

Environmental behaviour of a stabilised waste disposal in the framework of sustainable landfilling

*Presented at Sardinia 2005, Tenth International waste management and landfill symposium
(3-7 October 2005, S. Margherita di Pula-Cagliari, Sardinia, Italy),
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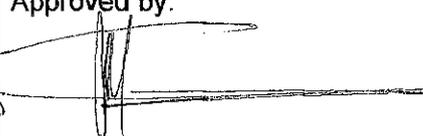
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OCTOBER 2005

Abstract

Stabilisation/solidification of (hazardous) waste materials is aimed at changing the release process from a percolation dominated to a diffusion or surface-dissolution dominated regime. For this form of treatment of hazardous waste for disposal in non-hazardous waste sites, the regulatory framework is still in development. In this study, stabilisation/solidification is done by addition of cement in order to create a monolithic material. This form of waste treatment and disposal is currently studied in a pilot experiment within the framework of a Dutch project on Sustainable Landfill. Results from a pilot scale experiment show that about 10% of the precipitation water is measured as percolate/run-off water, the majority of the precipitation water is evaporated. This is an important aspect in the scenario description specifically for monolithic waste landfills. As a result of the monofill design, the measured pH values in both the percolate and the run-off water are still generally between 7 and 9. Cores sampled from the monofill show that the surface of the waste material is significantly carbonated. It is suggested that the run-off water only comes in contact with the outer (carbonated) surface of the waste material, whereas the percolate is still neutralised by the soil layer protecting the bottom liner. The release of contaminants under field situations is controlled to a large extent by the pH (solubility controlled) of the outer layer of stabilised waste. This would imply that the chemical speciation derived from a pH-static leaching test could be used in order to estimate the release under field conditions (neutral to slightly alkaline pH), rather than only the results from a tank leaching test (which addresses leaching at the alkaline pH).

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1. Introduction

Stabilisation/solidification is a technology aimed at changing the physical/chemical properties of (hazardous) waste materials in order to reduce the release of contaminants in the environment. The technology aims at changing the release process from a percolation dominated to a diffusion or surface-dissolution dominated regime. For this form of treatment of hazardous waste for disposal in non-hazardous waste sites, the regulatory framework is still in development. In setting criteria for landfill classes in Annex II of the EU Landfill Directive (1999) it proved to be impossible to derive such values for stabilised monolithic waste due to lack of information on release and release controlling factors in stabilised waste monofills. Both at national and at EU level it was decided that additional information is needed to be able to develop proper criteria for this type of landfill. For the time being, regulatory controls are referred to the Member States.

Stabilisation of hazardous waste can be operated in various ways, in which recipe development and control of a stable and sustainable end product is a main objective. Work by Ludwig et al. (Ludwig et al. 2000) and by Fitch and Cheeseman (Fitch and Cheeseman 2003) on cement stabilised MSWI fly ash after preparation of large monolithic waste blocks has shown deterioration of the surface. In both studies carbonation was noted. In the study by Baur et al. (Baur et al. 2001) and Fitch and Cheeseman (Fitch and Cheeseman 2003) a very high pH in leachate was observed as would be expected for the highly alkaline matrix. In this study, cement stabilisation/solidification is studied in a pilot experiment within the framework of a Dutch project on Sustainable Landfill in conjunction with laboratory leaching studies, verification against full-scale field data and geochemical modelling. Sustainable in the framework of stabilisation should be read as a product with contaminant containment and minimal deterioration under the considered disposal scenario conditions.

Many complex physical/chemical processes control release from a stabilised waste monofill. Our first goal is to understand the physical/chemical processes in a stabilised waste monofill. 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. This gives more reliable estimates of the environmental impact on both short- and long-term, which then allows criteria to be established. A framework for environmental impact evaluation and testing of materials for construction and for disposal of waste was presented (Kosson et al. 2002), which is consistent with the methodology described in EN 12920 (2004).

