO_4 and, to a much lesser extent, $\text{Pb}_3(\text{VO}_4)_2$. Above pH 7, there is some sorption to HFO but the mineral $\text{Pb}(\text{OH})_2$ is the dominant phase that is controlling Pb solubility in the solid. Binding to solid organic matter (humic acid) is minimal in the pH range from 2 to 6.5.

The modelling results that have been presented here give a very detailed insight into the important solubility controlling processes in stabilised waste, and can form the basis for improving waste management decisions particularly in regard to the control of the actual and long-term leaching behaviour of stabilised waste. Moreover, this approach might enhance future recipes for stabilised waste as the chemical processes in these materials can be identified and actions can be taken to improve the residue leaching behaviour based on increased understanding of controlling factors.

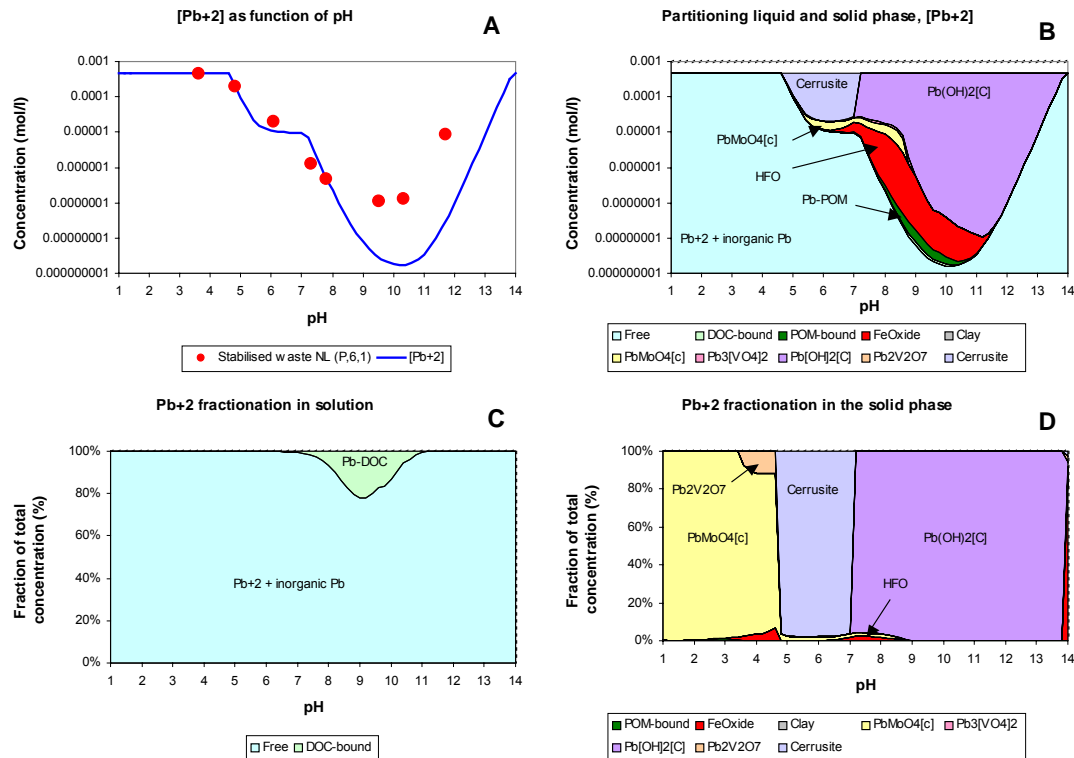


Figure 27 Measured and calculated Pb concentration as a function of pH in the leachate solution (A), the calculated speciation in the liquid and solid phase (B), the relative proportion of Pb species in solution (C) and the relative proportion of Pb species in the solid phase (D).

4.2.4 Geochemical modelling bioreactor data

The chemical speciation module of LeachXS has been applied to model pH dependence leaching test data of the waste mix that was used to fill the bioreactor pilot (Landgraaf, NL). The input parameters for respectively the relevant mineral phases, sorption surfaces, additional parameters and available quantities of major, minor and trace components are given in Table 7, Table 8 and Table 9.

The results of the full mechanistic modelling of the waste mixture are given in Figure 28 to Figure 31. All major, minor and trace elements have been taken along simultaneously at the same time taking into account relevant solubility controlling processes (mineral solubility, sorption onto Fe- and Al oxides and interaction with dissolved and particulate organic matter).

Table 7 *Calculated DOC concentrations as a function of pH based on measurement in pH-static leaching tests.*

DOC/DHA data					
pH	[DOC] (kg/l)	DHA fraction	[DHA] (kg/l)	Polynomial coefficients	
1.00	4.539E-04	0.55	2.496E-04	C0	3.600E-04
2.75	2.810E-04	0.40	1.124E-04	C1	-1.008E-04
3.69	1.790E-04	0.30	5.370E-05	C2	5.989E-06
6.37	1.470E-04	0.25	3.675E-05	C3	2.792E-07
6.81	1.730E-04	0.20	3.460E-05	C4	0.000E+00
7.48	1.740E-04	0.20	3.480E-05	C5	0.000E+00
8.78	3.330E-04	0.25	8.325E-05		
10.32	6.195E-04	0.35	2.168E-04		
11.66	8.380E-04	0.55	4.609E-04		
14.00	9.574E-04	0.90	8.617E-04		

Table 8 *Available concentrations of elements used in geochemical modelling of predominantly organic waste. Additional parameters to describe binding to the solid phase were: HFO (1E-2 kg/kg), total humic acid content (4E-2 kg/L) and clay (0.1 kg/kg).*

Reactant concentrations					
Reactant	mg/kg				
Ag+	not measured	Fe+3	1.341E+04	NO3-	not measured
Al+3	3.076E+03	H2CO3	3.901E+04	PO4-3	7.881E+01
H3AsO4	6.116E-01	Hg+2	not measured	Pb+2	5.878E+02
H3BO3	7.289E+01	I-	not measured	SO4-2	2.769E+03
Ba+2	1.567E+01	K+	1.584E+03	Sb[OH]6-	1.813E+00
Br-	9.010E+00	Li+	2.670E+00	SeO4-2	5.495E-01
Ca+2	2.272E+04	Mg+2	1.632E+03	H4SiO4	1.973E+03
Cd+2	1.695E+01	Mn+2	3.392E+02	Sr+2	6.760E+01
Cl-	2.330E+03	MoO4-2	7.673E+00	Th+4	not measured
CrO4-2	5.273E+01	Na+	2.079E+03	VO2+	4.727E+00
Cu+2	2.342E+02	NH4+	not measured	Zn+2	2.110E+03
F-	1.680E+02	Ni+2	8.473E+01		

Table 9 *Possible solubility controlling minerals in stabilized waste selected from speciation calculations. These minerals were subsequently used as input for the model predictions*

Selected Minerals			
Al[OH]3[a]	Ferrihydrite	CuCO3[s]	Anglesite
Wairakite	Fe2[OH]4SeO3	NiCO3[s]	Pb3[VO4]2
Ba[SCr]O4[96%SO4]	Cerrusite	Analbite	OCP
BaSrSO4[50%Ba]	Rhodochrosite	Brucite	alpha-TCP
Witherite	Magnesite	Huntite	Fe_Vanadate
Anhydrite	Strontianite	Nsutite	Zn[OH]2[B]
Ca2Zn[PO4]2	Calcite	CaMoO4[c]	hydrozincite
CaCu2[PO4]2	ZnCO3:H2O	PbMoO4[c]	Birnessite
Fluorite	Dolomite	Pb2V2O7	Manganite

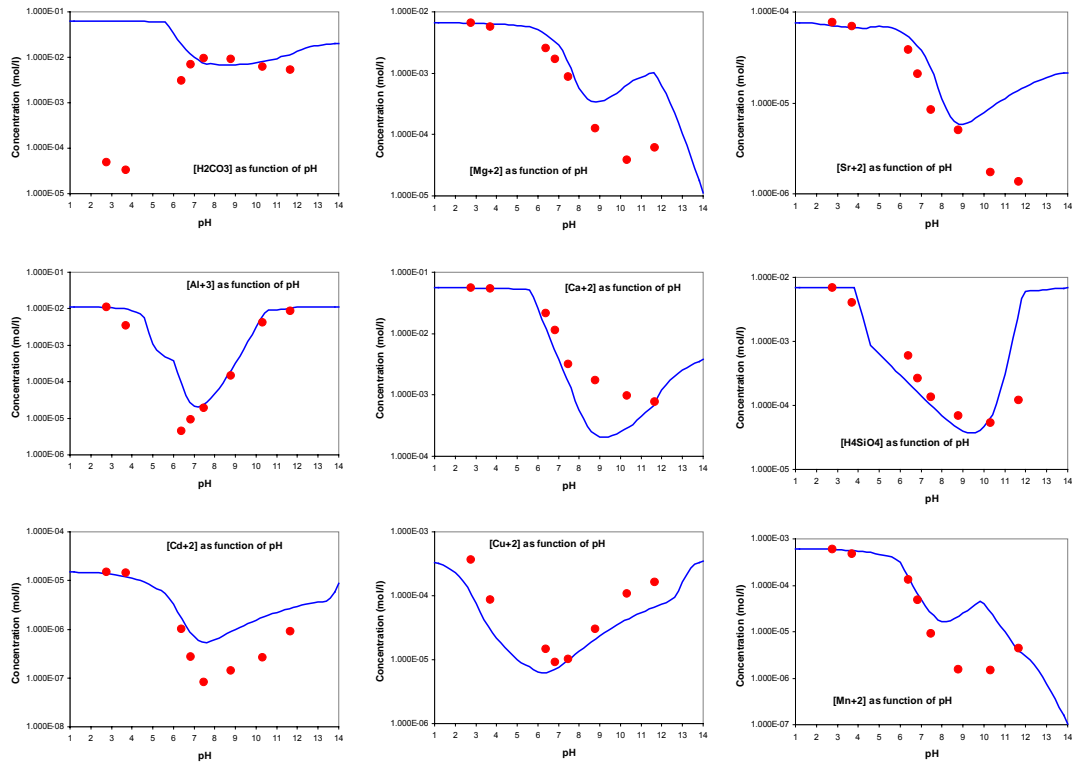


Figure 28 Measurement from a pH dependence leaching test (TS 14429) and the modelling results for CO_3^{2-} , Mg, Sr, Al, Ca, Si, Cd, Cu and Mn using the above mentioned input parameters.

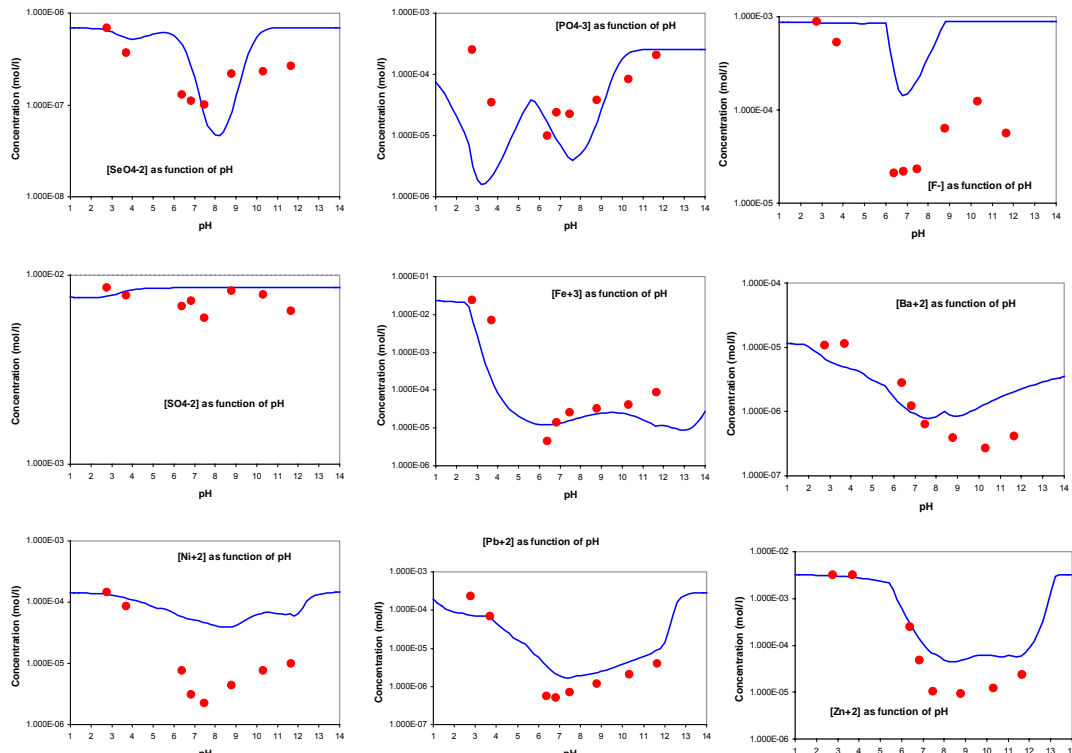


Figure 29 Measurement from a pH dependence leaching test (TS 14429) and the modelling results for Se, P, F, SO_4 , Fe, Ba, Ni, Pb, en Zn using the above mentioned input parameters.

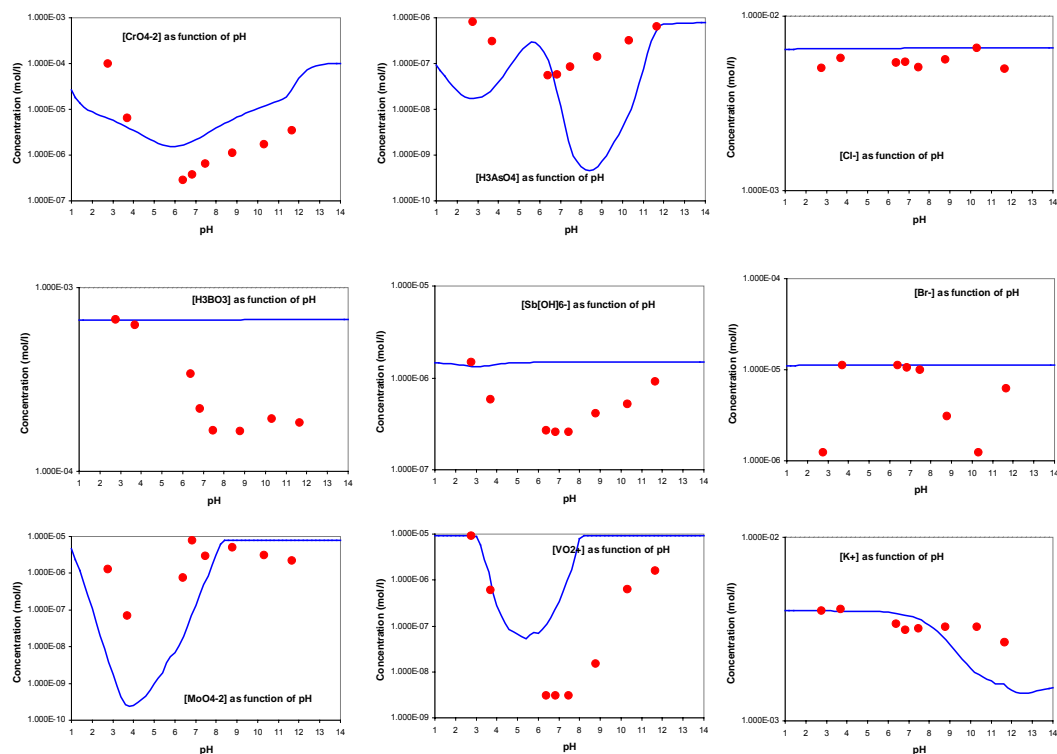


Figure 30 Measurement from a pH dependence leaching test (TS 14429) and the modelling results for Cr, As, Cl, B, Sb, Br, Mo, V and K using the above mentioned input parameters.

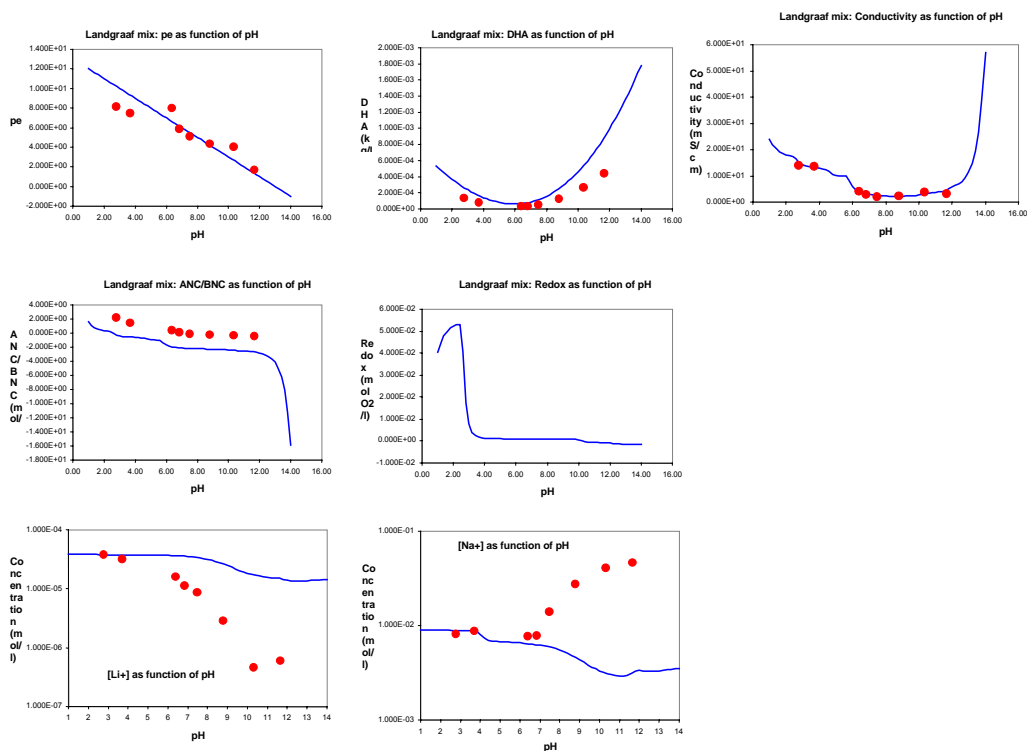


Figure 31 Measurement from a pH dependence leaching test (TS 14429) and the modelling results for pe, DHA, EC, ANC, redox capacity, Li and Na (NaOH artificially elevated at pH >7 by the use of NaOH for pH control) using the above mentioned input parameters.

In Figure 32 to Figure 34, the chemical speciation and partitioning between dissolved and particulate phases is provided for Cu, Pb and Zn in the predominantly organic waste mix from pilot Landgraaf (bioreactor). Figure 32 shows that Cu is strongly associated with both dissolved and particulate organic matter. Until rather low pH (<5-6) quite a significant fraction of the Cu in solution is bound to DOC. The release of Cu from predominantly organic waste is governed by complexation with organic matter.

Obviously, not all elements are described equally well. Still it is surprising to note how well, in terms of qualitative (match between curve shape and measurements) and quantitative (match between model and measurement) criteria, the overall modelling output matches the measured data points. This implies that there is significant understanding of the chemical processes leading to release of contaminants.

Several processes, depending on the pH range, control the leaching of Pb (Figure 33). In the neutral to alkaline region, Pb release is controlled by sorption to HFO. At pH values lower than 6, sorption to solid organic matter and solubility control by mineral phases becomes the dominating release process. A substantial part of the leached Pb is associated with DOC over a wide pH range.

The leaching of Zn is predominantly controlled by the solubility of several mineral phases (Figure 34). Sorption to solid organic matter is important at low and at very high pH. At neutral pH, ZnCO_3 and hydrozincite seem to be the main controlling phases. Sorption to HFO only plays a minor role in the binding of Zn to the solid matrix. A substantial part of the leached Zn is associated with DOC in the neutral to alkaline pH range.

