

Prediction of the leaching behaviour of waste mixtures by chemical speciation modelling based on a limited set of key parameters

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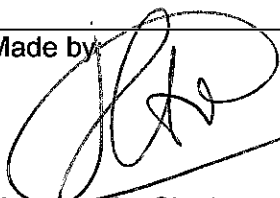

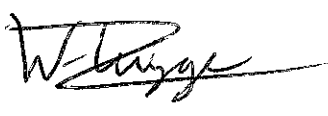
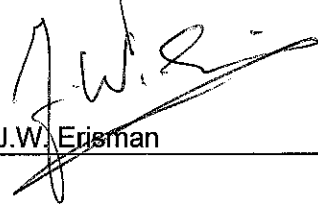
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Abstract

In previous work on a predominantly inorganic waste landfill, carried out in the framework of developing sustainable landfill concepts, detailed information on the leaching behaviour of the wastes submitted for landfilling was obtained. Chemical speciation modelling of the eluate composition obtained from testing the waste mix in a laboratory column leaching test (0.0005 m³) and of the leachates obtained from the lysimeter (1.5 m³) and field scale studies (12,000 m³ pilot cell) on the same waste mix with ORCHESTRA embedded in the database/expert system LeachXS, is showing a rather good agreement between modelling results on major, minor and trace elements and actual measurement. A limited set of input parameters consisting of element availabilities, relevant parameters for sub-models on adsorption to iron oxides, clay, particulate and dissolved organic matter and a selective set of minerals provides a revealing partitioning between dissolved and particulate phases. Apart from describing the release behaviour in the pH dependence-leaching test adequately, this information is most relevant for assessing changes in each of release controlling properties (element availabilities, amount of sorptive surfaces and redox). This type of modelling allows prediction of changes in leachate quality as a result of waste input as this may cause a change in element availability and quantity of sorptive surfaces. A few of such possible changes have been modelled. This type of modelling provides the potential for development of more sophisticated acceptance criteria as well as possibilities to assess the level of aftercare measures needed at the time of landfill closure.

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1. Introduction

Although more waste materials are recycled or re-used nowadays, landfilling of waste materials is still necessary in the future. The long term aftercare of landfills has raised concerns. In the Netherlands, a Sustainable Landfill Foundation was set up in order to stimulate the development of new landfill technologies to minimize impact and thus reduce or eliminate the need for long-term aftercare (Mathlener 2001). The project aims at creating a biogeochemical equilibrium between a landfill and the environment within a period of 30 years, in order to reduce the long-term risk and the aftercare needs.

Waste acceptance criteria such as specified in the EU landfill directive (1999) 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 an entire landfill. In earlier work (van der Sloot et al. 2001) 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). Relatively small additions (up to 10%) of contaminated waste materials in most cases 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 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 multicomponent 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 (e.g. Dijkstra et al. 2004 and refs therein) and waste materials (van Zomeren and Comans, 2004). These models were implemented within the modelling framework ORCHESTRA (Meeussen 2003).

The long-term leaching behaviour of a landfill is strongly affected by the macro-chemistry, which is currently largely ignored in monitoring of leachate. 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 that are occurring in landfills. 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. 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.

2. Materials and methods

2.1 Leaching tests

Laboratory experiments (percolation test – PrEN 14405, 2003; pH dependence test – PrEN 14429, 2003), lysimeter studies (1-1,5 m³) and a 12,000 m³ pilot demonstration project at landfill site Nauernasche Polder (the Netherlands) were performed. Results from the lysimeter study and the pilot demonstration project are described elsewhere (van der Sloot et al. 2001; van der Sloot et al. 2003).

From all waste samples collected during the filling of the pilot test cell, an integrated waste mixture was prepared by taking the waste mass per waste charge into account. The waste mixture was leached with a pH dependent leaching test (PrEN 14429). About 80 g of the waste material was leached with 800 mL water (L/S=10, corrected for the moisture content of the sample) and equilibrated at pH values between 3 and 12. The pH was adjusted at the start of the experiment and at several times during the experiment (up to 6 hours) with 14.4 M HNO₃ or 10 M NaOH. After 24 hours of equilibration by end over end rotation in PE containers the suspensions were filtered (0.45 µm) and analysed.

