

## Test method selection, validation against field data, and predictive modelling for impact evaluation of stabilised waste disposal

Hans A. van der Sloot<sup>a,\*</sup>, Andre van Zomeren<sup>a</sup>, Johannes C.L. Meeussen<sup>a</sup>,  
Paul Seignette<sup>a</sup>, Rob Bleijerveld<sup>b</sup>

<sup>a</sup> Energy Research Centre of the Netherlands (ECN), P.O. Box 1, 1755 ZG Petten, The Netherlands

<sup>b</sup> A&G Maasvlakte, P.O. Box 1016, 3180 AC Rozenburg, The Netherlands

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### Abstract

In setting criteria for landfill classes in Annex II of the EU Landfill Directive, it proved to be impossible to derive criteria for stabilised monolithic waste due to the lack of information on release and release controlling factors in stabilised waste monofills. In this study, we present a scientific basis, which enables a realistic description of the environmental impact of stabilised waste landfills. The work in progress involves laboratory testing of different stabilisation recipes, pilot scale studies on site and evaluation of field leachate from a full-scale stabilisation landfill. We found that the pHs in run-off and in percolate water from the pilot experiment are both around neutral. The neutral pH in run-off is apparently caused by the rapid atmospheric carbonation of those alkaline constituents that are released. The soil, used as a liner protection layer, controls the release to the subsurface below the landfill. This soil layer buffers pH and binds metals. The modelling results show that the chemistry is understood rather well. Differences between predicted and actual leaching might then be attributed to discrepancies in the description of sorption processes, complexation to organic matter and/or kinetic effects in the leaching tests. We conclude that this approach resulted in a new scientific basis for environmental impact assessment of stabilised waste landfills. The integrated approach has already resulted in a number of very valuable observations, which can be used to develop a sustainable landfill for monolithic waste and to provide guidance for the management of waste to be stabilised (e.g. improved waste mix design).

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### 1. Introduction

The technology of waste stabilisation/solidification seeks to change the physical and/or chemical properties of (hazardous) waste materials in order to reduce contaminant release to the environment [1]. The technology aims to change the release process from a percolation dominated mechanism to a diffusion- or surface-dissolution dominated regime. Hazardous waste can be stabilised in a variety of ways, but the main objective is to develop a recipe that produces a stable and sustainable end product, that will pose minimal threat to the environment.

#### 1.1. Regulatory framework

The European regulatory framework is still in development for hazardous waste treatment for disposal in non-hazardous waste sites. In setting criteria for landfill classes in Annex II of the EU Landfill Directive [2], it proved impossible to derive values for stabilised monolithic waste due to the lack of suitable information for relating release from stabilised waste in monofills to environmental impact at a given point of compliance (POC). The European Commission decided that additional information was needed prior to setting criteria for this type of landfill. For the time being, regulatory controls for stabilised waste landfills have been referred to the Member States (MS). Several MS are currently studying this topic to fill the knowledge gaps [3–6]. The main information required for judging this landfill type relate to unknown or insufficiently quantified factors affecting contaminant release. These factors include net

*Abbreviations:* CEN, European Standardisation Organization; HFO, hydrous ferric oxide; POC, point of compliance

\* Corresponding author. Tel.: +31 224 564249; fax: +31 224 568163.

E-mail address: vandersloot@ecn.nl (H.A. van der Sloot).

infiltration, evaporation and run-off, the degree of saturation of the monolithic waste forms, the monolith's durability in terms of crack formation and other causes of loss of integrity, effects of carbonation, and the dominant mechanisms controlling release (e.g. diffusion, solubility limitations, and kinetics). The assumption that contaminant release is controlled solely by diffusion is too simple since solubility limitations are also important [7]. An important limitation to deriving a proper impact scenario has been the lack of actual field data. The aim of this study was to identify the relative importance of release controlling factors such as hydrology, carbonation, diffusion processes and solubility limitations through geochemical reaction and transport modelling of data obtained from laboratory experiments, a stabilised waste pilot experiment [7] and a full-scale stabilised waste site. With the better understanding of the chemical processes controlling the release of contaminants from stabilised waste, we aim to develop a scenario description for a stabilised waste landfill. This will provide the basis for the development of acceptance criteria for Annex II of the Landfill Directive.

### 1.2. Test methods

Many complex physical and chemical processes control contaminant release from a stabilised waste monofill. Kosson et al. [8] 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. [8] and with the methodology described in EN 12920 (2004).

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 [8–11].

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. The mass transfer rate is estimated by performing a tank-leaching test on the intact monolithic material. 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 monofill can be predicted by geochemical and transport models. This gives more reliable estimates of the envi-

ronmental impact in both the short- and long-term, which then allows regulatory criteria 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 [12]. 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 [12–14].

### 1.3. Pilot scale studies

Several authors have studied the environmental behaviour of cement-stabilised waste in lysimeter or pilot scale experiments. Work by Ludwig et al. [15] and by Fitch and Cheeseman [16] on large monolithic blocks of cement-stabilised MSWI fly ash showed deterioration of the surface. In both studies carbonation by atmospheric CO<sub>2</sub> uptake was also noted. In the study by Baur et al. [17] and Fitch and Cheeseman [16] leachate pH was very high, as was expected for the highly alkaline matrix.

Fruchter et al. [18] and Meij and te Winkel [19] studied the environmental behaviour of coal fly ash and pulverised fuel ash, respectively, in lysimeter experiments. Although these materials were not stabilised with cement and emissions were probably controlled by percolation rather than diffusion (which is the presumed emission controlling mechanism for stabilised waste), these studies are similar in that highly alkaline waste materials were leached under environmental conditions. Solubility controlling solid phases were identified by Fruchter et al. [18] for Al, Ba, Ca, Cr, Cu, Fe, S, Si and Sr by geochemical modelling coal fly ash pore water and leachate. They concluded that equilibrium of the solid phase with the leachate was established within days. It can be assumed that the contact time of pore water with stabilised waste is of the same order of magnitude, and therefore, solubility controlling phases might control contaminant emission from stabilised waste materials.

In this study, cement stabilisation through solidification is studied in a pilot experiment within the framework of a Dutch project on Sustainable Landfill. Information was gathered from laboratory leaching studies, and both the pilot and laboratory tests were verified against full-scale field data. Leach data was subjected to geochemical modelling [7,20]. The results from this study will be used to identify the mechanisms that control contaminant release. This work supports the choice of laboratory leach tests to properly account for the behaviour of stabilised waste under environmentally relevant conditions.

## 2. Materials and methods

### 2.1. Stabilised waste samples

Stabilised waste samples were taken from the full-scale installation just after mixing of all materials, and were cured for at least 28 days prior to testing. The most common haz-

ardous waste materials that are stabilised include MSWI fly ash, filter ashes, metal sludges and filtercake from wastewater treatment.

Duplicate stabilised waste cores were drilled from the upper layer of a waste compartment containing an MSWI fly ash mixture on three separate occasions. The first cores were sampled 1 week after the stabilised waste was landfilled, the second sampling round was about 4 months after landfilling and the third after about 6 months. Waste cores were drilled manually from a depth of approximately 20 cm using stainless steel cores. The cores were transported to the laboratory, stored at 4 °C and sliced, manually crushed to reduce particle size and leached within 1 week of sampling.

## 2.2. pH-static leach test

A pH-static test (TS14429, 2005) was used to characterise the stabilised waste. In short, this leaching test involves leaching the crushed material at eight pH values ranging from pH 2 to 13, each at a liquid to solid ratio (L/S) of 10. HNO<sub>3</sub> (10 M) and NaOH (10 M) were used to adjust the pH to the desired value. The pH was checked and adjusted accordingly after 6 h of equilibration. After 48 h, the final pH and electrical conductivity (EC) was measured, and the eluates were filtered (0.45 µm) and analysed.