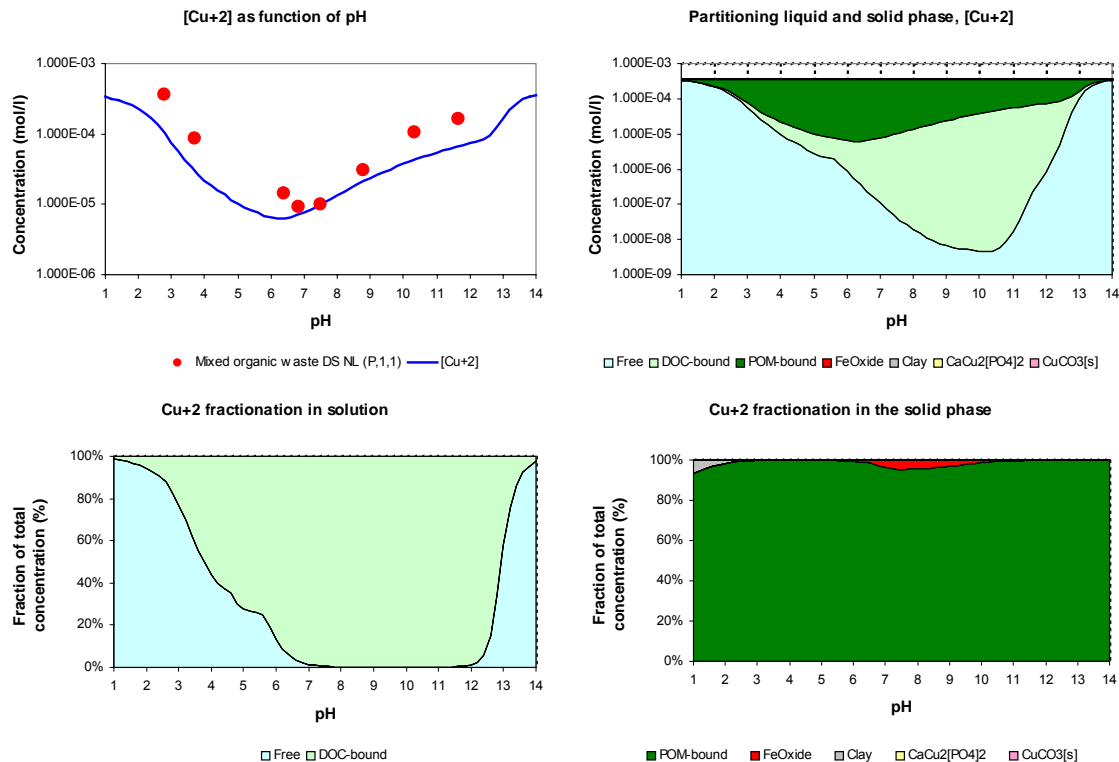


Figure 32 Chemical speciation and fractionation of Cu in the predominantly organic waste mix.

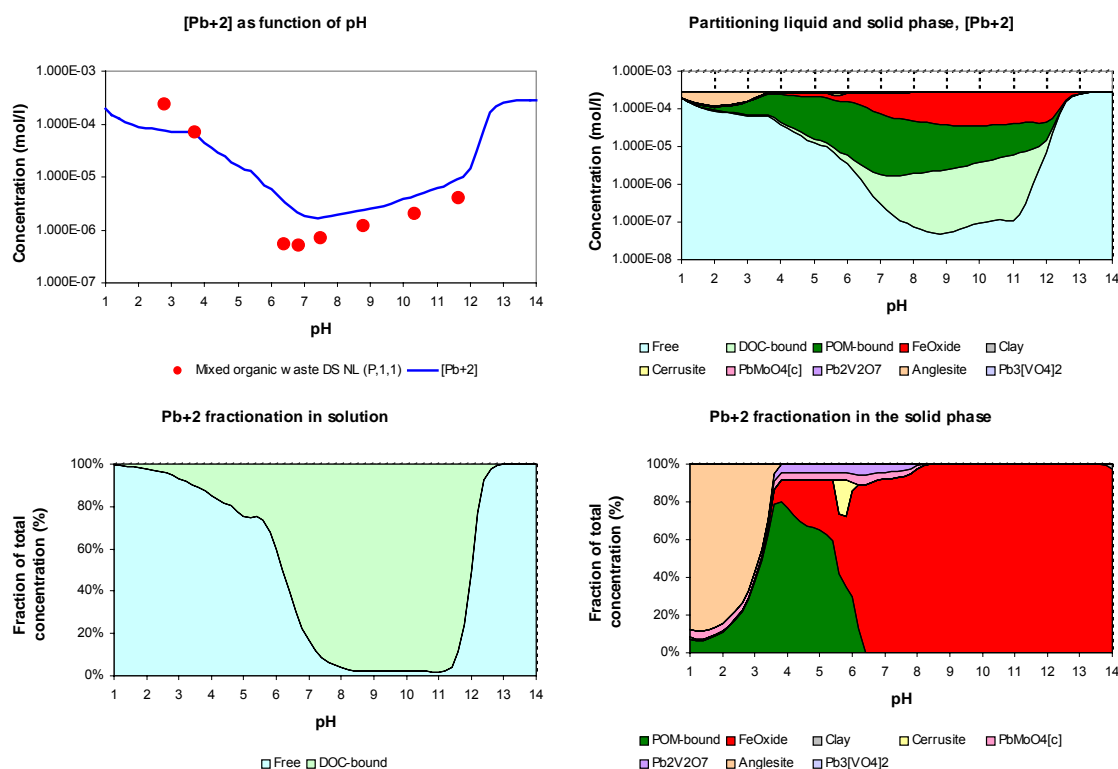


Figure 33 Chemical speciation and fractionation of Pb in the Landgraaf waste mix

4.3 Comparison of contaminant speciation in organic to predominantly inorganic waste materials

As indicated in earlier work (41) an organic matter dominated landfill will tend to develop in a predominantly inorganic waste landfill after degradation. This was illustrated before by direct comparison of the leaching behaviour of fully degraded waste from a laboratory pilot (42) with the predominantly inorganic waste from the pilot Nauerna.

The comparison shown in Figure 35 to Figure 37, illustrates the main differences in the chemical speciation aspects of the organic matter dominated versus the fully degraded organic matter rich material from the Essent bioreactor and the predominantly inorganic waste.

In all cases, it is clear that organic matter plays an important role in all landfill concepts. However, the emphasis shifts going from organic to fully degraded to predominantly inorganic from binding to dissolved organic matter to binding on particulate organic matter. Thus the release to the environment is reduced and more stable conditions develop.

Cu is fully dominated by either dissolved or particulate organic matter in all systems. Pb is largely dictated by DOC in solution, but mainly controlled by sorption on to Fe-oxide surfaces in the solid phase, whereas Zn is to a large extent controlled by DOC in solution, but mainly by mineral solubility in the solid phase. These observations hold definite decision power as it allows the stability of the release controlling factors to be identified and thus conclusions can be drawn, if due to foreseeable external circumstances changes in release behaviour are likely to occur. In the evaluation, the acid neutralisation capacity of the system plays an important role as it determines to what extent pH changes towards lower pH are likely to occur. Based on the present evaluation, the stability of the system is quite substantial as both calcite and organic matter are maintaining a buffered condition.

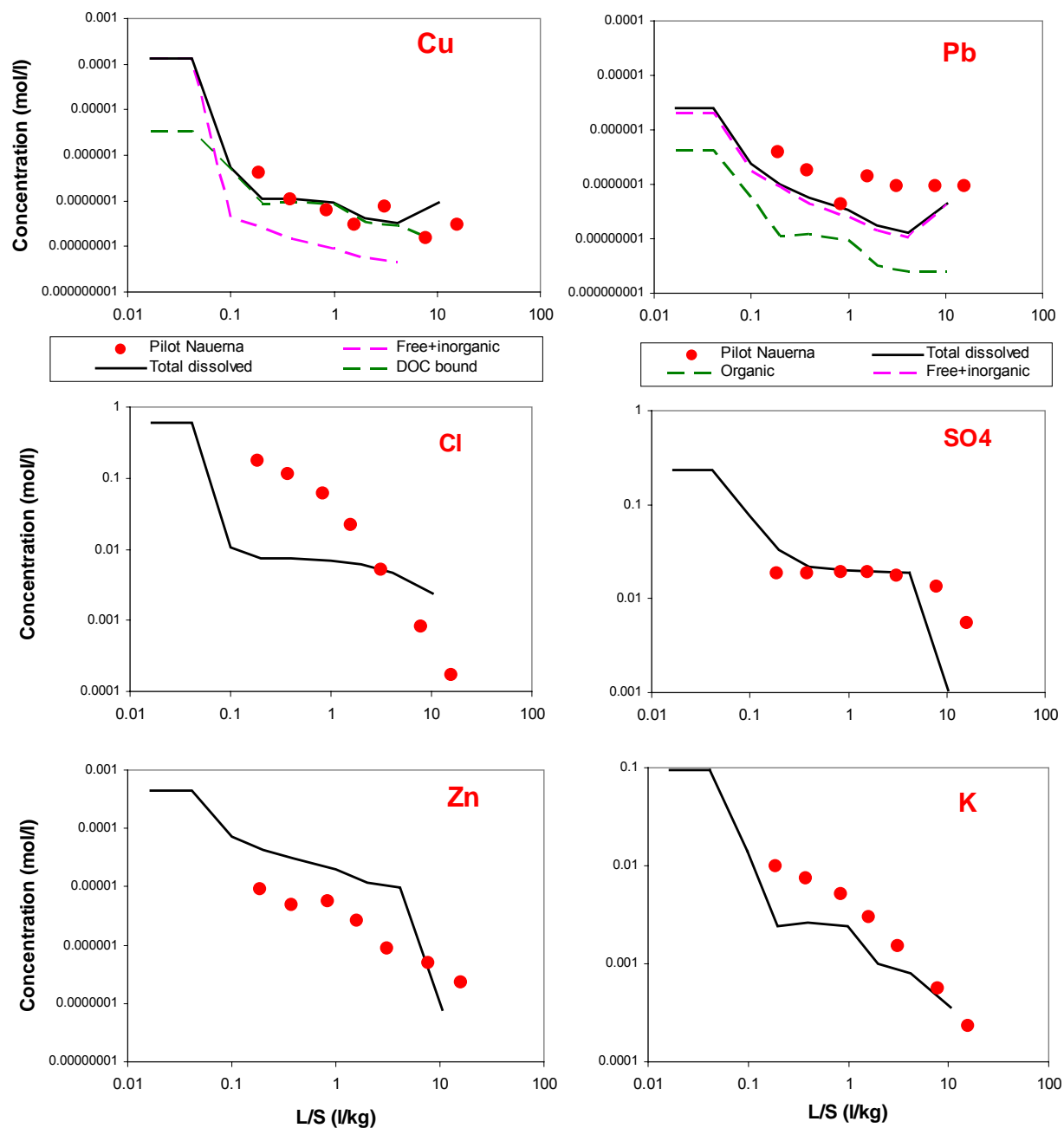


Figure 34 Chemical speciation and fractionation of Zn in the Landgraaf waste mix.

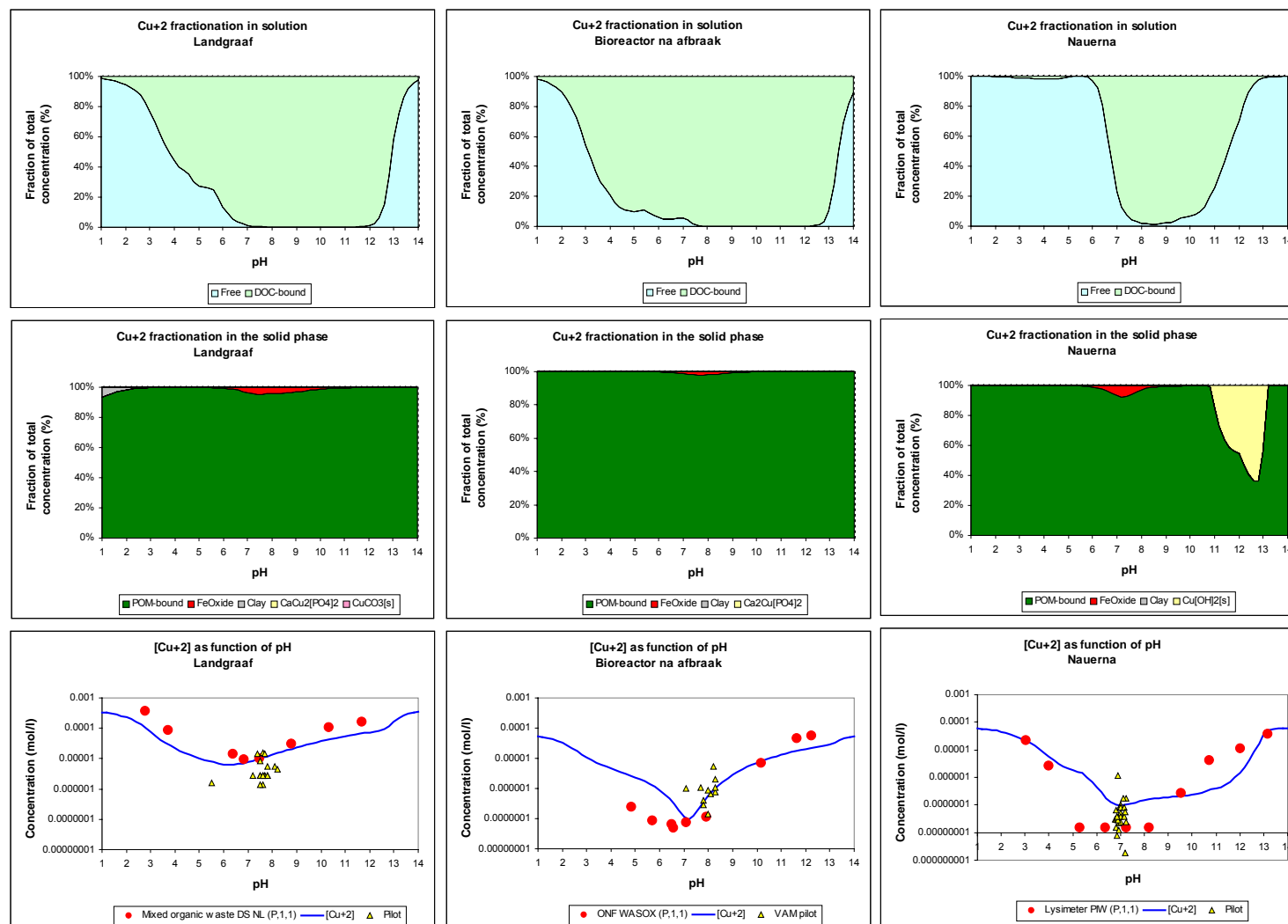


Figure 35 Comparison of chemical speciation of Cu in organic (Bioreactor and Landgraaf) and predominantly inorganic waste (Nauerna) landfill concepts. Top graphs show partitioning in the water phase, middle graphs show the partitioning in the solid phase and bottom graphs show the model prediction based on the minerals, sorption to Fe, Al and organic matter compared to the actual measurement. Data points are field leachate data.

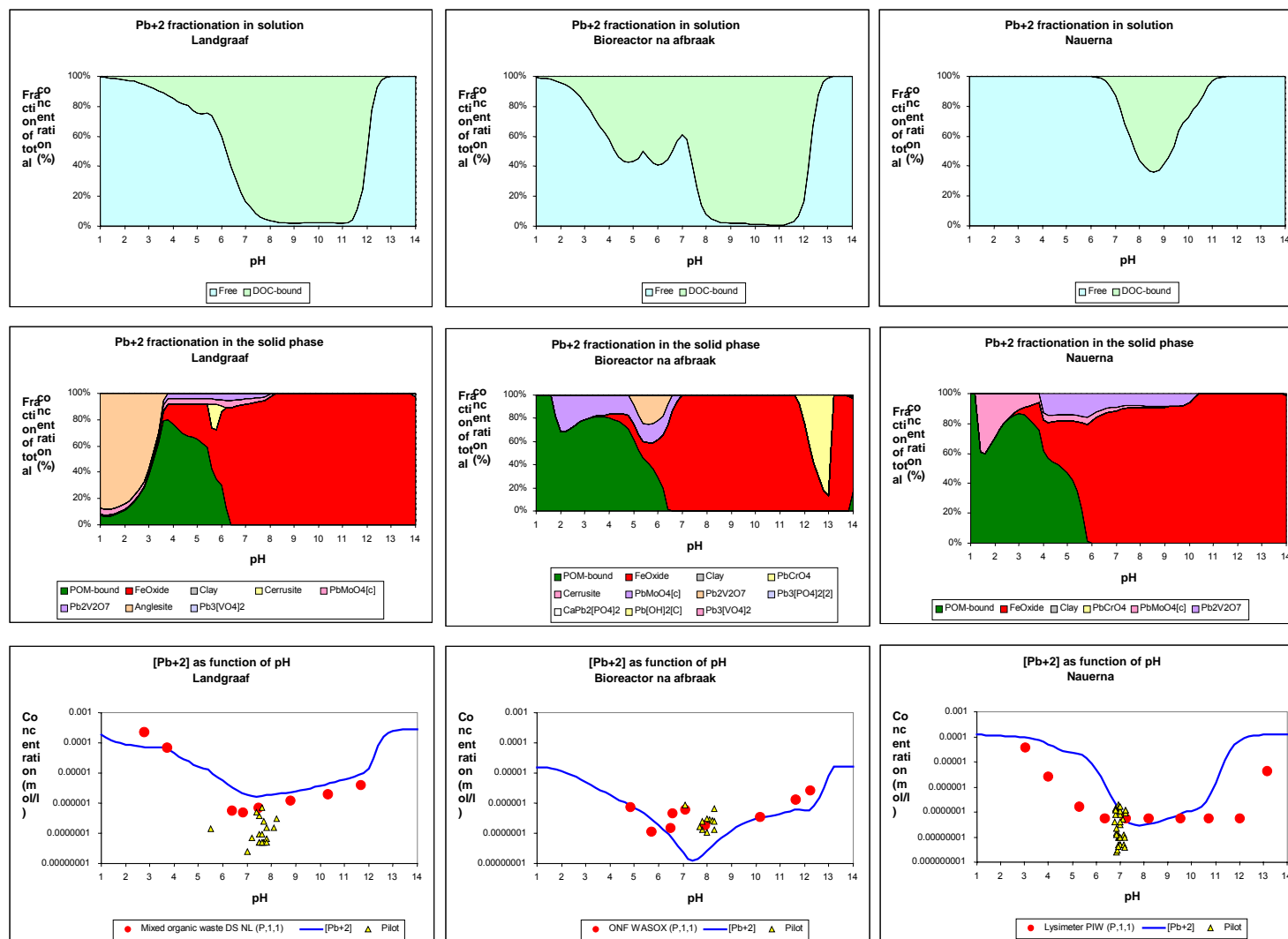


Figure 36 Comparison of chemical speciation of Pb in organic (Bioreactor and Landgraaf) and predominantly inorganic waste (Nauerna) landfill concepts. Top graphs show partitioning in the water phase, middle graphs show the partitioning in the solid phase and bottom graphs show the model prediction based on the minerals, sorption to Fe, Al and organic matter compared to the actual measurement. The data shown in the graph are field leachate data.

