LEACHING BEHAVIOUR OF ESSENT BIOREACTOR REST PRODUCT AT DIFFERENT STAGES OF DEGRADATION IN LAB AND PILOT SCALE TO ASSESS POTENTIAL UTILIZATION OPTIONS.

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SUMMARY:
Detailed characterization of the leaching behaviour of Mechanically Separated Organic Residue (MSOR) and the rest product from degradation in a lysimeter (ca. 0.2 m^3) and in full-scale bioreactor (38.000 m^3) demonstration has been carried out. This means of characterization has yielded valuable new insights in how to manage this material. Dissolved organic carbon (DOC) at neutral pH can be used as a quick method to identify status of degradation. The Acid Neutralization Capacity (ANC) shows that long term stability can be ensured. Furthermore, evaluation of the leaching behaviour of individual constituents provides means to improve quality. After degradation, material with soil-like leaching characteristics remains. Measures to improve the morphological aspects could lead to a reusable product.

Keywords: Flushing bioreactor, Residues, Leaching, Trace elements, Environmental impact, Reuse.

1. INTRODUCTION

At ESSENT (formerly VAM) a bioreactor study (Woelders and Oonk, 1999) was initiated in 1996 with the Mechanically Separated Organic Residue (MSOR) of a waste separation plant at the ESSENT treatment facility. As in many other studies, the aim of the work was largely focused on the degradation aspect of MSOR (Oonk and Woelders, 1999). This work focuses on the aspect of the ultimate quality of the end product from the bioreactor for possible reuse. The existing information on the ultimate quality of the end product is limited (Heyer et al, 1999) as in many cases the end product is only considered as a residue for final disposal, therefore not requiring detailed characterization. When the emphasis shifts to possible reuse or changing the disposal regime, more information on the long-term quality of the end product is needed. The characterization of the MSOR described in this work consists of an evaluation of its leaching behaviour to assess long-term environmental impact. Since the material has specific characteristics not common to other materials for which evaluation criteria exist, new criteria for evaluation may need to be developed. These relate in particular to the residual generation of dissolved organic carbon, which acts as a carrier for trace contaminants – both inorganic and organic, morphological aspects and environmental impact. This work aims at characterizing the leaching behaviour at different stages of the degradation process in the bioreactor to be able to predict material behaviour in the long term. The residual release of contaminants in dissolved organic carbon (DOC) associated form is a key issue in this respect. The use of DOC measurement at neutral pH as a means of establishing the status of degradation will be discussed in relation to measurements carried out after 2.5 years of degradation in the full-scale pilot. This also allows a comparison between the leaching behaviour of material degraded under optimal conditions at laboratory scale (2 m high columns) and material degraded in the full-scale demonstration.

2. EXPERIMENTAL

2.1 Materials

The materials studied are: the source material for the ESSENT bioreactor (Woelders and Oonk, 1999), which is the wet organic fraction (Coded: MSOR) obtained form the pre-sorting of MSW at the ESSENT Incinerator facility; the reducing rest product (Coded: RED) obtained directly from the TNO test columns (ca. 0.2 m^3) after accelerated degradation by flushing (Vroon et al, 1999), the same material after oxidation (Coded: OX) in a fermentation reactor, both materials washed to remove soluble components (Washred, washox) and samples taken from the full-scale bioreactor (38.000 m^3) 2.5 years after placement (Coded BioFS). 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 Methods

The materials have been leached in a percolation test as currently standardized in CEN TC 292 WG6 (2000) with similarities to NEN 7343 (NNI, 1997) to address the long-term behaviour in percolation dominated conditions. In this standard, 7 eluate fractions are collected in the range of L/S = 0.1-10 l/kg. The leachant is demineralized water (DMW). Due to the heterogeneous character of the waste a column with a diameter of 10 cm was selected, which allows use of particles up to 10 mm. The column is operated in up-flow to minimize channelling. The test is used to simulate leaching from different types of waste in the short, medium and long term by relating the L/S to time by the infiltration rate and the height of the application (Hjelmar et al., 1990). To address the factors controlling leaching and to evaluate changes in material conditions due to external influences a pH dependent leach test, which is now standardized in Working Group 6 of CEN TC 292 Characterization of Waste (2000), has been applied. The pH-static leaching test consists of a combination of individual batch leaching test, in which pH is maintained at a constant value at L/S =10 for 24 hours using automated pH control equipment (8 positions) with NaOH or HNO_3 addition. An alternative option is to use a batch test, in which predetermined amounts of acid/base are added to reach a given end point pH (ANC mode). This method has been used for the full-scale bioreactor samples. A common pH range covered ranges from pH = 4 to pH = 12. From the acid/base consumption of the material to reach a certain end pH the acid/base neutralization capacity can be derived expressed in mol/kg. Both the time dependent leaching behaviour as reflected in a column leach 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.

