

## **CHARACTERISATION OF THE LEACHING PROPERTIES OF C-FIX PRODUCTS AND COMPONENTS**

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## SUMMARY

This study focuses on a detailed characterisation of the leaching properties of C-fix products and their individual components. It is intended to give more insight in the processes controlling the leaching of possible contaminants, as a basic characterisation and as a reference for the further development of C-fix with other possible filling materials. The leaching of both inorganic and organic contaminants is addressed, the latter in anticipation of possible near-future developments in the environmental assessment of construction materials. Although standardised leaching tests are not yet available for organic contaminants, recently developed draft procedures are applied to make a first assessment of the leaching of mineral oil and PAH from C-fix products.

In addition to the characterisation of the leaching properties of C-fix products and standard components (binder and filling materials) in freshwater, three special situations are evaluated. The effect of the use of two alternative filling materials (finest fraction), (uncontaminated) river sludge and biomass-ash from the combustion of (uncontaminated) wood is evaluated. In addition, the leaching of C-fix products is measured in a seawater environment, to simulate possible contaminant emissions during the potential use of C-fix bricks in dikes along the sea shore.

For the majority of the measured major and trace elements, leaching from C-fix products was found to be substantially lower than from cement-based products, both for the ground granular material (relevant for end of life/demolition stage) and for the intact products. For all three of the tested intact C-fix products, i.e. with limestone, heated river sludge or biomass ash as fine filling material, all of the measured inorganic elements show cumulative emissions well below the limits of the Dutch Building Materials Decree for both Category 1 and Category 2 construction materials. The product with river sludge was tested in seawater.

Particularly as a result of the acid nature of the C-fix binder, the pH and buffer capacity of the (fine) filling material that is used in the filler-mixture has a significant effect on the leaching properties. From a leaching point of view, the (original) mixture containing limestone is to be preferred over that containing river sludge, although in the latter case contaminant leaching remains limited. A number of heavy metals (Co, Ni, Zn and Cd) show up to an order of magnitude higher cumulative emissions from the C-fix product containing river sludge in a seawater environment, compared to the products containing limestone and biomass ash in freshwater. This effect is most likely due to complexation of these metals with Cl in seawater. However, it cannot be excluded that the lower pH of the C-fix product with river sludge also plays a role in the enhanced leaching of these metals.

A first assessment of the leaching of mineral oil and PAH from C-fix products, based on non-standardised draft leaching procedures, shows limited leaching of these organic contaminants. The cumulative emission of mineral oil, measured using an experimental modification of the standard NEN 7345 procedure, suggests that the leaching of these organic contaminants occurs only initially as a result of wash-off and possible steric hindrance of the diffusion process. The total cumulative amount leached is only of the order of 2 mg/kg. Leachable ("available") PAH concentrations in the C-fix binder and products are low (100-300 µg/kg), considering that the conditions in the test procedure are very favourable for the leaching of PAH because of their strong solubility enhancement by the high concentration of humic acid in the leachate.



## 1. INTRODUCTION

C-fix (“carbon fixation”) is a novel construction material developed by Shell Global Solutions on the basis of a carbon-rich binder that is produced during the refining of crude oil. Until recently, the heavy refinery fractions from which C-fix is obtained could only be used as fuels for ship engines and power plants, and as such contributed substantially to CO<sub>2</sub>-emissions. C-fix has been developed to contribute to the emission reduction of CO<sub>2</sub>, by applying the C-rich binder to produce a beneficial construction product, rather than burning it as a heavy refining residue. A number of projects on the application of C-fix have started in the period 2000-2002. The current projects focus on selected applications, but are intended to extend to the large-scale application of C-fix, which would enable significant contribution to the reduction of CO<sub>2</sub>-emissions.

In addition to the assessment of the civil-technical properties of C-fix products in specific constructions, a thorough environmental assessment of the materials is equally important to enable its large-scale introduction. In The Netherlands, the environmental properties of construction materials have to comply with the Building Materials Decree. In the European Union, the Construction Products Directive is in the process of being formulated. The environmental criteria are based on limit values for the leaching of contaminants in prescribed standardised leaching tests.

A number of standard leaching tests have been performed in the development-phase of C-fix (INTRON, 2000), and has indicated that the leaching of inorganic contaminants is well below the limits of the Dutch Building Materials Decree. Limits for organic contaminants in this Decree are (still) based on total amounts rather than leaching limits. Polycyclic Aromatic Hydrocarbons (PAH) and extractable halogenated organic compounds have been detected, but were also well below the specified concentration limits. Only total concentrations of mineral oil were found to be 7-8 times higher than the limit values. However, this value for mineral oil in the Building Materials Decree has been declared not to apply to construction materials with a high organic matter content, such as asphalt and bituminous roof paving materials. C-fix is likely to fall under this category of materials.

This report focuses on a more detailed characterisation of the leaching properties of C-fix products and their individual components. It is intended to give more insight in the processes controlling the leaching of possible contaminants, as a basic characterisation and as a reference for the further development of C-fix with other possible filling materials. The leaching of both inorganic and organic contaminants is addressed, the latter in anticipation of possible near-future developments in the environmental assessment of construction materials. In the last few years, both at the national (The Netherlands) and European level, there is growing interest in the development of leaching tests for organic contaminants and their possible implementation in environmental legislation (e.g. Comans, 2001). Although standardised leaching tests are not yet available for organic contaminants, the current state-of-the-art is applied to make a first assessment of the leaching of mineral oil and PAH from C-fix products.

In addition to the characterisation of the leaching properties of C-fix products and standard components (binder and filling materials) in freshwater, three special situations are evaluated. The effect of the use of two alternative filling materials (finest fraction), (uncontaminated) river sludge and biomass-ash from the combustion of (uncontaminated) wood is evaluated. In addition, the leaching of C-fix products is measured in a seawater environment, to simulate possible contaminant emissions during the potential use of C-fix bricks in dikes along the sea shore.





## 2. MATERIALS AND METHODS

### 2.1 Testing materials

The following materials, produced in February 2002, have been received from Shell Global Solutions and were used for for this study:

1. *Intact C-fix product (code F)* made from standard filling materials: gravel, sand and Wigro limestone
2. *Crushed (coarse) C-fix product (code F)* made from standard filling materials: gravel, sand and Wigro limestone. Crushed at ECN (jaw crusher) to < 4 mm
3. *Intact C-fix product (code S)* made from standard gravel and sand, but with heated river sludge as alternative fine filler
4. *Crushed (coarse) C-fix product (code S)* made from standard gravel and sand, but with heated river sludge as alternative fine filler. Crushed at ECN (jaw crusher) to < 4 mm
5. Separate gravel, sand and Wigro limestone (standard filling materials), mixed by ECN in the appropriate proportions (as in intact products): 44% : 44% : 12%
6. *Separate gravel, sand and heated river sludge*, mixed by ECN in the appropriate proportions (as in intact products): 44% : 44% : 12%
7. *C-fix binder*, crushed at ECN to < 2 mm (material was too sticky for jaw crusher, but decomposed in liquid N<sub>2</sub> and was then sieved)
8. *Intact C-fix product (code BM)* made from standard gravel and sand, but with biomass ash (from the combustion of clean wood) as alternative fine filler

### 2.2 Leaching procedures and analyses

#### 2.2.1 pH-stat leaching test

Because both major element and contaminant leaching are generally strongly dependent on pH, batch pH-static leaching experiments were performed for the basic characterisation of the leaching properties of the (crushed) C-fix products, filler mixtures and crushed binder. In this procedure, which is in preparation to become a European EN standard (WI 292034), the pH is monitored and adjusted to setpoint in 250-mL Teflon PFA reactors simultaneously at a number of pH values in the range of pH 4-13. Suspensions of the granular samples were prepared in nanopure deionized water at a liquid/solid (L/S) ratio of 10 L/kg. The reactors were kept open to the atmosphere at 20±1 °C and were stirred continuously during a 48-hour equilibration period, using a teflon-coated magnetic stirring bar. The pH of the suspensions was continuously monitored by a computerized pH-stat system and was automatically adjusted to setpoint by addition of 1 M analytical grade HNO<sub>3</sub> or NaOH, when the measured pH deviated by more than a preset value from setpoint.