2.2 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 (van Zomeren and Comans 2005), which is derived from the procedure currently recommended by the International Humic Substances Society (IHHS) for solid samples (Swift 1996) and liquid samples (Thurman and Malcolm 1981), respectively. In short, the procedure is based on the solubility behaviour of HA (flocculation at 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 (Kostka and Luther III 1994). The amount of amorphous aluminium (hydr)oxides were estimated by an oxalate extraction (Blakemore et al. 1987). The extracted amounts of Fe and Al were summed and used as a surrogate for hydrous ferric oxides (HFO) in the model.

2.3 Chemical analysis

The leachates and extracts from laboratory tests were analysed for major, minor and trace elements by ICP (Al, As, B, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Mo, Na, Ni, P, Pb, S, Sb, Se, Si, Sn, Sr, Ti, V, Zn). DOC and TIC were analysed by a Shimadzu TOC 5000a analyser. Cl, F, ammonium and sulfate were analysed by ion-chromatography.

2.4 Geochemical speciation and release modelling

Chemical speciation of the solutions was calculated with the ORCHESTRA modelling framework (Meeussen 2003). 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 (Kinniburgh et al. 1999), with the generic adsorption reactions as published by Milne et al. (Milne et al. 2003). Adsorption of ions onto iron and aluminium oxides was modelled according to the generalized two layer model of Dzombak and Morel (Dzombak and Morel 1990).

The database/expert system LeachXS 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 (van der Sloot et al. 2003; van der Sloot et al. 2001). 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 consists 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 (Meima and Comans 1998)), particulate organic matter and a description of the DOC concentration as a function of pH. 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.

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.

3. Results and discussion

3.1 Interpretation of results

To facilitate the interpretation of the figures regarding the measured and predicted leaching behaviour, an example is given in Figure 3.1. The leaching data is represented as a function of pH by the red data points. 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 3.1 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.

3.2 Geochemical modelling

The availability of all elements used as input for geochemical speciation modelling is given in Table 1. It should be noted that the availability was determined as the maximum concentration 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.

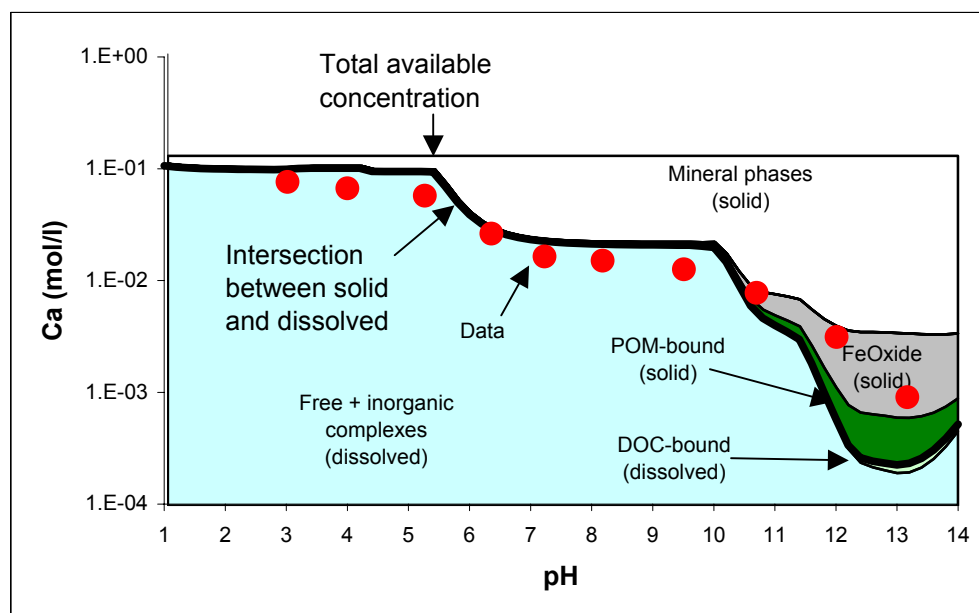


Figure 3.1 *Example of integrated data presentation for pH-static leaching test results and geochemical speciation modelling. Red data points represent leaching data, black solid line is the predicted leached concentration. Areas represent the element speciation: White=minerals, Gray=FeOxide sorption, Dark green=complexation to solid organic carbon, Light green=complexation to dissolved organic carbon and Light blue=free+inorganically complexed form in solution.*