The sliced core samples were leached with demineralised water (L/S ratio = 10) at the own pH of the sample. Suspensions were leached for 48 h, filtered (0.45 µm) and analysed.

## 2.3. Tank leach test

The tank leach test was performed on cylindrical product samples from stabilised waste (diameter 11 cm, height 12 cm) according to the Dutch NEN 7375 standard. The European standard for monolithic materials is still under development. The specimen was subjected to leaching in a closed tank. Demineralised water was used as the leaching solution at a leachate-to-product volume ratio (L/V) of approximately 5. The leaching solution was renewed after 8 h, 1, 2.25, 4, 9, 16, 36 and 64 days. The pH, electrical conductivity (EC) and, occasionally, Eh were

measured in all eluates before filtration (0.45 µm) and chemical analysis.

## 2.4. Chemical analysis

The leachates from the laboratory tests were analysed for major and trace elements using ICP-AES, for DOC using a Shimadzu 5000-a TOC analyser, for anions using ion-chromatography and for cyanides (total and free) using photometry.

## 2.5. Pilot experiment

At the site of VBM (Maasvlakte, The Netherlands) a pilot experiment with four stabilised waste compartments was set up. A simplified diagram of the experiment is given in Fig. 1. The pilot-scale experiment has four sections (cells A–D) in which the solidified/stabilised waste is landfilled, and effects of height, carbonation and different waste recipes can be studied. The waste is stabilised in situ in layers of approximately 0.5 m and separated at intervals of 1.5 m by a vertically placed geotextile membrane (see Fig. 1). The inclusion of a geotextile membrane was designed to improve the sustainability of stabilised/solidified waste by creating preferential flow channels for water, instead of creating one very large waste body. This was designed to reduce the amount of water that reaches saturation when it percolates through stabilised waste. Part of the rainwater that falls on top of the stabilised waste material is evaporated due to the relatively high porosity of the surface layer and the low permeability (possibly even partial pore sealing) of the deeper layers in the stabilised waste monofill. Finally, a layer of mildly contaminated soil was used at the bottom of the compartment as a protection layer for the liner system. As will be discussed further, this soil layer is able to neutralise the alkaline percolate water and can bind leached contaminants [7].

Sampling facilities were installed to sample the leachate that percolated through the geotextile membrane, and that permeated through the waste material itself. Furthermore, the run-off water that flowed along the top layer towards the side of the compartment was collected. pH, EC and water volumes were monitored

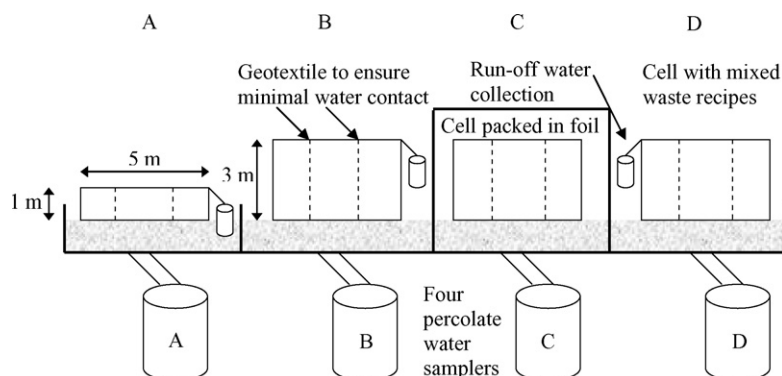


Fig. 1. Front view of the experimental set-up of the pilot scale experiment using stabilised waste. Each compartment was 8 m long and the space between the compartments was filled with sand to obtain good physical stability during the experiment.

periodically. Chemical analysis of the samples was performed after filtration (0.45  $\mu\text{m}$ ).

### 2.6. Geochemical release modelling from stabilised waste

The geochemical modelling framework ORCHESTRA [21], which uses an extended MINTEQA2 database with thermodynamic constants for inorganic reactions, was coupled to a database/expert system (LeachXS) [22] containing the pH-dependent leach test data, the tank test data, pilot and field leachate data. The use of LeachXS allowed for quick data retrieval, processing and presentation.

The generalized two-layer model of Dzombak and Morel [23] was used to take complexation to iron (hydr)oxide surfaces into account. The amount of amorphous iron/aluminum (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 [24]. DOC was used as the input for humic acid in the NICA-Donnan model [25] and might be quantified according to [26]. 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.

### 2.7. Characterisation, quality control and judging treatment methods

Fig. 2 shows the central role of stabilised 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.

## 3. Results and discussion

### 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 Fig. 3 as examples. It can be seen that the concentration leached from waste stabilised using different recipes can vary by up to two orders of magnitude in both the pH-dependent leaching test (in  $\mu\text{g/L}$ ) and the tank-leaching test (cumulative emission in  $\text{mg/m}^2$ ). 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

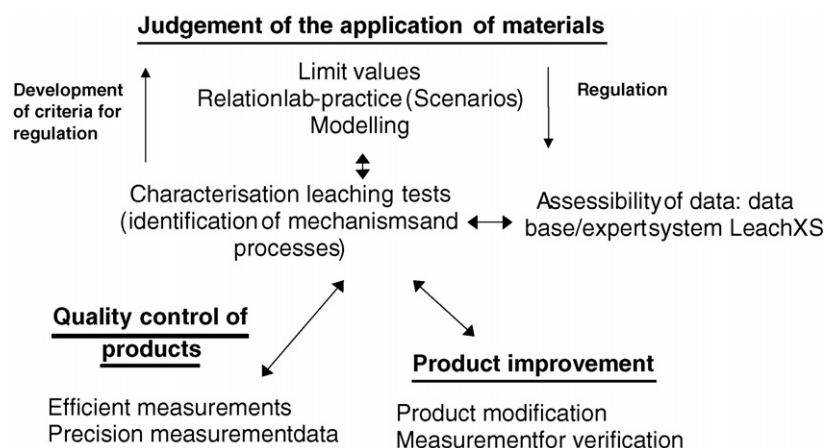


Fig. 2. Role of characterisation leaching tests in environmental judgement of materials.