After 48 hours reaction time, the suspensions were pre-centrifuged at 2000 x g for 0.5 h in 200-mL polycarbonate centrifuge tubes to facilitate the separation of leachate and particulate matter. Subsequently, the leachates were filtered through 0.2 µm membrane filters.

#### 2.2.2 Draft “availability” leaching test for non-volatile organic contaminants

A draft “availability” leaching test for non-volatile organic contaminants has been developed in the framework of the European Standards, Measurements and Testing programme (Comans (2001)). The test is based on the strong solubility-enhancement of hydrophobic organic contaminants (PAH) by natural dissolved (humic) organic carbon (DOC) in soil environments

and is intended to indicate the maximum amount of contaminants that can be leached from a solid (soil/waste) material.

The procedure is described in detail in Appendix I. The availability for leaching is determined by extracting a sample of ground (95% <1 mm) solid (soil/waste) material with a solution of a commercial (Aldrich) humic acid (1000 mg-C/L) at a high liquid/solid (L/S) ratio of 100 L/kg and a pH of 12 for 48 hours. This high pH-value is necessary to keep the DOC in solution by preventing its adsorption to the solid phase. The concentration of DOC is chosen as an upper limit that can be reached, e.g. when alkaline materials react with organic soils. The leaching principles and development of this test are described in detail in Comans (2001) and Comans & Roskam (2002). The test was used to measure both the leaching of PAH and mineral oil, although it has not been applied earlier for the latter contaminants.

### 2.2.3 Diffusion test for monolithic construction materials (NEN 7345)

The diffusion (tank) test has been performed according to NEN 7345 to evaluate the emission of inorganic contaminants from the intact C-fix products as a function of time. The C-fix product with river sludge is evaluated for its possible use in dikes along the sea shore and was, therefore, leached in Doggersbank seawater.

Although the NEN 7345 test has been developed for inorganic contaminants, in this study a modified NEN 7345 procedure was used to measure the emission of mineral oil. The test modifications concerned particularly the use of all glass containers for the test and sample vials, and the rinsing of the container walls with ca. 50 mL of acetone after each refreshment of the leachate. The intact C-fix products were used as delivered by Shell Global Solutions (i.e. cylinders of Ø 10 cm and 10 cm length; volume approximately 815 cm<sup>3</sup>). The leachate volume was 600 mL, of which 400 mL was used for the extraction and analysis of mineral oil (see 2.2.5).

### 2.2.4 Extraction and analysis of PAH

PAH were extracted from leachates by a 3-step sequential liquid/liquid extraction with dichloromethane (water:DCM ratio's were 75:10, 75:5 and 75:5, for 16, 3 and 3 hours, respectively). The extract was dried by adding sodium sulphate (Merck, anhydrous granulated for organic trace analysis). The volume of DCM was reduced to 0.5 ml under a gentle flow of nitrogen and transferred to an HPLC-vial. Subsequently, 1 ml of acetonitrile was added and the volume was reduced to 1 ml by evaporating the DCM. If necessary (in case of a turbid extract), a final clean-up of the acetonitrile extract by percolation through aluminium oxide tubes (Supelco, Supelclean<sup>TM</sup> LC-Alumina-N 6-ml SPE tubes) was added to the procedure. The PAH were analysed by HPLC, using a C<sub>18</sub> PAH Column (Varian, Chromospher PAH; length 20 cm, 3 mm internal diameter, particle size stationary phase 5 µm), and a mobile phase consisting of an acetonitrile/water mixture. The fluorescence detector was used for quantification of the PAH concentrations, whereas the diode array detector was used for confirmation of the individual PAH peaks, except for acenaphthylene, which can only be detected by the diode array detector.

### 2.2.5 Extraction and analysis of mineral oil

For the extraction of mineral oil from aqueous leachates a slightly modified procedure according to ISO 9377-2 was used. The leachate solutions from the "availability" test (ca. 750 mL) and the diffusion test (ca. 400 mL) were extracted by a 3-step sequential liquid/liquid extraction with hexane (suprasolv) volumes of 50, 25 and 25 mL (750 mL leachate volume "availability" test), and 30, 15, 15 mL (400 mL leachate volume diffusion test). In the case of the diffusion test, mineral oil was also analysed in acetone (ca. 50 mL) that was used to rinse the walls of the glass container in which the test was performed. The mineral oil was first

transferred from acetone to hexane by reduction of the acetone volume to ca. 10 mL under a gentle flow of nitrogen, addition of 20-30 mL hexane (Suprasolv) and further volume reduction to ca. 10 mL. The further handling of the hexane samples was identical.

The hexane solutions were dried by addition of sodium sulphate (Merck, anhydrous granulated for organic trace analysis), purified by percolation through a Florisil column (Supelco, Supelclean<sup>TM</sup> LC-Florisil 6ml, 1g SPE tubes) and reduced to 1 ml under a gentle flow of nitrogen.

The analysis of mineral oil was performed by GC-FID, according to NEN 5733.

#### 2.2.6 Analysis of inorganic components

For a thorough characterisation of the leaching properties of C-fix products, filling materials, and binder, a wide selection of inorganic components has been analysed, with the analytical techniques in brackets:

- Li, B, Na, Mg, Al, Si, P, S, K, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Sr, Mo, Cd, Sn, Sb, Ba, Pb (axial plasma ICP-OES)
- Cl-Br (ion chromatography)
- TIC-TOC (Shimadzu TOC 5000A carbon analyser)

These analyses are Sterlab and AP04 certified (Raad voor Accreditatie (RvA) registration number L135).



### 3. RESULTS

#### 3.1 pH-dependent leaching

The leaching properties of the C-fix products, filler-mixtures and binder have been characterised by measuring the release of a large range of chemical (major and trace) elements over a wide pH-range (pH = 2-12), using the pH-stat procedure. The results are shown in Appendix 2. The solubility and leaching of major and trace elements is strongly dependent on pH and, therefore, the pH-stat results provide a geochemical “fingerprint” of the underlying processes that control their solubility/leaching. Four general features can be observed in pH-stat leaching curves:

1. Increasing concentration towards low pH, with maximum around pH 2-4 (Li, Mg, Ca, Mn, Co, Ni, Sr, Ba). This feature represents the typical increased solubility of metals at low pH. The maximum concentration at low pH can be taken as the maximum “availability” of the contaminants for release from the solid matrix.
2. Increasing concentration towards high pH, with maximum around pH 10-12 (B, As, TIC, TOC). This feature represents typical anion solubility behaviour, with maximum solubility at high pH. The maximum concentration at high pH can be taken as the maximum “availability” of the contaminants for release from the solid matrix.
3. V-shaped concentration curves, with maximum at pH 2-4 and/or pH 10-12 (Si, Al, P, Ti, V, Cr, Fe, Cu, Zn, Cd). This feature is typical for metals which form soluble complexes with ligands such as  $\text{OH}^-$ ,  $\text{CO}_3^{2-}$  and DOC at high pH.
4. Approximately constant concentrations (K, S, Cl (pH 12 probably analytical error)), typical for pH-independent solubility and leaching.

The increase of Na towards high pH is an artefact of the experimental setup and caused by the addition of NaOH in the pH-stat to increase pH. The leaching of Br was at all pH-values below the detection limit and, consequently, the curve has no meaning. The extreme reduction in the concentration of Cl at pH 12 cannot be explained and is probably an analytical error.

Except for the binder, the general leaching behaviour of the ground C-fix products and filler-mixtures are very similar to those of other mineral (construction, waste, soil) materials (e.g. van der Sloot et al., 1997). When the pH-dependent leaching of C-fix products is compared to that of cement-based products (van der Sloot, 2000), the general picture is that smaller amounts are leached from the C-fix products. Only at high pH, the concentrations of oxyanions such as B, V, Cr, As are higher for C-fix than for cement-based products, due to the absence of immobilisation reactions of these ions with alkaline cement minerals such as ettringite and Ca-silicates. However, given that the “natural” pH of C-fix products is between slightly acid and slightly alkaline (Table 1), while that of cement-based products is strongly alkaline, the absence of this fixation mechanism is less relevant for C-fix than it is for cement.