2. Materials and methods

2.1 Pilot experiment

At the site of VBM (Maasvlakte, The Netherlands) a pilot experiment with four stabilised waste compartments has been realised. The experimental set-up is given in Figure 2.1, note that this is a simplified scheme of the experiment. In the pilot-scale experiment, there are four sections (Cell A to D) in which the solidified/stabilised waste is landfilled and effects of height, carbonation and mixing of recipes are studied. The waste is stabilised in-situ in layers of approximately 0.5 m and in the pilot experiment it is separated at intervals of 1.5 m by a vertically placed geotextile membrane (see Figure 2.1). The space filled by geotextile is part of the sustainable concept for stabilised/solidified material to create preferential flow channels for water instead of creating one very large waste body. This reduces the amount of water that reaches saturation when it percolates through the stabilised waste. Part of the rainwater that falls on top of the stabilised waste material is evaporated due to a relatively high porosity in 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 stabilisation layer for protection of the bottom liner system. As will be discussed below, this soil layer is able to neutralise the alkaline percolate water and can possibly bind leached contaminants.

Sampling facilities were installed to sample the water that has reached the drainage by percolation along the geotextile membrane and through the waste material itself. Furthermore, the run-off water that flows along the top layer towards the side of the compartment was collected. pH, E.C. and watervolumes were monitored periodically. Chemical analysis of the samples was performed after filtration (0.45 μm).

2.2 Leaching tests and chemical analysis

For characterisation of the stabilised waste a pH-static test (PrEN 14429, 2003) was used. In short, this leaching test involves the leaching of crushed material at a liquid to solid ratio (L/S) of 10 at eight different pH values ranging from 2 to 13. After 24 hours, pH is measured and the eluates are filtered (0.45 μm) and analysed.

Batch leaching tests at the native pH of the suspension (L/S ratio of 10) were performed on crushed samples from cores sampled in the pilot experiment (see below). The suspensions were filtered (0.45 μm) after measurement of pH and E.C.

The leachates and extracts from laboratory tests were analysed by several chemical analysis techniques. All major- and minor elements were measured by ICP-AES, anions by ionchromatography and cyanides (total and free) by photometry.

2.3 Sampling of stabilised waste cores

About one year after completion of the waste compartments, several cores were drilled in the upper layer of waste (0-55 cm) to study carbonation effects as a function of depth. The sampled cores were sliced in the laboratory and the sub fractions were leached with a batch leaching test (L/S ratio of 10, 24 hours).