3. RESULTS AND DISCUSSION

3.1 Physical properties and morphological properties

In table I relevant physical properties of the rest products from MSOR reactors are given, which have been taken largely from German studies (Huyer et al, 1999). For potential reuse some of these parameters (hydraulic conductivity and CEC) are important as they hold the key to potential beneficial application.

Tabel I. Physical properties of starting material and rest product (Heyer et al, 1999).

Parameter	MSOR	Bioreactor rest product
Wet Density (kg/m3)	1200 - 1600	1700 – 1800
Dry density (kg/m3)	800 - 1000	900 - 1300
Particle size mm	100 % < 100 mm; 50% < 10 mm	60 – 80 % < 10 mm
Hydraulic conductivity (m/s)	ND *	$10^{-7} – 10^{-9}$
CEC (mequiv/100 g)	29.8	31.1
ANC/BNC mol/kg	0.01	0.1
pH	5.34 – 6.93	7.5 – 8 (lysimeters)
		6.4 – 7.8 (field samples)

*ND = not determined

The morphological properties, such as the appearance of the materials and possible odour, are aspects to be addressed in an evaluation of practical application of the material. The nature of the material from the full-scale bioreactor will not differ substantially from the material reported in several studies carried out in Germany and Austria (Heyer et al, 1999). The prominent visibility of plastics may form a limitation for the use of the rest product. Options to cure this problem are size reduction or separation of plastics from the end product. The reducing material taken straight from the columns does smell. After the oxidation step, however, the odour is almost completely gone.

3.2 Comparison of environmental properties of starting material and rest product

Limited leaching data are available on the quality of residues from MSOR bioreactor systems (Heyer et al.,1999). This lack of leaching data is largely explained by the fact that the material is generally disposed, for which no further testing is required. For an evaluation of residue quality for potential reuse more extended leaching information is important to ensure that no adverse environmental impact occurs. The results for the MSOR rest product obtained after full degradation in flushed columns (Vroon et al, 1999) are compared with the leaching behaviour of samples taken from the full-scale bioreactor pilot at ESSENT. The comparison is based on the pH dependence leaching test data as this allows a good comparison of chemical changes in materials. From this test three types of information can be derived:
- leaching behaviour of DOC as a function of pH
- acid/base neutralization capacity and
- leaching behaviour of different elements as a function of pH.

3.2.1 Leaching behaviour of DOC
The leaching behaviour of DOC (=TOC in eluate) as a function of pH for the different samples from the bioreactor study (figure 1) is very interesting as it reveals a feature that can potentially be very 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 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 soil or mildly contaminated soil (Harmonization project, 2000) 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.
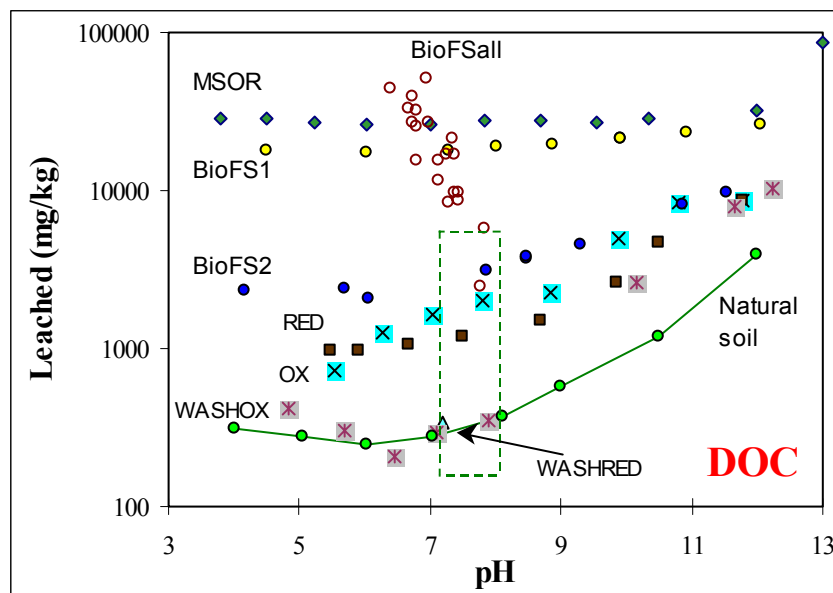