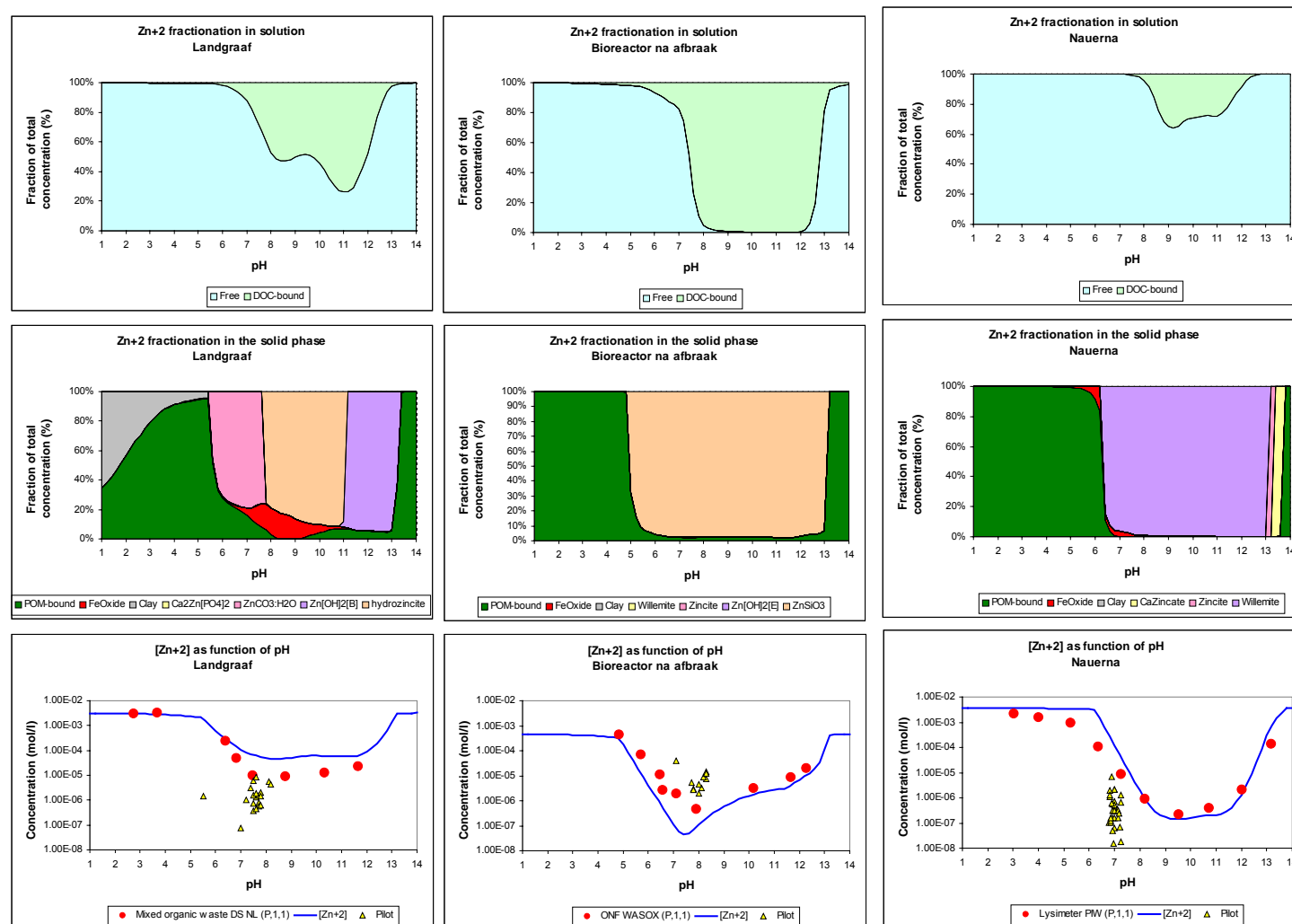


Figure 37 Comparison of chemical speciation of Zn in organic (Bioreactor and Landgraaf) and predominantly inorganic waste (Nauerna) landfill concepts. Top graphs show partitioning in the water phase, middle graphs show the partitioning in the solid phase and bottom graphs show the model prediction based on the minerals, sorption to Fe, Al and organic matter compared to the actual measurement. The data shown in the graph are field leachate data.

4.4 Geochemical modelling of diffusion controlled release in a tank leach test

Besides predicting leaching behaviour in the pH dependent leach test, it is important to model the release in a tank test to ensure that the geochemical characterisation of the material (obtained from the pH dependent leach test) leads to a good prediction of the monolithic material's release behaviour. This modelling takes into account the material's physical parameters and the test conditions. Thus the physical properties of the material, such as its dimensions, leachant volume, porosity, tortuosity and density, and the exposure conditions of the test (e.g. leachant renewal cycles, exposure to the atmosphere) need to be quantified for input into the transport model (defined in ORCHESTRA). The complex interface phenomena occurring in monolithic materials due to the strong concentration gradients in the interface region (e.g. pH) have a major influence on the release of contaminants.

In Figure 38, both the tank test results and the modelling results are given for pH, Cl, K, Pb, Cr and Mo. The measured element concentration represents the total leached into solution by the end of each time step, whereas the model calculates these as well as the concentration increase in the leachant during each leaching cycle. The concentration profile in the product's porewater is an output of the model. Partitioning of phases as a function of depth can be obtained, but this is not presented here.

The leaching of many solubility controlled elements is highly dependent on pH; therefore, it is crucial to correctly predict pH. It should be noted that pH is calculated in this type of model (where emissions are predicted as a function of time) whereas the pH is fixed in models that calculate emissions as a function of pH.

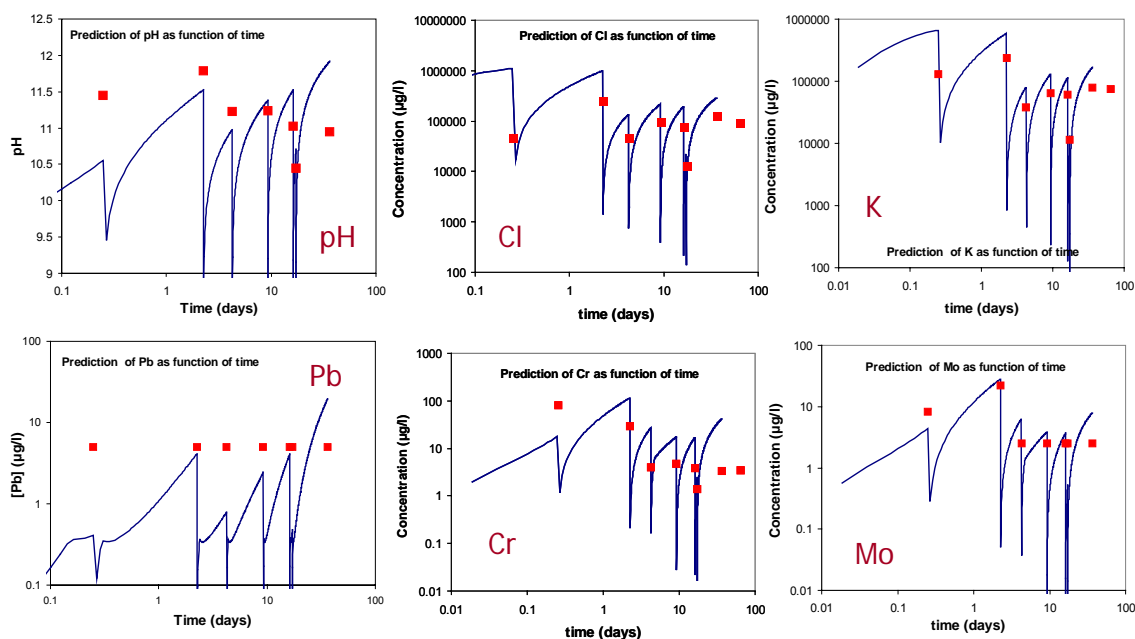


Figure 38 Comparison of measured and predicted concentrations in a tank leach test on stabilised waste.

Figure 38 shows that, except for the first and the last fraction, the pH is generally predicted to within 0.5 units of the measured values.. The pH is clearly under-estimated (by one unit) in the

first fraction. This might be the result of surface wash-off effects that occur in the tank test that are not yet adequately described in the model. It can be seen that the measured pH steadily decreases with each subsequent refreshment step during the tank test, which is the result of leachate carbonation by CO_2 uptake from air, which even in a closed vessel cannot be entirely avoided due to the very long contact times used in this experiment, since gases can diffuse through polyethylene. This carbonation is not yet quantified properly, and therefore it is not currently addressed in our model definition.

4.5 Geochemical reaction transport modelling of release to soil and groundwater.

The next modelling step is to evaluate the interaction of the material with soil in both monolithic (service life) and crushed form (after degradation). This implies modelling release by diffusion and by percolation. The geochemical characterisation of the stabilised waste has been used as input for the layer of stabilised waste. For the soil characteristics the geochemical characteristics of Eurosoil 4 (43) have been used as an example of a common soil type in Europe. In the transport modelling a diffusion coefficient of $3 \cdot 10^{-11} \text{ m}^2/\text{s}$ is applied, whereas in the case of convective flow a flow rate of $9 \cdot 10^{-6} \text{ l/s}$ (corresponding to an infiltration of 280 mm/yr) is applied. In Figure 39 and Figure 40 the pH and concentration profiles of Cl, Cu and Mo in the pore water solution of stabilised waste and soil (separated by 0.03 m) is

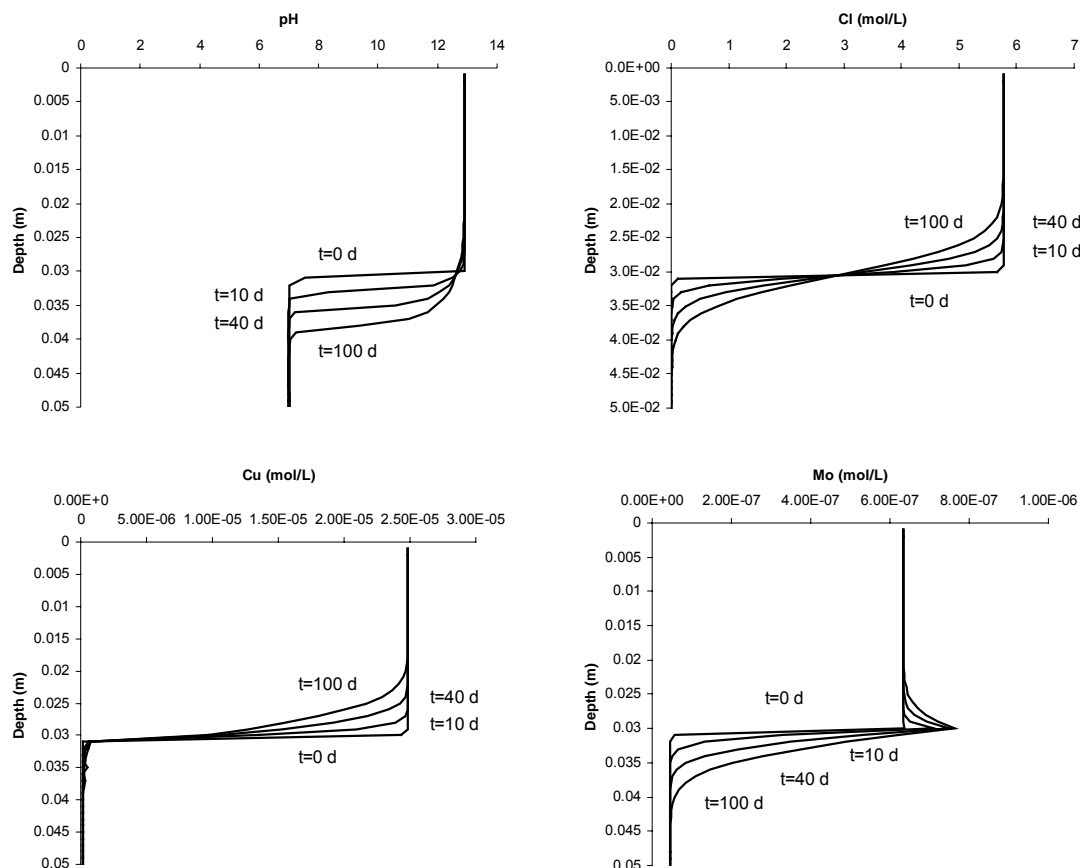


Figure 39 pH and concentration Profile (Cl, Cu and Mo) of Soil impact from Monolithic Cement-Stabilised material. The emission is controlled by diffusion and plotted at different times ranging from 0 to 100 days.

shown for both the diffusion dominated and percolation driven cases respectively. Diffusion dominated transport is slow and this implies that concentration fronts are also slow moving. The pH front progression into the soil layer is slow. In judging this profile it should be realised that pH is in log units, while the concentration scale for the other elements is linear. Cl simply diffuses out of the material. Cu may be somewhat over-predicted at high pH (see pH dependence test results) and it is predicted to be slightly mobilised in the soil as a result of DOC mobilisation. The slight pH drop in the stabilised waste layer directly in contact with soil leads to increased Mo leaching at the interface. It is subsequently released into the soil and from there its transportation is almost uninhibited.

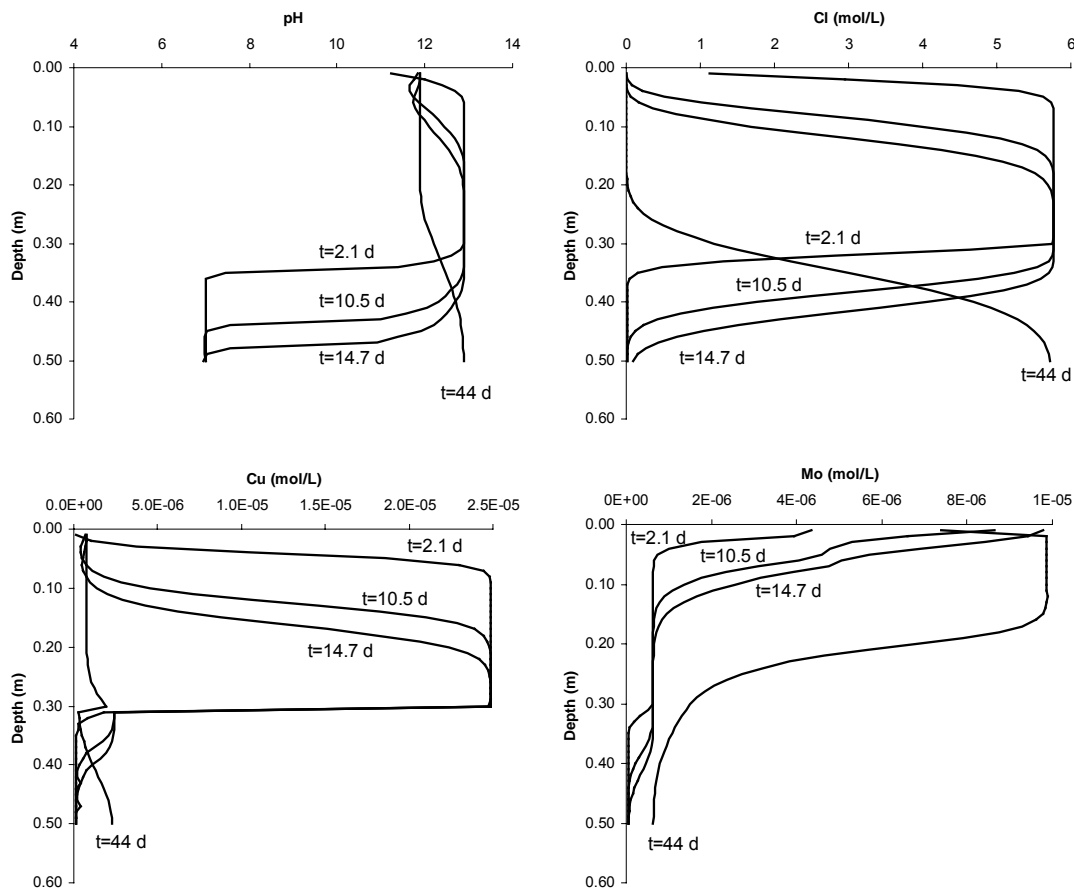


Figure 40 pH and concentration Profile (Cl, Cu and Mo) of Soil impact from Monolithic Cement-Stabilised material. The emission is controlled by percolation and plotted at different times ranging from 0 to 100 days.

In Figure 40, the effect of percolation from a stabilised waste layer on top of a soil layer is shown for up to 44 days (280 mm/yr). It can be seen that the mass transfer is substantially greater from percolation than diffusion. The pH and Cl fronts move down from the stabilised waste into the soil layer. The Cl concentration is depleted in the upper layer of the stabilised waste, the pH in the upper layer decreases from 12.9 to about 12 after 44 days. Cu is transported through the stabilised waste layer but is bound to and/or precipitated in the soil layer. The release of these elements into the environment is substantially reduced by application of the soil layer. It should be noted that carbonation processes are not taken into account in these model calculations. Moreover, the percolation results are not directly comparable to the measured values in the pilot experiment because the model calculation

assumes that the stabilised waste material is crushed (whereas the pilot experiment deals with a monolithic material). These results show the potential to give a detailed description of the chemical processes occurring under field conditions and may lead to the foundation of reliable limit values based on predicted contaminant emission.

Based on the current evaluation, the building blocks that are required for impact modelling to subsequently derive landfill criteria for monolithic waste can be identified as follows

(Figure 13):

- release by diffusion from monolith directly to soil drainage layer
- release by crushed monolith to soil drainage layer (brittle layer resulting from salt being completely washed out)
- infiltration through preferential flow channels to soil drainage layer including
 - * carbonation
 - * degree of sealing by carbonation
- pH buffering by soil drainage layer
- leakage through bottom liner and transport to subsoil and groundwater

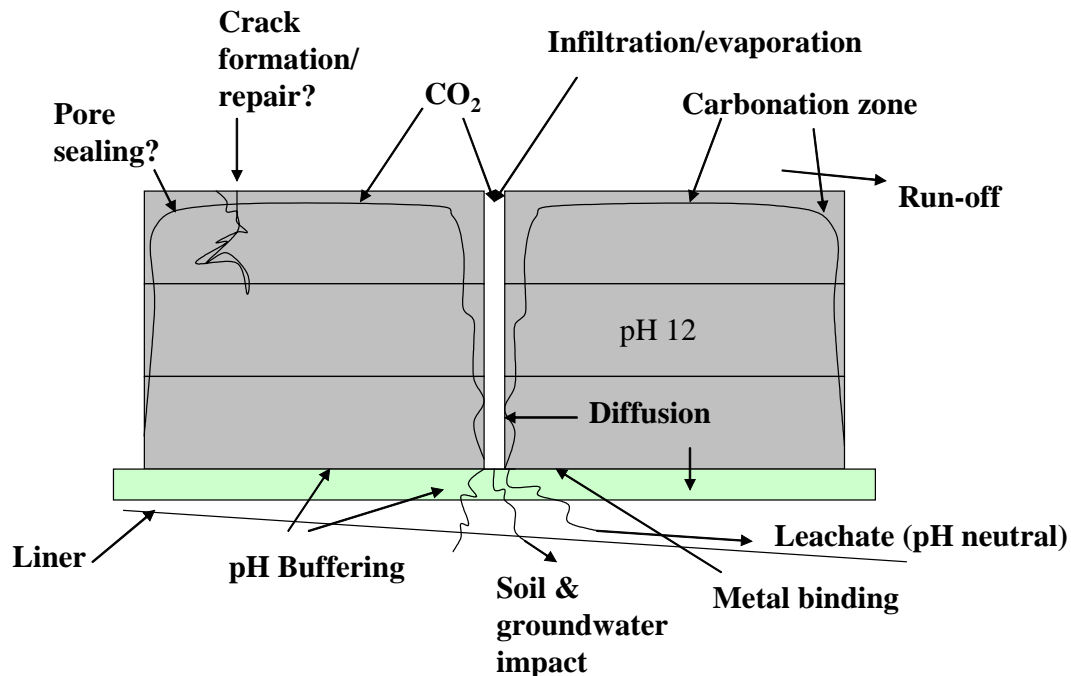


Figure 41 Scenario description for impact evaluation of monolithic waste disposal

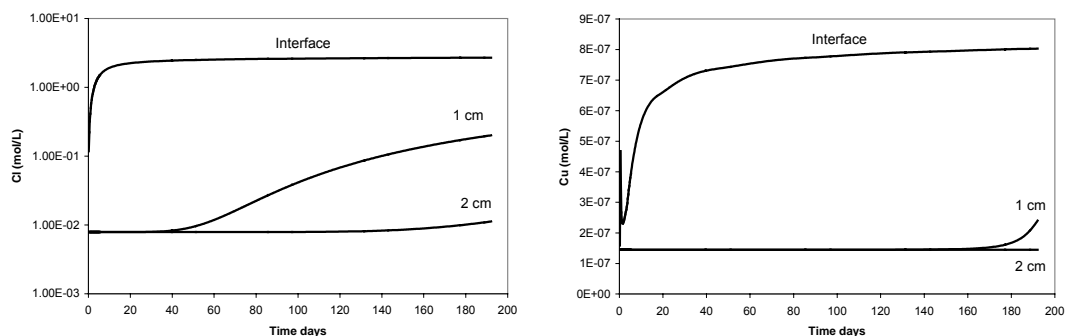


Figure 42 Profile of Cl and Cu concentrations at the stabilised waste interface and the underlying soil at 1 and 2 cm depth as a function of time.

