# SIMILARITIES IN THE LONG TERM LEACHING BEHAVIOUR OF PREDOMINANTLY INORGANIC WASTE, MSWI BOTTOM ASH, DEGRADED MSW AND BIOREACTOR RESIDUES.

H.A. VAN DER SLOOT*, R.P.J.J. RIETRA *, R.C. VROON**, H. SCHARFF[O] AND J.A.WOELDERS[OO].

*ECN, P.O. Box 1, 1755 ZG Petten, The Netherlands,
**TNO-MEP, P.O. Box 342, 7300 AH Apeldoorn, The Netherlands.
[O] Afvalzorg Deponie B.V., P.O. Box 6343, 2001 HH Haarlem, The Netherlands,
[OO]ESSENT, P.O. Box 5, 9418 ZG Wijster, The Netherlands

SUMMARY: There is a strong desire to reduce the need for long term aftercare measures in landfill operation. This requires more knowledge of the processes within the landfill and the factors influencing leachate quality. New methods have become available through standardisation in CEN TC 292 that provide such more detailed characterisation. In separate studies on different types of landfilled waste, a combination of laboratory leaching tests, lysimeter studies and field scale measurements were carried out. The comparison of these different types of landfilled waste, such as predominantly inorganic waste, partially degraded municipal solid wasted (MSW), municipal solid waste incinerator bottom ash (MSWI BA) and the rest product of degradation of mechanically separated organic waste (MSOR) in a Bioreactor, has revealed that the end point to which all of these "mixed" materials converge is very much the same in terms of their long term leaching behaviour. The end pH is a neutral pH due to the pH buffering imposed by calcite and the almost non-degradable residual organic matter. The leaching behaviour in all of these "mixed" materials proves to be dominated for many constituents by dissolved organic carbon (DOC) similar to topsoil's. The results suggest that DOC measured at neutral pH can be used as a measure to assess the status of degradability by comparing measured DOC release levels to a reference data set. It appears that DOC levels as observed for topsoils can be used as a reference for final storage quality.

## 1. INTRODUCTION

In this work the leaching behaviour of representative portions of the wastes from four distinct landfill scenarios are compared and discussed in the light of reaching a final storage quality of disposed waste to reduce the need for costly aftercare. Samples of freshly disposed waste have been sampled and analysed as well as material taken from large-scale demonstration projects of the four types of landfill. The four types of landfill comprise two predominantly inorganic waste landfills and two biologically active landfills. In the latter case the evaluation is focussed on the leaching behaviour of fresh bioreactive waste, and the situation after full degradation, and also on

intermediate stages of degradation. The role of DOC resulting from degradation is an important carrier for inorganic and organic contaminants and as such plays a major role in the evaluation of final storage quality of waste.

In a comparison of four different types of landfilled waste, a combination of laboratory leaching tests, lysimeter studies and field scale measurements were carried out in various related studies (see references in Table 1). These are a predominantly inorganic waste, a partially degraded municipal solid wasted, municipal solid waste incinerator (MSWI) bottom ash and the rest product of degradation of mechanically separated organic waste (MSOR) in a bioreactor (see Table 1). The goal in all of these studies was to elucidate the reactions taking place within the landfill and to understand controlling factors determining leachate quality. In view of the widely different nature of wastes taken to landfills, a better understanding of the waste-waste interactions in landfills is needed to be able to identify which wastes unproportionally affect the leachate quality of an entire landfill.

Table 1 - Types of materials evaluated in this study. Reference is given to work where the materials have been described in more detail.

| code | origin | short description | Reference | type of data |
|---|---|---|---|---|
| MSOR | ESSENT bioreactor | bioreactor* filled with wet organic fraction after pre-sorting of MSW at incinerator | Woelders and Oonk, 1999 | pH dependence test, field leachates |
| RED | TNO test columns | reduced rest product obtained directly from test columns (ca. 0.2 $m^3$) after accelerated degradation by flushing | Vroon et al., 1999 | percolates from columns, pH dep. test, percolation test after full degradation |
| OX | TNO test columns | material RED after oxidation in a fermentation reactor | Van der Sloot et al, 2001 | pH dependence test |
| Washred | TNO test columns | washed material RED, to remove soluble components | Van der Sloot et al, 2001 | pH dependence test |
| Washox | TNO test columns | washed material OX | Van der Sloot et al, 2001 | pH dependence test |
| BioFS | ESSENT bioreactor | samples taken from the ESSENT bioreactor 2.5 years after placement. | Van der Sloot et al, 2001 | pH dependence test, batch test at own pH |
| MSW | Landfill Braam-bergen | MSW landfill, field samples and material sampled after 8 years of field degradation | Scharff et al., 2001 | field-extracted pore water, pH dependence test on sampled waste |
| Equistort | Landfill Nauerna Assendelft | pilot demonstration of predominantly inorganic waste landfill (12000 $m^3$) | Van der Sloot et al, 1997; , 2001 | field-extracted pore water, leachate from pilot and pH dep. test and percolation test |
| Soil | Hagen Germany | topsoil from | EU SMT4-CT96-2066 | pH dependence test |
| MSWI BA[1] | MSWI Netherlands | MSWI bottom ash after the customary ageing for 6 – 8 weeks | Meima, 1997 | pH dependence test |
| MSWI BA[2] | Landfill Denmark | MSWI bottom ash monofill | Hjelmar et al., 1997 | field leachates, pH dependence test |
| MSWI BA[3] | Landfill Denmark | aged MSWI-bottom ash from the monofill after 10 years of exposure | Meima, 1997 | pH dependence test |