*Table 1. “Natural” pH values of the granular filler mixtures and ground C-fix products at a liquid/solid ratio of 10 L/kg.*

| Sample                                   | “Natural” pH* |
|--|---------------|
| C-fix product (gravel/sand/limestone)    | 8.78 ± 0.33   |
| C-fix product (gravel/sand/river sludge) | 6.27 ± 0.45   |
| Filler mixture: gravel/sand/limestone    | 8.96 ± 0.05   |
| Filler mixture: gravel/sand/river sludge | 7.85 ± 0.24   |
| C-fix binder                             | 5.46 ± 0.98   |

\*Average and standard deviation of 6 measurements (4 measurements for C-fix binder)

Given that the pH-stat test is performed at a liquid/solid (L/S) ratio of 10 L/kg, the results at the “natural” pH (not adjusted by the addition of acid or base) of the materials can be used as a first approximation of the cumulative emissions in a column test at L/S = 10. For granular materials, the limit values in the Dutch Building Materials Decree are based on these values. Table 1 indicates the “natural” pH of the different samples.

None of the measured elements at these pH-values reach the limit values for Category I construction materials according to the Building Materials Decree, which is relevant with regard to evaluation of the end of life properties of construction materials (after demolition). However, the pH of the products is important in this respect. The pH of the product based on limestone as the finest filling material (8.78) is more favourable than that of the product with river sludge, which is substantially lower (6.27), particularly for the heavy metals. Particularly the leaching of Co is at pH 6 about equal to the limit for Category 1 construction materials (0.4 mg/kg)<sup>1</sup>, while at pH >8 it is insignificant. Also metals such as Zn and Ni are only a factor of 2-3 away from this limit at pH 6, while their leaching at pH 8 is about an order of magnitude lower. Table 1 shows that the C-fix binder reduces the pH of the (ground) product, relative to the filler mixtures. The limestone-containing mixture is well-buffered and only slightly reduced in pH, but the mixture containing river sludge apparently has only a limited buffer capacity and is reduced by 2.5 pH-units. This pH effect is a factor to be taken into account when selecting (fine) filler materials, and is possibly also noticeable for Co Ni and Zn in the results of the diffusion tests on the intact products (see section 3.2).

When comparing the results of the ground C-fix products with the filler-mixtures, the leaching curves are generally very similar. This observation is consistent with the inert leaching properties of the C-fix binder, which is for virtually all elements considerably lower than that of the filler-mixtures (the apparently higher oxyanion concentrations (As, Se, Sb, Mo, V, Sn) in binder leachates are not significant, and are well below detection limits)<sup>2</sup>. Therefore, the binder does not seem to contribute to the leaching of the measured inorganic components. There is one noticeable and positive exception; the C-fix binder has a positive effect on the leaching of chromium. The higher leaching of Cr from the (oxidised) filler-mixtures relative to the ground C-fix products between pH 6 and 12 is indicative of the mobile (and toxic) Cr(VI) (chromate) species, which is possibly reduced by reaction with the organic binder to the less mobile Cr(III) species. Finally, the very similar leaching properties of the filler-mixtures and the corresponding ground products also enables a relatively rapid batch leaching test (at L/S = 10 L/kg) to be used for quality control purposes, using the pH-dependent leaching curves in Appendix 2 as a reference.

### 3.2 Diffusion tests

The results of the diffusion tests are shown in Appendix 3. For the relevant elements, the limit cumulative emission values of the Dutch Building Materials Decree for Category 1 (BSB-1) and Category 2 (BSB-2) construction products are indicated in the graphs. All of the measured inorganic elements show cumulative emissions well below the limits for both Category 1 and Category 2 construction materials. This is also true for C-fix with biomass ash as the finest filling material.

The C-fix product with river sludge is evaluated for its possible use in dikes along the sea shore and was, therefore, leached in (Doggersbank) seawater. All results shown in Appendix 3 are corrected for the concentrations of the measured elements in the seawater sample that was used. This correction may have contributed to irregularities in the leaching curves of some elements, such as Al K, and Se. Also under seawater conditions, the cumulative emissions remained

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<sup>1</sup> Concentrations in the leachate in mg/L can be multiplied with L/S ratio of 10 L/kg to obtain emissions in mg/kg solid material.

<sup>2</sup> Please note that detection limits may vary between samples. Values < DTL are plotted in the graphs as 0.5\*DTL.

below the limits of the Building Materials Decree. A number of heavy metals (Co, Ni, Zn and Cd) show up to an order of magnitude higher cumulative emissions from the product with river sludge in seawater, compared to the products containing limestone and biomass ash in freshwater. This effect is most likely the result of complexation of these metals with Cl in seawater. However it cannot be excluded that the lower pH of the C-fix product with river sludge (see section 3.1) also plays a significant role in the enhanced leaching of these metals. The average pH-values in the diffusion tests (8 fractions) were  $8.09 \pm 0.20$  (product with limestone in freshwater),  $7.70 \pm 0.13$  (product with river sludge in seawater), and  $10.54 \pm 0.22$  (product with biomass ash in freshwater). A diffusion test of this product in freshwater could help to distinguish between these two possible causes.

The cumulative emission of mineral oil, although measured using an experimental modification of the standard NEN 7345 procedure, suggests that the leaching of this organic component is an initial wash-off effect and/or due to steric hindrance of the diffusion process (large molecular size relative to pore diameters inside the product). The total cumulative amount of mineral oil leached during the 64 days of the test was only approximately 2 mg/kg, relative to total amounts (reported in the INTRON (2000) study) of 3500-4100 mg/kg.

Overall, the diffusion tests confirm the observation based on the pH-stat tests on the ground materials (section 3.1) that the leaching of major and trace elements from C-fix products is generally lower than that of cement-based products.

### 3.3 Availability tests for PAH and mineral oil

The recently developed draft availability test for non-volatile organic components (Comans, 2001 and Appendix 1) was applied to the C-fix binder as well as to the ground products with limestone filler (F2) and river sludge (S2). Leachates were analysed for both PAH and mineral oil. The test was not developed nor tested earlier for the latter components. It was found that the concentration of mineral oil in the leachates was only slightly higher than that in the (relatively high) blanc leachates containing only humic acid and close to (1.5-2.5x) the detection limit. Corrected for the blanc, the leached concentration of mineral oil was approx. 0.01 mg/L, corresponding to a concentration of approx. 1 mg/kg in the binder. This value is low relative to the cumulative release of about 2 mg/kg from the intact product (which contains about 8% m/m binder), possibly as a result of the relatively high humic acid blanc. However, these findings are another indication that the leachability of mineral oil from the C-fix binder is limited.

The availability of PAH is shown in Figure 1, both for the sum of the 16 EPA-PAH and for the different size groups (2-6 rings).

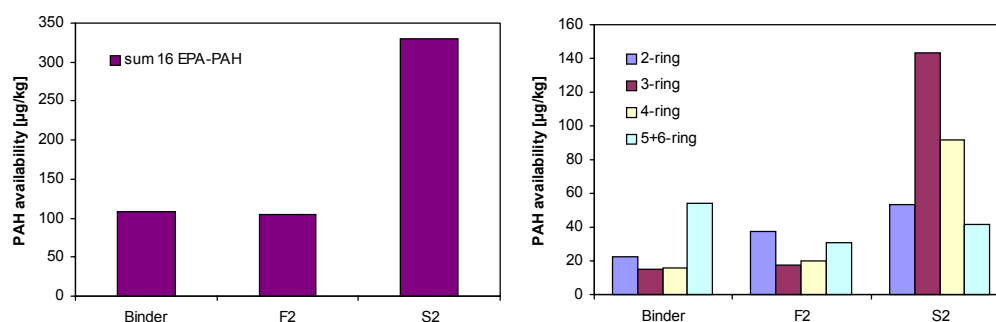


Figure 1. Availability of the sum of 16 EPA-PAH and different PAH size groups in the C-fix binder and the ground products with limestone filler (F2) and river sludge (S2).