In the case of percolation, a front may be seen passing a pre-defined POC. In Figure 42 an example of such a front is given. Based on the available pieces of information, a full chemical reaction transport model to describe release from a monolith waste is possible by taking into account the different factors and mechanisms controlling release. In Figure 41 all of these aspects are shown. Ongoing work is focussed on completing this fundamental model description.

4.6 Geochemical modelling of changes in leaching behaviour as a result of altered waste properties

4.6.1 Influence of waste properties on the leaching behaviour.

The results from geochemical modelling show that there is understanding of the chemical processes that determine the leaching behaviour of a significant amount of elements from the waste mixture. With this information a basis is formed for sensitivity analysis. With sensitivity analysis, influences of changing contaminant availability, amounts of organic matter and/or HFO can be assessed. The outcome can serve as a basis for waste management decisions for landfill owners.

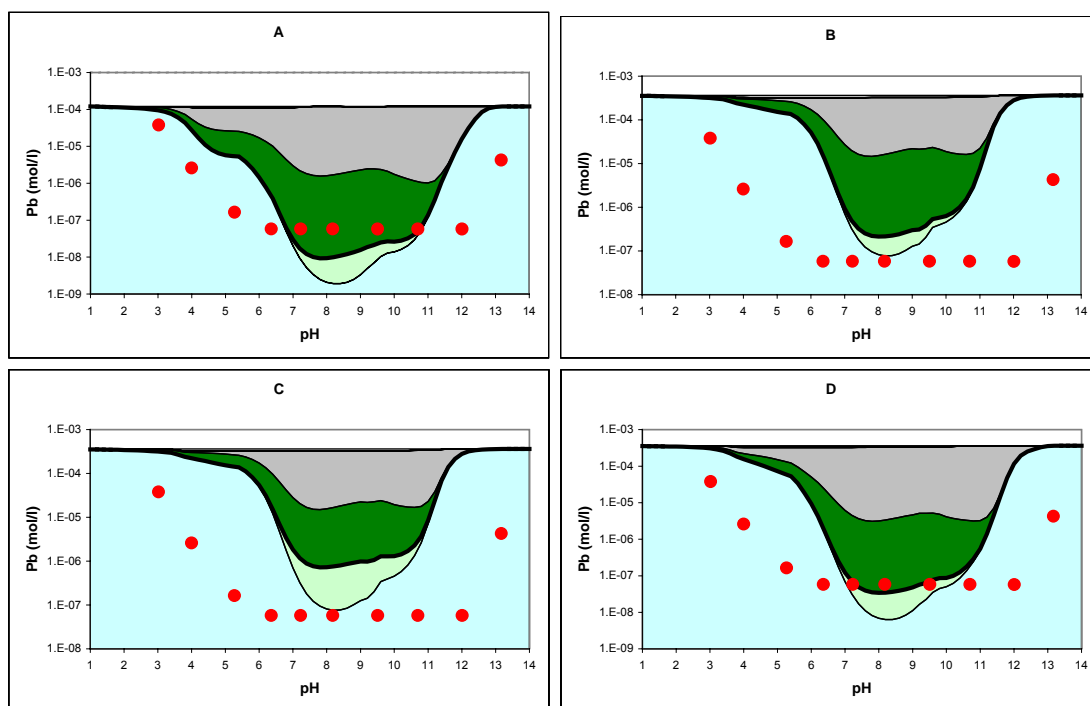


Figure 43 Prediction of Pb leaching as a function of pH from a predominantly inorganic waste mixture under varying conditions. A: Initial calculations; B: Pb availability is increased by a factor 3; C: Pb availability and DOC concentration is increased by a factor 3; D: Pb availability and the content of HFO is increased by a factor 3.

Two examples have been worked out in detail, the first example deals with the calculated Pb emissions in the waste mixture as a result of an increased Pb availability. The initial calculations are given in Figure 43A, it can be seen that Pb is substantially bound to HFO in the solid phase at neutral to slightly acidic pH values. Figure 43B shows the measured and predicted pH dependent leaching behaviour of Pb where the availability of Pb was increased by a factor 10. In Figure 43C, the Pb availability is increased 10 fold and and the DOC

concentration is increased by a factor 3 in the model. It can be seen that the predicted Pb emissions in the neutral to acidic pH region significantly increase as a result of the increased availability. This implies that increasing Pb availability under unchanging conditions of the waste mixture will directly result in an increasing Pb emission.

Figure 43C shows the effect of increased DOC concentrations on the predicted Pb emissions. It can be seen that Pb emission become higher, mainly as a result of a higher concentration of organically complexed Pb. Increase of both the Pb availability as well as the HFO content of the waste mixture will lead to a subsequent reduction of the Pb emissions (Figure 43D) compared to Figure 43B and C. The leaching behaviour of Pb is almost equal to the initial calculation in Figure 43A. Only at pH values lower than 6, an increase in the emissions is observed as already shown in the initial calculations (Figure 43A). Binding to HFO will not be the dominant solubility controlling mechanism at these conditions. However, these low pH values will probably not be relevant in practice.

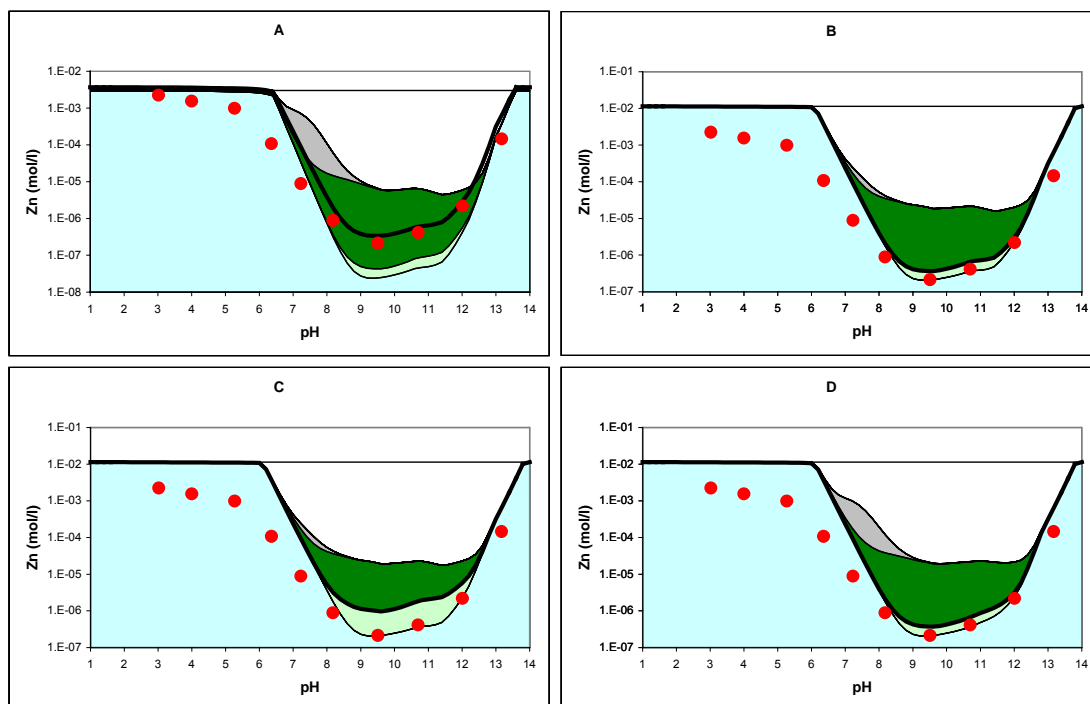


Figure 44 Prediction of Zn leaching as a function of pH from a predominantly inorganic waste mixture under varying conditions. A: Initial calculations; B: Zn availability is increased by a factor 3; C: Zn availability and DOC concentration is increased by a factor 3; D: Zn availability and the content of HFO is increased by a factor 3.

The second example of the sensitivity analysis is given for the leaching of Zn. The initial model results are given in Figure 44A and show that Zn is primarily in the form of mineral phases at neutral to alkaline pH values. We have calculated the effects on Zn leachability in case the availability is 10 times higher without changing any of the other parameters. Figure 44B shows that there is a limited effect on Zn leaching in the neutral to alkaline pH range when the availability is increased to a factor 10. The solubility controlling mineral Willemite determines the dissolved Zn concentrations and this does not depend on the total amount of (available) Zn in the system. However, Zn leaching increases at very low pH values to the available concentration.

Increasing DOC concentrations will have an effect on Zn leaching (Figure 44C) but not to the same extent as shown for Pb (Figure 43). The increased HFO content does not effect the leached Zn concentrations (Figure 44D). However, it can be seen that the speciation in the solid phase changes in the neutral pH region. Sorption to HFO will be a more important process in the binding of Zn to the solid matrix.

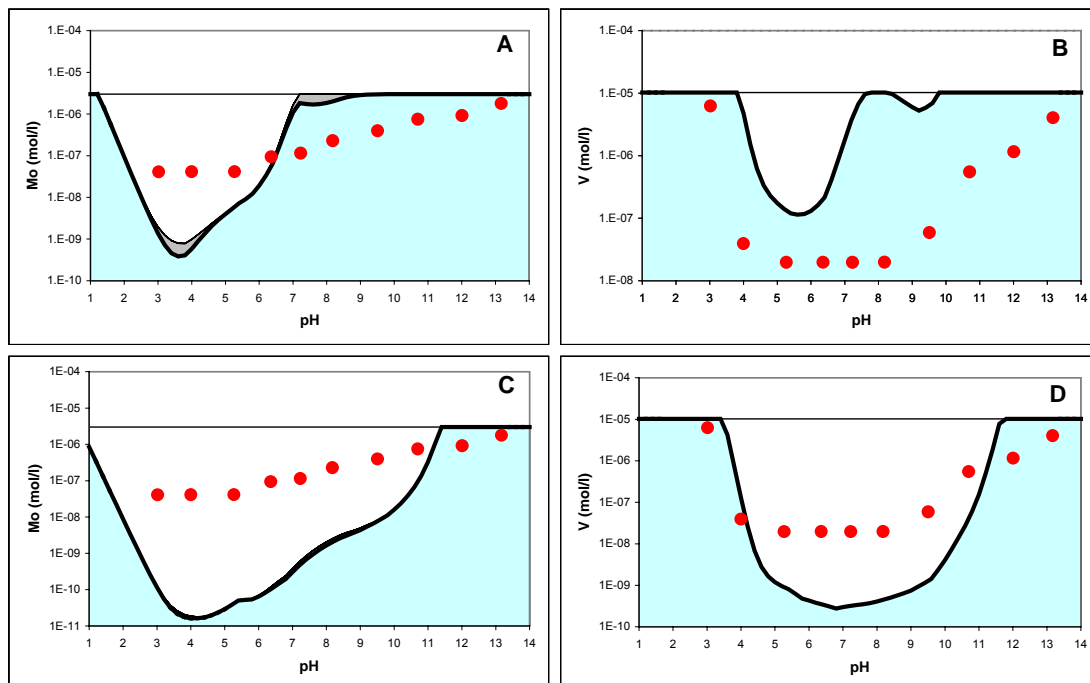


Figure 45 Prediction of the leaching behaviour of Mo and V as a result of an increased Pb availability. Figure A and B shows the initial prediction for Mo and V. Mo (C) and V (D) leachability after increasing Pb availability by a factor of 10.

4.6.2 Influence of increased availability on the leaching behaviour of other elements

The results presented in Figure 43 and Figure 44 already showed that the leaching behaviour of contaminants could be adjusted when changing properties of the waste mixture. In this way, there are opportunities to improve waste management options by introduction of tolerances in available contaminant concentrations. This can be practiced by administration of the total available amounts of contaminants in relation to the amounts of HFO and solid organic matter. However, increasing availabilities for one metal might affect the leaching behaviour of other elements by competition of elements for binding sites on HFO and solid organic matter or mineral formation.

Figure 45 shows the effect of increased Pb availability (factor 10) on the leaching behaviour of Mo and V. As mentioned before Pb influences the leachability of Mo and V through formation of Pb-molybdate and Pb-vanadates. Increasing the Pb availability changes the predicted Mo and V leachate concentrations significantly. In this example, the predicted leaching behaviour of Mo and V is substantially lower as a result of an increased Pb availability. However, changing contaminant availabilities could also result in enhanced leaching of other contaminants due to competition processes on surfaces (HFO and/or organic matter). These results stress that the improvement of the environmental quality of waste materials must be

assessed by studies, which include measurements and modelling of all relevant elements/compounds.

4.6.3 Influence of reducing conditions on the leaching behaviour of Cu, Fe and Mn

Reducing conditions will be dominant in a landfill scenario for a significant amount of time. However, laboratory leaching tests are generally performed under atmospheric conditions. This aspect needs to be taken into account for estimation of the long-term prediction of contaminant emissions. Reducing conditions have a pronounced effect on the leaching behaviour of waste materials in a landfill.

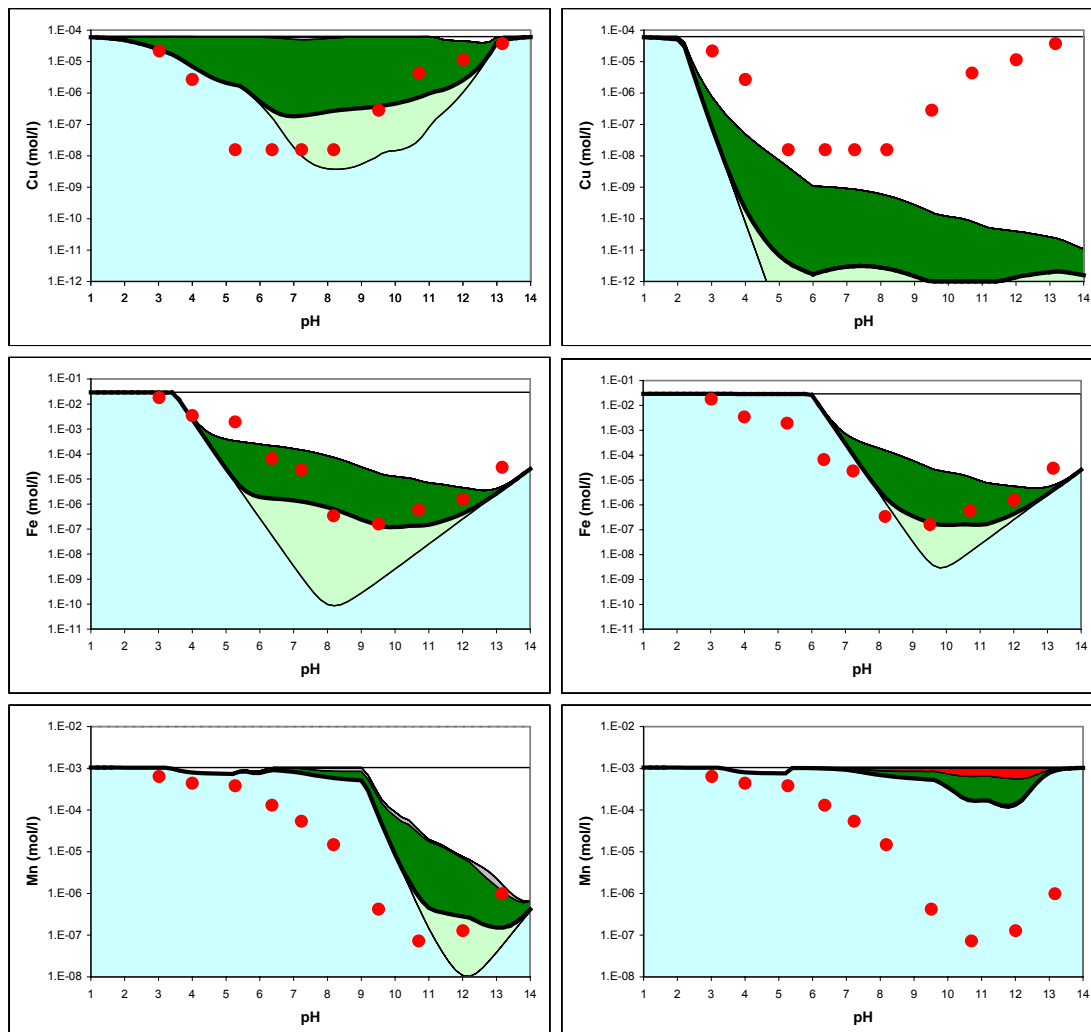


Figure 46 Prediction of Cu, Fe and Mn leaching behaviour in a predominantly inorganic waste mixture as a function of pH. The upper graphs show the initial modelling results, lower graphs show the results under assumption of reducing conditions.

Figure 46 shows the change in leachability of Cu, Fe and Mn after imposing reducing conditions on the system ($p_e + pH = 6$). Cu leachability is significantly reduced after imposing reducing conditions. In case of Fe the solubility curve shifts to higher pH as the more mobile Fe^{2+} is formed. The increase mobility of Mn is noticed, which is explained by the formation of the more mobile Mn^{2+} .

4.7 Numerical elaboration of hydrology and biochemistry

Hydrological and the biochemical algorithms are modeled in Orchestra. This program describes the waste bulk as a cascade of stirred tanks as depicted in figure 4.1, where in all tanks the biochemical reactions described in chapter 5 take place. Within Orchestra additionally the situation can be simulated in which leachate is nitrified and recirculated into the waste. The input and output of Orchestra are depicted in Figure 47.