Figure 1. pH dependent leaching of DOC from the starting material (organic wet fraction: MSOR), the reducing bioreactor end product after "complete" degradation (RED), the same material after oxidation (OXID) and two samples taken from the full-scale bioreactor (BioFS 1, 2 and all). For comparison, natural soil DOC is given (EU project Harmonization of Leaching/Extraction test, 2000).

The data points as obtained from different locations in the full-scale bioreactor indicate different stages of degradability by the points between starting product and fully degraded material. 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 characterization test. The DOC measurement at high pH (pH>13) can provide a measure of residual degradability in case of inhibition of biological activity by comparing the DOC response with natural soil. This aspect is subject of further study.

3.2.2 Acid neutralization capacity

The acid or base neutralization capacity is obtained from the acid or base addition 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, as buffering at neutral pH and limited influence of external factors affecting this stable end point is important. In figure 2 the acid/ base neutralization 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. 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 the 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).
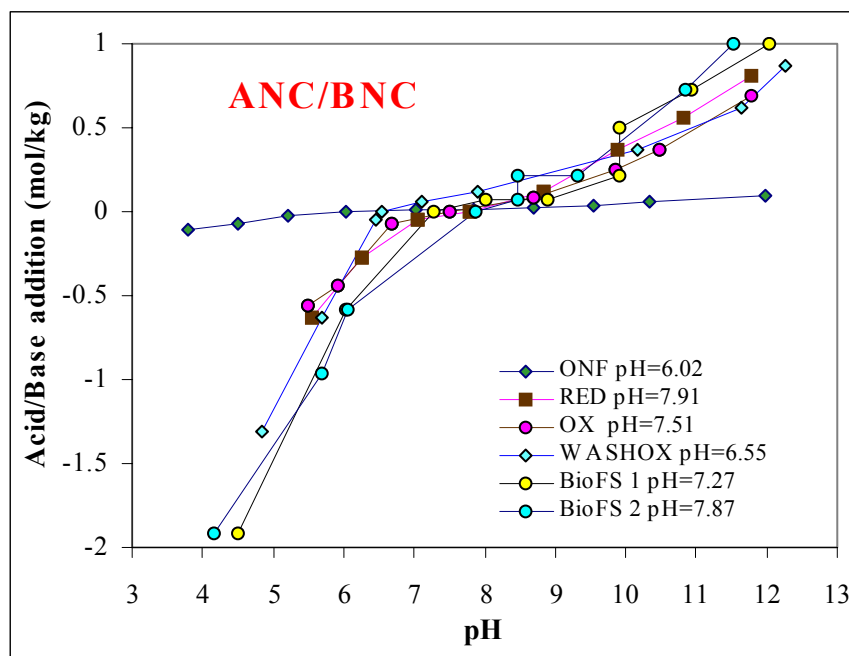

Figure 2. Acid/base titration data for the starting material (organic wet fraction: MSOR), the reducing bioreactor end product after "complete" degradation (RED), the same material after oxidation (OXID) and two samples taken from the full-scale bioreactor (BioFS 1 and 2).