Total PAH concentrations in the C-fix binder and products have not been measured (INTRON (2000) mentions only “traces” of PAH). However, Figure 1 shows that “available” PAH concentrations are low (100-300 µg/kg), given that the conditions in the test are very favourable for the leaching of PAH because of their strong solubility enhancement by the high concentration of humic acid in the leachate. As a reference, tar-containing asphalt granulate was shown to have a 3-orders of magnitude greater PAH availability in the same test (Comans, 2001). Given the low PAH concentrations in the test, it is questionable whether the concentration differences between the C-fix binder and the two products are significant.



## 4. CONCLUSIONS

- For the majority of the measured major and trace elements, leaching from C-fix products was found to be substantially lower than from cement-based products, both for the ground granular material (relevant for end of life/demolition stage) and for the intact products.
- Particularly as a result of the acid nature of the C-fix binder, the pH and buffer capacity of the (fine) filling material that is used in the filler-mixture has a significant effect on the leaching properties. From a leaching point of view, the (original) mixture containing limestone is to be preferred over that containing river sludge, although in the latter case contaminant leaching remains limited. Addition of an alkaline component to the river sludge mixture could further improve the leaching properties. These results show the great value of pH-static characterisation of the leaching properties of products/filler mixtures.
- The very similar leaching properties of the filler-mixtures and the corresponding ground products offer a good basis for quality control (QC). This relationship enables a relatively rapid batch leaching test (at L/S = 10 L/kg) to be used for QC-purposes, using the pH-dependent leaching curves in Appendix 2 as a reference. The close match between the properties of the filler-mixtures and ground products is also beneficial with regard to possibilities for recycling at the end of life phase.
- For all three of the tested intact C-fix products, i.e. with limestone, heated river sludge or biomass ash as fine filling material, all of the measured inorganic elements show cumulative emissions well below the limits of the Dutch Building Materials Decree for Category 1 construction materials. The product with river sludge was tested in seawater.
- A number of heavy metals (Co, Ni, Zn and Cd) show up to an order of magnitude higher cumulative emissions from the C-fix product containing river sludge in a seawater environment, compared to the products containing limestone and biomass ash in freshwater. This effect is most likely due to complexation of these metals with Cl in seawater. However, it cannot be excluded that the lower pH of the C-fix product with river sludge also plays a role in the enhanced leaching of these metals. A diffusion test of this product in freshwater is recommended to distinguish between these two possible causes.
- The cumulative emission of mineral oil, although measured using an experimental modification of the standard NEN 7345 procedure, suggests that the leaching of these organic contaminants occurs only initially as a result of wash-off and possible steric hindrance of the diffusion process. The total cumulative amount leached is only of the order of 2 mg/kg.
- Leachable (“available”) PAH concentrations in the C-fix binder and products are low (100-300 µg/kg), considering that the conditions in the test procedure are very favourable for the leaching of PAH because of their strong solubility enhancement by the high concentration of humic acid in the leachate.



## 5. REFERENCES

Comans, R.N.J. (ed.) (2001) Development of standard leaching tests for organic pollutants in soils, sediments and granular waste materials. Final Report EU project SMT-4-CT97-2160. ECN-C--01-121.

Comans, R.N.J. & Roskam, G.D. (2002) Leaching procedure for the availability of polycyclic aromatic hydrocarbons (PAHs) in contaminated soil and waste materials. In: P. Quevauviller (ed.) *Methodologies for Soil and Sediment Fractionation Studies - Single and Sequential Extraction Procedures*. Royal Society of Chemistry, Cambridge, pp. 123-141.

INTRON (2000) Toetsing ontwikkelingsmateriaal aan Bouwstoffenbesluit. Uitloogonderzoek en samenstelling. INTRON report A804420/R20000306.

NEN 7345 (1994) Determination of leaching from monolithic construction materials and waste materials by means of a diffusion test. Netherlands Normalisation Institute, Delft.

van der Sloot, H.A., Heasman, L. & Quevauviller, Ph. (1997) Harmonization of Leaching/Extraction Tests. *Studies in Environmental Science* 70. Elsevier, Amsterdam. 292 p.

van der Sloot, H.A. (2000) Comparison of the characteristic leaching behavior of cements using standard (EN 196-1) cement mortar and an assessment of their long-term environmental behavior in construction products during service life and recycling. *Cement & Concrete Research* **30**, 1079-1096.



# APPENDIX 1: “AVAILABILITY” TEST FOR THE LEACHING OF NON-VOLATILE ORGANIC CONTAMINANTS

*Draft organic availability test SMT4-CT97-2160, Version 1.1, 23-05-01 11:54*

## Draft method for the determination of the availability of non-volatile organic components for leaching

### Contents

1. Principle
2. Samples for analysis
3. Reagents
4. Apparatus
5. Procedure
6. Calculation
7. Report

#### 1 Principle

The purpose of the availability test is to indicate the quantity of a particular component that may leach out from a (soil/waste/building) material exposed to extreme conditions (such as e.g. in the very long term, after disintegration of the material and/or full oxidation in an aerobic environment). The generally low aqueous solubility of particularly hydrophobic organic pollutants limits the availability of these components for leaching in water, but association with dissolved organic carbon (DOC) can considerably enhance their solubility and leaching in the (soil) environment. Therefore, this availability test is based on the premise that the exposure of a material in the environment to water containing DOC, particularly in the form of humic acids, is the major process that controls the availability of hydrophobic organic contaminants for leaching.

The availability for leaching is determined by extracting a sample of the ground material with a solution of a commercial (Aldrich) humic acid (1000 mg-C/l) at a high liquid/solid ratio (L/S) of 100 l/kg and a pH of 12. This high pH-value is necessary to keep the DOC in solution by preventing its adsorption to the solid matrix of the (soil/waste/building) material. The concentration of DOC is chosen as an upper limit that can be reached, e.g. when alkaline materials react with organic soils. The quantities of the various organic components present in the material that are available for leaching may be calculated on the basis of the results of this availability test.

#### 2 Samples for analysis

To carry out a single availability test, a sample for analysis of at least 10 g dry matter is needed, the use of a smaller amount should be avoided because of the variability within the sample. The moisture content (MC) has to be known and at least 95 % (dry mass) of the particles should have a grain size of less than 1 mm. This grain size is chosen to allow for practical handling of the material in a batch laboratory leaching test and is otherwise based on the premise that organic contaminants are generally present at the grain surfaces rather than in the interior of grains.

##### 2.1 Particle size reduction

If the amount of oversized material exceeds 5% (dry mass), the entire oversized fraction shall be crushed with a crushing equipment (4.1). Non-crushable material (e.g. metallic parts such as nuts, bolts, scrap) in the sample shall be separated and the weight and nature of the material shall be recorded. The method of size-reduction applied shall be documented in the test report.

#### NOTE

Where the sample intended for the availability test has to be pre-dried to prepare the

sample for analysis, this may not be carried out at a temperature higher than 40°C to prevent components from evaporating and/or chemical conversions taking place during the drying process which may affect the leaching behaviour. If the material already has the appropriate grain size distribution, no pre-drying should be carried out.

**NOTE**

Fibrous materials and plastics can often be size-reduced after cryogenic treatment (with liquid N<sub>2</sub>).