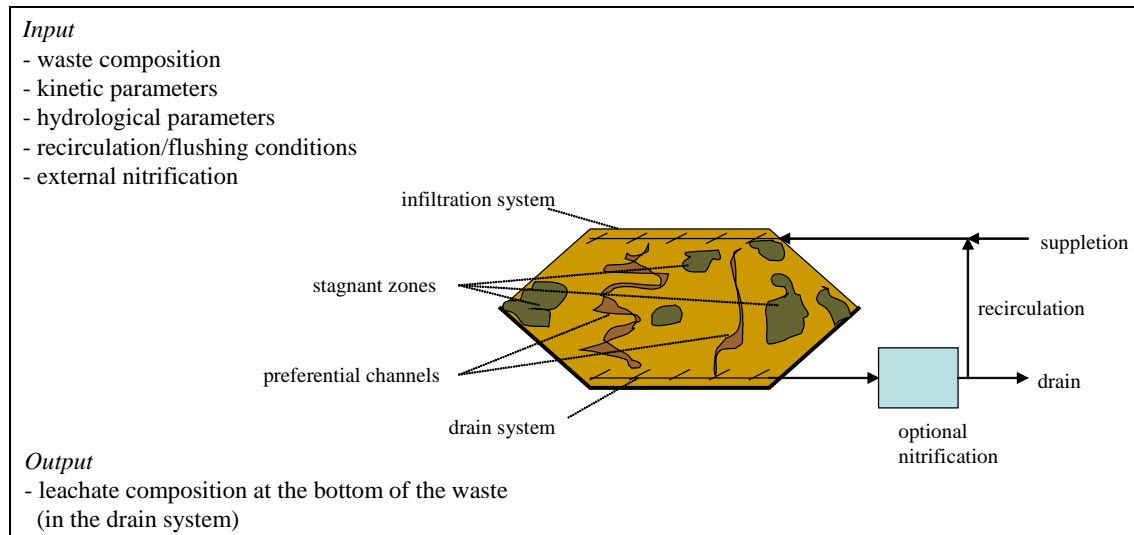


Figure 47 Description of the Orchestra-model

4.7.1 Validation

Orchestra is validated by comparing results with results from column experiments from a previous bioreactor demonstration in the Netherlands in which biodegradation of waste was enhanced through leachate recirculation. During this experiment, the formation of biogas and concentrations of pollutants in the liquid phase was intensely followed (42).

The column was flushed upwards; leachate was pumped in at the bottom of the column and extracted at the top. The expected effects were:

- a co-current flow of gas and water, both flowing upwards from the bottom to the top
- all columns were saturated upon flushing
- a slight reduction in density and most likely an increase in permeability

the result of this is most likely a very complete and homogeneous way of infiltrating the columns.

These columns are modelled in Orchestra as a system in which all waste is in the mobile phase. Other input parameters were:

- waste composition as determined prior to the test (organic dry matter: 210 kg per ton, 70% is biodegradable, water content 50% and a Cl-content of 2 g per kg d.s)
- leachate supply of 10 m³ per m³ waste per year and a composition of : BOD: 50 mg l⁻¹; COD: 3000 mg l⁻¹; N_{kj}: 1200 mg l⁻¹; Cl⁻: 5000 mg l⁻¹;
- a rate of hydrolysis, which results in a rate of biogas formation as observed in the column tests;
- a rate of methanogenesis, resulting in leaching of 10 % of the gas formation potential in the water phase (as observed in the column tests).

Figure 48 and Figure 49 show the results of the model calculations are compared with the results from the column tests. Both calculated and modelled results refer to concentrations in the extracted leachate in the course of time.

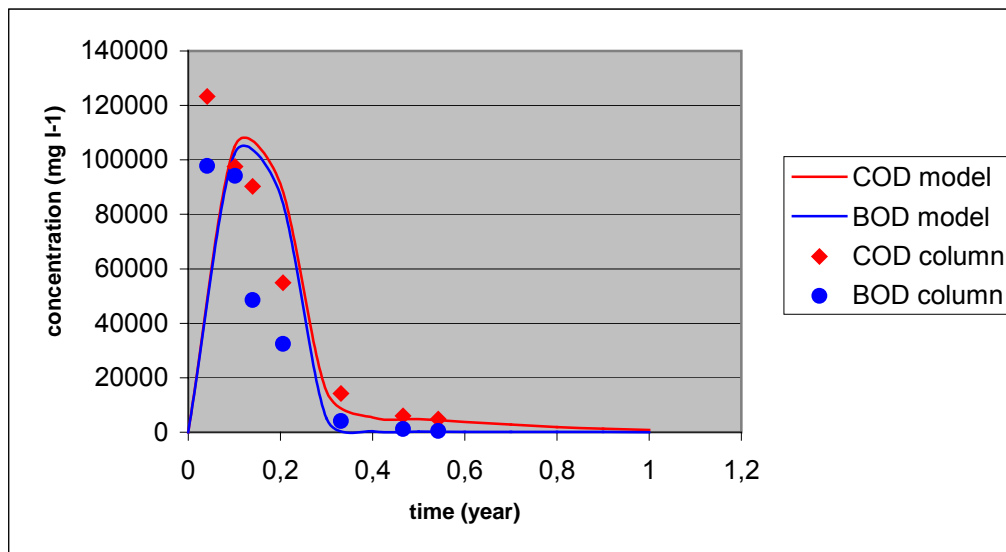


Figure 48 Development of BOD and COD in the leachate

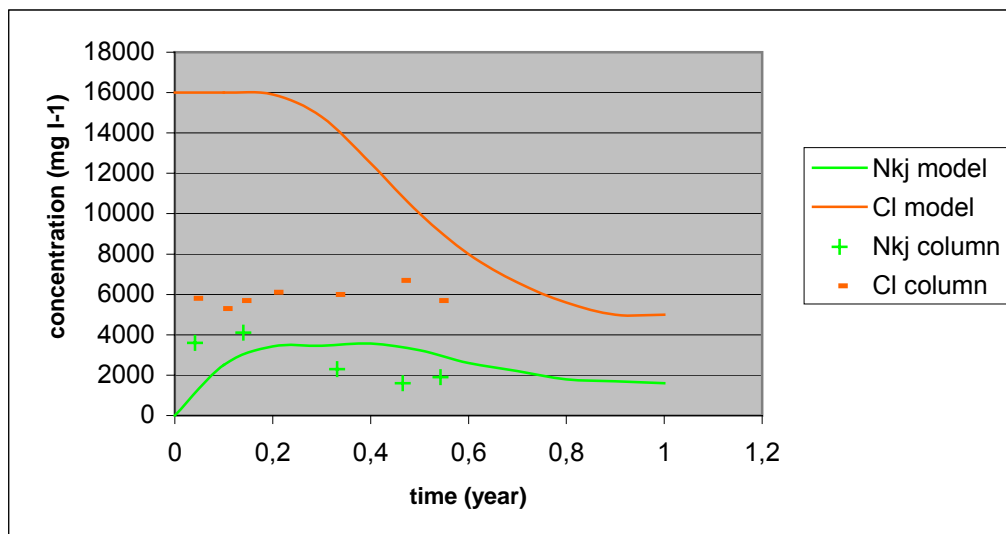


Figure 49 Development of Cl and N_{kj} in the leachate

Both figures show that, except for Cl^- , the model predicts the order of magnitude of concentrations quite well. However in reality the peak in concentrations seems to occur somewhat earlier in time and decreases subsequently somewhat faster. This might have two reasons:

- The model calculation assumes that the column is filled in day one, after which infiltration/flushing is immediately fact. In the real columns it took three months before leaching was effective (after first attempts to infiltrate leachate top down failed). In this time, significant amount of organic material was converted and available for flushing.
- The column is modelled as a cascade of 10 reactors in series, which results in a strong plug-flow and as a result reduced initial concentrations.

The calculated chloride concentrations are much higher than the measured ones. Also the total amount actually being flushed out is much less than the calculated amount being flushed out. Obviously the C-analysis on which the calculation was based was not representative for the whole column.

4.7.2 Example calculations for the pilot in Landgraaf

The main application of the biological decay model within the integrated Dutch project on sustainable landfilling is the prediction of long-term emissions of the Landgraaf-bioreactor cell and evaluate the effects of different operating procedures. For the full evaluation of the Landgraaf bioreactor-cell, please see the background document of this experiment (Luchien et al, 2006). In this chapter a few first explorations are presented of long-term emissions from this bioreactor. The calculations in this chapter mainly refer to N_{kj} , which proves to be the most problematic component to abate (44). At the end of this paragraph a few results for COD are presented as well.

These preliminary calculations of Landgraaf are performed assuming three time-phases of infiltration/recirculation:

- In the first 5 years leachate is mainly recirculated with a liquid/solid ratio of 167 l m^{-3} waste per year;
- In the next 15 years the waste is flushed with clean water, also with a liquid/solid ratio of 167 l m^{-3} waste per year;
- an infinite time afterwards (of which 15 years are simulated) in which forced infiltration is stopped and only natural infiltration with clean rainwater takes place at a liquid/solid ratio of $0,33 \text{ l m}^{-3}$ waste per year.

Hydrology is characterised by the following factors, estimated on the basis of the experimental data of the Landgraaf bioreactor demonstration (44):

- preferential channels make up 10% of the waste volume; 60% of the liquid flows through preferential channels;
- the mobile phase makes up 50% of the waste volume; 40% of liquid transport proceeds here;
- the stagnant bulk makes up 40% of the waste volume.

In these conditions, N_{kj} -concentrations in the leachate after the treatment period of 20 years are mainly determined by two factors which are not that well known: delayed supply of N_{kj} as a result of decaying biomass and delayed supply of N_{kj} from the stagnant bulk. In Figure 50, the effect of decay rate of dead biomass on long-term N_{kj} -emissions is illustrated, while diffusion of N_{kj} from the stagnant bulk is negligible. Calculations show that when the rate at which dead biomass decays becomes longer, the long-term concentrations of N_{kj} will be higher.

Figure 50 shows that when decay of dead biomass is fast compared to the time-frame of flushing, most N_{kj} is available for flushing at an early stage and most of the N_{kj} can be flushed out in between years 6 and 20. After ending forced infiltrations after year 20, concentrations of N_{kj} hardly rise. However when the rate of decay slows down, N_{kj} is increasingly released towards the end of the flushing period. As a result, N_{kj} is not completely flushed out, which results in increased N_{kj} -concentrations when forced infiltration is stopped after 20 years. This effect can already be noticed when the flushing period is about 4 times the half-time of decay of methanogenic biomass.

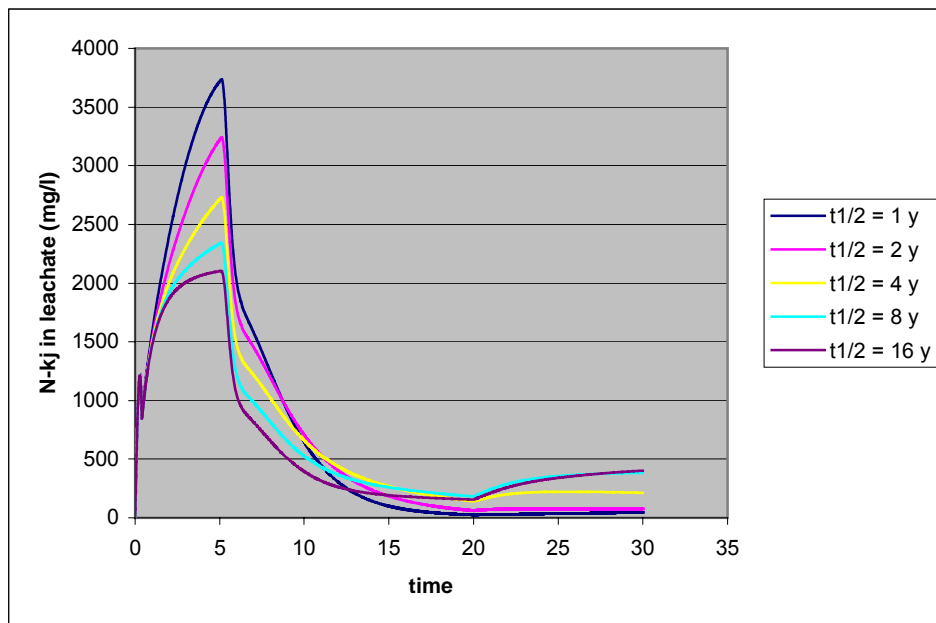


Figure 50 N_{kj} concentrations in time, assuming different half lives of decay of dead biomass, ranging from 1 year to 16 years.

Figure 50 illustrates the effect of delayed supply of N_{kj} from the stagnant bulk. These calculations were performed assuming a rapid decay of methanogenic biomass and thus negligible increase of N_{kj} from the methanogenic biomass after 20 years (see above).

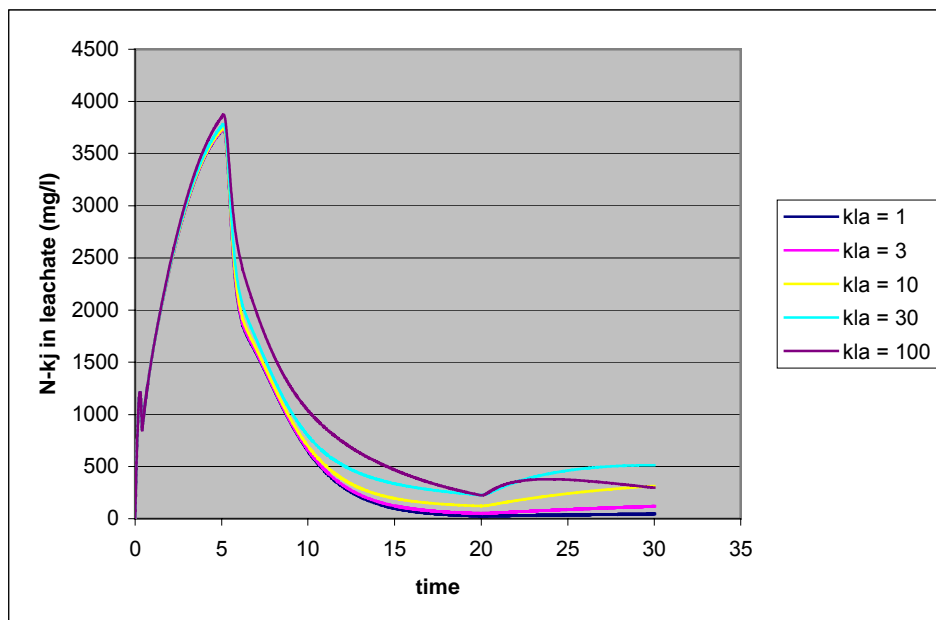


Figure 51 N_{kj} concentrations in time, assuming different diffusion coefficients from the stagnant zone.

Figure 51 shows that when mass-transfer is increased, the concentrations of N_{kj} after 20 years are increased as well. When the mass-transfer is very high, the supply of N_{kj} in the stagnant

phase run out, ultimately resulting in a reduction of N_{kj} -concentrations in the leachate that is produced.

4.7.3 Effectiveness of nitrification/denitrification

External nitrification and recirculation of the nitrified leachate is sometimes proposed as a possible solution for high N_{kj} -concentrations in a bioreactor. In the figures below (Figure 52 and Figure 53) the effect of this measure is depicted, both for a case when N_{kj} is supplied from the methanogenic biomass (half life of 4 years) and for a case when N_{kj} is supplied from a stagnant bulk ($k_1 a = 10$).

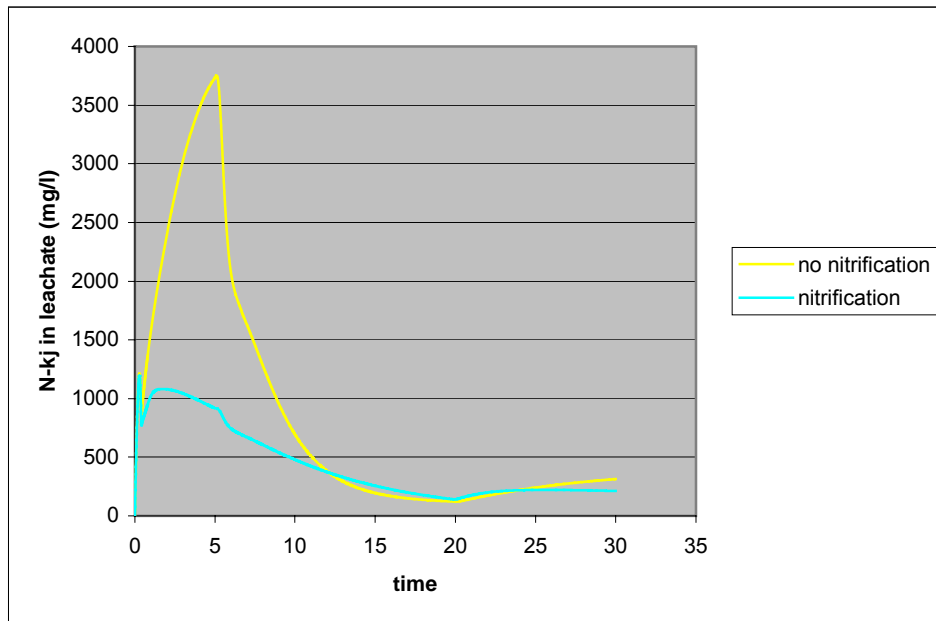


Figure 52 Effect of nitrification/denitrification in case of delayed release of N_{kj} from methanogenic biomass

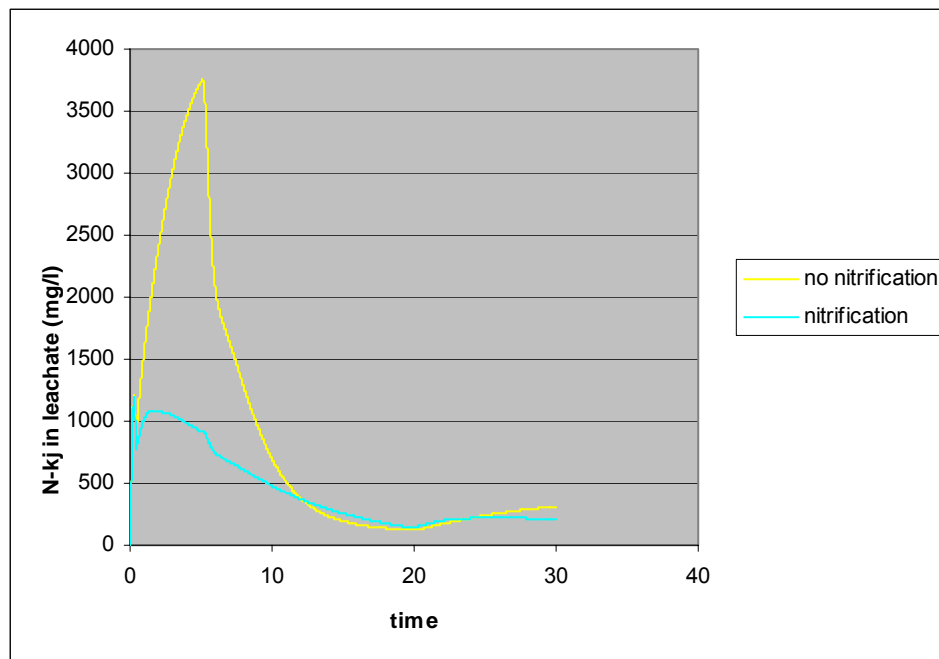


Figure 53 Effect of nitrification/denitrification in case of delayed release of N_{kj} from stagnant zones ($k_d A = 10$)

In both cases, recirculation of nitrified leachate results in a reduction of N_{kj} in the leachate during the treatment period. However effects on longer terms are negligible. Recirculation of nitrified leachate seems to be more a cost saver for leachate treatment rather than a solution to reduce long-term N_{kj} -concentrations in the leachate.