3.2.3 Evaluation of leaching mechanisms and long term release

In figure 3 the leaching results for MSOR and the reducing and oxidised rest products from accelerated biodegradation are given in comparison with leaching data for samples taken from the full-scale bioreactor. In addition, the leaching behaviour of a largely inorganic waste mixture (Van der Sloot et al., 1999) is given. This can serve as an indication for the possible end point for the fully degraded and washed material. Although some 30 major, minor and trace elements have been measured, here only a selection is presented. The box with the broken line represents the most relevant pH domain for the material in the long term. The comparison between original material and fully degraded product illustrates that a significant reduction in leachability of an order of magnitude to almost 2 orders of magnitude is achieved. The high metal leachability from the raw MSOR is attributed to the very high DOC level in the leachate from this material. The reduction in leachability is therefor largely linked to the reduction in DOC. The increase in metal leachability with increasing pH is related to the mobilization of dissolved organic matter (DOC).
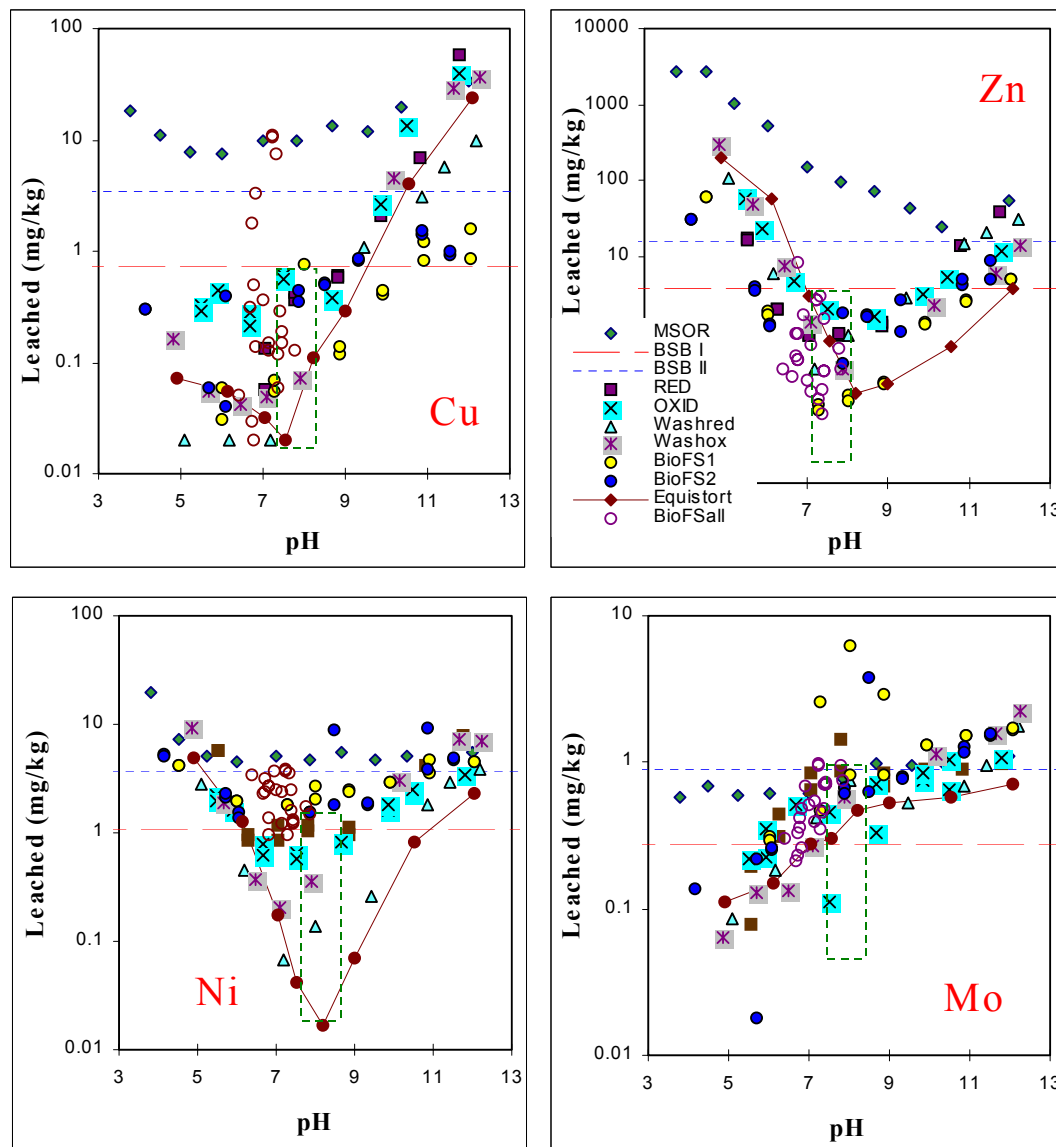

Figure 3. pH dependence test data for MSOR (◇)and rest products of MSOR (Red: □;Oxid:○) from ESSENT in comparison with leaching data from the full-scale bioreactor. The box with broken line represents the most relevant pH domain for the material in the long term. Regulatory thresholds BMD (Building Materials Decree1995) are indicated.