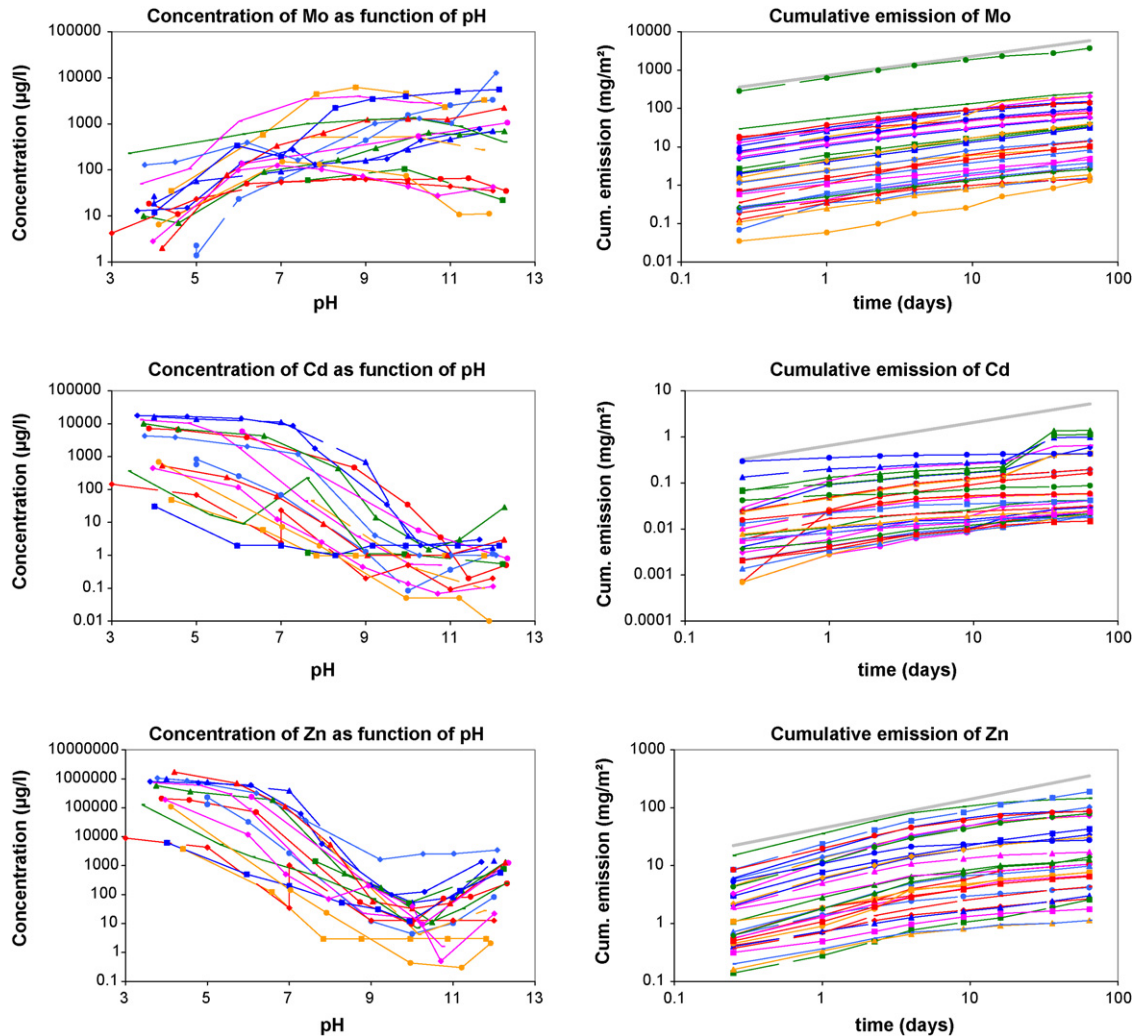


Fig. 3. Results of the pH-dependent and tank leach test on crushed stabilised waste and the intact material, respectively.

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 Fig. 3 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.

### 3.2. Field observations

The pHs of both the percolate and the run-off water from the pilot experiment are generally neutral to very mildly alkaline, ranging from 6.8 to 9.3 (average 7.9). This is quite remarkable since the alkaline waste material has a pH of greater than 12. In addition, other field experiments with cement-stabilised MSWI fly ash have produced a leachate of about pH 13 [15–17]. Presumably, the run-off water only comes into contact with the outer (carbonated) surface of the waste material (see below) or it undergoes atmospheric carbonation relatively quickly. The soil layer at the bottom of the waste compartment buffers the pH in the percolate water. In an earlier study [7], we estimated

that the soil layer can neutralise the alkaline percolate water for a period of 55–115 years based on a constant infiltration rate of 300 mm/year. Adding a top cover to the landfill may increase percolate alkalinity by decreasing the water volume, and hence causing gradient relaxation in the exposed waste layer. Future work should determine whether or not the combination of increased alkalinity and decreased water volume affects the calculated buffering period of the soil layer. Indications of pore sealing as a result of carbonation have been observed and should also be taken into account. Fitch and Cheeseman [16] have identified  $\text{CaCO}_3$  minerals in environmentally exposed stabilised waste. Pore sealing can lead to lower alkalinity and contaminant release from waste.

The EC values in the percolate water samples (63–217 mS/cm) are roughly a factor 10–30 higher than the EC values in run-off water samples (0.9–6.8 mS/cm). This can be attributed to the difference in contact time of the water with the waste (relatively short for run-off water) and possibly depletion of soluble salts from the surface layer.

Cu, Mo, Pb and Zn concentrations in stabilised waste leachates (specifically laboratory data, landfill percolate and core leachates, pilot experiment percolate and run-off, and lysimeter samples) are shown as a function of pH in Fig. 4. 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 percolate water and the pilot experiment percolate and run-off water (Fig. 1) 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 (Fig. 4). 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.

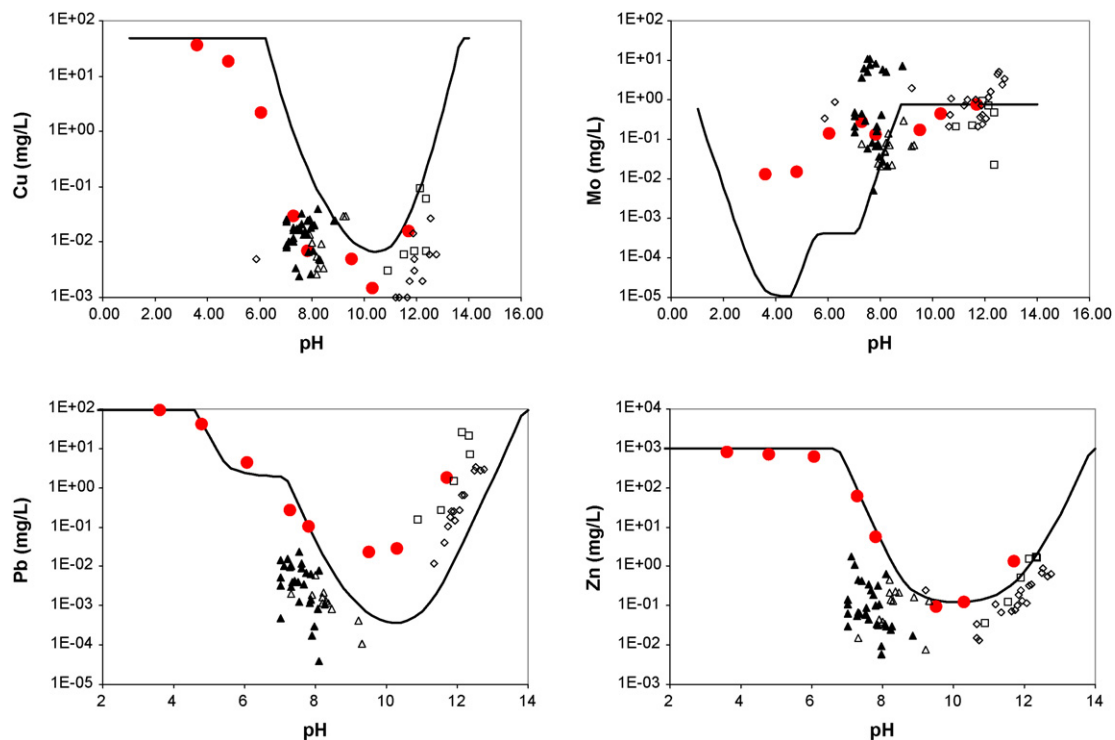


Fig. 4. pH-dependent leaching of Cu, Mo, Pb and Zn from laboratory tests on stabilised waste (●) compared with landfill and pilot experiment percolate data (▲), pilot experiment run-off data (△), landfill core leachates (□) and lysimeter data (◇, taken from [20]). The solid line represents the leaching behaviour predicted by geochemical equilibrium modelling.