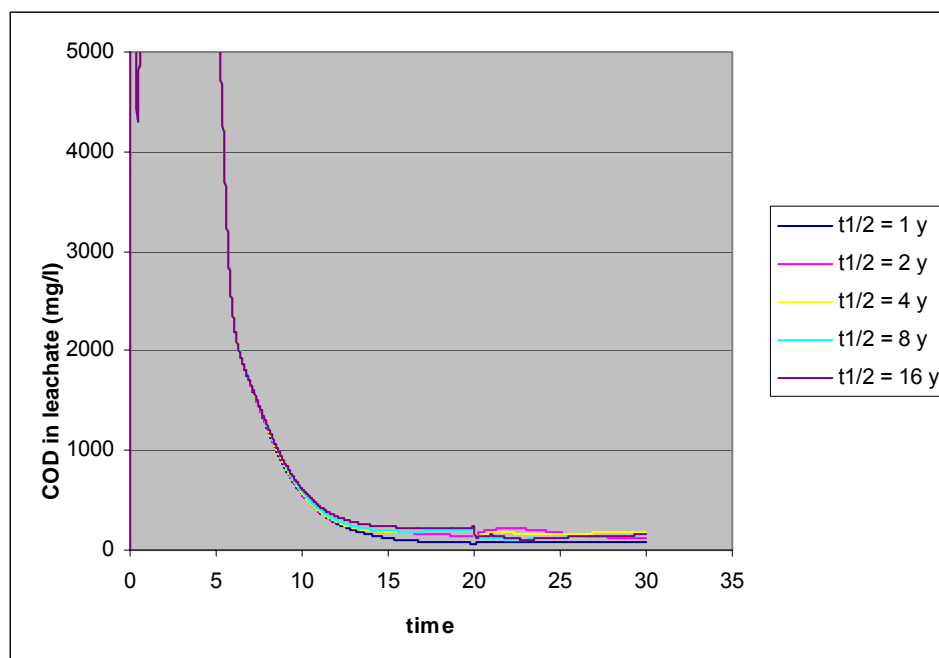


Figure 54 COD-concentrations in time, assuming different half lives of decay of dead biomass, ranging from 1 year to 16 years.

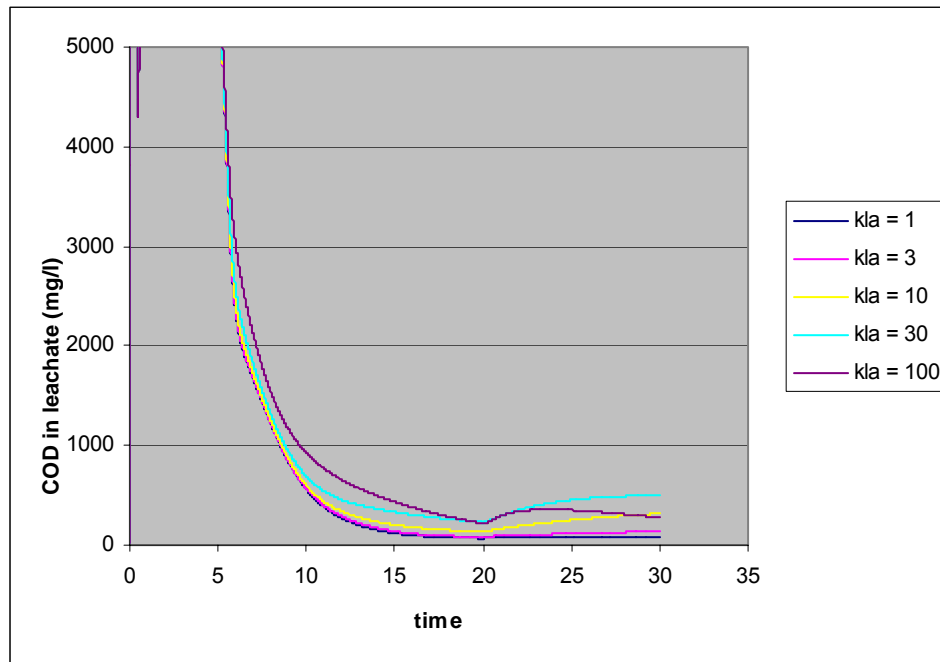


Figure 55 COD-concentrations in time, assuming different diffusion coefficients from the stagnant zone.

Figure 54 and Figure 55 show the COD concentrations, calculated during the simulations described above. In general, increase of COD due to delayed release from methanogenic biomass does not result in an increase in concentrations. Delayed release from the stagnant zones does.

5. Conclusions

The work presented in this report shows the developments in the level of understanding of the three tested landfill concepts (predominantly organic waste, predominantly inorganic waste and cement stabilised hazardous waste). In general, data storage in a uniform data format and the developed database proved to be an important basis for data comparison. The database can be extended with future data from both regular quality control as well as with research project results. One of the goals of this project was to compare laboratory and field data to draw conclusions on the pilot experiments. Since detailed test results should be made more widely accessible, the development of an expert system comprised of methodology guidance, databases of laboratory and field data, geochemical speciation modelling tools, and multiple scenario simulations, will provide a very useful tool for waste and material producers, landfill owners, end-users, consultants and regulators.

Recent developments with the database/expert system LeachXS during the later stages of the project made it feasible to predict the leaching behaviour in the pilot experiments based on laboratory leaching tests. Major progress has been made in understanding the chemical processes leading to release of contaminants. This allows drawing more general conclusions about release controlling processes in landfills. A striking example of the modelling capabilities is the ability to predict the leaching behaviour of a mixture of waste materials, based on the chemical properties of the individual materials. Waste-waste interactions influence the behaviour of a landfill body. This finding forms the basis for judgement of the long-term environmental behaviour of a landfill compartment instead of the currently practised waste-by-waste judgement.

Organic matter plays an important role in both the predominantly organic and inorganic landfill concepts. However, the emphasis shifts going from organic to degraded predominantly inorganic waste. Binding to dissolved organic matter in the leachate is dominant in the organic waste landfill. In the predominantly inorganic waste landfill, binding to particulate organic matter is mainly dominant. Thus the release to the environment is reduced and more stable conditions develop with the degradation of organic waste materials.

In the next paragraphs, conclusions on the pilot experiment results are given for each sustainable landfill concept. The reader is referred to the sustainable landfill project reports for more specific information (44-47).

Stabilised waste

The integration of laboratory, lysimeter and pilot scale testing with long term release modelling and impact assessment to soil and groundwater provides the basis for proper criteria development for stabilised monolithic waste landfills. It must be emphasized that further work is needed to integrate the most relevant processes in the overall scenario. The carbonation of the material by atmospheric CO₂ is one of the more complex processes to deal with. However, this work has already led to significant improvements in understanding the environmental behaviour of stabilised waste landfills.

The leaching behaviour of different stabilised waste materials is far more systematic than might be concluded from the single step leaching tests most commonly applied in judging stabilised waste performance. For judging monolithic waste behaviour, a limited number of leaching tests can provide the crucial answers needed to assess long-term impact: the combination of pH dependence test and a form of tank leach test is suitable. It is important not to confuse characterisation of monolithic waste behaviour with regular quality control testing. The first is designed to develop criteria and to judge the performance of stabilised waste prepared according to various recipes in specific scenarios. The latter is undertaken to show consistency with the characterisation information and thus comply with regulatory criteria. For compliance testing and quality control, a short (1 day) tank leach test will suffice provided that this test is related to results from a characterisation tank leach test (e.g. NEN 7375).

Monolithic waste landfill design is in its infancy and the processes leading to release have not been addressed systematically. When evaluating the complex issue of environmental impact of stabilised waste, using approaches that are too simple lead to poor management decisions. In this project, significant progress has been made in understanding the leaching processes in a monolithic waste landfill. The results of this study show that several aspects of the scenario description can be addressed adequately.

Chemical speciation modelling using mineral solubility, sorption and organic matter interactions provides identification of minerals controlling release and highlights similarities amongst widely different materials. Understanding chemical speciation provides insights into system improvement and enhances long-term release prediction for many constituents of concern. Dissolved organic carbon (DOC) proves to be quite relevant for cement stabilisation, and in particular, for cement stabilisation of contaminated soil.

Predominantly inorganic waste

In this study, geochemical speciation modelling was used to identify important chemical processes that determine leaching from mixed waste materials in short and long term. pH-static leaching tests in combination with model predictions of the leaching behaviour and the speciation of contaminants in both the solid phase and solution provides detailed knowledge of chemical processes in these apparent heterogeneous materials. Significant progress in geochemical modelling has been made, whereas the pH dependent solubility of many elements can be adequately predicted simultaneously by model calculations. This is particularly true for the pH domain around the native pH of the material (neutral pH). There are gaps between data and model predictions for a number of constituents, which are due to missing thermodynamic data, as yet unidentified mineral phases or kinetics of dissolution and precipitation reactions. The advantage of the applied integral approach is that more guidance can be derived as to which factors need further work. Kinetics have been shown to be of relevance in the type of leach test used in this work, which may help to decide that at what level a match between measurement and prediction is sufficiently accurate for a subsequent decision. The potential to predict leaching behaviour under conditions that have not yet been tested before (low L/S, imposed redox condition, increased contamination, external influences) provide important insight on how to design verification experiments. In general, the results show that the approach of characterisation and geochemical modelling provides an increased level of understanding the relationships between major, minor and trace elements, which helps significantly to make choices through the acceptance of waste to reach a more sustainable landfill practice. Modelling results show that the interactions between major, minor and trace elements forms a very significant limitation for studies in which only a limited set of elements is

evaluated, let alone the unjustified omission of major elements, which dictate the leaching conditions that are imposed on trace constituents of concern.

We have shown the ability to predict the leaching behaviour of a mixture of waste materials, based on the chemical properties of the individual materials. Waste-waste interactions influence the behaviour of a landfill body. This finding forms the basis for judgement of the long-term environmental behaviour of a landfill compartment instead of the currently practised waste-by-waste judgement.

If the relevant parameters (Sum of dissolved and particulate organic matter, sum of Fe and Al oxide surfaces, relevant minerals) describing the leaching behaviour of the landfilled mix can be derived from the mass contribution and properties of disposed waste in a cell, a reasonably accurate prediction of leachate quality may prove feasible for that cell. This type of prediction may be useful for deciding about the level of aftercare measures to be defined at the time of landfill closure. Thus the preliminary sensitivity analysis of the leaching behaviour under varying conditions indicates that there is a scientific basis for more focused waste selection/acceptance criteria in order to reduce the environmental impact of landfills, thereby creating a landfill with minimal impact which in that way can help to reduce or eliminate the need for long-term aftercare.

Predominantly organic waste

The hydrological/biochemical model described in the previous chapters is simple, but gives good insight in factors that govern the effectiveness and long-term emission potential of bioreactors. Some important insights are described in this paragraph.

- *N_{kj} -concentrations are less easily reduced than COD.*

Due to growth of methanogenic biomass, which is high in nitrogen content, large part of the nitrogen is not immediately available for flushing out. Calculations indicate, that in some cases up to 50% of all nitrogen might be stored into the biomass. This is something that was already observed by Beaven (1997) in laboratory tests. COD is also incorporated in methanogenic biomass, but this amount is relatively of less importance and is limited to about 15% of total COD-potential.

This temporary storage of N in the methanogenic biomass results in a delayed release of N_{kj} , and thus increased N_{kj} -concentrations in the leachate on longer terms. This is illustrated in Figure 56, where for one of the simulations of Landgraaf COD and N_{kj} -concentrations in the leachate are depicted, along with the ratio of both.

- *Non-homogeneous flow reduce leachate concentrations significantly*

Flow through waste bodies does not proceed homogeneously. Liquid flow preferably takes place through preferential channels, while other parts of the waste will not be reached by flow of water at all. Pollutants in the latter regions can only be released by diffusion to mobile zones (Figure 57).

Model calculations show that the hydrology has an enormous impact on long-term emissions, and the end term emissions are dependent on (i) the effectiveness of flushing out pollutants in the mobile phase; (ii) remaining convective transport (flow*concentration) of pollutants from this mobile phase and (iii) remaining diffusive transport of pollutants from stagnant zones. In more qualitative terms, several situations can be identified that result in low emissions of pollutants after longer terms:

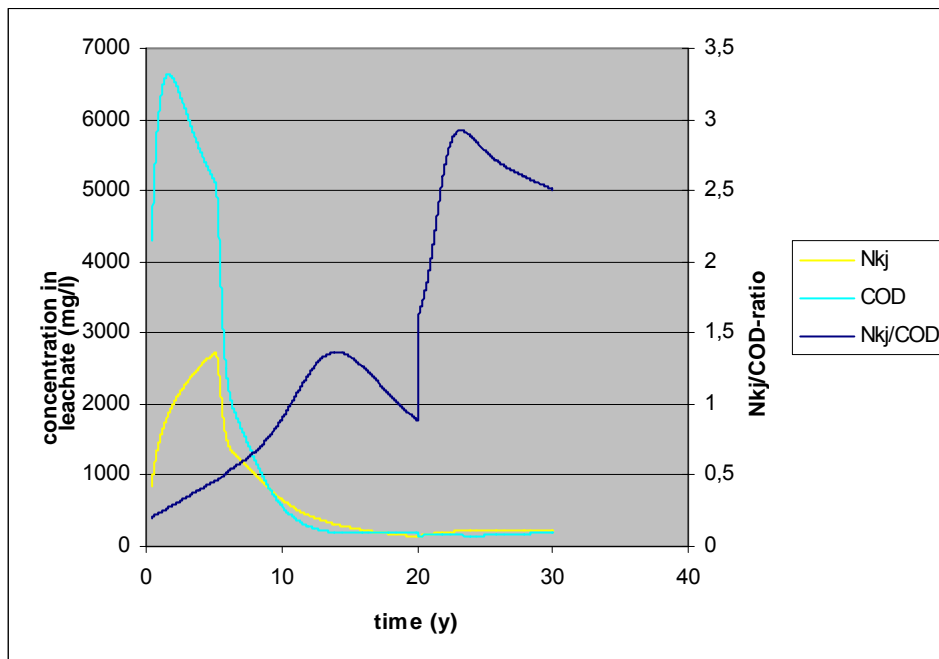


Figure 56 Development of COD and N_{kj} concentrations in a bioreactor effluent

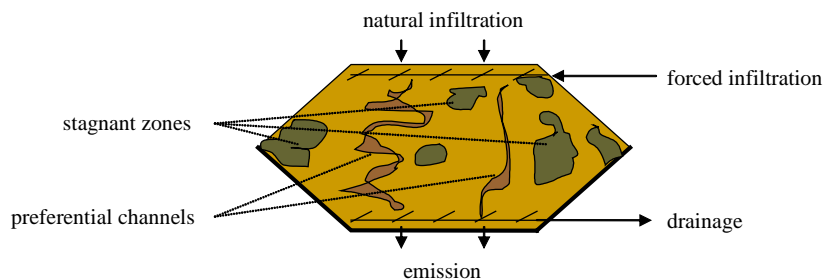


Figure 57 Graphical representation of mobile and stagnant zones in a landfill. Forced infiltration was used in the predominantly organic waste pilot experiment at Landgraaf.

- small preferential channels through which most leachate is transported. Flow through the mobile zone is low combined and diffusive mass-transfer is limited. In this case the pollutants in the preferential channels are flushed out rapidly, and due to the low supply of pollutants from other phases, long-term emissions remains low. This might be the case in many normal landfills, where a relative low flow through the landfill body (excess rainfall at maximum) is combined with highly inhomogeneous waste;
- increased infiltrations, resulting in a relative high flow through the stagnant zones (resulting in flushing out pollutants from this phase as well) combined with low mass transfer from the stagnant zones. This might be the case in many bioreactor situations where infiltration is not completely homogeneous;
- increased infiltration in combination with high mass-transfer from the stagnant zone, in combination with a small fraction of the entire body that is still in a stagnant zone. In this case all pollutants from the entire waste body might be flushed out, resulting in low long-term emissions. This is a close to ideally functioning bioreactor.

Problems do occur in situations where efficient flushing does not reach the entire waste in combination with a moderate mass-transfer from stagnant and mobile phases. Here large part

of the pollutants are not flushed out after initial treatment, but are available for release through convection or diffusion after the initial 20 or 30 years. In such a case, increased concentrations might occur for longer times after closure of the landfill. In the example calculations of Landgraaf, described in 6.2, this is illustrated.

- *Hydrology and decay of methanogenic biomass govern leachate concentrations*

By changing the values of kinetic parameters, mass-transfer and convection, insight is obtained in what factors are most important for the long-term emissions. Table 10 gives an overview of the most important findings for biochemistry (hydrolysis, methanogenesis) and convective transport in series.

In general the rate of biodegradation is higher than the speed at which pollutants are flushed out from the waste, so hydrology is the factor that determines long-term emissions. This is the case in normal landfill operation, where decay proceeds with half-times of about 7 years, but leaching of pollutants continues for centuries. This is also the case in bioreactors, where increased moisture movement results in accelerated degradation (half-times of a few years) where flushing out pollutions might take 20 to 30 years. Only when flushing rates are increased into extreme situations, the rate of biological reactions govern overall release of pollutants, and of all biological reactions decay of methanogenic biomass is the rate-determining step.

Table 10 *Rate-determining factors for leachate concentration*

Flushing	Conclusion
Landfill: normal infiltration (~ 300 mm yr ⁻¹)	Conversion is fast compared to flushing. Concentrations on longer terms (> 30 years) are completely determined by hydrology (flows/homogeneity)
Bioreactor: increased infiltration (~1500 mm yr ⁻¹)	Both conversion and flushing is accelerated. Concentrations on longer terms (> 50 years) are determined by hydrology. On the mid-term (10-30 years) N _{kj} is increased due release from decaying biomass
High-low reactor: largely increased (> 3000 mm jr ⁻¹)	N _{kj} and to some less extent COD on the mid-term (5-20 years) are increased and are determined by decay of methanogenic biomass.

An important conclusion is that in most cases the speed of decay of organic material (neither hydrolysis of methanogenesis) doesn't have a large impact on the leachate quality on longer terms. In other words in bioreactor concepts it is not of primary importance to accelerate the decay of the waste. It is much more important how waste can be flushed as efficiently as possible. Second important aspect is how to deal with the large amounts of nitrogen that is stored in biomass and subsequently released in a delayed way.

6. Recommendations

- The major element chemistry (e.g. Al, Ca, Fe, Mg, Si) is important in the behaviour of contaminants. However, little work has been done yet to analyse these elements for a wide range of landfills. It is recommended to include major elements in the monitoring of landfill leachates to obtain a basis for geochemical speciation modeling.
- Improved understanding of chemical processes from modeling of pH-stat leaching tests has provided the basis for detailed modeling of column test and tank leach test data in LeachXS. The next step should be to model transport processes in laboratory leaching tests as the basis for modeling the transport processes in lysimeter and field scale studies.
- Coupling the organic matter degradation model to the other geochemical models in LeachXS. This will enable to describe emissions in a bioreactor during the degradation process, focused on the changing role of organic matter to emissions of contaminants.