PROCESSES IN STABILISED WASTE

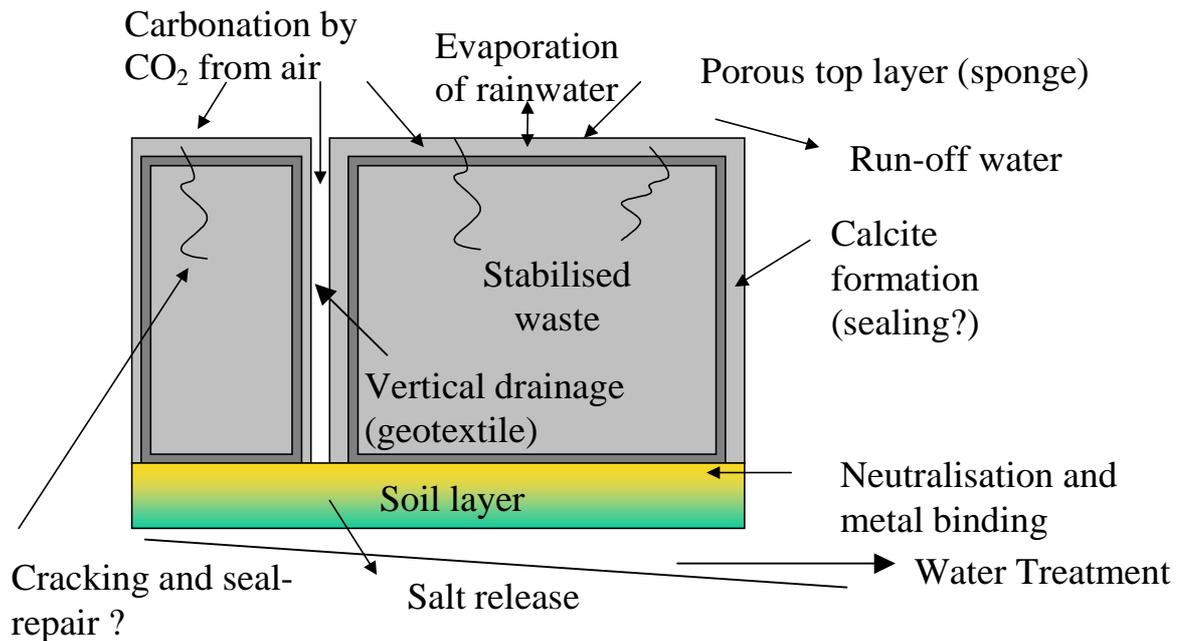


Figure 2.1 *Schematic representation of important processes in a stabilised waste landfill during the operational phase based on the results from the Sustainable Landfill project*

2.4 Geochemical release modelling from stabilised waste

The geochemical modelling framework ORCHESTRA (Meeussen 2003), using an extended MINTEQA2 database with thermodynamic constants for inorganic reactions, was coupled to a database/expert system (LeachXS)(van der Sloot et al. 2003) containing the pH dependence leaching test data, the tank test data, lab pilot and field leachate data for quick data retrieval, processing and data presentation. 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 (Kostka and Luther III 1994). The extracted amounts were summed and used as an estimate for hydrous ferric oxides (HFO) in the model. DOC was used as input for humic acid modelled with the NICA-Donnan model. The availability of all elements was estimated and used as input, the model calculates the predicted concentrations and the speciation in both the leachates and the solid matrix.

3. Results and discussion

Several relevant aspects of the scenario for stabilised waste as shown in Figure 2.1 have been worked out in more detail and are explained below. The scenario aspects include the water balance in the waste compartment, effects of carbonation, neutralisation and metal binding by the soil layer and the release of contaminants under field situations.

3.1 Production of percolate and run-off water in the pilot experiment

The amount of precipitation and the production of percolate and run-off water was monitored and graphically presented in Figure 3.1 (results from cell B are shown). The precipitation was measured daily; the percolate and run-off water volumes were usually measured monthly. Figure 3.1 shows that after an initial start up period, the amount of percolate water amounts to only 10% of the actual precipitation as measured on site. The volume run-off water is even less. However, it should be noted that the run-off water is collected at two sides of the compartment. Possibly, more run-off water (about a factor 2) is produced that is not collected in our sampling system or could possibly be measured as percolate water. It should be noted that the hydrology will be affected after placement of a top cover on the landfill, resulting in a significant lower infiltration in the order of 5 mm/yr. Our results are in good agreement with Ludwig et al. (Ludwig et al. 2000), who have shown that about 10-30% of the precipitation was measured as percolate water. Our results indicate that the majority of the precipitation water is evaporated before this water comes to run-off or to form percolate water. This is an important aspect in the scenario description for monolithic waste monofills.

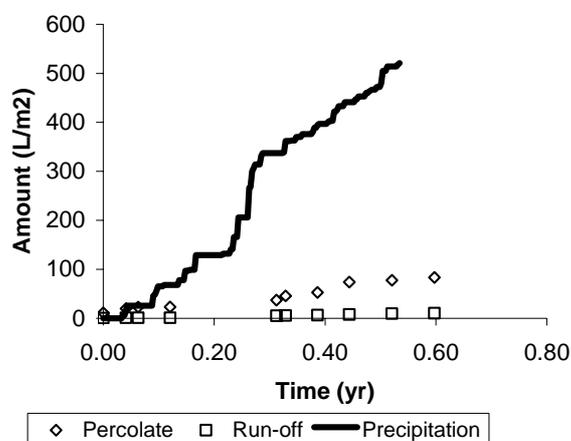


Figure 3.1 Amount of precipitation and percolate and run-off water production as a function of time. The cell height is 3 m, the surface of the top side is 40 m²