*The full scale bioreactor had a size of 38000 $m^3$. The materials have been size reduced to less than 10 mm after taking out some materials, which are either irrelevant for the leaching process (glass, stones), too complicating in leaching (large pieces of plastic) or can not be size reduced (metal pieces).

2

## 2. MATERIALS AND METHODS

From several studies information has been combined to build a clearer picture of the leaching behaviour of different types of landfilled waste. In table 1 the materials examined in this work, their origin, a reference where more background information is published and the type of data (test method or leachate) are listed.

Standardised test methods are a prerequisite in being able to make comparisons between different types of landfilled waste (van der Sloot et al, 1997). It is also clear that single step leaching tests, such as currently used for evaluation of waste to be landfilled, are absolutely inadequate for such a comparison. In CEN TC 292 characterisation leaching test methods have been standardised that are suited for this purpose. Several materials have been leached by a percolation test as currently standardised in CEN TC 292 WG6 (2000) to address the long-term behaviour in percolation dominated conditions. To address the factors controlling leaching and to evaluate changes in material conditions due to external influences a pH dependent leach test has been applied. This is also standardised in Working Group 6 of CEN TC 292 Characterisation of Waste (2000). The pH dependence leaching test consists of a combination of individual batch leaching test, in which pH is maintained (constant L/S =10 for 48 hours) using automated pH control equipment (8 positions) with acid/base addition. An alternative option is to use pre-determined amounts of acid/base to reach given end point pH values (ANC mode). This latter method has been applied in most cases. From the acid/base consumption of the material to reach a certain end pH the acid/base neutralisation capacity can be derived, expressed in mol/kg. Both the time dependent leaching behaviour as reflected in a percolation leaching test and the pH dependence of leaching are used to predict the release and changes in release of constituents in short and long term due to external influences. Besides these characterisation leaching tests, a single batch test at own pH was applied on samples taken from the full-scale bioreactor to assess the DOC level in the field-exposed samples.

In all lysimeter, large-scale column experiments and pilot-scale experiments leachate data have been obtained. These data have been used to evaluate the relationship with laboratory measurements.

## 3. RESULTS AND DISCUSSION

In the comparison of the different types of landfilled waste the pH dependence test plays a major role as it reflects better than any other test changes in chemical speciation of the elements of interest (van der Sloot et al, 1997). Two of the materials studied are highly degradable – mechanically separated organic residue resulting from separation of MSW (MSOR) and regular municipal sold waste (MSW). The two other materials are mainly inorganic by nature – Municipal solid waste incinerator bottom ash (MSWI BA) and the predominantly inorganic waste from the pilot Nauernasche Polder.

### 3.1 Degradation of organic matter

The role of organic matter is important from different viewpoints. It creates a highly reactive landfill that without additional measures will result in methane emissions long after the landfill has been completed. It leads to the formation of DOC capable of mobilizing metals and organic pollutants. The DOC complexed compounds are carried with the percolate, which then needs to be treated to meet discharge criteria.

In an optimised upflow percolation experiment with MSOR (Vroon et al, 1999) a complete degradation of MSOR was achieved in less than 20 months. The same MSOR in the full-scale