Table 3.1 *Available concentrations of elements used in geochemical modelling. Additional parameters to describe binding to the solid phase were: HFO ($4.3E-3$ kg/kg), total humic acid content ($1.03E-3$ 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	Mg	3002	CO3-2	55000	SO4-2	12715
As	2.57	Mn	574	Cr	19.2	Sb	0.39
B	18.7	Mo	2.87	Cu	39.8	Se	0.32
Ba	7.54	Na	1400	F	50	Si	3015
Br	34.5	NH4	609	Fe	16360	Sr	176
Ca	50150	Ni	23.2	K	1158	V	5.22
Cd	2.76	PO4-3	81.6	Li	3.02	Zn	2401
Cl	5268	Pb	251				

DOC is a sum parameter for all organic carbon species. 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. The DOC data from the pH dependence test were fitted to a polynomial function in order to describe the pH dependent leaching of DOC for intermediate pH values. Initial speciation calculations have indicated several possible solubility controlling minerals (SI saturation index close to 0). From this, a set of minerals was selected for the model prediction calculations.

The geochemical model results for several major and minor elements in comparison with the measurements in the pH-static leaching test are given in Figure 3.2 and Figure 3.3. 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 reckon with in judging the results. These effects will result in an apparent deviation of the model prediction, whereas the leached concentrations might still increase or decrease due to equilibrium and/or kinetic processes. Recent work (Dijkstra et al. 2005) 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, Ca, Fe and Mg are presented in Figure 3.2. There can be deviations in the model description compared to the actual leaching data, as for instance the leaching of Fe is underestimated for about one to two orders of magnitude in the pH range 5 to 7. The deviation of Mg is expected to be largely related to kinetics. Despite the model deviations in the leaching of the described elements (others not shown here), 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 3.3 shows the pH dependent leaching behaviour and results from geochemical modelling for Cr, Mo, Pb and Zn. The leaching behaviour of Zn is 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. The leaching behaviour of Cr is quite well described, whereas Mo is reasonably well described. The latter is controlled by Pb and thus any change in Pb partitioning will affect Mo leachability. 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.

3.3 Influence of waste properties on 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.

An example has been worked out in detail; it 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 3.4A, it can be seen that Pb is substantially bound to HFO in the solid phase at neutral to slightly acidic pH values. Figure 3.4B shows the measured and predicted pH dependent leaching behaviour of Pb where the availability of Pb was increased by a factor 3.