3.2 Release of contaminants under field conditions

The measured pH values in both the percolate and the run-off water are generally neutral to slightly alkaline, ranging from 6.8 to 9.3 (average 7.9). This is quite remarkable since the alkaline waste material has an own pH > 12. Also, other field experiments have shown a high leachate pH of about 13 (Fitch and Cheeseman 2003; Baur et al. 2001; Ludwig et al. 2000). Presumably, the percolate and run-off water only comes in contact with the outer (carbonated) surface of the waste material (see below). This could explain the relatively low pH values in the water. Moreover, the pH in the percolate water is buffered by the presence of the soil layer at

the bottom of the waste compartment {van Zomeren, van Wetten, et al. 2003 398 /id}. Gradient relaxation in the exposed waste layer as a result of a decreased water volume after completion of the top cover may cause an increased alkalinity of the percolate water. Future work should point out whether the combination of an increased alkalinity and a decreased water volume affects the calculated effective period of the soil layer after construction of a top cover. The effect of pore sealing as a result of carbonation should also be taken into account. Fitch and Cheeseman {Fitch & Cheeseman 2003 512 /id} have identified CaCO_3 minerals in environmentally exposed stabilised waste. Pore sealing can lead to a lower release of alkalinity and contaminants from the waste.

The EC values in the percolate water samples (63 to 217 mS/cm) are roughly a factor 10 to 30 higher than the E.C. values in run-off water samples (0.9 to 6.8 mS/cm). This can be attributed to the difference in contact time of the water (relatively short for run-off water) and illustrates that salts are released fairly readily, while pH remains almost neutral.

The leached concentrations of Cd, Cu, Mo and Zn in percolate and run-off water are shown in Figure 3.2. It can be seen that the leached concentrations in the percolate water are generally higher than the concentrations in run-off water, except for Zn. There are no obvious differences in the concentrations between the different compartments, which differ in height (cell A is one 1 m high, cell B and D are 3 m high) and stabilised waste recipe (cell A and B both contain a MSWI fly-ash recipe, cell D contains several waste recipes). It is remarkable that the relatively large differences in E.C. between percolate and run-off water are generally not reflected as strongly in the release of contaminants. This is probably due to a pH dependent (solubility controlled) leaching of these elements, which do not significantly contribute to E.C. This would imply that a pH-static leaching test could be used in order to estimate the release under field conditions, rather than only the results from a tank leaching test. In addition, the low volume to area ratio in this type of scenario and wet/dry periods lead to significant delays in projected release in comparison with the common assumption of a zero boundary condition for diffusion in a tank leaching test. In general, the concentrations of Mo are high whereas Pb, Cu and Zn are relatively low. This would imply that anions are more relevant for emissions than heavy metals in this type of disposal scenario. The monitoring will be continued for a longer period to validate these initial results and to check whether the range in observed concentrations will change.

3.3 Effects of carbonation in stabilised waste under field conditions

About one year after the start of the pilot experiment, cores with stabilised waste were drilled from the upper layer of the compartment. Results from leaching tests ($L/S=10$) on sliced samples are presented in Figure 3.3. It can be seen that Cl is depleted from the exposed material, concentrations increase substantially as a function of depth. This is a typical behaviour for soluble salts and is independent of the pH of the waste material. The leaching behaviour of Mg is pH-dependent and this explains the observed concentration profile. The exposed material is carbonated (pH 8.5 to 11) in the upper layers (0-2 cm) which causes high Mg leaching in this region. Inside the material the pH is about 12, leaching of Mg is then generally controlled by the mineral brucite, which results in a much lower leachability. Mo is an anion which is very soluble and exhibits about the same leaching behaviour as Cl, although the extent of difference in concentrations is less for Mo. Pb shows the highest concentration inside the waste material and low concentrations at the (carbonated) surface from 0-10 cm. This pattern can be explained by the strong pH dependent leaching of Pb, which has a solubility minimum around pH 8-10. These results indicate that for the prediction of release solubility controlled elements should be judged by taking the pH of the (carbonated) surface of the waste material into account rather than by projecting release on results from a laboratory leaching test on a freshly produced (alkaline) sample assuming unchanged conditions.

