ANNEX 5 COMPACTED GRANULAR LEACH TEST HORIZONTAL STANDARD

Desk study HORIZONTAL-23

Title
DETERMINATION OF THE RELEASE OF INORGANIC CONTAMINANTS FROM GRANULAR MATERIALS BEHAVING AS MONOLITH FROM A LEACHING PERSPECTIVE - THE COMPACTED GRANULAR LEACH TEST.

Based on Dutch pre-standard NVN 7347 (1992)
Preliminary edition: September 2003

1. Subject and area of application

This standard describes a method for the determination of leaching characteristics of inorganic (and possibly organic constituents) from powders and granular materials and materials of mainly inorganic nature under conditions where transport by diffusion is more important than transport by convection. The method allows for the determination of physical retardation and chemical retention factors at low liquid to solid ratios (LS 0.3), which are representative of conditions in practice.

2. Principle

The maximum leachable quantity is determined by two subsequent extractions of the fine-ground material at a liquid to solid ratio (LS) of 100 (L/kg), while the pH is subsequently maintained at pH 7 and 4. The concentration of components of interest is analyzed in the combined extract.
The diffusion controlled flux of components from powders and granular materials is assessed by transfering the material to be tested in a beaker and covering the surface of the material to be exposed to the leachant with a layer of glass beads, subsequently placing the beaker in a larger container, which is filled with demineralized water so as to immerse the beaker completely and replacing the water at regular time intervals. The extracts are analyzed for the components of interest. The measurement of an inert species allows the determination of the physical retardation in the granular matrix. For components interacting with the matrix, the chemical retardation can be calculated.

3. Material

The sample to be tested should be representative for the bulk material to be assessed for its environmental properties.
At least 1 kg of material should be available for testing.

4. Reagents

Use only analytically pure reagents and demineralized water.

Water, acidified with "Suprapur" 1 M HNO_3 to pH=4.
Nitric acid, concentration: 6 M HNO_3
Nitric acid, concentration: 1 M HNO3

5. Equipment and appliances

Standard laboratory equipment and appliances in particular the following:

Leaching vessel or tank

Round glassbeaker with a diameter of at least 20 times the maximum particle size to be placed in a larger glassvessel or tank, which can be closed to avoid prolonged contact with the air. The contact with the air is avoided to limit uptake of CO_2 or O_2 from the air. The size of the vessel should be chosen such that the beaker can be immersed with at least 5 cm water over the rim of the beaker. Depending on the emission rate and the duration of the experiment, the height of the beaker should be more than $10^1(2\mathbf{D_e}.\mathbf{t})$ in meter. $\mathbf{D_e}$ is the effective diffusion coefficient (m^2/s) and t is the contact time (s)

Rinse with nitric acid (4.3) before use.

In Figure 1 the equipment is shown.

Membrane filter

Membranefilter with pore-diameters of 0.45 micrometer. The filter needs to be rinsed prior to use with nitric acid (4.3).

Polyethene bottles

Apply polyethene bottles of 1 liter and 100 ml. Rinse with nitric acid (4.3) before use.

Wire sieve, NEN 2560, ISO 565 - 125 micrometer.

6. Determination of the maximum leachable quantity

This test estimates the fraction of the total concentration present, which can be leached under worst case conditions in the long term.

Equipment and reagents

Pyrex glass beaker of 1 liter
Magnetic stirrer
pH-stat apparatus with acid dosing equipment
Membrane filter

Membranefilter with pore-diameters of 0.45 micrometer. The filter needs to be rinsed prior to use.
Filtration unit

6.1 Sample preparation

Crush and grind part of the specimen until 95 % of the weight passes the wire sieve NEN 2560, ISO 565 - 125 micrometer.

Remark

Contamination of the sample by the crusher and grinding equipment has to be avoided.