bioreactor equipped with leachate recirculation by downflow percolation has shown different degrees of degradation in different parts of the cell (Oonk et al, 1999). In figure 1a the estimated half-life of degradation is shown based on measured COD measurements in leachate. The more scattered nature of the data of the full-scale bioreactor is indicative of the level of heterogeneity in the cell. In figure 1b the positive correlation between DOC and metal concentration in leachate is illustrated for the large-scale TNO column experiments.
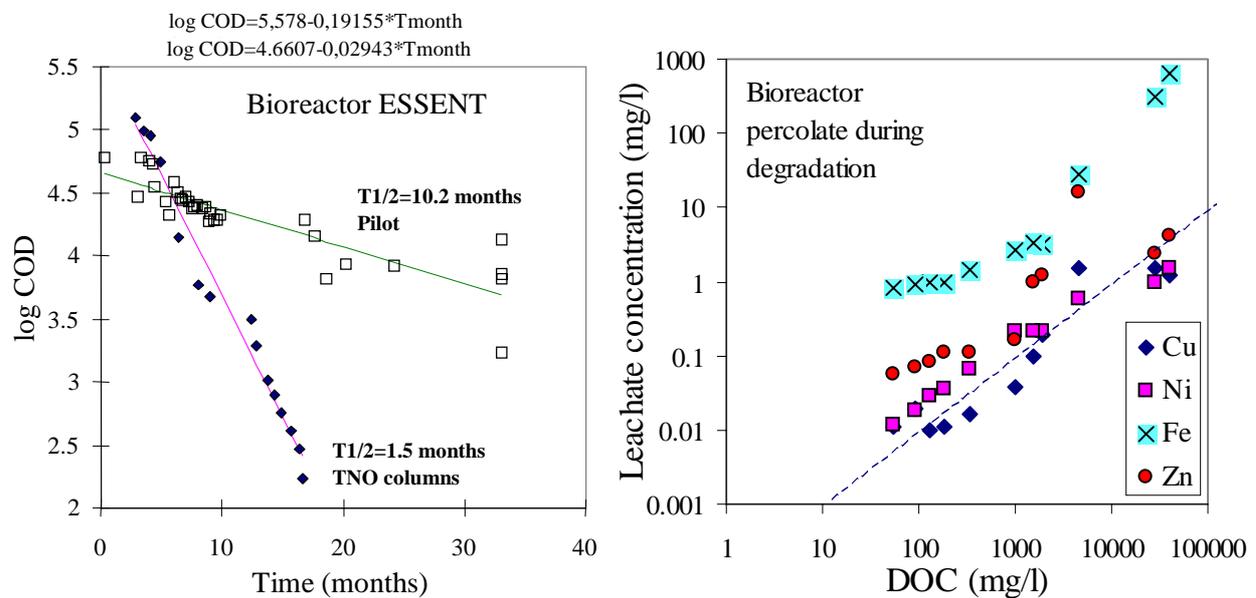


Figure 1 (a) Half life of degradation derived from COD measurements in percolate under optimised laboratory conditions (TNO columns) and from the full scale ESSENT bioreactor (38,000 m$^3$), (b) Correlation between DOC and metal concentrations in percolate from the optimised laboratory scale degradation experiment.

   If low leachate concentrations of metals and other constituents is aimed for then DOC levels should be decreased as quick as possible. Well-controlled conditions in the laboratory lead to full degradation in a relatively short time. The challenge is to enhance these favourable degradation conditions in larger scale systems. The extent to which moist conditions can be achieved in a bioreactor cell determines to a large extent how fast degradation will occur. In the field sampling of the bioreactor rather dry unreacted spots were found, where very little degradation had occurred. On the other hand continuous full saturation does not appear to be favourable either. So a form of wet/dry cycling would seem most desirable.

## 3.2 Leaching behaviour of DOC

The leaching behaviour of DOC (measured as TOC in eluate) as a function of pH for the different samples from the bioreactor study (figure 2b) is very interesting as it reveals a feature that can be potentially attractive in judgement of materials containing organic matter. The highly reactive starting material (MSOR) shows a DOC release pattern, which is almost independent of pH. Upon full degradation (RED), which is evidenced by a drastic drop in biological reactivity and CH$_4$ production (Oonk and Woelders, 1999), the DOC leachability in the neutral pH range drops dramatically (factor of about 30), whereas the drop at high pH only amounts to a factor of 3 – 4. The latter represents high molecular weight organic matter fractions, which are also less degradable. Lower molecular weight DOC is produced in a material in significant quantities when it is biodegraded. The DOC at neutral pH therefore reflects the degree of degradability of a

4

material. The more DOC at neutral pH the more (bio-) reactive the material.