3.4 Geochemical modelling release controlling mechanisms from stabilised waste

The results from the pH static leaching tests on stabilised waste for Cu, Cr, Al and Pb and the subsequent model prediction of the leaching behaviour are presented in Figure 3.4. The leaching data is given as the (red) data points, the (black) solid line represents the predicted leaching behaviour. As can be seen from the Cu graph, the colored areas represent different chemical species in both the solid matrix (minerals, sorption to HFO and complexation to solid organic carbon) as well as in solution (free ion+inorganic metal complexes and organic metal complexes). The predicted leaching behaviour is therefore the intersection between all dissolved and the solid species.

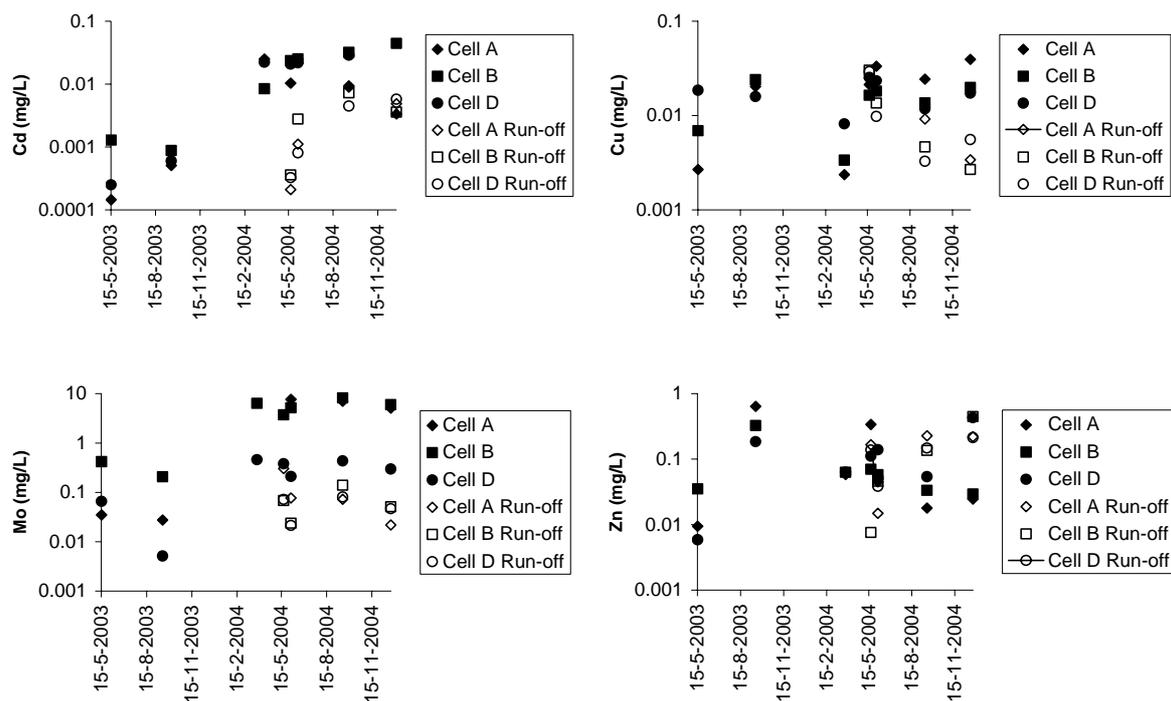


Figure 3.2 Release of Cd, Cu, Mo and Zn in percolate and run-off water from the pilot experiment with a stabilised waste monolith landfill

It is crucial for these calculations that the model parameters (e.g. availability, amount of HFO and solid organic matter and relevant mineral phases) are known because they determine the distribution of a contaminant between the solid matrix and the leachate solution. However, in this study, the amount of HFO and solid organic matter was estimated based on general knowledge of this waste material. In general, the model describes the data well considering the complex processes and interactions of all elements. The qualitative trend in predicted concentrations is already very good, future model improvements could fill the gaps. Moreover, kinetic constraints in the laboratory experiments (24 hrs) are also a reason for the observed deviations between data and the model predictions.