6.2 Procedure

Determine the maximum leachable fraction (U_{max}) of all components of interest by weighing 8 g of the dried sample (6.2). The temperature during the test should be 25 ± 5 ◦C and record the average temperature. Record the actual weight (**G**). Pour 800 ml of demineralized water in the beaker and add the ground sample. Stir for 3 hours at controlled pH (pH = 7). Record the acid consumption ($\mathbf{V_1}$) in ml. Allow the solid to settle. Filter the solution over a membrane filter. Transfer the extract to a prerinsed polythene bottle. Resuspend the sample (filter included) in 800 ml ($\mathbf{V_b}$) demineralized water and stir for 3 hours at controlled pH (pH=4). Allow the solid to settle. Filter the solution over a membrane filter and acidify the extract with HNO_3 (4.3) to pH=2. Combine the extracts from both extraction steps and analyze the extract for all components of interest by normalized procedures. Analyze the blanc of the extractant used. Record the acid consumption ($\mathbf{V_2}$) in ml.

6.3 Calculation

Calculate the maximum leachable fraction for each component from the formula:

$$\mathbf{U}_{max} = \frac{\mathbf{c}_{max} \cdot (2.\mathbf{V}_b + \mathbf{v}_1 + \mathbf{v}_2)}{1000 \cdot \mathbf{G}}$$

with:

$\mathbf{U_{max}}$ the maximum leachable quantity in mg/kg

$\mathbf{c_{max}}$ the concentration of the component of interest in the extract in µg/l (corrected for blanc of the extractant).

$\mathbf{V}_b$ is volume of extractant step 1 in L

v_1,$\mathbf{v}_2$ is volume of acid used in step 1 en 2 in L

G is weight sample in kg

7. Determination of the release of contaminants from granular material

7.1 Procedure

Rinse the beaker and outer container (5.1) with nitric acid (4.3) and subsequently several times with water.

Fill the beaker with powder or granular material and saturate the sample with water. Ensure a smooth surface area corresponding with the cross-sectional area of the beaker. Cover this surface with a layer of 2 cm glass beads (3mm). Allow 24 hours of equilibration prior to starting the experiment.

Fill the outer container with demineralized water such that the glass beads are covered with at least 5 cm of water. Maintain a temperature of 20 ± 5 ◦C during the experiment.

Replace the water in the vessel after 0.25, 1, 2, 4, 8, 16, 32, and 64 days (N=8). Note the volume and the time of replacement accurately.

Remark

The eight renewal cycles are chosen such as to coincide as much as possible with calculated time intervals according to:

$t_n = n^2 . t_1$

with:
t_n the renewal time of the n^{th} period
n the period sequence number
t_1 the renewal time of the first period

The proposed renewal time series follows from the formula given above using t_1 = 0.25 days and n= 1, 2, 3, 4, 6, 8, 12 and 16. The larger steps in later periods allows measurement of components featuring a slow release.
If slow leaching components are not of interest, n=16 can be replaced by n=10 (25 days).

Remark

In renewing the solution care must be taken to avoid disturbing the diffusion layer between the glassbeads.

Filter the solution through a membranefilter (5.2) and acidify the sample with nitric acid to pH=2 after measurement of pH, conductivity and, possibly, E_H. Do not acidify part of the sample in case major anions and halogens (sulfate, nitrate, chloride, e.g.) have to be analyzed.

Analyze the acidified samples as soon as possible, but all in one analytical sequence according to standardized procedures.

7.2 Calculations

Emission of component per time interval

Calculate the emission of each component per time interval with the formula:

$$\mathbf{B_i} = \frac{\mathbf{c_i . V_i}}{1000.\mathbf{A}}$$

with:
B_i the emission in period i, expressed in mg/m^2
c_i the concentration of the component in the i-th period, expressed in
µg/l.
V_i the volume of the contactsolution, in Liter
A   the geometrical surface area of the specimen in m^2.

The first and/or second interval can be biased by the use of the glass beads, which form a diffusion barrier.

Measured and calculated cumulative emission

Determine the measured cumulative emission of all N periods according to:

$$\mathbf{B_n}^* = \sum^{j} (\mathbf{B_i}) \quad \text{for j=1 to N}$$

$i=1$

with:
$\mathbf{B_n}^*$ the cumulative emission of the component until period i=j, in mg/m^2
$\mathbf{B_i}$ the emission in period i, in mg/m^2
N the number of periods (fractions), normally 8.