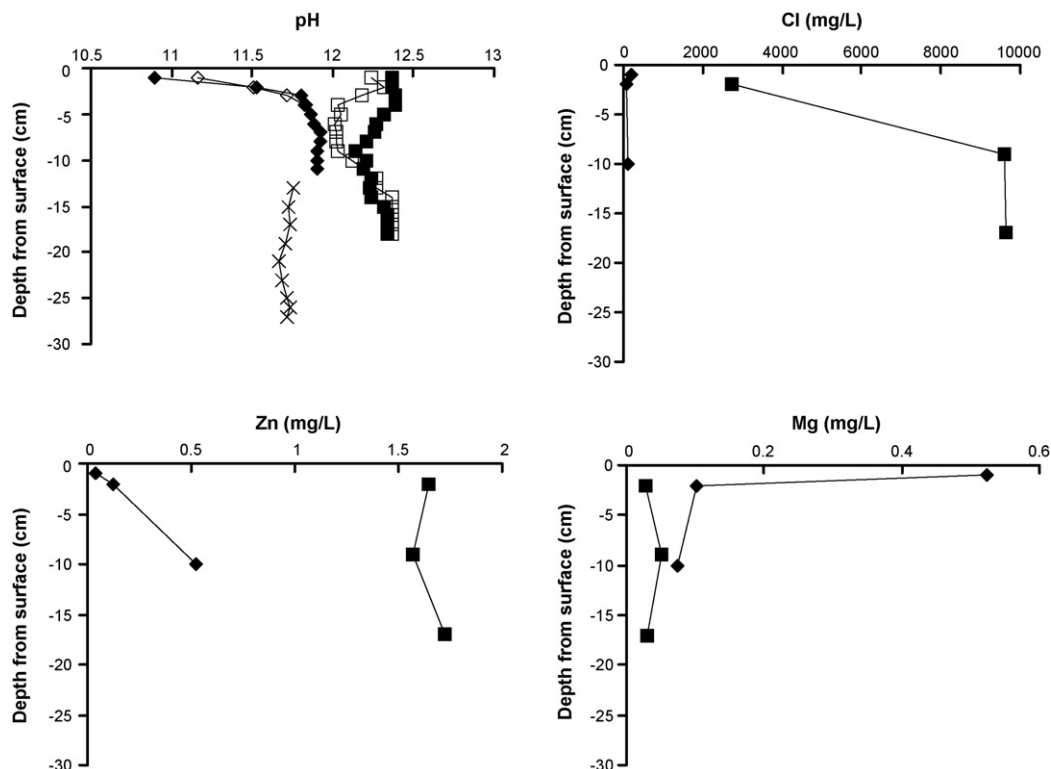


Fig. 5. pH and leaching of Cl, Zn and Mg as a function of depth in cores from stabilised waste sampled 1 week (■ and □), 4 months (◆ and ◇) and 6 months (×) after landfilling.

Results from leach tests ( $L/S = 10$ , 24 h at the samples' native pH) on the sliced core samples are presented in Fig. 5.

The pH of the fresh material (1 week old) was between 12 and 12.5, whereas the pH of the older samples (4 months) increased with depth from 10.9 to 11.9. After 6 months, the pH of the stabilised waste at 15–25 cm below the surface had decreased to about 11.7.

Fig. 5 shows that Cl is depleted from the first few centimetres of the material after 1 week. The deeper layers appear to be unaffected at this time. This behaviour is typical for soluble salts and is independent of the waste material pH. After 4 months, Cl is depleted from at least the first 10 cm of the stabilised waste, indicating substantial wash out of this mobile element.

The leaching of Zn is strongly pH-dependent and its solubility is controlled by equilibrium with the mineral zincite. This results in a V-shaped leaching curve with a leaching minimum around pH 10. The observed Zn leaching in Fig. 5 is consistent with the pH-dependent leaching behaviour shown in Fig. 4; Zn concentrations are lower in the 4-month-old sample (lower pH) than in the fresh samples (higher pH).

The Mg concentrations in the eluates of the fresh sample are relatively low due to the high pH. At high pH, Mg leaching is controlled by brucite solubility. In the 4-month-old sample, the Mg concentrations are significantly higher at 2 cm depth than deeper in the core because of the lower pH closer to the surface (about 10.9). Leaching is still controlled by brucite, but this mineral is more soluble at lower pH.

Information generated in this way will provide the basis for deciding whether to cover the monolithic waste cell or to keep it

exposed to the atmosphere longer and allow the stabilised waste to act as a  $\text{CO}_2$  sink. The latter process is enhanced by natural wet and dry cycles. Better understanding of these mechanisms may well lead to new design concepts for sustainable monolithic stabilised waste landfills.

### 3.3. Geochemical modelling of release as a function of pH

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 [21] 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.

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 Tables 1 and 2.

Table 1  
Available concentrations of elements used in geochemical modelling

| Element                       | Availability (mg/kg) | Element | Availability (mg/kg) | Element                       | Availability (mg/kg) |
|-------------------------------|----------------------|---------|----------------------|-------------------------------|----------------------|
| Al                            | 6565                 | Cu      | 485                  | Pb                            | 955                  |
| As                            | 0.145                | F       | 1904                 | PO <sub>4</sub> <sup>3-</sup> | 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 <sub>4</sub> <sup>2-</sup> | 19660                |
| Cd                            | 202.2                | Mn      | 175                  | Sr                            | 206                  |
| Cl                            | 53500                | Mo      | 7.7                  | V                             | 0.58                 |
| CO <sub>3</sub> <sup>2-</sup> | 30000                | Na      | 25625                | Zn                            | 10020                |
| Cr                            | 9.69                 | Ni      | 11.29                |                               |                      |

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).

The mineral phases were selected by means of calculated saturation indices obtained from preliminary speciation calculations of the leachates.

The results, given in Fig. 6 through to Fig. 8, 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 (Figs. 6–8). 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

Table 2  
Possible solubility controlling minerals selected from speciation calculations

| Mineral name                                    |
|---|
| Analcime  |
| BaSrSO <sub>4</sub> [50%Ba]                     |
| Boehmite  |
| Brucite   |
| Calcite   |
| Cd[OH] <sub>2</sub> [c]                         |
| Cerrusite                                       |
| CSH.ECN   |
| Cu(OH) <sub>2</sub>                             |
| Ferrihydrite                                    |
| Fluorite  |
| Gypsum  |
| Manganite                                       |
| Ni[OH] <sub>2</sub> [s]                         |
| Pb[OH] <sub>2</sub> [c]                         |
| Pb <sub>3</sub> [VO <sub>4</sub> ] <sub>2</sub> |
| PbMoO <sub>4</sub> [c]                          |
| PbV <sub>2</sub> O <sub>7</sub>                 |
| Portlandite                                     |
| Zincite   |

These minerals were subsequently used as input for the model predictions.

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. [27]. This type of modelling will highlight any lack of mineral or other phases controlling the release (e.g. Cd in pH range 7–10).

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 Fig. 9, 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 (Fig. 9B) is controlled predominantly by mineral solubility and sorption to HFO (between pH 3 and 7). In the pH range from 1 to 7, a significant proportion of Pb is found in the minerals PbMoO<sub>4</sub> and, to a much lesser extent, Pb<sub>3</sub>(VO<sub>4</sub>)<sub>2</sub>. Above pH 7, there is some sorption to HFO but the mineral Pb(OH)<sub>2</sub> 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.