## 2.2 Determination of the moisture content

The moisture content of the sample must be determined on a separate sub-sample that is dried at 105 ± 5 °C. The moisture content is expressed as the (wt) percentage of water relative to the amount of dried sample.

$$MC = 100 * \frac{(m_w - m_D)}{m_D}$$

where *MC* is the moisture content (%)  
*m<sub>w</sub>* is the mass of undried sample (g)  
*m<sub>D</sub>* is the mass of the dried sample (g)

The quantity of (wet) solid material (*m<sub>w</sub>*) to be used in the test, based on the required dry weight of 10 g, is calculated as follows:

$$m_w = \left( \frac{MC}{100} + 1 \right) * 10$$

## 3 Reagents

- 3.1 Sodium hydroxide p.a. *c*(NaOH) = 5 ± 0.1 mol/l.
- 3.2 Nitric acid of analytically pure quality *c*(HNO<sub>3</sub>) = 1 ± 0.1 M
- 3.3 Demineralised, deionised or distilled water or water of equivalent purity (5 < pH < 7.5) with a conductivity < 0.5 mS/m.
- 3.4 Aldrich humic acid, sodium salt (techn.).

## 4 Apparatus

- 4.1 Crushing equipment: e.g. a jaw crusher or a cutting device.

**NOTE**

Both metal and ceramic grinding equipment can be used for this purpose

- 4.2 Sieving equipment with sieves of 2-mm nominal screen size.

**NOTE**

Both grinding (4.1) and sieving (4.2) can be omitted when the sample only contains particles smaller than 2 mm

- 4.3 Analytical balance with a measurement range up to at least 1000 g and a measurement

accuracy better than  $\pm 10$  mg.

- 4.4 Volumetric flask (glass) with a volume of 1 litre.
- 4.5 Reaction vessel (glass) with a volume of 1 litre.
- 4.6 Glass collection bottles with screw cap.
- 4.7 Glass coated magnetic stirring rod.
- 4.8 Magnetic stirring device.
- 4.9 pH meter with a measurement accuracy better than  $\pm 0.05$  pH units.
- 4.10 pH-stat (optionally)
  - NOTE
  - A pH-stat system that can automatically maintain pH at a constant value is very suitable and recommended for this purpose.
- 4.11 Centrifuge.
- 4.12 Centrifuge tubes of glass (low-speed  $\leq 2000 \times g$ ), Teflon FEP (high speed  $> 2000 \times g$ ), or stainless steel.
- 4.13 Filtration apparatus, suitable for either pressure or vacuum filtration.
- 4.14 Membrane filters for the filtration apparatus (4.13) with a pore size of  $0.45 \mu\text{m}$ , rinsed with demineralised water (3.3). Filters should be able to resist  $0.01 \text{ M NaOH}$ .

## 5 Procedure

The availability is determined by successively:

- determining the requirements of the eluate samples to be analysed in accordance with 5.1;
- carrying out the availability test in accordance with 5.2;
- analysing the eluate in accordance with 5.3;
- carrying out the calculation in accordance with Section 6.

### 5.1 Eluate samples

Determine the quantity of eluate needed to analyse the leached components and the way in which the eluate samples must be stored in accordance with the following procedure:

- a) first check how much, for what components and by what methods analyses must be carried out;
- b) check for what components the eluate must be preserved and in what way;

#### NOTE

In case it is not possible to (extract and) analyse the eluates immediately after the availability test, preservation may be necessary to prevent biological degradation of organic (macro/micro) components. Bacteriocides that can be used for this purpose are Na-azide and  $\text{CuSO}_4$ .

- c) determine in the light of the above the minimum quantity of eluate necessary for each component to be analysed and the way in which the eluate samples must be preserved.

## 5.2 The availability test

### 5.2.1 Preparation of the leachate solution

The leachate solution is an Aldrich humic acid solution of 1000 mg C/l in 0.01 M NaOH. Weigh 3.6 g of Aldrich humic acid (3.4) into a 1-l volumetric flask, add 2 ml of 5 M NaOH solution (3.1) and add demineralised water (3.3) to obtain a 0.01 M solution. Filter the solution over a membrane filter (4.13 and 4.14). Analyse a sample for the exact DOC-concentration.

### 5.2.2 The availability test

The availability test is carried out at room temperature ( $20 \pm 5$ °C). All previously used glassware should be heated overnight in an oven at 550 °C in advance to remove organic contaminants. Rinse the reaction vessel (4.5) consecutively with nitric acid (3.2) and demineralised water (3.3). Weigh the reaction vessel to an accuracy of 10 mg. Transfer the sample for analysis ( $m_W$  as mentioned in section 2.2) to the reaction vessel and weigh again to an accuracy of 10 mg. The difference between the two is the quantity of solid material ( $m_W$ ). Add a quantity of Aldrich humic acid solution (prepared according to 5.2.1) of  $100 \times m_D \pm 10$  g and weigh again. The difference between the total weight ( $m_{tot}$ ) and the sum of the mass of the reaction vessel and the solid material is the mass of the leachant ( $L$ ). Specify  $m_W$  and  $L$  in the report. Place the stirring rod (4.7) in the reaction vessel. Stir the mixture with the aid of the magnetic stirring device (4.8) and set the speed in such a way that all the material is brought into suspension. Prevent aeration of the solution due to intensive stirring, in order to reduce absorption of CO<sub>2</sub> and to minimise evaporation losses. With the aid of the pH meter (4.9) read the initial pH of the contact fluid (pH<sub>A</sub>) after one minute and the stabilised pH (pH<sub>B</sub>) after 10 min. Add sodium hydroxide until pH =  $12 \pm 0.1$  and maintain this value during the test period of 48 hours, by either automated (pH-stat) or manual addition of 5 M NaOH solution when the pH deviates from 12.0 by more than 0.1 pH unit. Record the volume of NaOH solution that is added during the experiment.

#### NOTE

For some samples (with a high base neutralising capacity, BNC) it may be necessary to initially add NaOH at a higher concentration than 5 M (e.g. 10 M) to reach the required pH, while limiting the volume of added NaOH.

After 48 hours, record the pH<sub>final</sub> and let the suspension settle for 15 minutes. Decant in a centrifuge tube and centrifuge at 27000 x g for half an hour. If centrifugation according to these specifications is not possible, the details of the applied procedure (centrifugational force and time) should be specified in the report.

#### NOTE

Samples that settle insufficiently may be pre-centrifuged at a lower speed (in glass centrifuge tubes).

Transfer the quantity of the thus obtained eluate intended for analysis into a suitable bottle (4.6). Preserve the eluate samples according to the procedure described in 5.1. Where more than 1 ml of preservation fluid is needed per 250 ml of eluate, the concentrations determined according to 5.3 must be corrected for the added volume.

## 5.3 Analysis

Analyse the eluate samples obtained in accordance with 5.2.2.

#### NOTE

Details of the applied extraction and analytical methods should be specified in the



report.

## 6 Calculation

Calculate for each component separately the quantity available for leaching (availability), on the basis of the dry mass of solid material, by using the formula;

$$A_i = c_i * \left[ \frac{(L + V)}{m_D} + \frac{MC}{100} \right]$$

Where:

- $A_i$  is the availability of component  $i$ , in  $\mu\text{g/kg}$  dry matter;
- $c_i$  is the concentration of component  $i$  in the eluate, in  $\mu\text{g/l}$ ;
- $L$  is the added amount of the leachate solution, in g;
- $V$  is the added volume of NaOH solution, in ml;
- $m_D$  is the dry weight of the sample for analysis, in g;
- $MC$  is the moisture content (as expressed in section 2.2), in %;

The concentration  $c_i$  referred to in the formula is the concentration originally present in the eluate; the measured value determined in accordance with 5.3 must be corrected for the quantity of preservation fluid added in 5.2 where this is more than 1 ml per 250 ml of eluate.

Where the concentration of a component in the eluate is below the lower limit of detection, for that component the upper limit of the availability must be calculated by making  $c_i$  in the formula equal to the lower limit of detection.