Determine the calculated cumulative emission for all n periods according to

$$\mathbf{B_n} = \mathbf{B_i} \cdot \frac{\sqrt{\mathbf{t_i}}}{\sqrt{\mathbf{t_i}} - \sqrt{\mathbf{t_{i-1}}}} \qquad \text{for } j=1 \text{ to } N$$

$\mathbf{B_n}$ the cumulative emission of the component until period i=j, in mg/m^2.
$\mathbf{t_i}$ the contact time after the period i in seconds
$\mathbf{t_{i-1}}$ the contact time after the period i-1 in seconds

Remark
In the measured cumulative emission ($\mathbf{B_n}^*$) the measured emission from previous periods is summed. This implies that deviations in a given period accumulate in the subsequent periods, which may hamper interpretation. In the calculated cumulative emission ($\mathbf{B_n}$) , the cumulative emission until the i th period is estimated only from the emission in the i th period assuming diffusion control. These values can be used to check, whether the emission is diffusion controlled (see 7.2.3). $\mathbf{B_n}^*$ and $\mathbf{B_n}$ are equal, when the emission is indeed diffusion controlled.

Relation between cumulative emission and time

Plot the logarithm of the calculated cumulative emission ($\mathbf{B_n}$) against the logarithm of the time ($\mathbf{t_i}$) for j=1 to N. Plot in the same figure the logarithm of the measured cumulative emission ($\mathbf{B_n}^*$).
Verify the slope of the log ($\mathbf{B_n}$) - log ($\mathbf{t_i}$) relation for all points and for time intervals omitting the first fractions:

0. fractions 1 to 8
1. fractions 2 to 8
2. fractions 3 to 8

Remark
From the slope of the graph the mechanism of leaching can be derived: Components dissolving from the surface (**slope > ¸ 0.8**), short initial release of surface deposited components (**initial traject slope < ¸ 0.4**) and diffusion controlled release (**slope 0.5**). Only in case the emission proves to be diffusion controlled an effective diffusion coefficient can be calculated ($\mathbf{D_e}$).

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table

Effective diffusion coefficient

When the slope in one of the trajects is 0.5 ± 0.1 , all respective fractions can be used in the calculation of the effective diffusion coefficient.
Calculate the effective diffusion coefficient ($\mathbf{D_e}$) for the component of interest from each period for the emission per period ($\mathbf{B_i}$) (7.2.1) using only those datapoints for which the slope is 0.5 ± 0.1 with a

deviation of less than 50 % and the slope at the end-traject smaller than 0.6.

$$\mathbf{D}_{e,i,x} = \frac{\pi \cdot \mathbf{B}_i^2}{4.(\mathbf{U}_{max}.\mathbf{d})^2.\ (\sqrt{\mathbf{t}_i}-\sqrt{\mathbf{t}_{i-1}})^2}$$

with:

$\mathbf{D}_{e,i,x}$ the effective diffusion coefficient of component x calculated from the emission in period i, in m^2/s

$\mathbf{B}_i$ the emission in period i in mg/m^2

$\mathbf{d}$ the bulk density of the product, in kg/m^3

$\mathbf{U}_{max}$ the maximum leachable quantity in mg/kg

$\mathbf{t}_i$ the contact-time until period i in s

$\mathbf{t}_{i-1}$ the contact-time until period i-1 in s

Express the effective diffusion coefficient in the negative logarithm:

$$p\mathbf{D}_{e,i,x} = -\log(\mathbf{D}_{e,i,x})$$

Calculate the average effective diffusion coefficient for component x from:

$$\mathbf{D}_{e,x} = \frac{\sum_{i=n_1}^{n_2} \mathbf{D}_{e,i,x}}{n_2-n_1+1}$$

with:

$\mathbf{D}_{e,x}$ the average effective diffusion coefficient of component x, in m^2/s

n_1,n_2 the first and the last fraction number of the sampling intervals in The traject with a slope 0.5 ± 0.1.

Determine the standard deviation and report the number of fractions n_2-n_1+1.