The leaching behaviour of Cu is overestimated from pH 5 to about pH 9. This overestimation can possibly be the result of an underestimation of the HFO and/or solid organic matter content. In addition, $\text{Cu}(\text{OH})_2$ controlled Cu leaching between pH 7.2 and 13.6. However, sorption to HFO and solid organic matter are important processes to bind Cu to the solid phase as can be seen from the gray and green areas in Figure 3.4. Further improvements in the model can provide a better description of the leaching behaviour for Cu in this pH range. The leaching behaviour is predicted reasonable at pH values above 9. It can be seen that the leached Cu concentra-

tions are fully in free and inorganic complexes, this is due to the very low DOC concentrations in this waste material.

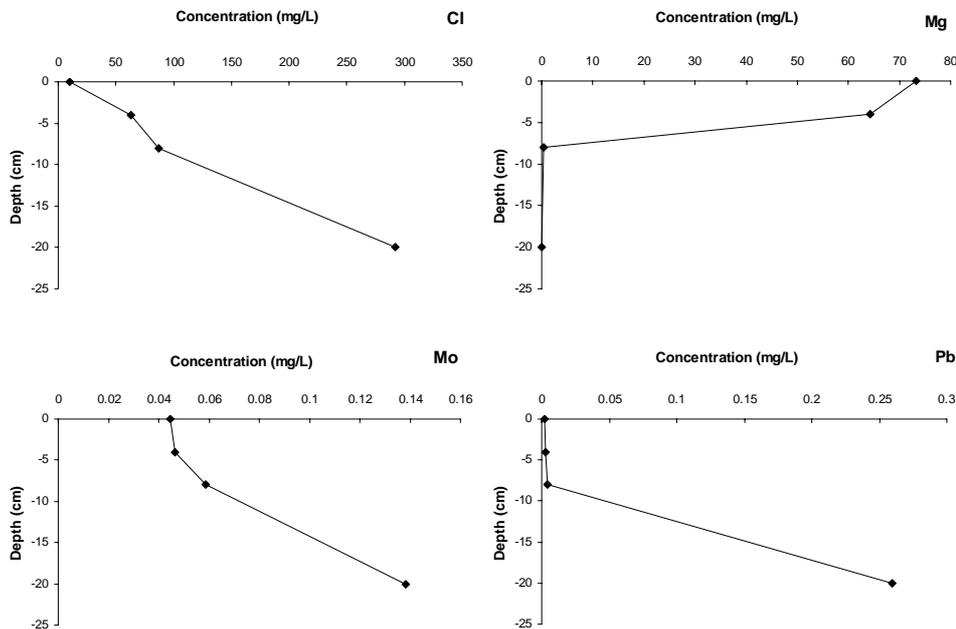


Figure 3.3 Results from leaching tests on sliced core samples from stabilised waste

Cr leaching decreases strongly between pH 4 and 6 and increases again until pH 11. Above pH 11, Cr leaching decreases again. This trend is qualitatively described by our model prediction, although the extent of these processes are not quantitatively followed in the calculations for the same reasons as explained for Cu. However, the qualitative description of the leaching behaviour of Cr is already very promising and would never be possible without the extended model calculations. At very high pH, substitution of Cr as Cr III or as CrO₄ in ettringite controls Cr leaching and below pH 11 the leaching is controlled by sorption to HFO, PbCrO₄ and solid organic matter. In solution, Cr is predominantly free and inorganically complexed. At neutral pH, organically complexed Cr may also be present.