Geochemical modelling, in which sorption and interaction with dissolved and particulate organic matter is taken into account, will provide a better understanding of release controlling factors. The degree of $CaCO_3$ solubility, which buffers the pH of the material, is addressed that way and can help to quantify the minimum required concentration of Ca to ensure long term stability. Cu is almost entirely dominated by its interaction with particulate and dissolved organic matter (Dijkstra et al., 2000). 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. Mo as oxyanion ($MoO4-$) has a significantly different leaching behaviour than metals as leachability drops towards lower pH and increases at neutral to mildly alkaline pH. In view of the rather strict criteria in the Building materials Decree (1995) for Mo, this element can be critical from a reuse point of view. The material can be applied as category II material, which implies under infiltration reduced conditions. In addition, sulphate, Se and Sb can be critical relative to the Category I (free application) criteria. Br and Cl can be critical in the raw degraded material, when more flushing or a washing step is applied the levels are readily reduced to below critical levels. (Figure 4).
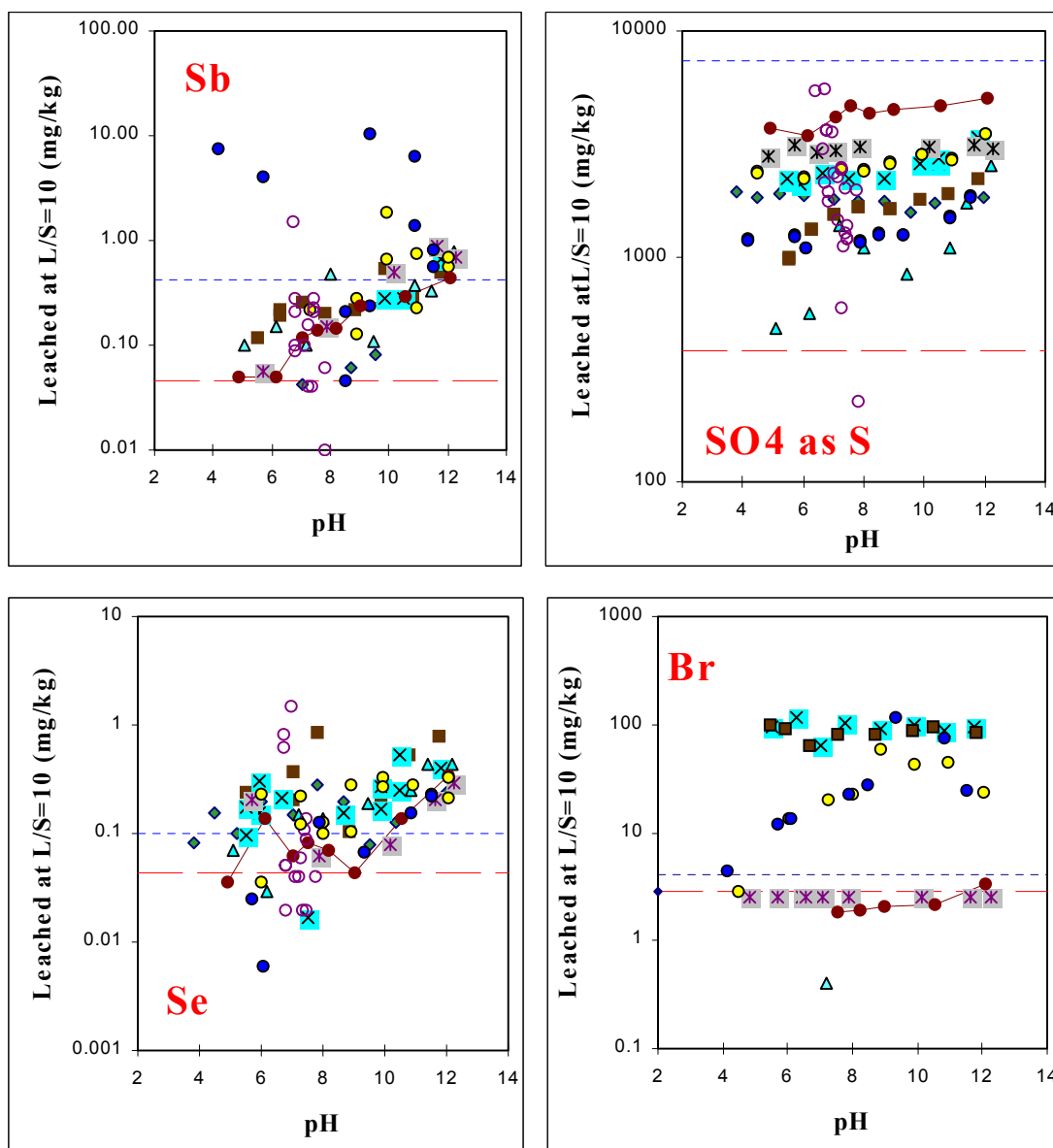

Figure 4. pH dependence test data for MSOR (◇)and rest products of MSOR (Red: □;Oxid:○) from ESSENT in comparison with leaching data from the full-scale bioreactor. The box with broken line represents the most relevant pH domain for the material in the long term. Regulatory thresholds BMD (Building Materials Decree 1995) are indicated.