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Annex A

Materials for which Extended Leaching Information is Available

Aggregates, synth. (coal fly ash, mining waste)	Lava stone
Alkaline batteries	Lime stone
Al-production ash	Light weight concrete
Asphalt/asphalt rubble	Lime silicate bricks
Basalt	Metallurgical sludge (CaO-type)
Biomass ash	Metallurgical slag
Bioreactor residue (after degradation)	Milling residues
Blast furnace slag	Mine stone (coal)
Bottom ash (coal)	Mixed waste (70% landfilled waste largely inorg.)
Brown coal ash	MSWI residues (bottom & fly ash, APC residues)
Bricks (ceramic)	Municipal solid waste, fly ash
Catalyst cracker, Cat. ox. RVC	Natural gas production sludge
Chemical sludge (Ni electroplating)	Ni sludge
Clay bricks	Non-purifiable sand blasting dust
Coal fly ash	Oven waste from primary Al production
Compost	PAH, PCB and metal polluted soil
Concrete	Paper sludge
Concrete with coal fly ash	Pb/Zn slag
Construction debris	Phosphate slag
Contaminated soil	Phosphating sludge
Crushing waste	Phosphogypsum
Cryolite waste (zeolite production)	Pigment sludge
Detox., neutralized dewatering sludge	Plastic waste material
Dredging sludge	Preserved wood
Drinking water pipes	Purification sludge from industrial purification
Drinking water product. sludge (ground water)	Purification sludge from textile paint production
Dust from a sand blasting unit	Purification sludge from polymer production
Expanded clay pellets	Refuse derived fuel ash
Fe-Cr catalyst residue	Sand blasting waste
Fe-norit waste from pharmaceuticals industry	Sediments (river, lake, canal)
FeOH sludge needle factory	Sewage sludge
Filter cake MSWI	Shredder waste
Filter dust (ceramic industry)	Sieve sand from demolition breaker
Flot. concentrate/sand blasting waste purific.	Soil (various natural soils: sand, loam, clay)
Fl contaminated dust - primary Al production	Soil amended with sewage sludge
Fluorescent powder	Soil purification extraction residue
Fly ash from isolation material production	Spent catalyst (activated Al)
Fly ash industrial waste and RDF incineration	Stabilized galvanic sludge
Foundry sand (waste material)	Stabilized waste (various)
Foundry oven dust	Steel slag
Galvanic sludge	Tannery sludge
Glass-oven rubble from glass production	TBBA recovery sludge from production of Te

Glaze/enamel sludge	Tiles (ceramic)
Gravitational concentrate/sand blasting waste	Sb containing sludge
HCH soil purification residue. (phys. purific.)	Vitrified MSWI fly ash
Incinerated sewage sludge	Zn-Fe-salt residue from Zn-varnish installation
Jarosite	Zn-MnO- batteries

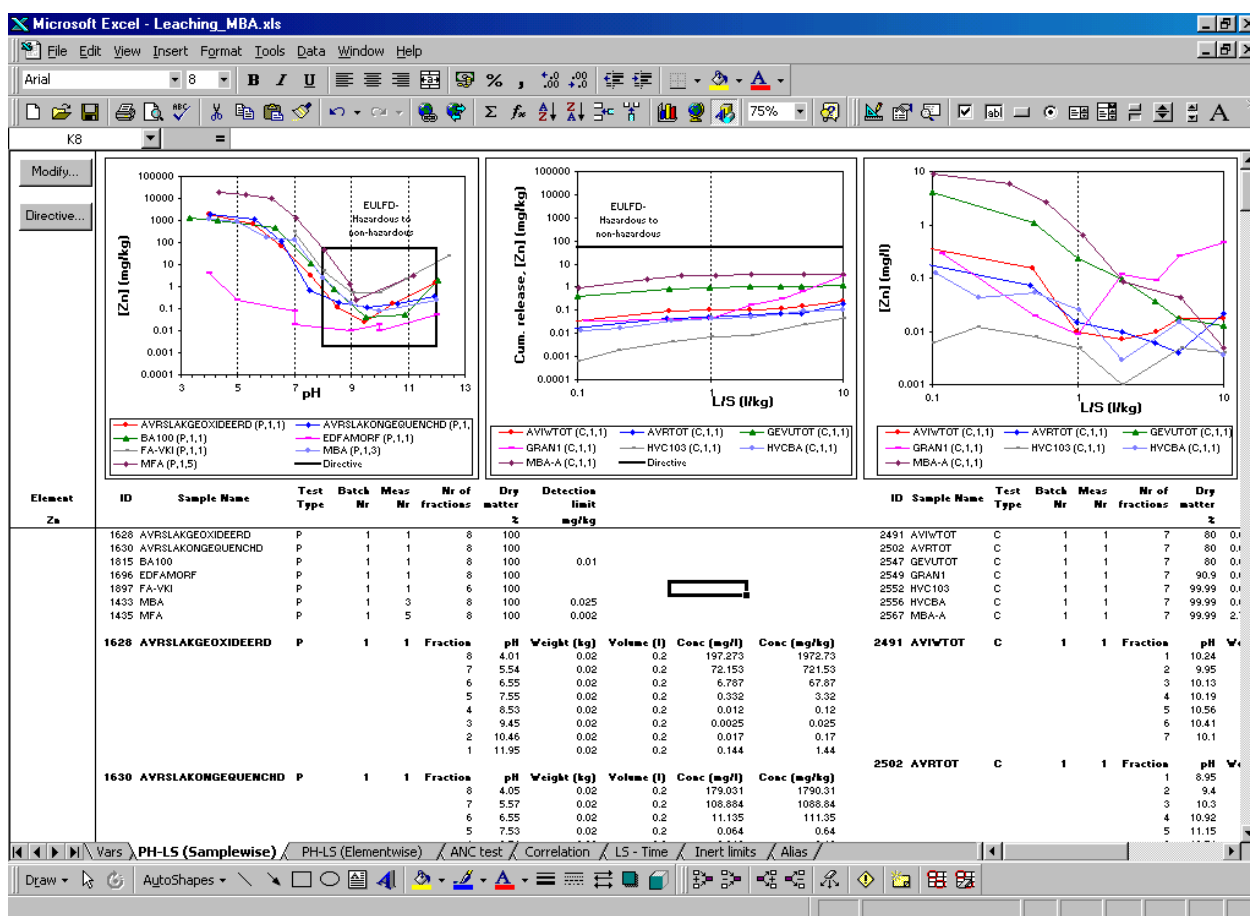
Sources: Mammoet project, RIVM studies, EU Harmonisation work (ECN, DHI, INSA, WRC, IBAC, NNI, UB), ECN research, Dutch Building Materials Decree certification, others.

Annex B

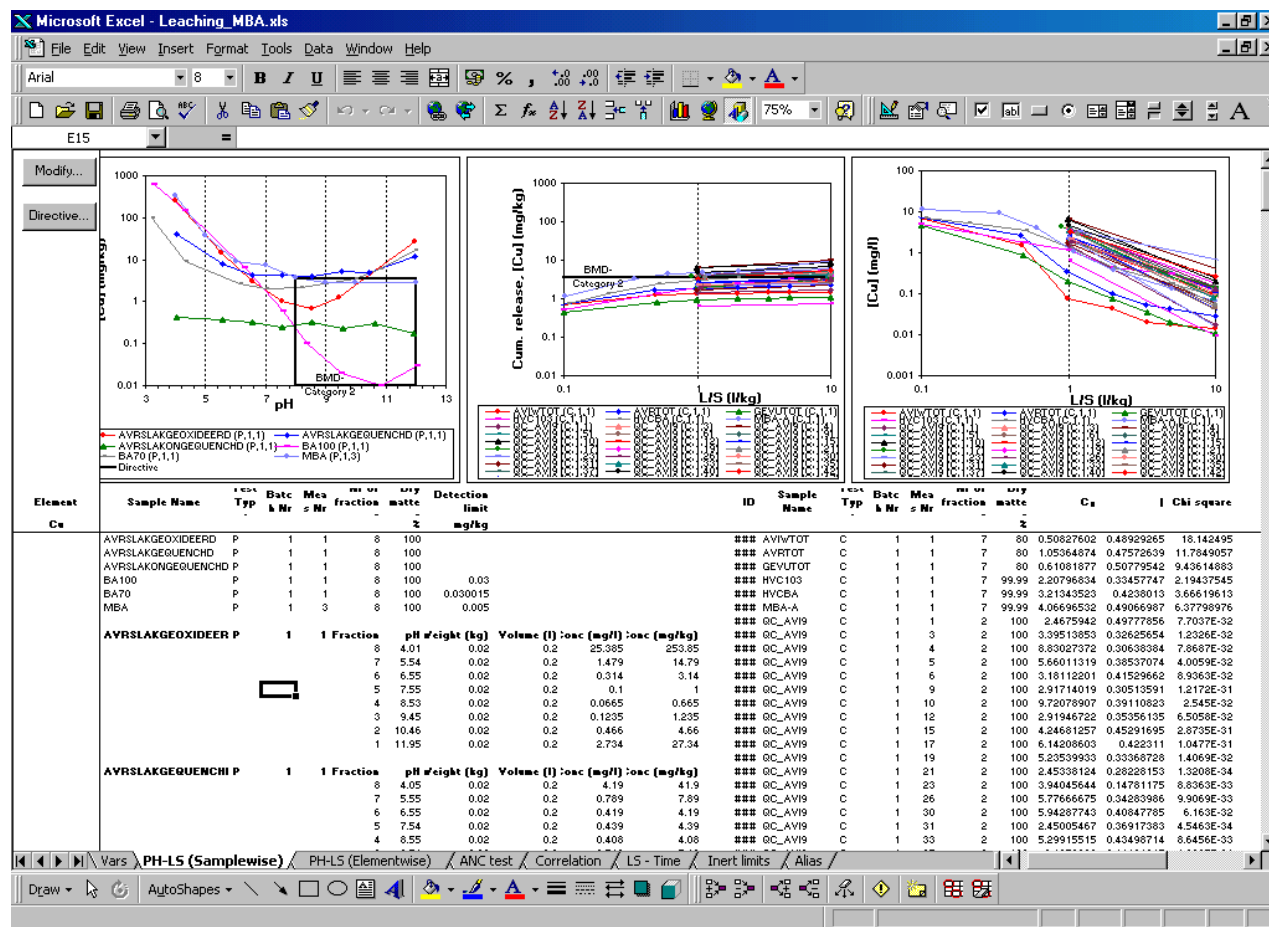
Graphical data presentation examples

Below several forms of data presentation are highlighted.

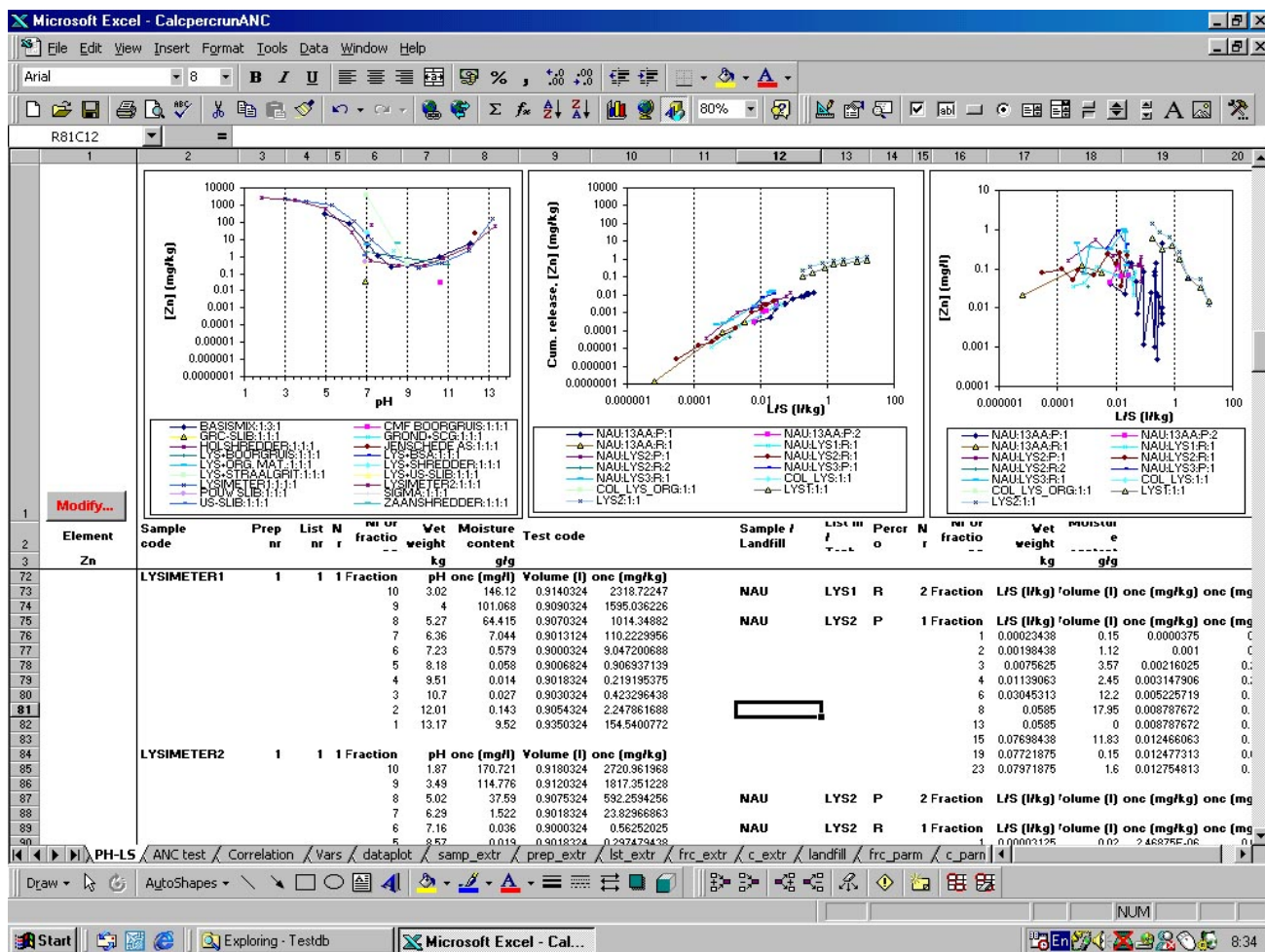
Leaching of Zn as a function of pH and L/S for widely different granular materials



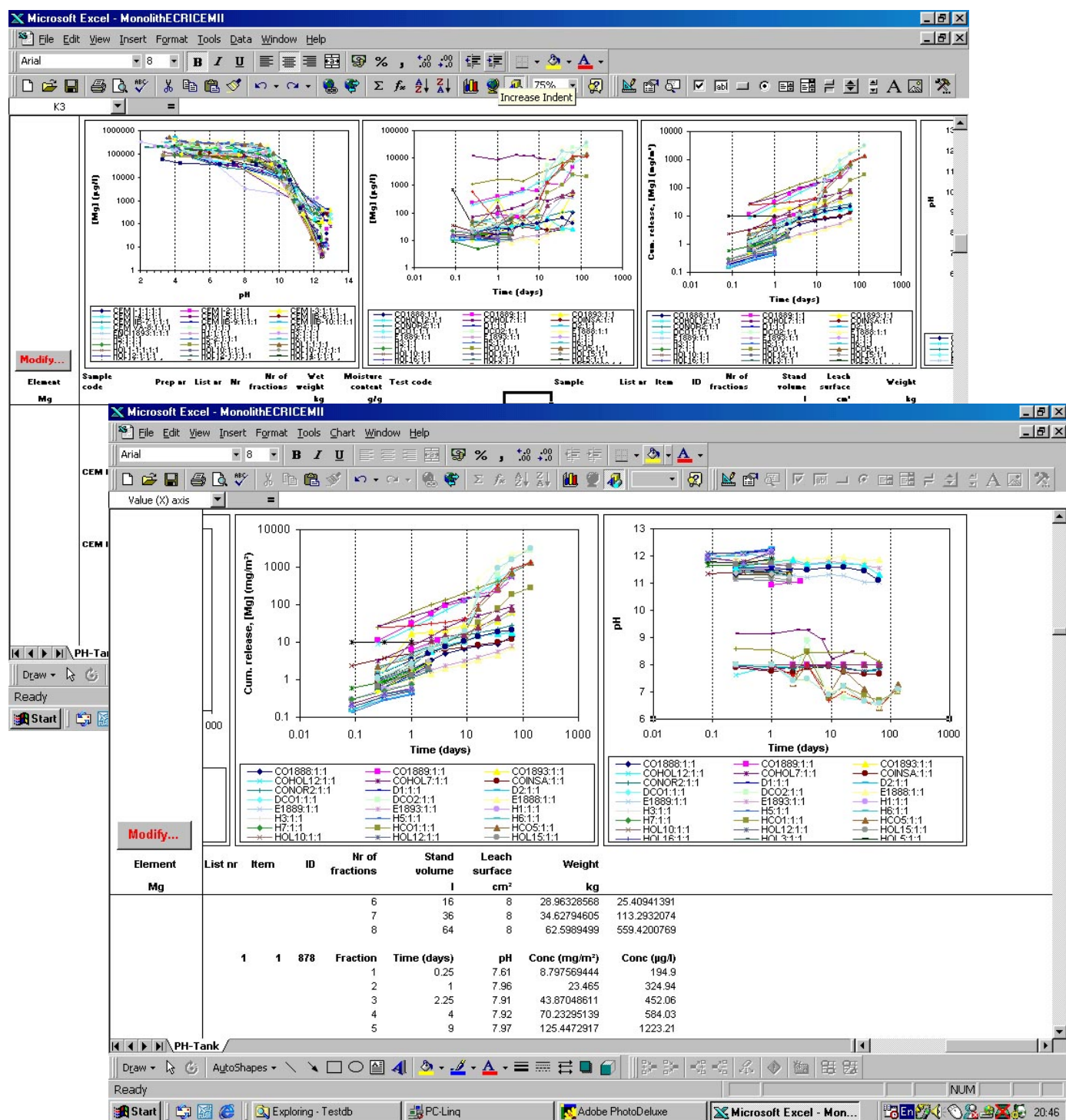
MSWI bottom ash characterisation of leaching behaviour and comparison with compliance testing with reference to regulatory criteria.



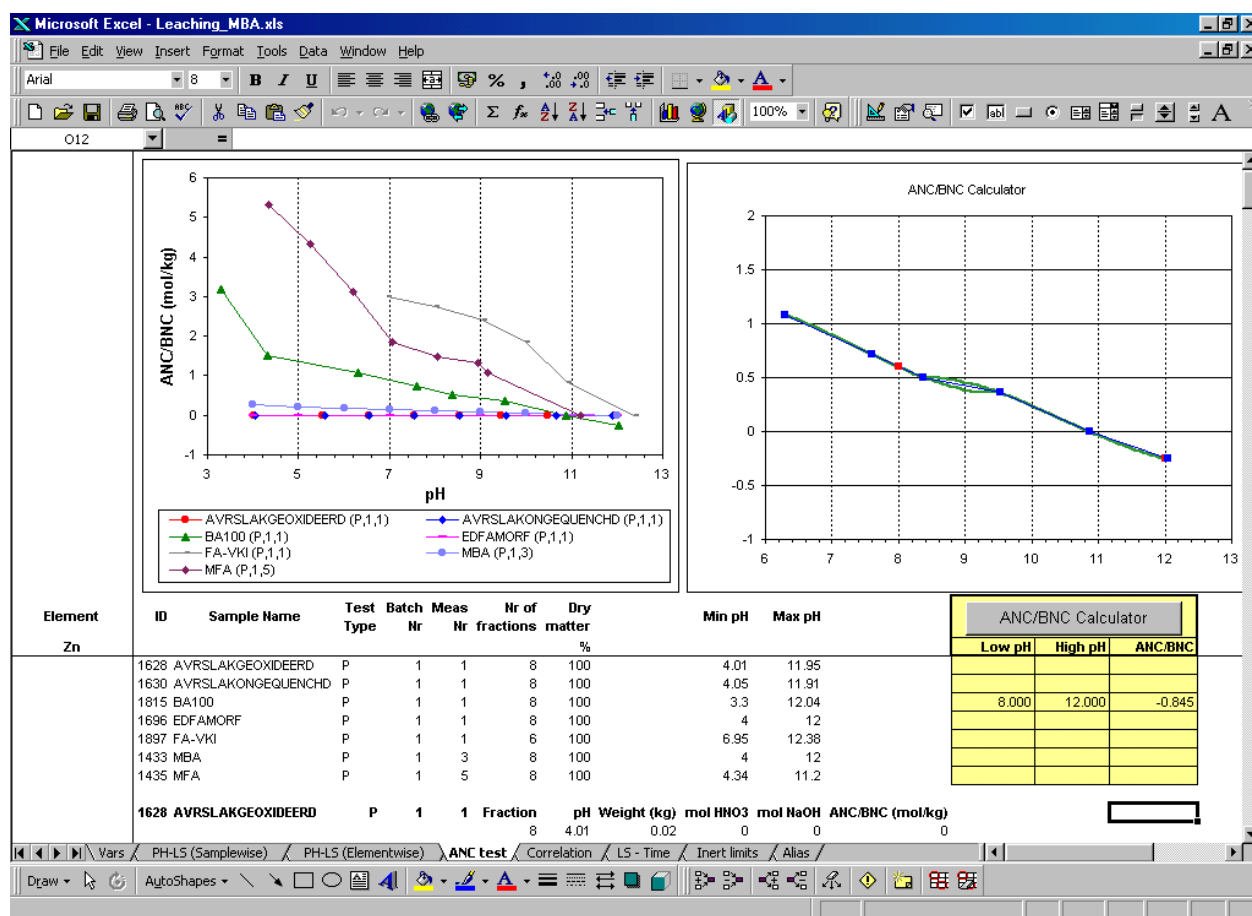
Relationships between laboratory, lysimeter and field data for a non-hazardous waste landfill