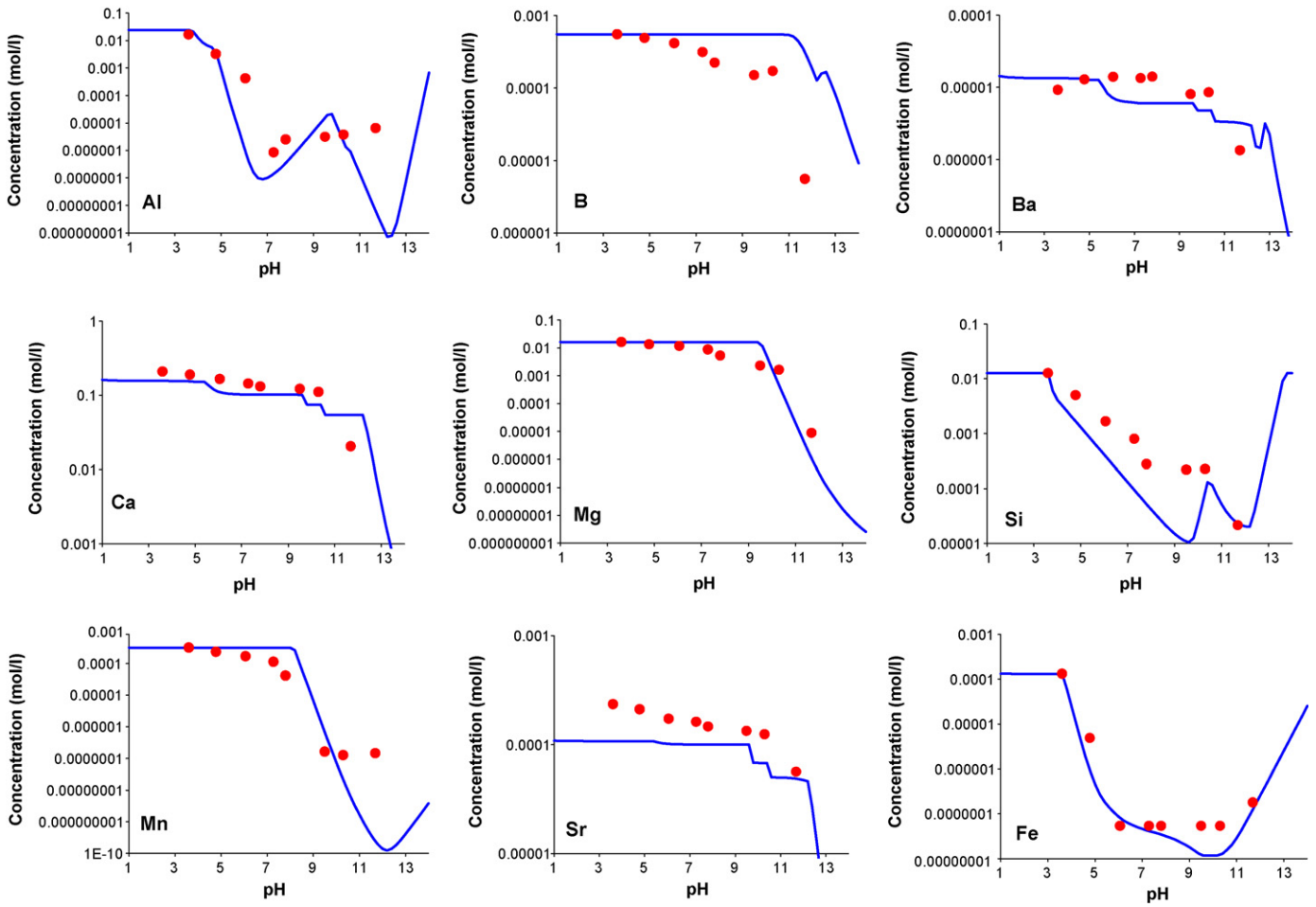


Fig. 6. Measured and predicted leaching behaviour of major elements as a function of pH in a stabilised MSWI fly ash recipe.

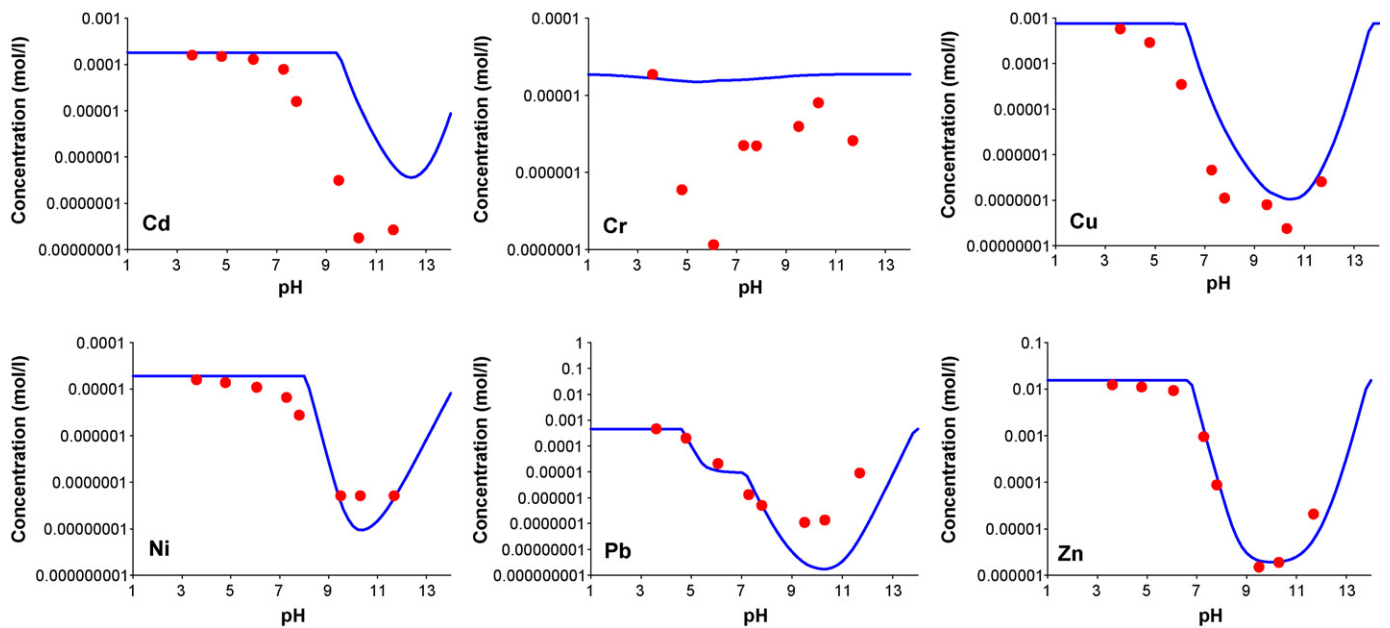


Fig. 7. Measured and predicted leaching behaviour of heavy metals as a function of pH in a stabilised MSWI fly ash recipe.