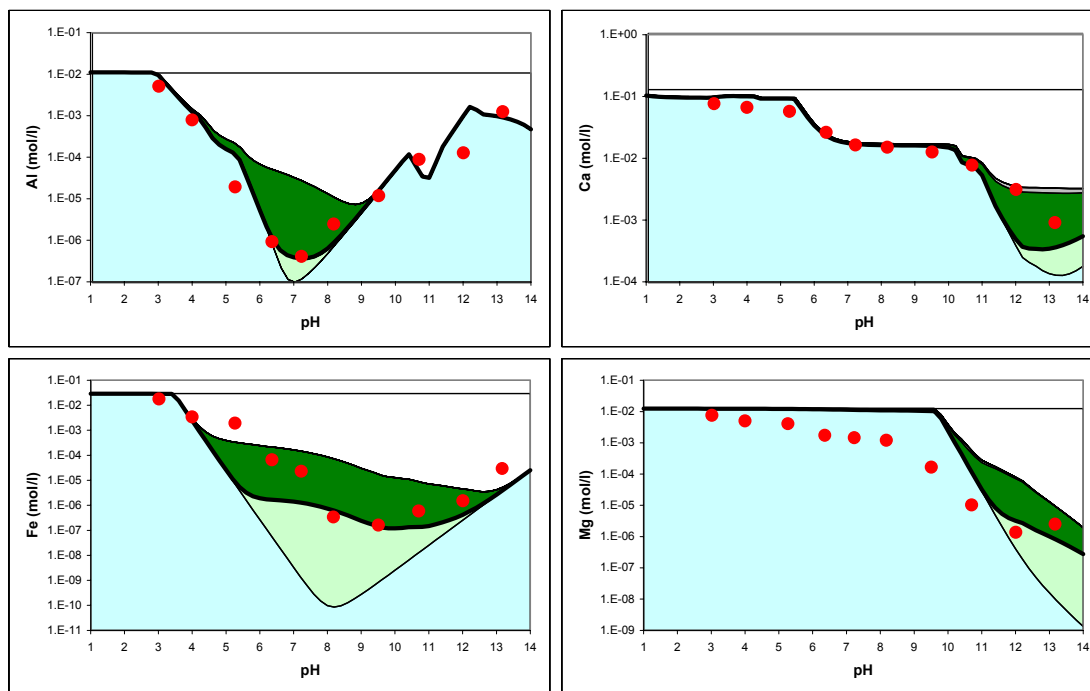


Figure 3.2 *pH-static results and geochemical modelling for the major elements Al, Ca, Fe and Mg (For color codes and lines see Figure 3.1). Minerals identified as solubility controlling are: albite, boehmite, $AlOHSO_4$, anhydrite, gypsum, CaZincate, calcite, ferrihydrate, brucite.*

In Figure 3.4C, the Pb availability 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 3.4C shows the effect of increased DOC concentrations on the predicted Pb emissions. It can be seen that Pb emissions become higher, mainly as a result 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 3.4D). Only at pH values lower than 6, an increase in the emissions is observed as already shown in the initial calcula-

tions (Figure 3.4A). 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.

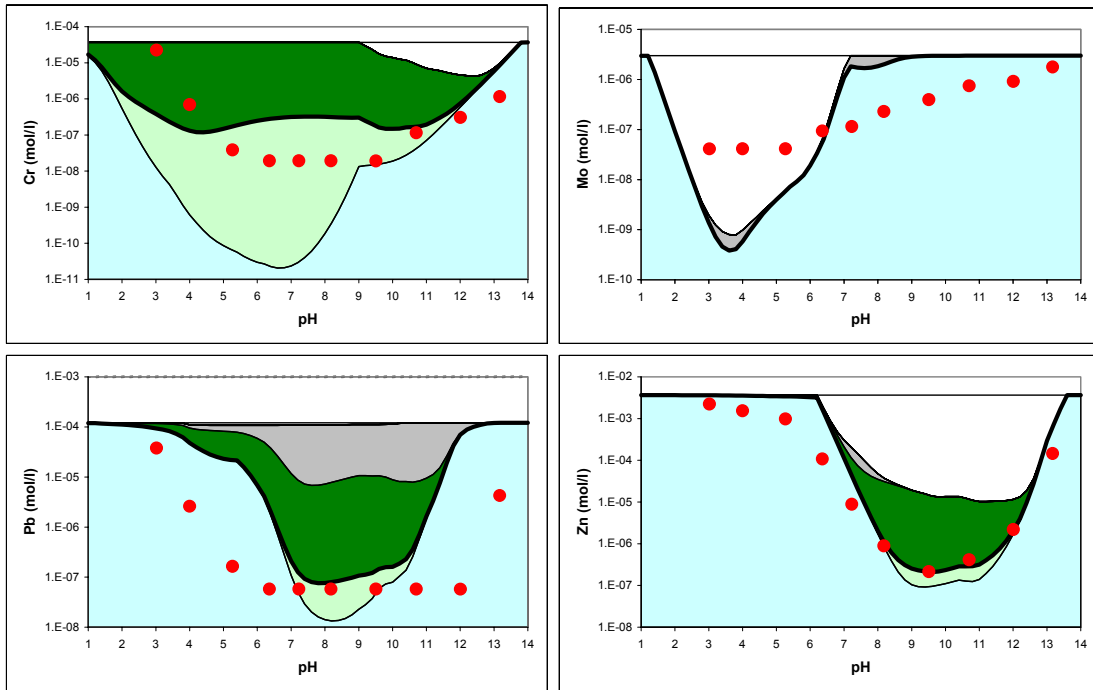


Figure 3.3 *pH-static results and geochemical modelling for the elements Cr, Mo, Pb and Zn. The relevant solubility controlling phases are: $PbMoO_4$, PbV_2O_7 , $Cr(OH)_3$ and Willemite.*