The model very well describes the leaching behaviour of Al. Between pH 5 and 7 a mineral phase may be missing. It can be seen that the leaching of Al is predominantly controlled by the solubility of mineral phases (Al(OH)SO₄, Boehmite, Albite[low] and monosulfate were found to be controlling). Binding to solid organic matter is only relevant around neutral pH.

Pb is very well described in the pH range between 4 and 8. At higher pH, the model does describe the data qualitatively. However, there is an underestimation of 1-2 orders of magnitude for Pb. This implies that there is an important solubility controlling process missing in the prediction of the leaching behaviour for Pb. Pb(OH)₂ was found as the solubility controlling mineral between pH 8.2 to 13.8.

These preliminary extended model calculations will form the basis for environmental impact modelling, in which the calculated pH dependent release will be transported into a layer of soil. The transport of contaminants through the soil layer can then be assessed in order to estimate the final release of contaminants.

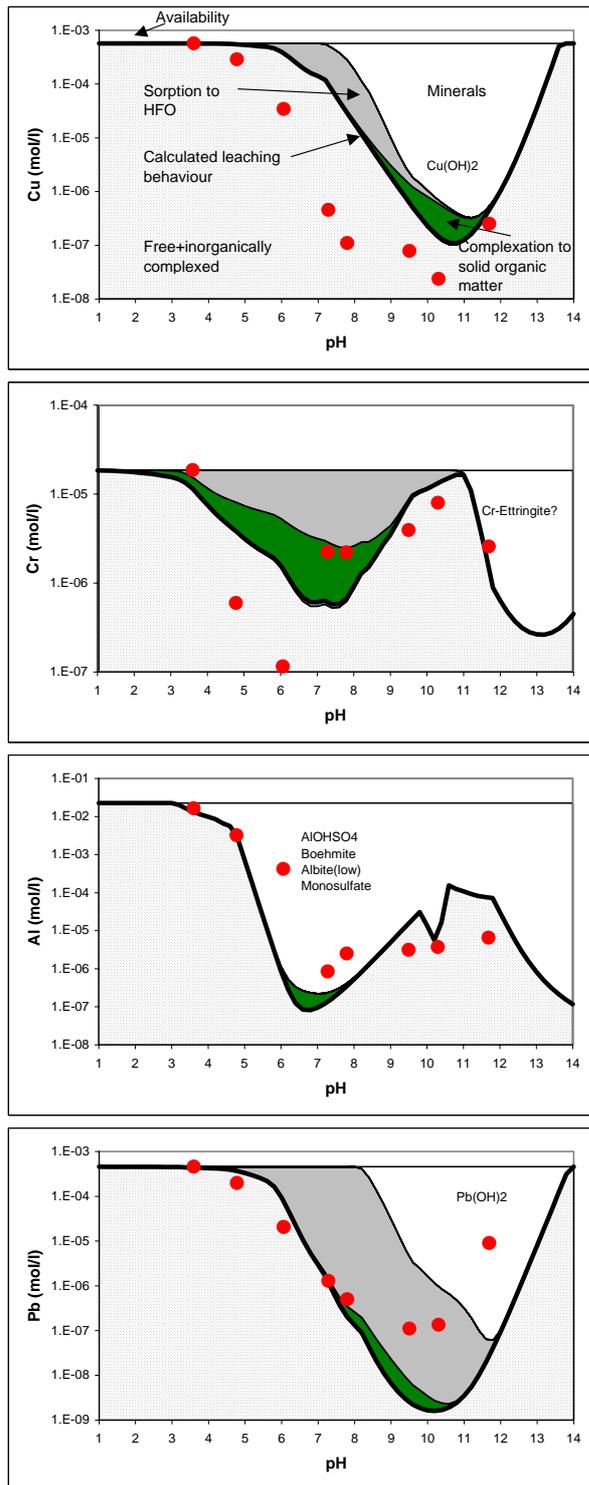


Figure 3.4 Results from pH-static leaching tests (red data points) on stabilised waste and prediction of the leaching behaviour by geochemical modelling (Black solid line). Areas represent the element speciation: White=minerals, Gray=FeOxide sorption, Dark green=complexation to solid organic carbon, Light green=complexation to dissolved organic carbon (minor importance in these calculations) and Dotted area=free+inorganically complexed form.