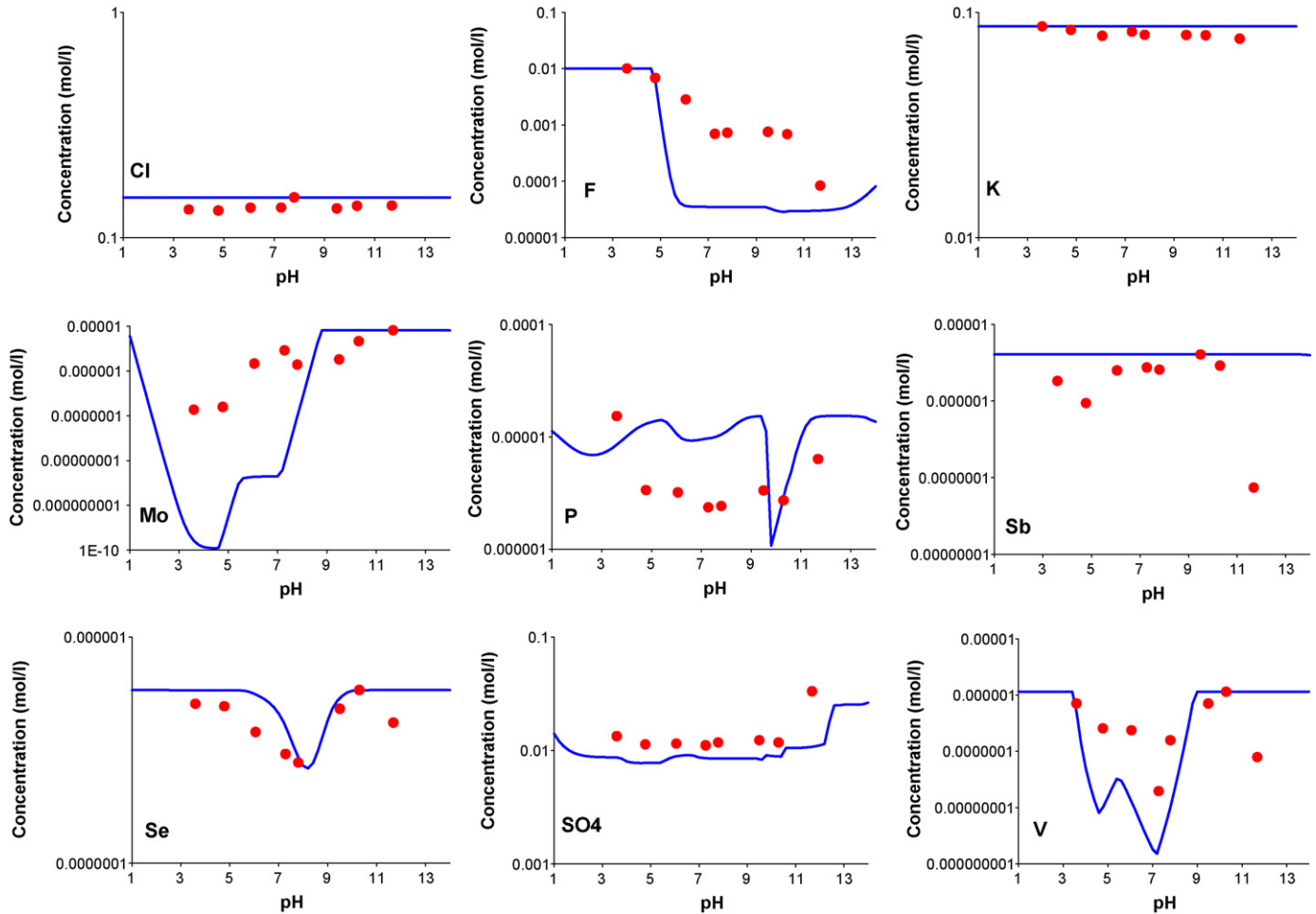


Fig. 8. Measured and predicted leaching behaviour of salts and oxyanions as a function of pH in a stabilised MSWI fly ash recipe.

#### 3.4. 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 Fig. 10 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.

Fig. 10 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  $\text{CO}_2$  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.

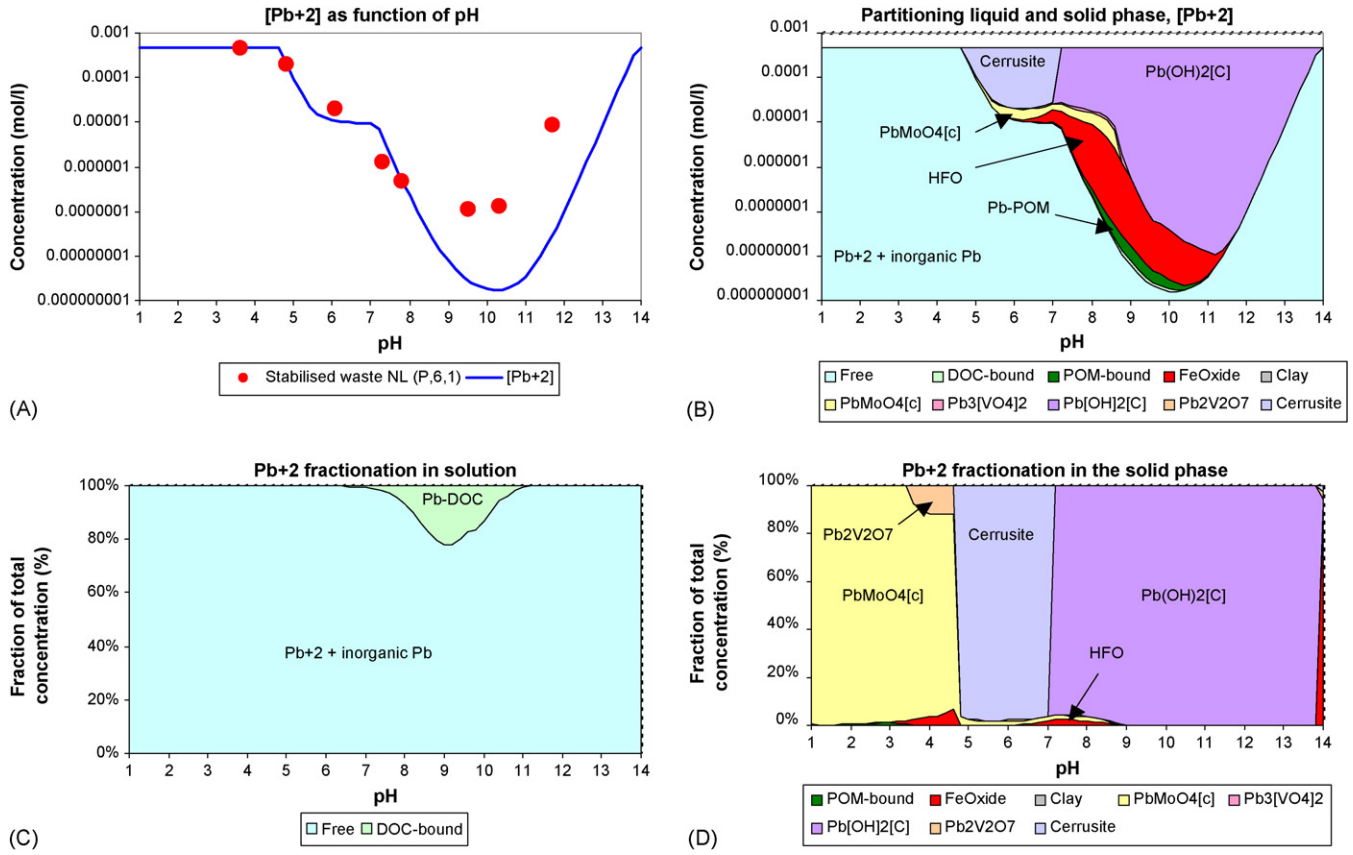


Fig. 9. Measured and calculated Pb concentration as a function of pH in the leachate solution (A), the calculated speciation in the liquid and solid phase (B), the relative proportion of Pb species in solution (C) and the relative proportion of Pb species in the solid phase (D).