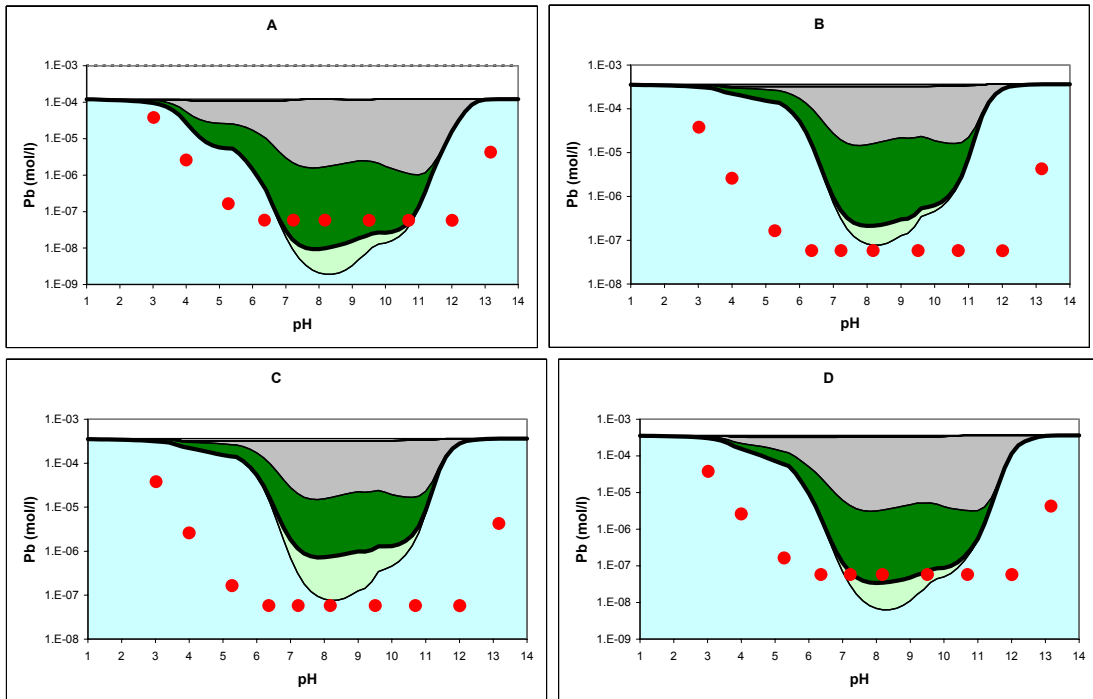


Figure 3.4 *Prediction of pH dependent Pb leaching from a waste mixture under varying conditions. A: Initial calculations; B: Pb availability increased by a factor 3; C: Pb availability and DOC increased by a factor 3; D: Pb availability and HFO increased by a factor 3.*

4. Conclusions

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 many elements can be adequately predicted simultaneously by model calculations. This is particularly true for the pH domain around the own 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.

The advantage of the integral approach applied here 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 test used in this work, which may help to decide at what level a match between measurement and prediction is sufficiently accurate for a subsequent decision. The potential to predict behaviour under conditions that have not yet been tested before (e.g. low L/S, imposed redox condition, increased contamination) 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 significantly helps to make choices through the acceptance of waste to reach a more sustainable landfill practice. From the modelling it has become very clear 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. The parameter settings for the prediction will be used in subsequent work on combined chemical reaction/transport to predict percolation behaviour at lab, lysimeter and field scale.

If the relevant parameters (sum of dissolved and particulate organic matter, sum of Fe/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 decisions 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.