## 7 Report

The report must contain at least the following data:

- a reference to this method;

concerning the sample for analysis:

- the data needed for sample identification;
- the origin and specifications;
- the nature of the material examined;
- the date of reception in the laboratory;
- storage conditions between reception and extraction of the sample;
- preparation of the test portion (method of size reduction, fraction above 2 mm, character of non-crushable material);

concerning the test:

- the date at which the test was carried out;
- moisture content, wet en dry weight of the sample for analysis;
- weight of the added leachate;
- the temperature range within which the availability test has been carried out;
- centrifugation procedure (centrifugational force and time);
- type of centrifugation tube (volume and material);
- duration between the end of agitation and beginning of the separation;
- $\text{pH}_A$ ,  $\text{pH}_B$  and  $\text{pH}_{\text{final}}$ ;
- added amount and type of bacteriocide;

concerning the analysis:

- duration and storage conditions between the test and the extraction of the eluates;
- the applied extraction and analytical method (in case of a liquid-liquid extraction: type of solvent, solvent:solution ratio, extraction time; in case of any extraction: initial volume of

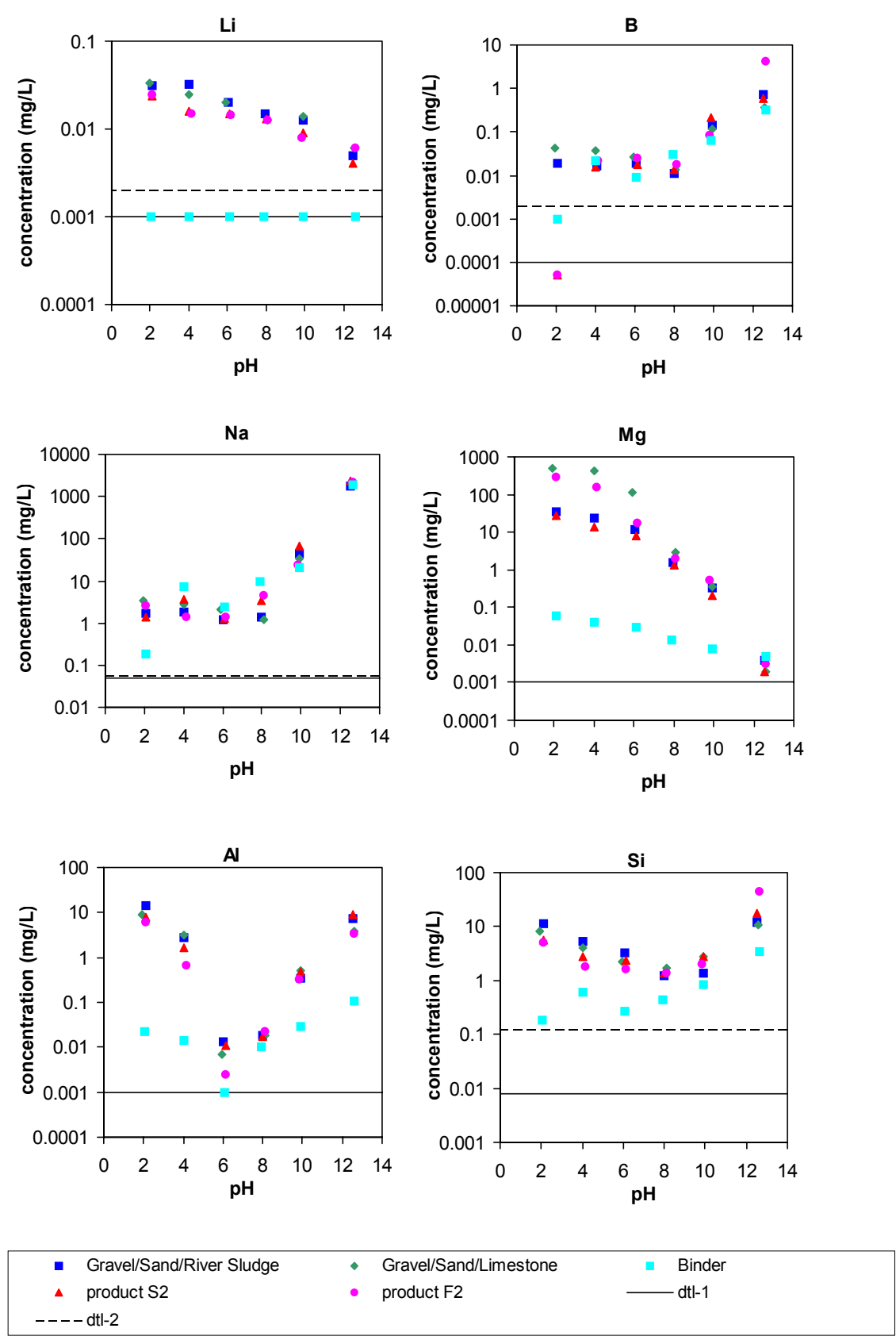
- eluate and final volume of solvent for analysis);
- specifications of the apparatus used for the analysis;
- the components which are analysed and the lower limit of detection of these components in the eluate;

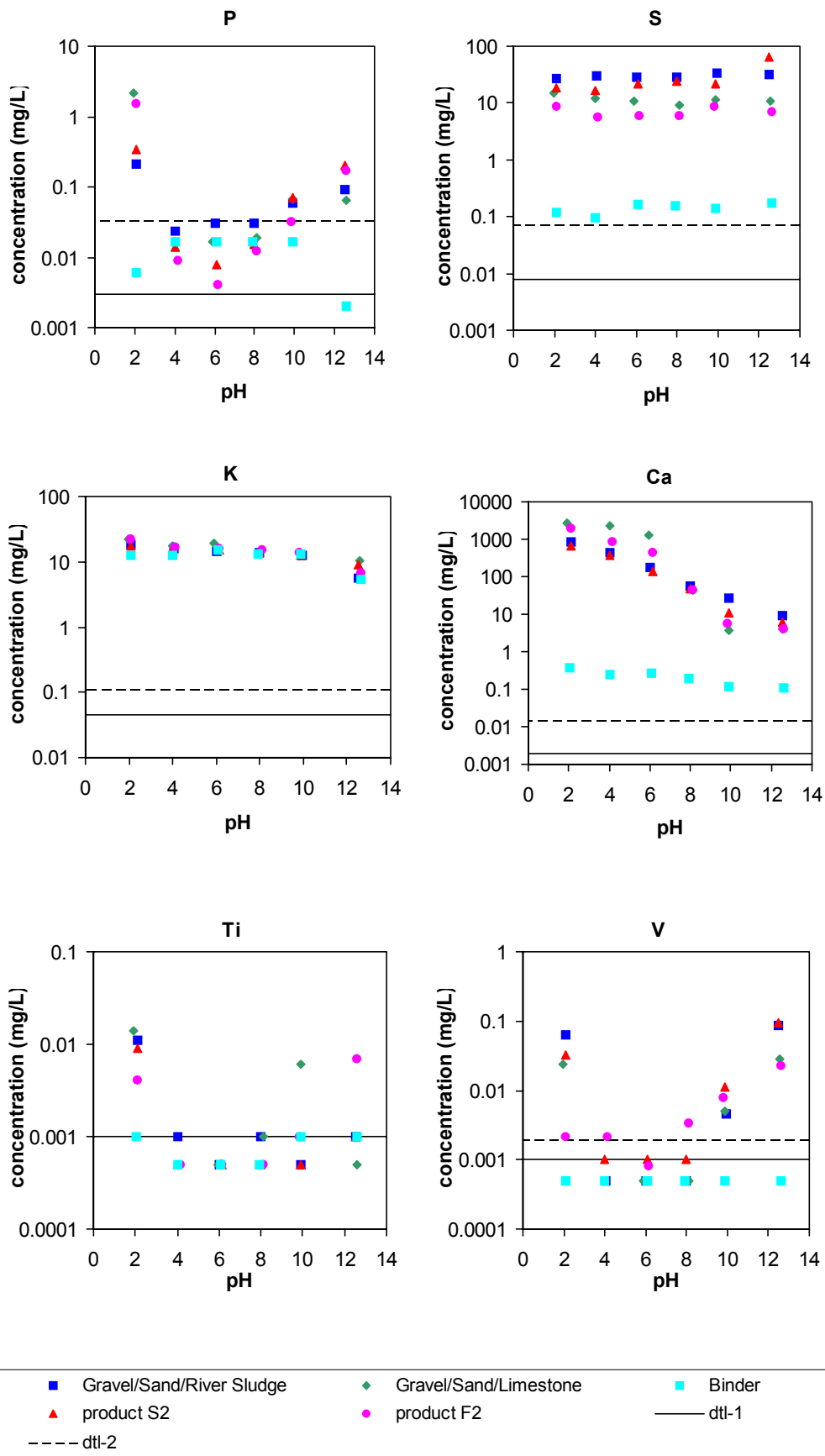
concerning the results:

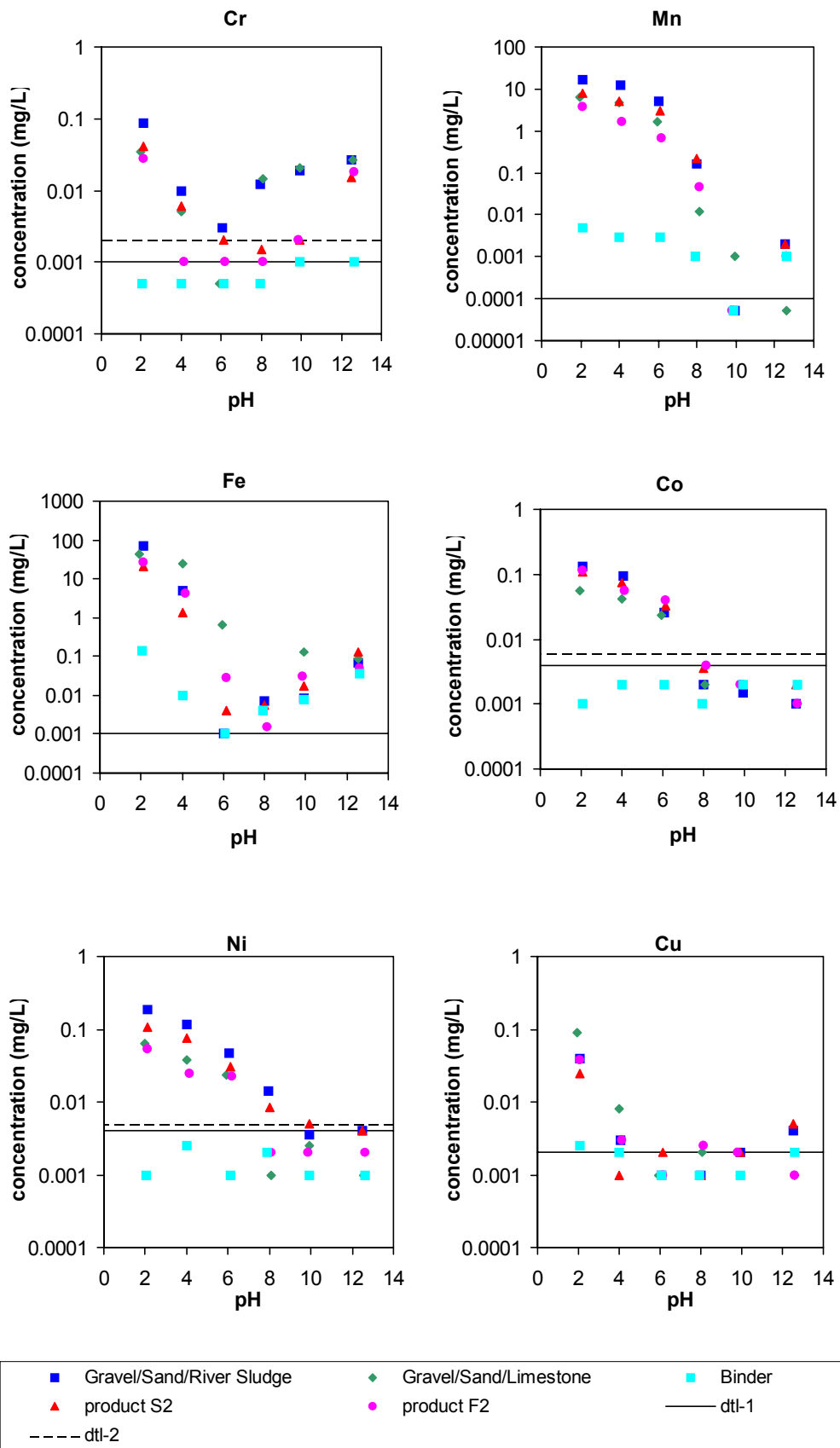
- all measured concentrations;
- the quantity of preservation fluid added in accordance with 5.1 where this is more than 1 ml per 250 ml eluate;
- the calculated availabilities in µg per kg dry weight;
- when analysis results are below the lower limit of detection, the upper limit of the availability is calculated for the relevant component;

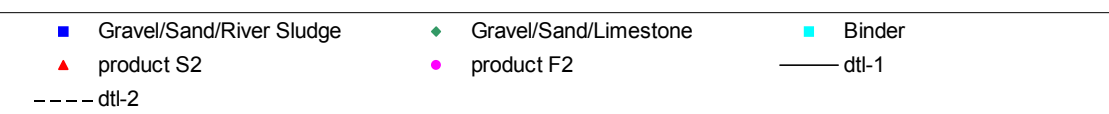
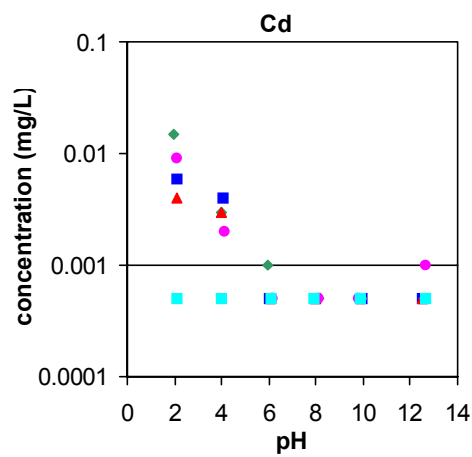
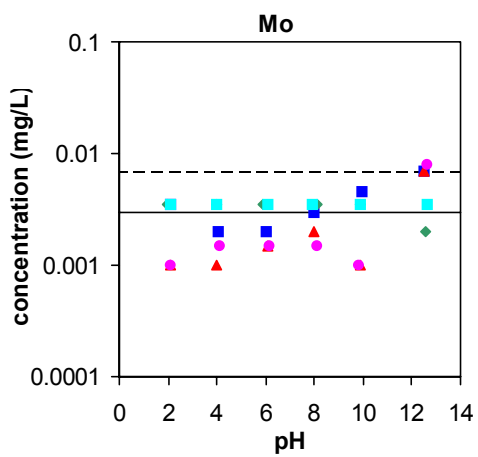
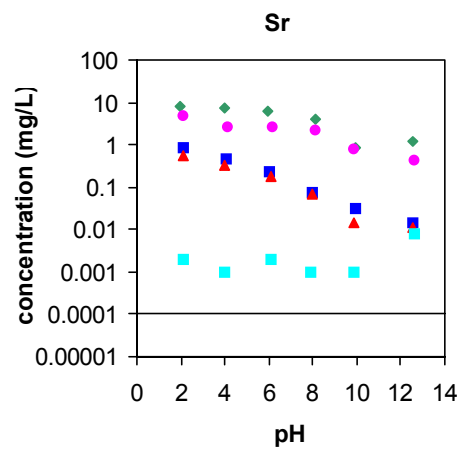
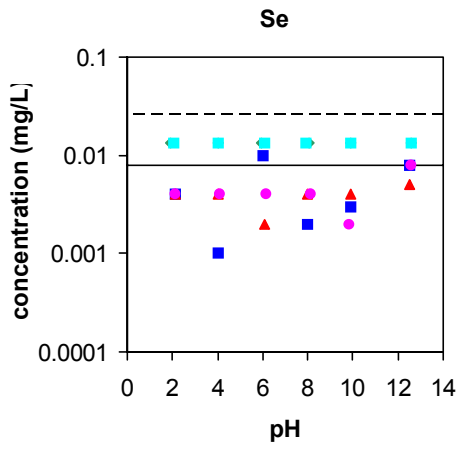
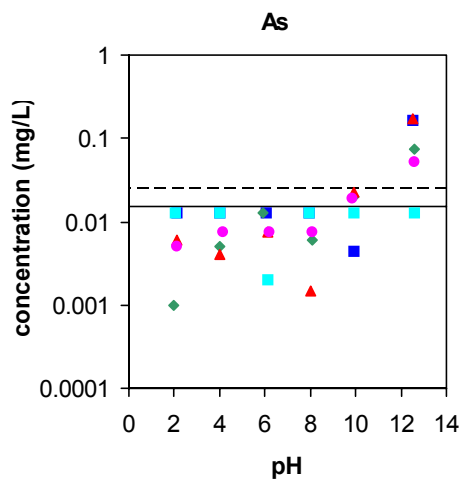
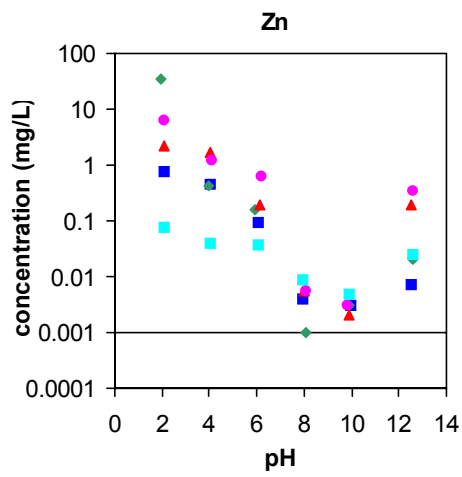
Where the availability test is not carried out fully in accordance with this method, reference may only be made in the report in case all deviations from the procedures prescribed in this standard are indicated in the report supported by argumentation.