The fact that the DOC from the fully degraded bioreactor material (TNO columns) starts to approach the DOC leachability of regular topsoil or mildly contaminated soil (Van der Sloot et al, 2001) indicates that a final low level of biological activity is reached. Any level in between can then be an indication of the stage of degradability.
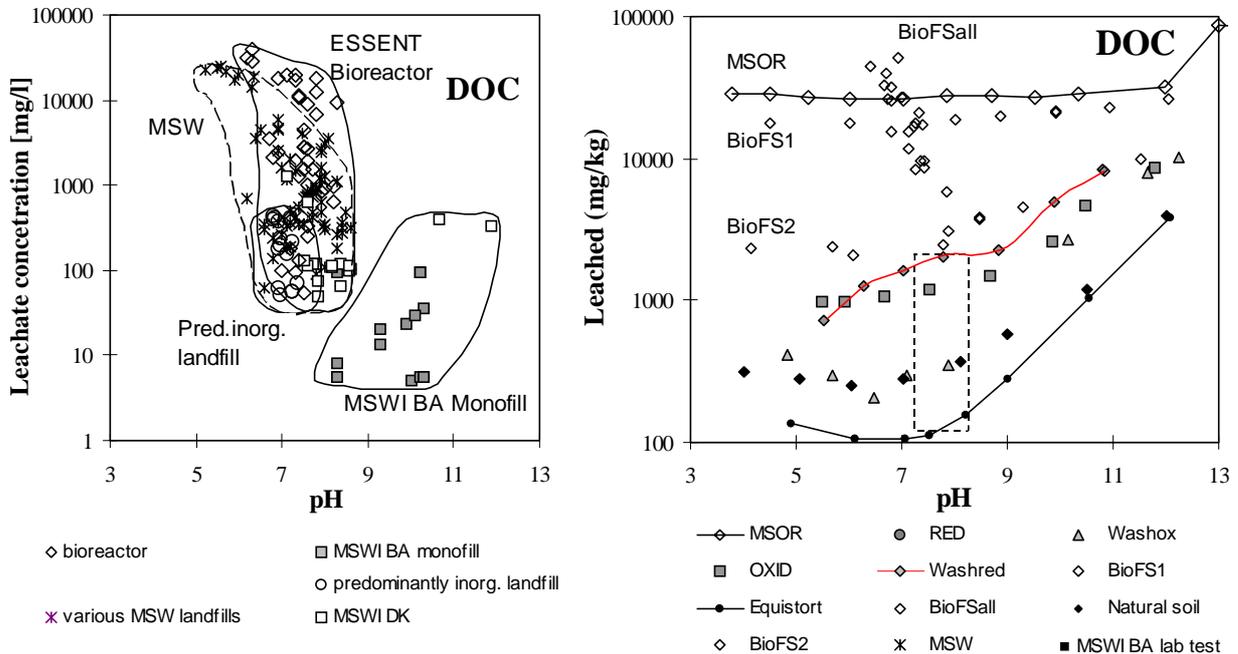


Figure 2. pH dependent leaching of DOC (a) DOC in leachate from the different types of landfills (b) pH dependence test: starting material (MSOR), the reducing bioreactor end product after "complete" degradation (RED), the same material after oxidation (OXID) and two samples taken from the full-scale bioreactor (BioFS 1, 2 and all). For comparison, natural soil DOC is given. The box represents the desired final storage condition.

The data points as obtained from different locations in the full-scale bioreactor indicate different stages of biodegradability by the points between starting product (MSOR) and fully degraded material (RED). As a quick verification, the extraction and subsequent analysis of DOC is a simpler and straight forward alternative for the more elaborate respiration test used to assess biodegradability (Binner et al., 1998). The DOC determination at neutral pH can be seen as a compliance test, while the respiration test has the features of a characterisation test. The DOC measurement at high pH (pH>13) can provide a measure of potentially leachable DOC at the long term. The type of DOC is different at neutral pH and at high pH. At high pH the nature of the DOC is largely of the humic acid type whereas at neutral pH fulvic acid and - in case of highly bioactive materials - lower carbonic acids form a significant contribution to the total DOC level in solution. Further work on the nature of DOC is needed for the materials studied.

The DOC measurements in leachate from MSW landfills (van der Sloot et al, 1997), from the bioreactor pilot and column experiments at TNO, the field data from the Danish MSWI bottom ash monofill and leachate measurements at the Nauerna pilot are given in figure 2a. The domains can be clearly identified. The main difference between MSW and MSOR is the significantly higher initial DOC level without the acidification phase. Both the predominantly inorganic waste landfill and the old MSWI bottom ash landfill are low in DOC. In MSWI bottom ash one has to be aware that the initial DOC is around 300 to 500 mg/l, which decreases fairly rapidly to levels between 10 and 100 mg/l.