References

- Blakemore, L.C., P.L. Searle and B.K. Daly (1987): *Methods for chemical analysis of soils*. Sci. rep. 80. Lower Hutt, New Zealand, NZ Soil Bureau.
- Comans, R.N.J. and C. Zevenbergen (1997): *Beoordeling van het effect van grondreiniging op de uitloogbaarheid van grond*. ECN-C--97-055, 1-86.
- Council Directive (1999): 1999/31/EC of 26 April 1999 on the landfill of waste.
- Dijkstra, J.J., H.A. van der Sloot and R.N.J. Comans (2005): *The leaching of major and trace elements from MSWI bottom ash as a function of pH and time*. Appl. Geochem., submitted.
- Dijkstra, J.J., J.C.L. Meeussen, and R.N.J. Comans (2004): *Leaching of heavy metals from contaminated soils; an experimental and modelling study*. Environ. Sci. Technol., vol. 38, Iss. 16, pp. 4390-4395.
- Dzombak, D.A. and F.M.M. Morel (1990): *Surface complexation modeling: hydrous ferric oxide*. John Wiley & Sons, Inc., New York.
- Kinniburgh, D.G., W.H. van Riemsdijk, L.K. Koopal, M. Borkovec, M.F. Benedetti and M.J. Avena (1999): *Ion binding to natural organic matter: competition, heterogeneity, stoichiometry and thermodynamic consistency*. J. Colloids Surf., A, Vol. 151, pp. 147-166.
- Kostka, J.E. and G.W. Luther III (1994): *Partitioning and speciation of solid phase iron in saltmarsh sediments*. Geochim. Cosmochim. Acta, Vol. 58, pp. 1701-1710.
- Mathlener, R.A. (2001): *The savings of sustainable landfilling*. Proceedings Sardinia 2001, Eight International landfill symposium, Cagliari, vol. I, 265-269.
- Meeussen, J.C.L. (2003): *ORCHESTRA: An object-oriented framework for implementing chemical equilibrium models*. Environ. Sci. Technol., vol. 37, pp. 1175-1182.
- Meima, J.A. and R.N.J. Comans (1998): *Application of surface complexation/precipitation modeling to contaminant leaching from weathered municipal solid waste incinerator bottom ash*. Environ. Sci. Technol., Vol. 32, pp. 688-693.
- Milne, C.J., D.G. Kinniburgh, W.H. van Riemsdijk and E. Tipping (2003): *Generic NICA-Donnan model parameters for metal-ion binding by humic substances*. Environ. Sci. Technol., Vol. 37, pp. 958-971.
- Sloot, H.A. van der, A. van Zomeren, J.J. Dijkstra, D. Hoede, J. Jacobs and H. Scharff (2003): *Prediction of long term leachate quality and chemical speciation for a predominantly inorganic waste landfill*. Proceedings Sardinia 2003, Ninth International landfill symposium, Cagliari, vol. I, 36-38.
- Sloot, H.A. van der, A. van Zomeren, R.P.J.J. Rietra, D. Hoede and H. Scharff (2001): *Integration of lab-scale testing, lysimeter studies and pilot scale monitoring of a predominantly inorganic waste landfill to reach sustainable landfill conditions*. Proceedings Sardinia 2001, Eight International landfill symposium, Cagliari, vol. I, 255-264.
- Swift, R.S. (1996). *Organic matter characterization, In Sparks, D.L. (Eds), Methods of soil analysis. Part 3. Chemical methods*. Soil Sci. Soc. Am., Madison, WI, pp. 1011-1069.
- Thurman, E.M. and R.L. Malcolm (1981): *Preparative isolation of aquatic humic substances*. Environ. Sci. Technol., Vol. 15, pp. 463-466.

Zomeren, A. van and R.N.J. Comans (2004): *Contribution of natural organic matter to copper leaching from municipal solid waste incinerator bottom ash*. Environ. Sci. Technol., vol. 38, iss. 14, pp. 3927-3932.

Zomeren, A. van and R.N.J. Comans (2005): *Rapid batch procedure for the quantitative determination of humic and fulvic acid concentrations*. Environ. Sci. Technol., Submitted.