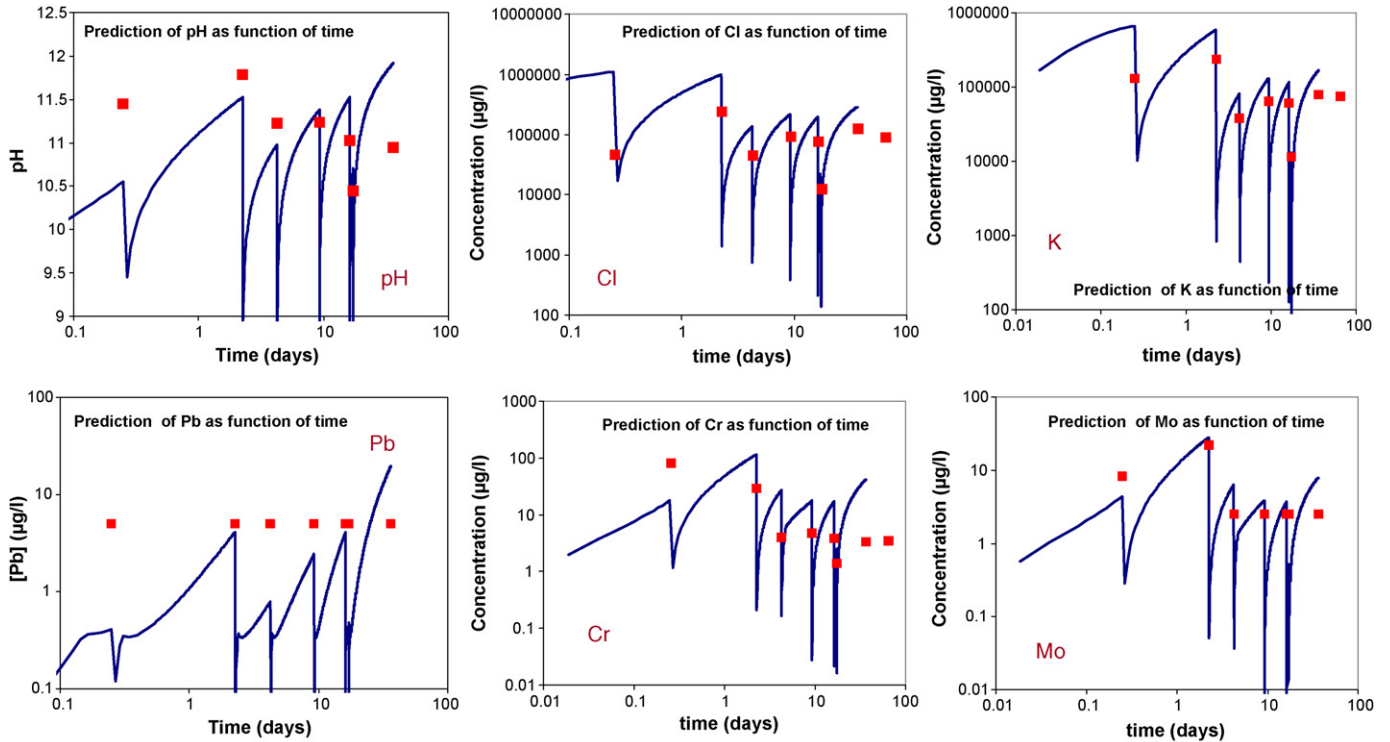


Fig. 10. Comparison of measured and predicted concentrations in a tank leach test on stabilised waste.

### 3.5. 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 [28] have been used as an example of a common soil type in Europe. In the transport modelling a diffusion coefficient of  $3 \times 10^{-11} \text{ m}^2/\text{s}$  is applied, whereas in the case of convective flow a flow rate of  $9 \times 10^{-6} \text{ l/s}$  (corresponding to an infiltration of 280 mm/year) is applied. In Figs. 11 and 12 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 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.

In Fig. 12, the effect of percolation from a stabilised waste layer sitting on top of a soil layer is shown for up to 44 days (280 mm/year). 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

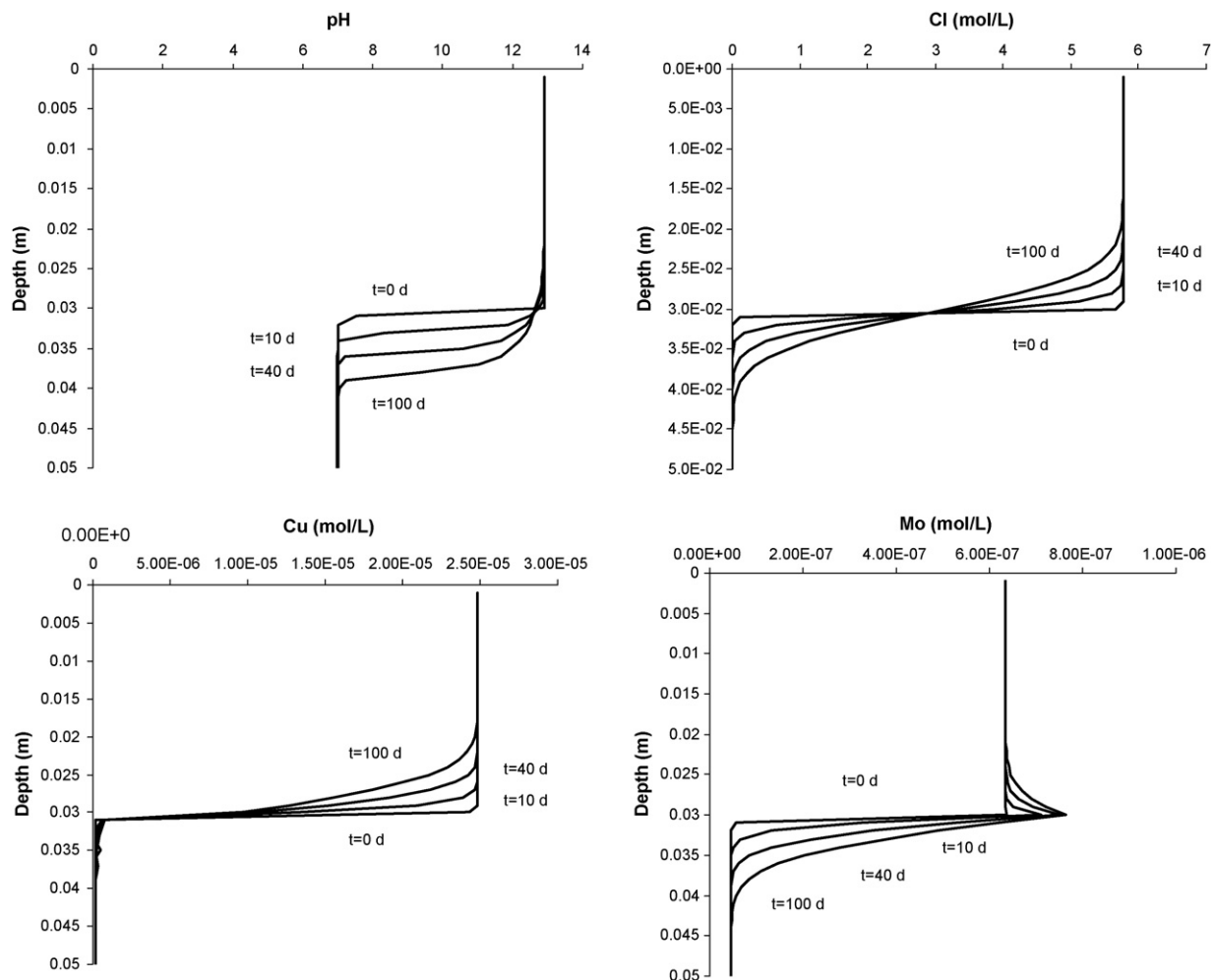


Fig. 11. pH and concentration profile (Cl, Cu and Mo) of soil impact from monolithic cement-stabilised material. The emission is controlled by diffusion and plotted at different times ranging from 0 to 100 days.