### 3.3 Acid neutralisation capacity

The acid or base neutralisation capacity is obtained from the amount of acid or base needed to reach a certain end pH in the pH dependence test. This property is important to assess the sensitivity of the material to external influences. This aspect is crucial to address long term environmental impact and for long term stability. For long term stability buffering at neutral pH is important, as it provides for the smallest deviation from the surrounding environment, a minimum in DOC solubility and favourable sorption conditions for metals and oxyanions. A good buffering ensures limited influence of external factors affecting this stable end point. In figure 3 the acid/ base neutralisation capacity for the MSOR starting material, the fully degraded rest product (Red and Ox) and samples from the full-scale bioreactor after 2.5 years of degradation under field conditions (BioFS) are presented. From the curve it is clear that pH buffering in the final product is much larger than in the original material. The formation of $CaCO_3$ buffer as a result of $CO_2$ production by organic matter degradation plays an important role as well as the buffering provided by residual organic matter. In the pH dependence test at pH 4 and 5 significant gas evolution is observed in all degraded materials, which illustrates the liberation of matrix bound $CO_2$. This may lead to a requirement on a minimum Ca concentration to ensure sufficient buffer formation to maintain a constant pH over a long term. The rest product taken from the full-scale bioreactor already shows similar buffering as the fully degraded product (TNO columns; Vroon et al, 1999). The pH in the largely degraded bioreactor material (BioFS2) is higher than that of the less degraded bioractor material (BioFS1) and resembles fairly closely the pH of the fully degraded material (RED).
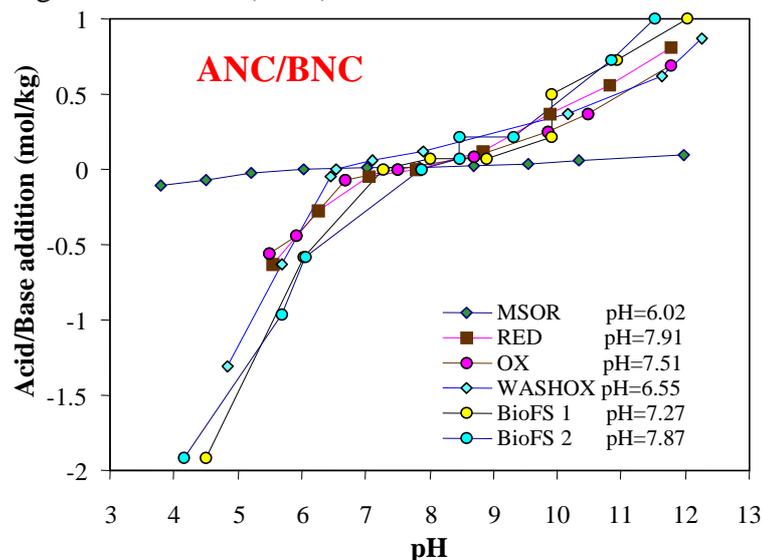


Figure 3. Acid/base titration data for the starting material (organic wet fraction: MSOR), the reducing bioreactor end product after "complete" degradation (RED), the same material after oxidation (OXID) and two samples taken from the full-scale bioreactor (BioFS 1 and 2)

### 3.4 Characterisation of leaching behaviour of landfilled waste.

As more knowledge is needed on behaviour of waste in the landfill, a more detailed testing is required. The methods recently standardised in CEN TC 292 have been applied on the range of wastes listed in table 1. In figure 4 results of the pH dependence leaching test on a variety of fresh wastes and samples taken from pilot and field demonstration experiments are shown (on the right) together with data on leachate quality from the same locations (on the left). The samples

include partially and largely degraded materials. Some 30 major, minor and trace elements have been measured, here only a selection is presented. Here Cu, Ni and Zn results are shown. Cu is almost entirely dominated by its interaction with particulate and dissolved organic matter. The same is to a large extent the case for Ni. For Ni, the carbonate concentration in solution may prove to be important. Zn is affected by DOC to a lesser extent than both Cu and Ni.

MSWI bottom ash can be seen as the inorganic fraction in MSW. If the organic matter does not affect the leaching of a specific component, the leachability of MSW and MSWI bottom ash may be the same. For some major and minor elements this has in fact been observed. Cu leaching from MSWI bottom ash is strongly dictated by complexation with dissolved organic matter (Meima et al, 1997, Dijkstra et al., 2000). After several years the dissolved organic matter is degraded or washed out and a low Cu leachability remains, which is reflected in the MSWI bottom ash monofill leachate data. Ni and Zn data from the MSWI bottom ash monofill are generally consistent with the lab data. The leachability of Cu, Ni and Zn of MSOR reflects the strong influence of the high level of dissolved organic carbon in this very bioreactive material. After full degradation in the TNO columns the leaching behaviour is very consistent and still shows a significant effect of DOC in mobilising these metals. Upon washing the leachability is decreased as readily washable DOC is removed.