3.2.4 Time dependence of leaching

In figure 4, the release of K and V from the fully degraded material are given as a function of pH (steady state condition by leaching for 24 hours at LS=10). Also shown release as a function of L/S, which can be seen as a measure for time based on the infiltration rate. The $L/S_{field} = N * t/ h*d$ with N the net infiltration rate in mm/ year, t the time in year, h the average height of the application/disposal in meters and d the density in kg/m^3 (Hjelmar,1990) . In the release-L/S graphs the slope of 1 is indicated, which reflects solubility control or constant generation (equal concentration in time). The data obtained in the pH dependence test and at the end point of the column test (L/S=10) correspond generally well. From other work (Dijkstra et al, 2000) the role of local equilibrium at the outlet of the column has been stressed. The combination of pH dependent leaching behaviour and leaching as a function of L/S covers a very wide range of potential conditions a material can be exposed to.

K is not pH dependent. In the column test depletion of K is observed, which indicates that basically all of the K is washed out of the system after an L/S of about 2. V is strictly solubility controlled as can be seen from the slope of 1 in the release time plot. Release is strictly related to L/S and the level at which leaching takes place is dictated by the pH.
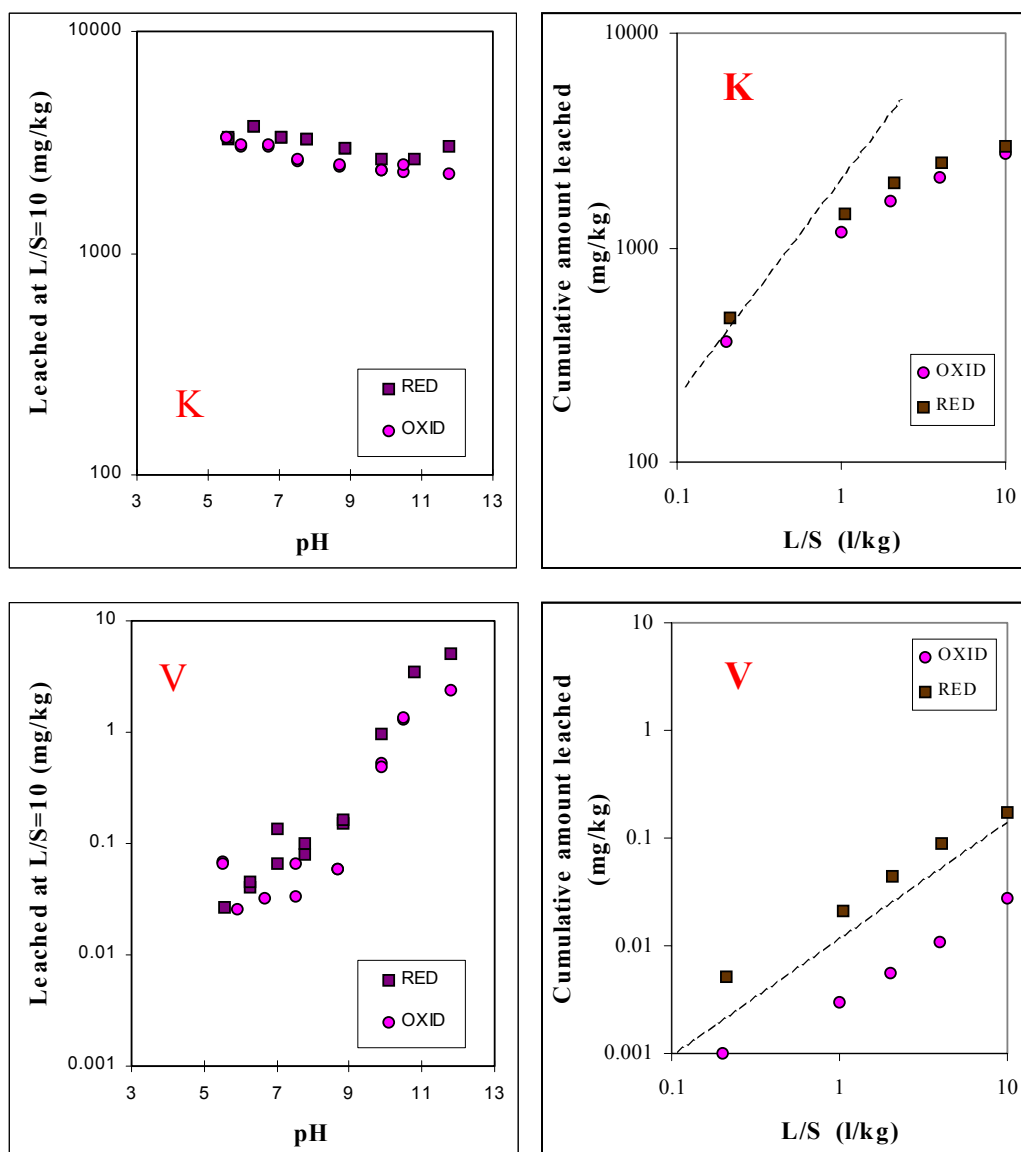