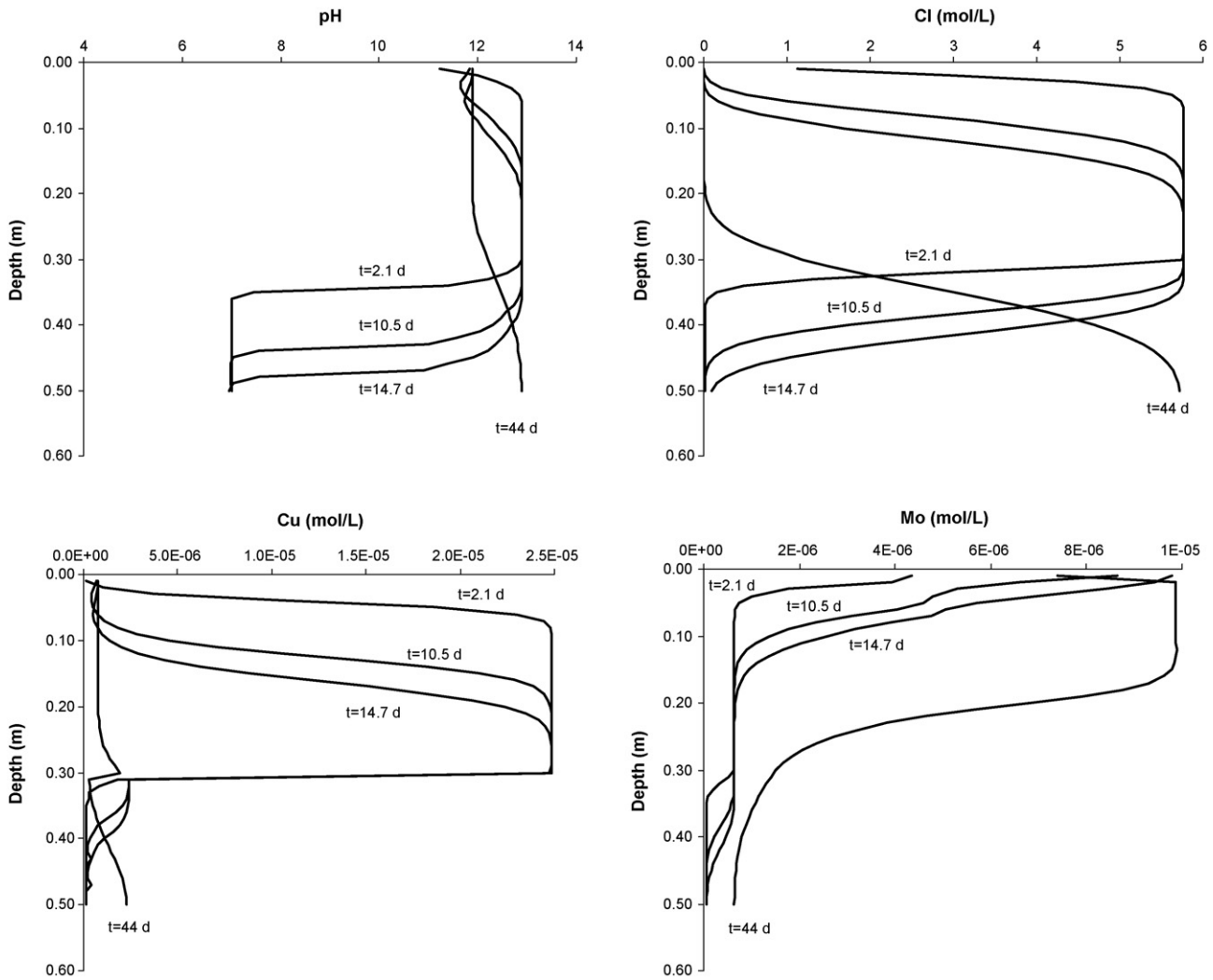


Fig. 12. pH and concentration profile (Cl, Cu and Mo) of soil impact from monolithic cement-stabilised material. The emission is controlled by percolation and plotted at different times ranging from 0 to 100 days.

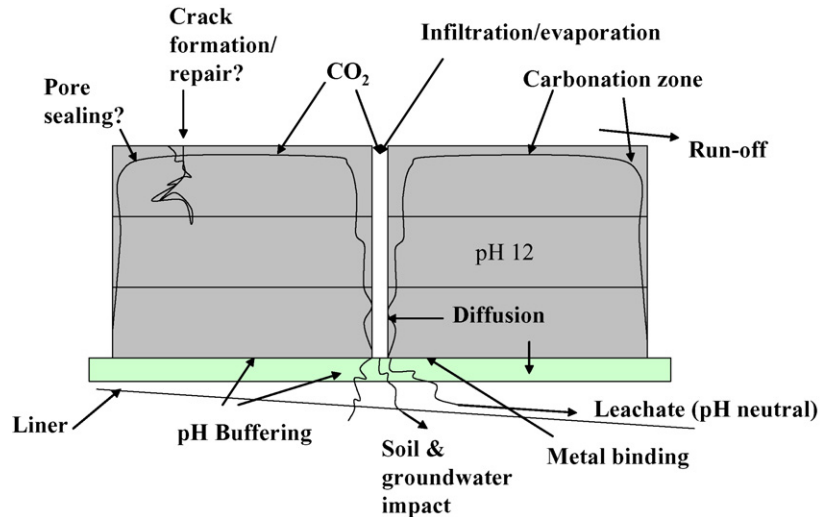


Fig. 13. Scenario description for impact evaluation of monolithic waste disposal.

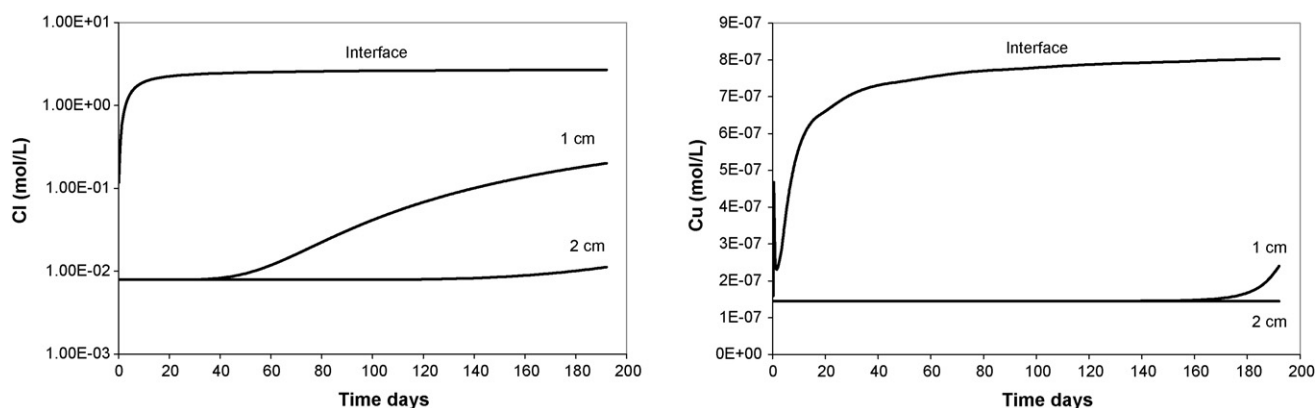


Fig. 14. Profile of Cl and Cu concentrations at the stabilised waste interface and the underlying soil at 1 and 2 cm depth as a function of time.

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 (Fig. 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 and degree of sealing by carbonation,
- pH buffering by soil drainage layer,
- leakage through bottom liner and transport to subsoil and groundwater.

In the case of percolation, a front may be seen passing a pre-defined POC. In Fig. 14 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 monolithic waste is possible by taking into account the different factors and mechanisms controlling release. In Fig. 13 all of these aspects are shown. Ongoing work is focussed on completing this fundamental model description.

#### 4. Conclusions

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  $\text{CO}_2$  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 test is suitable. It is important not to confuse characterisation of monolithic waste behaviour, which is designed to develop criteria and to judge the performance of stabilised waste prepared according to various recipes in specific scenarios, with regular quality control testing undertaken to comply with regulations. For compliance and QC, the first fractions of the tank leach test suffice.

In view of the widely different test protocols used today, harmonisation of test methods for environmental impact evaluation and assessment of stabilised waste treatment efficiency is badly needed [12,29]. The proposed hierarchy in testing provides the necessary detail required by regulators and developers of treatment techniques. It also provides for cost effective verification and QC testing.

When evaluating the complex issue of environmental impact of stabilised waste, using approaches that are too simple lead to poor management decisions. Significant progress has been made in understanding the leaching processes in a monolithic waste landfill. Monolithic waste landfill design is in its infancy. The processes occurring have not been addressed systematically. However, the results of this study show that several aspects of the scenario description can be addressed adequately. For example, the soil layer used in the monolithic waste landfill at VBM not only protects the bottom liner (as was intended), but also provides a buffer against the high pH from stabilised waste and retains metals. Soluble (non-interacting) constituents (e.g. Cl) will prove to be one of the more critical parameters for stabilisation of, for instance, MSWI incinerator fly ash.

Net infiltration into a stabilised waste monofill proves to be far less than previously anticipated. There appears to be a very high degree of water uptake during a rain event and subsequent evaporation of the retained water without producing leachate. This process also enhances the carbonation of the surface layer

leading to seal formation. If shown to be significant, this will reduce release from the bulk of the monolith by diffusion.

Chemical speciation 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. Using a too limited set of elements in geochemical modelling, as currently occurs in many modelling studies on stabilised waste, will have definite limitations in reaching a proper chemical description of release from a material. It is possible that a solution designed to reduce the leaching of one constituent will increase the release of other constituents.

Since more detailed testing 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.

## Acknowledgements

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