The results of the predominantly inorganic landfill (Equistort) match rather well with the results from the washed bioreactor residues. Both in terms of the shape of the leaching curve as well as in terms of the concentration levels observed. This is a rather special observation, which is not limited to the elements shown here. It implies that the predominantly inorganic waste consisting of soil cleaning sludge, contaminated soil, and dredge spoil has similar leaching characteristics as the fully degraded restproduct from a bioreactor test run on MSOR. For the predominantly inorganic waste this means that even at a moderate organic matter content, DOC still dictates the leachability of metals. The leaching test results at own pH of field samples from the full scale bioreactor demonstration (code BioFS) after 2.5 years of operation indicate that stabilisation has occurred for the metals faster than for DOC, as the leaching levels observed in all samples show a closer resemblance to the final fully degraded product than to the MSOR starting material. This is in contrast to the DOC levels. Apparently, residual organic matter possibly is capable of lowering the leached metal concentrations. The leachability curve shift for Zn in MSWI bottom ash in the pH range 6 - 8 relative to the material containing residual, virtually non-degradable organic matter may be attributed to this effect. Further experimental work and modelling work using Nicca-Donnan modelling in ECOSAT is needed to quantify these effects.

The concentration levels observed in the desirable pH domain (box in the graph) approach the levels found in natural topsoil. If there are no obvious reasons (external influences) why the landfilled waste would deviate from the "equilibrium" concentrations reached, then that level could be considered as final storage quality. This would then be the quality to aim for at the end of the period of filling of the landfill. The next question then is which (small) waste streams can jeopardise this balance. Waste streams unproportionally affecting the quality of the entire landfill (cell) should be identified and treated to maintain control over the long-term performance of the landfill.

The mix of MSW samples taken from a 2.5-year-old MSW landfill has been tested using the pH dependence test. Since this test uses individual test portions, the scatter in the data is a measure for the heterogeneity of the waste. It appears that consistent leaching curves matching with organic matter derived waste are obtained, which indicates that leachability controlling factors are the same and of about the same magnitude.

Mo as oxyanion ($MoO_4$) has a significantly different leaching behaviour than metals as leachability drops towards lower pH and increases at neutral to mildly alkaline pH (figure 5). With the exception of MSOR all other materials behave very much the same and even within a

relatively narrow range in spite of the widely different nature of the materials. Also Cr has some special aspects of leaching. In case of MSOR, virtually no influence of pH is noted and the Cr leachability matches the DOC curve. After degradation Cr leachability drops at pH< 7, however, it increase with pH at pH > 8. This is in case of Cr generally attributed to leaching of Cr VI. That is unlikely in the case of the reduced rest product from the bioreactor.
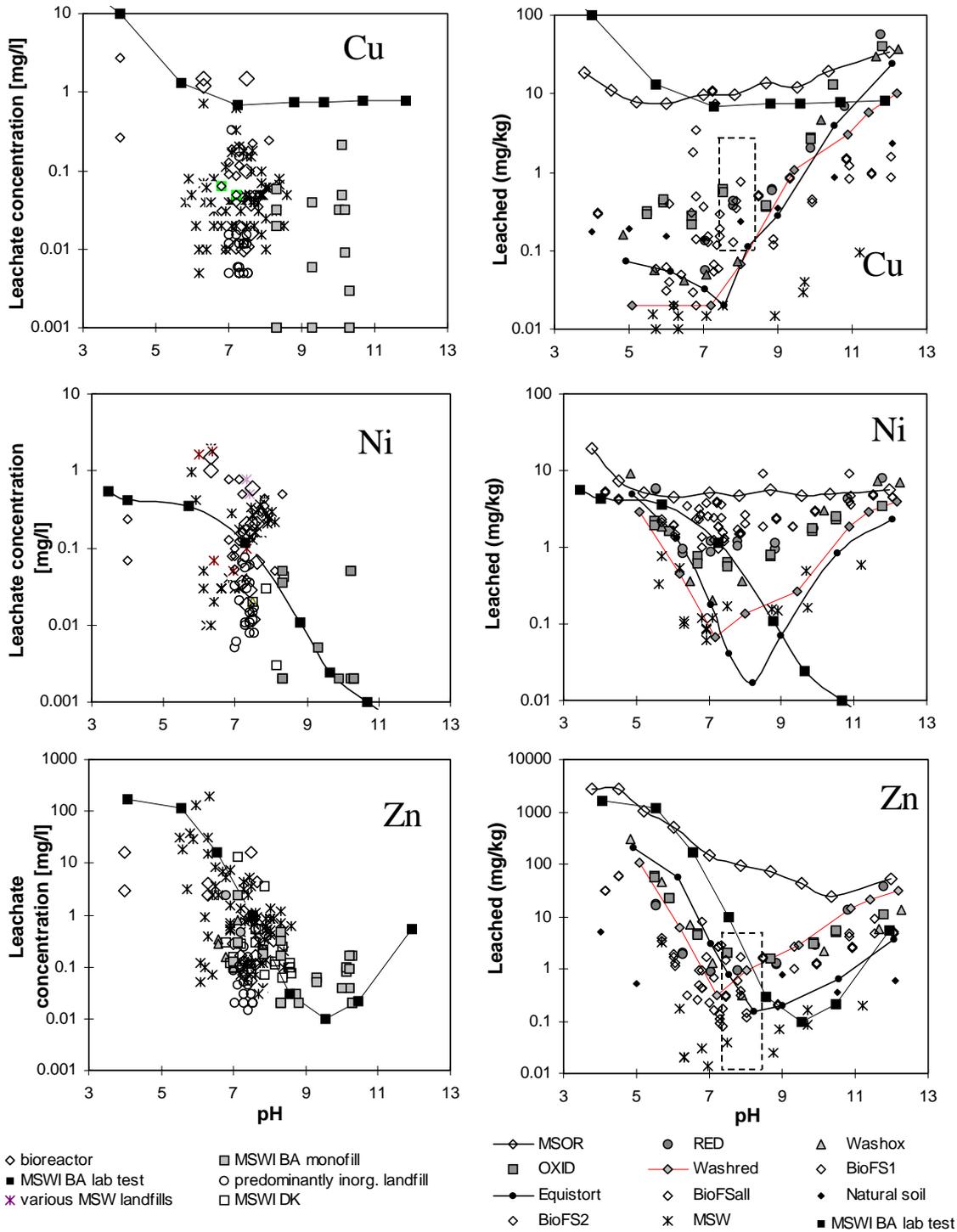