Figure 4. Leaching behaviour of K and V as a function of pH and L/S to evaluate release controlling mechanisms relevant for assessing long-term behaviour.

Factors controlling release of constituents can be classified based on the characterization of their leaching behaviour. This in turn provides an understanding that can be used to make conscious decisions to improve the quality of a material, thus improving the potential for reuse.

This type of release behaviour, which can not be obtained from a single extraction test does allow prediction at longer time scales. The level of metal release will be largely dictated by the DOC concentration in solution. For DOC also a consistent increase with time has been observed (van der Sloot et al, 1999) which reflects the degradation of organic matter with time.

3.5 Evaluation of potential use

These include potential use as a reactive metal/organic contaminant retaining barrier for instance as part of a bottom liner in landfills, use as part of a top cover construction for landfill and use as fill material in landscaping. The limits for applicability in each of the above mentioned scenarios has to be defined with regards to the conditions under which the final product is utilized. The materials from the bioreactor will be reducing initially. However, the results obtained so far indicate that reducing conditions will not last long after exposure to the atmosphere. The relevant properties in case of the use as part of a bottom liner are hydraulic conductivity, cation exchange capacity and sorption capacity for organic contaminants. Morphological aspects are not critical in this application. Compaction is required. The market potential seems good. Measures to avoid dusting are needed, when the material is placed. For use as part of a top cover the hydraulic conductivity is the key issue. Category II criteria for Building Materials Decree apply.

In case of use as fill material the morphological properties become important. In addition, the rest activity (gas generation) and physical stability (load bearing capacity) are important. The market potential is substantial, when properties can be shown to meet critical limits in release of contaminants. Criteria to be met are related to Category I of the Building materials decree.

4. CONCLUSIONS

Detailed characterization of leaching behaviour of MSOR and the final product from bioreactor provides an understanding of factors relevant to environmental assessment not addressed before. The leaching test applied here to characterize the rest product of MSOR in a bioreactor offer the possibility to assess the long-term behaviour of the material in different scenarios of application. The material behaviour tends to soil-like behaviour as far as leaching characteristics is concerned.

DOC measured in the pH dependence test illustrates characteristics of materials containing degradable organic matter not shown before. DOC at neutral pH can be used as a measure of biodegradability. High DOC at neutral pH is almost exclusively linked to biological reactivity. The DOC as a function of pH for degraded MSOR starts to approach the pattern for regular soil.

The acid/base neutralization capacity as obtained in the pH dependence test reflects the strongly increased buffering of the material after degradation. This inherent resistance to pH change ensures long term stability of the final product.

The leaching behaviour of individual constituents can be evaluated against regulatory criteria by selecting the pH range relevant for the application or disposal scenario considered. Evaluated against the Building Materials Decree category I, the material in its present state is critical for sulphate, Mo, Se and Sb. The critical elements Br and Cl can be reduced sufficiently by a washing step to fall within the specifications. The material can meet the criteria for category II applications. Measures to improve the morphological characteristics of the material are needed when reuse is considered.

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Figure captions and table captions

Tabel I. Physical properties of starting material and rest product (Heyer et al, 1999).

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