4. Conclusions

In this study, the results from a pilot scale experiment with stabilised waste were presented. Several aspects of the scenario description for a stabilised waste landfill were addressed. About 10% of the precipitation water is measured as percolate/run-off water in the pilot experiment. These results indicate that the majority of the precipitation water is evaporated before this water comes to run-off or to form percolate water. This is an important aspect in the scenario description specifically for monolithic waste landfills.

The measured pH values in both the percolate and the run-off water are generally between 7 and 9. This is quite remarkable since the alkaline waste material has a native pH of around 12 in laboratory measurements on crushed samples. Field measurements with cores sampled from the landfill show that the surface of the waste material is carbonated. It is suggested that the percolate and run-off water only comes in contact with the outer (carbonated) surface of the waste material. This could explain the relatively low pH values in the water. Moreover, the pH in the percolate water can also be buffered by the presence of the soil layer at the bottom of the waste compartment resulting in neutral percolate water on the long-term. This can be an important design criterion for sustainable landfill of stabilised waste.

The measured E.C. values in the percolate water samples are about a factor 10 higher than the E.C. values in run-off water samples. This can be attributed to the difference in contact time of the water where the run-off water has relatively short contact times compared to the percolate water.

It is concluded that there are no obvious differences in the concentrations between the different compartments, which differ in height and stabilised waste recipe (cell A and B both contain a fly-ash recipe, cell D contains several waste recipes). The relatively large differences in E.C. values between percolate and run-off water are not reflected as strongly in the release of contaminants. This is probably due to a pH dependent (solubility controlled) leaching of these elements. This would imply that a pH-static leaching test could be used in order to estimate the release under field conditions (neutral to slightly alkaline pH), rather than only the results from a tank leaching test (which addresses leaching at the native alkaline pH). The monitoring will be continued to validate these initial results and to check whether the range in observed concentrations will change.

References

- Baur, I., C. Ludwig and C.A. Johnson (2001): *The leaching behavior of cement stabilized air pollution control residues: a comparison of field and laboratory investigations*. Environmental Science and Technology 35 : 2817-2822.
- Council Directive (1999): 1999/31/EC of 26 April 1999 on the landfill of waste.
- Fitch, J.R. and C.R. Cheeseman (2003): *Characterisation of environmentally exposed cement-based stabilised/solidified industrial waste*. Journal of Hazardous Materials 101: 239-255.
- Kosson, D.S., H.A. van der Sloot, F. Sanchez and A.C. Garrabrants (2002): *An Integrated Framework for Evaluating Leaching in Waste Management and Utilization of Secondary Materials*. Environmental Engineering Science 19: 159-203.
- Kostka, J.E. and G.W. Luther III (1994): *Partitioning and speciation of solid phase iron in saltmarsh sediments*. Geochimica et Cosmochimica Acta 58: 1701-1710.
- Ludwig, C., C.A. Johnson, M. Kappeli, A. Ulrich and S. Riediker (2000): *Hydrological and geochemical factors controlling the leaching of cemented MSWI air pollution control residues: A lysimeter field study*. Journal of Contaminant Hydrology 42: 253-272.
- Meeussen, J.C.L. (2003): *ORCHESTRA: An object-oriented framework for implementing chemical equilibrium models*. Environmental Science and Technology 37: 1175-1182.
- Sloot, H.A. van der, P. Seignette, R.N.J. Comans, A. van Zomeren, J.J. Dijkstra, J.C.L. Meeussen, D.S. Kosson and O. Hjelm (2003): *Evaluation of environmental aspects of alternative materials using an integrated approach assisted by a database/expert system*.