Figure 4. Comparison between leachates from different landfills and leaching test data (pH dependence test) for Cu, Ni and Zn on fresh waste and samples taken from partially or fully degraded wastes from large scale pilot experiments.
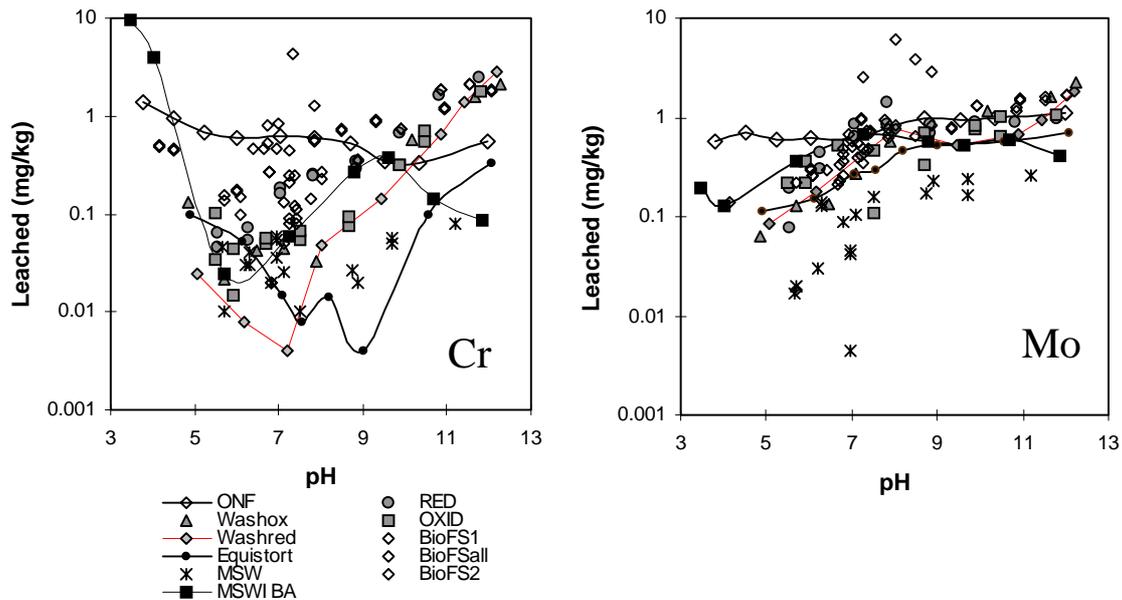
Figure 5. Comparison between leaching test data for Cr and Mo (pH dependence test) on fresh waste and samples taken from partially or fully degraded wastes from large-scale pilot experiments.