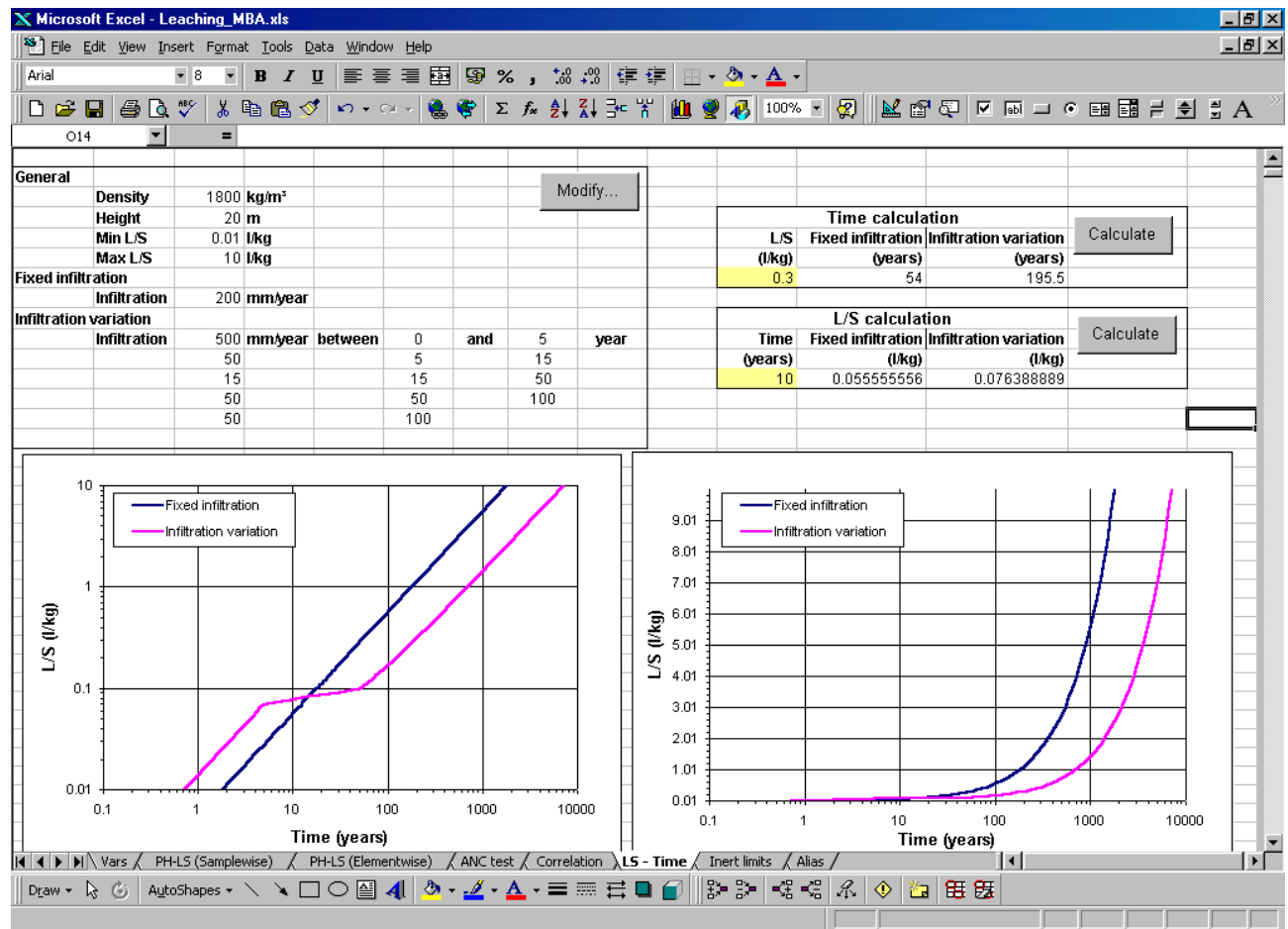
Leaching as a function of pH and time for monolithic materials



Acid Neutralization Curves and calculation of pH or ANC as required



L/S - Time relationship and calculation of time or L/S as required



Geochemical speciation of any leachate or eluate obtained from leaching: sample selection tool

Microsoft Excel - Speciation_BCR_INSA_A2100.xls

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100%

S12

Modify...

ID	Sample name	Test Type	Batch nr	Meas nr	Nr Fractions	Dry matter (%)	Cl (mol/l)	Co (mol/l)	Cr (mol/l)	Cu (mol/l)	DOC (mol/l)	F (mol/l)	Fe (mol/l)	K (mol/l)
4314	BCRDIFF	M	1	1	8	100								
4757	INSA	M	1	1	8	100								
4622	L2100	M	1	1	8	100								
5357	NOR2	M	2	1	8	100								
5366	REC60	M	2	1	7	100								
1457	A2100	P	1	1	8	100								
6328	BCR	P	10	2	8	100								
1796	INSA	P	1	1	3	100								
1773	NOR-2	P	1	1	8	100								

4314 BCRDIFF (M,1,1)	Fraction	Time (d)	Weight (kg)	Volume (l)	pH	pe
16002	1	0.25	0.0001344	0.25	11.86	8.74
16003	2	1	0.0001344	0.25	11.74	8.86
16004	3	2.25	0.0001344	0.25	11.84	8.76
16005	4	4	0.0001344	0.25	11.81	8.79
16006	5	9	0.0001344	0.25	11.89	8.71
16007	6	16	0.0001344	0.25	11.85	8.75
16008	7	36	0.0001344	0.25	11.86	8.74
16009	8	64	0.0001344	0.25	11.88	8.72

4757 INSA (M,1,1)	Fraction	Time (d)	Weight (kg)	Volume (l)	pH	pe
18871	1	0.25	0.000731	1.3	11.57	9.03
18872	2	1	0.000731	1.3	11.42	9.18
18873	3	2.25	0.000731	1.3	11.63	8.97
18874	4	4	0.000731	1.3	11.54	9.06
18875	5	9	0.000731	1.3	11.63	8.97
18876	6	16	0.000731	1.3	11.59	9.01
18877	7	36	0.000731	1.3	11.59	9.01
18878	8	64	0.000731	1.3	11.46	9.14

4622 L2100 (M,1,1)	Fraction	Time (d)	Weight (kg)	Volume (l)	pH	pe
17933	1	0.25	0.00144	4	10.98	9.62

Vars Sample selection Orchestra input Orchestra SI output Orchestra

Draw AutoShapes

Select samples

Sample filter

☐ pHStat and column samples ☒ pHStat and monolith samples

Available samples

Sample	TestType	Name	Batch	Measurementnr
B	AKTIEFKOOL		1	1
B	Alcoa_Red_mud		1	1
B	Alcoa_Red_mud		2	6
B	ASFALT_GRACOS		1	1
B	BAGGERBAGA		1	1
B	BAGGERSPECIE		1	1
B	BIOFS1		1	1
B	BIOFS2		1	1
B	BITUMEN		1	1
B	BITUMEN		2	1
B	BODEMAS_GRACOS		1	1
B	BOUWPUIN_RIVM		1	2
B	BOUWPUIN_RIVM		1	4
B	BSA		1	1
B	BSA		2	1
B	BSA		3	1

Selected samples

Sample	TestType	Name	Batch	Measurementnr
M	BCRDIFF		1	1
M	INSA		1	1
M	L2100		1	1
M	NOR2		2	1
M	REC60		2	1
P	A2100		1	1
P	BCR		10	2
P	INSA		1	1
P	NOR-2		1	1

Testtypes?...

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Table of SI units for all samples and all minerals

Microsoft Excel - Speciation_BCR_INSA_A2100.xls

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	A	B	AR	AS	AT	AU	AV	AW	AX	AY	AZ	BA	BB	BC	BD	BE	BF	BG	BH	BI	BJ	BK
1		Corrected Solubility Index																				
2		Min display value																				
3		Max display value																				
4																						
5		SampleFraction ID	5506	5505	5504	5503	5502	5501	27423	27424	27425	27426	27427	27428	27429	27430	6564	6563	6562	6517	6516	6515
6		Sample Name							BCR (P,10,2)								INSA (P,1,1)			NOR-2 (P,1,1)		
7		Fraction	6	5	4	3	2	1	1	2	3	4	5	6	7	8	3	2	1	8	7	6
8		pH	6.06	7.28	7.8	9.5	10.3	11.69	4.08	5.52	7.5	8.78	9.96	11	11.61	12.55	8	10	13	3.37	4.04	7.94
9		ID Minerals																				
10	919	AlBb	-212.27	-211.74	-211.73	-214.77	-215.44	-220.55	-210.67	-208.92	-210.67	-214.38	-215.83	-223.73	-220.06	-227.22	-213.08	-215.44	-223.81	-211.75	-210.37	-214.54
21	920	AlunK	-13.32	-15.18	-16.09	-22.64	-25.76	-29.60	-7.42	-9.23	-15.36	-21.52	-25.89	-28.94	-34.43	-38.18	-18.58	-28.50	-42.68	-6.16	-8.72	-20.12
22	921	Alunite	-2.90	-1.32	-1.14	-10.77	-15.33	-21.45	5.61	8.87	2.30	-8.65	-15.55	-18.77	-25.24	-32.00	-2.38	-20.06	-38.03	1.15	3.55	-6.96
23	922	Analcime	0.19	2.18	1.89	1.15	-0.19	-8.39	0.50	3.12	3.33	2.07	0.24	-2.49	-6.05	-13.84	3.07	-0.77	-18.09	-4.17	-2.60	0.45
24	923	Analcime	-0.25	2.06	2.24	1.78	0.91	-4.48	-0.52	2.35	3.28	2.07	0.81	-0.68	-3.01	-8.38	2.84	-0.35	-11.50	-5.01	-3.25	0.22
25	924	Anglesite	-1.01	-2.20	-2.63	4.37	2.70	-7.22	-0.40	-1.63	-2.82	4.13	2.07	-7.74	-10.60	-13.38	2.10	-1.19	-14.19	-3.42	-3.45	-3.71
26	925	Anhydrite	0.14	0.11	0.13	0.14	0.11	0.04	0.13	0.11	0.12	0.13	0.29	0.23	-1.56	-1.99	0.16	0.02	-2.70	-0.24	-0.31	-0.37
27	926	Anilite	-129.05	-130.52	-130.90	-132.23	-134.97	-137.06	-131.62	-130.50	-130.04	-130.82	-133.52	-136.40	-140.11	-144.00	-132.43	-134.95	-147.85	-135.08	-134.49	-132.75
28	927	Ansite	-29.53	-24.07	-23.49	-27.43	-31.14	-41.88	-31.02	-26.90	-22.27	-24.73	-27.68	-34.53	-37.51	-49.77	-16.64	-30.04	-57.06	-32.13	-31.33	-25.43
29	928	Anorthite	-6.03	-0.86	0.31	0.03	-0.80	-6.71	-5.97	1.06	3.53	1.18	-0.20	-0.86	-3.27	-9.94	3.41	-1.74	-12.95	-11.65	-7.76	0.03
30	929	Antlerite	-2.52	-3.32	-3.26	-3.16	-6.72	-8.83	-9.55	-5.59	-1.99	-1.52	-4.62	-8.11	-12.46	-17.98	-5.41	-6.84	-23.50	-16.37	-14.39	-5.83
31	930	Aragonite	-9.96	-8.51	-8.01	-6.96	-6.88	-7.07	-13.33	-10.80	-6.09	-7.12	-6.95	-6.82	-6.83	-6.93	-7.67	-6.84	-6.97	-14.93	-13.63	-7.81
32	931	Arzenosulfite	-127.74	-135.92	-140.60	-153.75	-160.30	-176.07	-140.21	-146.21	-158.77	-168.92	-178.55	-188.11	-194.33	-203.98	-142.72	-158.89	-191.59	-117.45	-120.05	-142.12
33	932	Artinite	-19.53	-15.82	-14.69	-10.91	-9.50	-10.90	-27.06	-21.52	-15.14	-11.75	-9.90	-10.98	-10.97	-10.51	-14.64	-11.66	-12.29	-30.62	-28.10	-14.65
34	933	Az2O5	-28.46	-32.55	-34.89	-41.46	-44.74	-52.62	-34.69	-37.69	-43.97	-49.05	-53.86	-58.64	-61.75	-66.58	-35.95	-44.03	-60.38	-23.31	-24.61	-35.65
35	934	Azcomite	-0.44	-0.59	-0.36	0.20	-1.90	-3.33	-16.74	-13.63	-10.58	-9.87	-11.67	-13.69	-15.30	-18.81	-12.74	-12.97	-21.96	-21.40	-19.83	-12.81
36	935	Azurite	-20.17	-20.42	-20.37	-21.55	-26.47	-30.88	-30.21	-23.63	-18.97	-19.10	-24.12	-29.47	-33.08	-39.54	-22.55	-26.11	-45.22	-38.26	-34.90	-22.40
37	936	Ba(OH)2.8H2O	-11.75	-15.33	-14.27	-11.11	-9.48	-7.54	-10.21	-10.33	-14.24	-12.95	-10.18	-2.10	-2.33	-4.33	-14.10	-10.30	-4.45	-22.94	-21.53	-13.91
38	937	Ba[SO4]0.4[77%SO4]	0.34	0.67	0.74	0.59	0.70	0.43	0.35	0.40	0.54	0.58	0.60	0.56	0.19	0.22	0.20	0.26	-1.33	0.33	0.44	0.59
39	938	Ba[SO4]0.4[96%SO4]	1.01	1.09	1.16	0.97	1.02	0.89	0.89	0.82	0.80	0.83	0.87	0.94	0.27	0.31	0.60	0.45	-1.29	0.81	0.81	0.72
40	939	Ba[AsO4]2	7.08	10.26	11.10	14.01	15.61	13.57	-10.70	-5.36	0.02	2.57	4.37	5.85	9.07	9.24	10.31	13.87	15.06	-3.32	-0.56	11.42
41	940	BaCsSO4[50%Ba]	0.88	0.88	0.92	0.83	0.83	0.75	0.80	0.75	0.73	0.74	0.85	0.84	-0.40	-0.59	0.65	0.49	-1.75	0.57	0.52	0.42
42	941	BaCsSO4[75%Ba]	1.15	1.15	1.22	1.07	1.09	1.00	1.03	0.96	0.92	0.94	1.02	1.05	0.07	0.00	0.80	0.62	-1.39	0.87	0.83	0.71
43	942	BaCrO4	-4.25	-2.88	-2.83	-2.79	-2.43	-3.28	-3.65	-3.14	-2.36	-2.27	-2.35	-2.30	-1.94	-2.02	-3.24	-2.36	-3.36	-3.45	-2.88	-1.74
44	943	BaF2	-6.08	-6.63	-6.56	-6.72	-6.76	-9.23	-9.12	-27.77	-24.85	-24.63	-24.51	-23.51	-23.50	-24.74	-24.55	-31.46	-30.57	-24.00		
45	944	Barite	1.41	1.43	1.51	1.31	1.34	1.25	1.26	1.17	1.12	1.14	1.19	1.25	0.54	0.59	0.94	0.76	-1.02	1.17	1.14	1.00
46	945	BaSeO3	-21.58	-21.67	-21.68	-21.68	-21.56	-22.50	-27.03	-27.13	-27.20	-27.21	-27.37	-27.34	-26.40	-26.46	-21.48	-22.71	-22.36	-21.79	-22.06	-22.00
47	946	BaSeO4	-7.35	-7.43	-7.45	-7.44	-7.33	-8.26	-12.80	-12.89	-12.96	-12.98	-13.13	-13.11	-12.16	-12.23	-7.25	-8.47	-8.13	-7.56	-7.83	-7.77
48	947	BaSrSO4[50%Ba]	0.20	0.21	0.26	0.16	0.17	0.28	0.12	0.07	0.04	0.06	0.17	0.20	-0.91	-0.76	0.02	-0.12	-1.90	-0.36	-0.40	-0.50
49	948	beta-TCP	-2.55	0.23	1.22	3.09	2.96	2.94	-9.28	-3.83	1.90	3.31	3.81	3.59	2.16	1.46	3.02	3.04	0.25	-11.94	-10.89	1.62
50	949	Bismutite	-4.03	-4.99	-6.00	-9.18	-10.65	-12.16	-4.97	-4.94	-6.64	-7.22	-10.25	-12.72	-15.65	-11.77	-7.09	-12.72	-21.75	-7.30	-7.49	-10.24
51	950	Birnessite	5.27	7.54	8.12	5.97	4.95	3.82	1.30	3.98	7.66	7.94	5.40	3.39	2.25	0.41	7.17	3.86	-1.26	-0.36	0.73	5.55
52	951	Bixbyite	6.13	10.67	11.84	7.53	5.50	1.23	-1.80	3.55	10.90	11.48	6.40	2.37	0.10	-3.60	9.94	3.32	-6.93	-5.13	-2.94	6.69
53	952	Blavickil	-118.07	-119.89	-120.49	-122.57	-124.89	-126.96	-118.31	-118.67	-119.85	-121.27	-123.77	-126.33	-129.71	-132.76	-121.69	-124.79	-135.73	-120.02	-120.17	-121.98
54	953	Blavickil	-123.58	-125.24	-125.74	-127.48	-129.99	-132.07	-124.89	-124.58	-125.00	-126.12	-128.71	-131.42	-134.96	-138.39	-127.09	-129.92	-141.77	-127.41	-127.22	-127.40
55	954	Bobierite	-9.94	-7.35	-6.31	-6.01	-6.49	-11.27	-17.35	-11.99	-6.36	-5.12	-5.73	-10.56	-13.50	-15.13	-6.56	-9.21	-20.12	-20.56	-15.64	-7.30
56	955	Bockite	-1.46	0.26	0.81	-0.73	-1.45	-2.59	-0.15	2.38	2.16	-0.23	-1.50	-1.58	-2.07	-3.57	-1.43	-2.45	-4.34	-2.01	-0.53	-0.09
57	956	Brochantite	2.53	2.85	2.44	-1.18	-2.39	-7.54	-13.19	-6.95	-0.84	0.63	-3.75	-7.25	-11.61	-18.44	-5.30	-5.63	-25.31	-22.70	-13.59	5.51
58	957	Brucite	-7.24	-4.92	-4.11	-1.06	0.38	0.77	-11.18	-8.35	-4.44	-1.96	-0.01	0.41	0.94	1.81	-3.91	-0.87	1.33	-12.96	-11.70	-4.00
59	958	Brushite[1]	-2.16	-1.96	-1.97	-2.72	-3.56	-4.56	-3.67	-2.38	-1.48	-2.05	-2.96	-4.05	-5.28	-6.22	-1.41	-3.36	-7.21	-4.20	-4.33	-1.95
60	959	Brushite[2]	-2.17	-1.97	-1.98	-2.73	-3.57	-4.56	-3.68	-2.39	-1.49	-2.05	-2.96	-4.06	-5.28	-6.22	-1.42	-3.37	-7.22	-4.21	-4.34	-1.96

Vars Sample selection Orchestra input Orchestra SI output Orchestra DOC output Element concentrations Alias

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