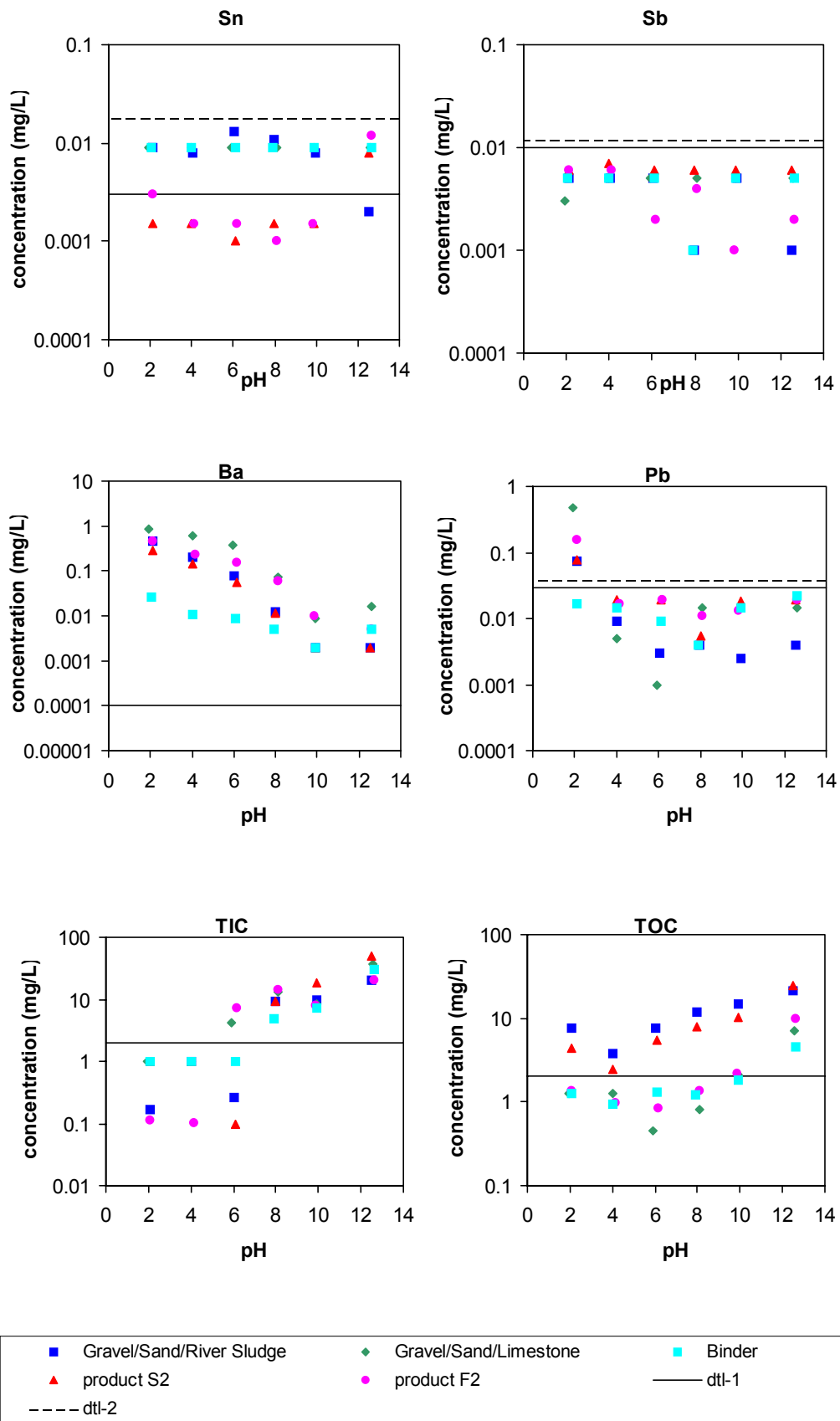
APPENDIX 2. GRAPHS pH-STAT LEACHING

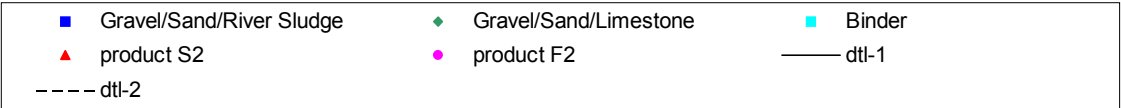
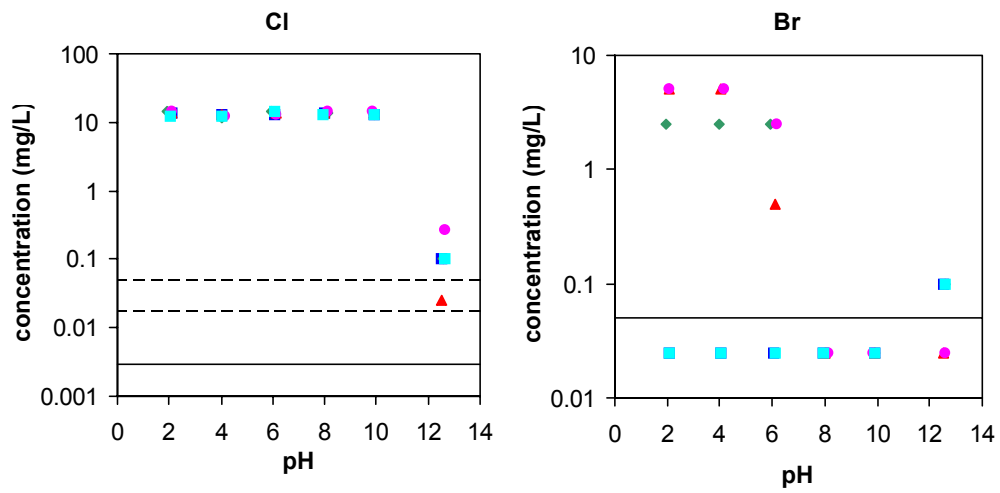














## APPENDIX 3. GRAPHS DIFFUSION TESTS

Note that samples with limestone (F1) and biomass ash (BM1) fillers are leached in freshwater, whereas the sample with river sludge (S1) was leached in seawater.