A quite reasonable explanation seems association of Cr III with DOC. In the predominantly inorganic waste, this may also be the case. The low Cr levels in samples of 2.5 year old MSW are consistent with predominance as Cr III. Cr leachability from MSWI bottom ash shows high leachability at low pH (Cr III) and a maximum at mild alkaline pH. In the quenched and aged samples, this is probably a trace of Cr VI.

## 4. CONCLUSIONS

The increased level of understanding that can be gained by carrying out characterisation leaching tests on wastes and mixed wastes taken from different types of landfill provides new options of waste acceptance at landfill to ultimately reach final storage quality at a projected point in time depending on the landfill type selected. For a largely inorganic waste landfill this point may be reached relatively quickly, whereas degradable waste when left alone may take a very long time to reach such a condition. From the laboratory operated large columns of MSOR it is clear that biodegradation can be completed much faster given the right conditions. There is room for optimisation in bioreactor design. Thus designing landfill types according to the rate at which one aims to reach final storage quality will most likely be feasible.

Consequences of the observations on the role of DOC are that the level of reactive (=degradable) organic matter in waste to be deposited needs to be defined better and set stricter to reduce long term emissions from landfills. The mostly applied methods for assessing degradable organic matter - LOI and TOC – are not suitable as they overestimate in several cases the proportion of degradable matter.

## ACKNOWLEDGEMENTS

# REFERENCES

Binner, E., Zach, A., Widerin, M., and Lechner, P. (1998) *Auswahl und Anwendbarkeit von Parametern zur Characterisierung der Endprodukte aus mechanisch-biologischen Restmuhlbehandlungsverfahren*. Bundes Ministerium fur Umwelt Jugend und Familie, Band 9.

Building Materials Decree. Staatsblad van het Koninkrijk der Nederlanden, 1995, 567.

Dijkstra, J. J., van der Sloot, H.A. and Comans, R.N.J. (2000) Process identification and model development of contaminant transport in MSWI Bottom ash. *Waste Management* (in press).

EU project SMT4-CT96-2066 (2000) Technical support to the Network Harmonization of Leaching/Extraction tests.

Heyer, K. U., Hupe, K.and Stegmann, R. (1999) Charakterisierung der Eigenschaften von Rückständen biologischer Behandlungsanlagen: Möglichkeiten zur Verwertung und Beseitigung.

Meima, J.A. Geochemical modelling and identification of leaching processes in MSWI bottom ash, Thesis, University of Utrecht, Netherlands, 1997.

Oonk, H.and Woelders,H.(1999). Full scale demonstration of treatment of MSOR in a bioreactor at VAM in Wijster, In*: Proceedings Sardinia 99, Seventh International Landfill Symposium*, CISA publisher, Cagliari, vol. V, 375-382..

Oonk, H., van der Sloot, H.A.,Vroon, R., Luning L. and Woelders, H. (2001) Treatment of mechanical separation organic residues in a landfill-bioreactor. This conference.

Percolation simulation test CEN TC 292 Working Group 6 Characterisation leaching test, Work item 292016 (in prep.)

pH dependence leaching test. CEN TC 292 Working Group 6, Characterisation leaching test: Work item 292015 (in prep.).

Van der Sloot, H.A. Heasman, L. and Quevauviller, Ph.(eds.)(1997) *Harmonization of leaching/extraction tests*. Studies in Environmental Science, Volume 70, Elsevier Science, Amsterdam, 292 pp.

Van der Sloot, H.A., Cnubben, P.A.J.P. and Scharff, H. (1999) Predominantly inorganic equilibrium disposal – part of the total concept sustainable recycling and storage of solid waste. In: *Proceedings Sardinia 99, Seventh International Landfill Symposium*, CISA publisher, Cagliari, vol. I, r, 103-110.

Van der Sloot, H.A., Hjelmar, O., Mehu, J., Blakey, N. (1999) Relevance of waste characterization by means of sophisticated leaching tests to assess treatment options, reuse potential and disposal of waste. In: *Proceedings Sardinia 99, Seventh International Landfill Symposium*, CISA publisher, Cagliari, vol. V, 3-10.

Van der Sloot, H.A., Heyer, K. U., Hupe, K.and Stegmann, R. (1999) Environmental properties and potential for utilization of MSOR stabilised in a bioreactor. In: *Proceedings Sardinia 99, Seventh International Landfill Symposium*, CISA publisher, Cagliari, vol. I,, 353 -360.

Vroon, R. C., Oonk, H. and van Marwijk, W. G. (1999) A Lab-scale exploration of the long-term behaviour of mechanically separated organic residue in a flushing bioreactor, In*: Proceedings Sardinia 99, Seventh International Landfill Symposium* CISA publisher, Cagliari, vol. I, 305-312.