Overall judgement of diffusion coefficients

$p\mathbf{D}_e > 12$: component with very low mobility

$p\mathbf{D}_e$ 10.5 - 12 : component with intermediate mobility

$p\mathbf{D}_e$ 9 - 10.5 : component with high mobility

Comparison of the mobility of a specimen and its free mobility in water

Calculate the tortuosity of the product with the formula:

$$\mathbf{T} = \frac{\mathbf{D}_{Na}}{}$$

$\mathbf{D_{e,Na}}$

with:

T the tortuosity of the product

$\mathbf{D_{Na}}$ the diffusion coefficient of Na in water ($pD_{Na} = 8.88$ at 22 ◦C) in m^2/s

$\mathbf{D_{e,Na}}$ the effective diffusion coefficient of Na in the product in m^2/s

Remark

The tortuosity is a measure for the physical retardation in the granular matrix and reflects the extended path length a diffusing ion has to travel in a porous matrix. This property is independent of the type of ion. For the calculation of the tortuosity, an ion should be chosen, which does not interact with the matrix. In many cases, sodium is an appropriate choice.

This value is biased by the layer of glass beads and has to be corrected for T= ...

Calculate the chemical retardation factor (**R**) for the component of interest from:

$$\mathbf{R} = \frac{\mathbf{D_x}}{\mathbf{D_{e,x}} \cdot \mathbf{T}}$$

with:

R the chemical retardation factor (-)

$\mathbf{D_x}$ the diffusion coefficient for component x in water, in m^2/s

$\mathbf{D_{e,x}}$ the effective diffusion coefficient for component x in the product, in m^2/s

T the tortuosity of the product (-)

Remark

The retardation factor is a measure for the chemical retardation of a component in the product. For a component, which does not interact with the matrix this value is 1.

Calculations of derived properties

Determination of the emission

Calculate the emission ($\mathbf{B_{2,1}}$) from time $\mathbf{t_1}$ to $\mathbf{t_2}$ with the formula:

$$\mathbf{B_{2,1}} = \mathbf{d}.\ \mathbf{U_{max}}.\sqrt{(4\mathbf{D_e}/\pi)}\ (\sqrt{\mathbf{t_2}} - \sqrt{\mathbf{t_1}})$$

with:

$\mathbf{B_{2,1}}$ the emission between times $\mathbf{t_1}$ and $\mathbf{t_2}$, in mg/m^2

$\mathbf{D_e}$ the effective diffusion coefficient, in m^2/s

$\mathbf{U_{max}}$ the maximum leachable quantity expressed in mg/kg

$\mathbf{t_1,t_2}$ start and end of period considered, in s

d bulk density of the product kg/m^3

Calculation of the leached quantity

Calculate the quantity of a component leached at time **t** from:

$$\mathbf{U_t} = \frac{\mathbf{A} \cdot \mathbf{d} \cdot \mathbf{U_{max}} \cdot \sqrt{(4\mathbf{D_e}.\mathbf{t}/\pi)}}{\mathbf{m}}$$

with:
U_t the leached quantity, in mg/kg
t the leaching period, in seconds (only wet periods)
A the surface area of the product, in m^2
m the weight of the product, in kg
D_e the effective diffusion coefficient, in m^2/s
U_{max} the maximum leachable quantity, in mg/kg
d the bulk density of the product, in kg/m^3

The percentage of the leachable fraction that is leached in a given period can be obtained from:

$$\mathbf{U_p} = \mathbf{U_t} \cdot \frac{100}{\mathbf{U_{max}}}$$

with:
U_p the percentage leached in period t, expressed in % based on the leachable quantity.

Calculation of the average concentration

Calculate the average concentration in the contact solution in the time period $t_1 - t_2$ from:

$$\mathbf{c_{2,1}} = \frac{\mathbf{B_{2,1}} \cdot \mathbf{A} \cdot 1000}{\mathbf{V_{tot}}}$$

with:
$c_{2,1}$ the average concentration in the contact solution from time t_1 to t_2, in µg/l
$B_{2,1}$ the emission in time interval t_1 to t_2, in mg/m^2
A the surface area of the product, in m^2
V_{tot} the total volume of the contact solution, in liter.

APPENDIX

Choice of pH

The maximum leachability test is a estimate of the fraction of the elements that can be leached, when the material is completely deteriorated. This is assessed by testing at high dilution (minimal solubility constraints), fine grained material (limitation of solid phase diffusion) and a maximum pH of 4, which is considered the maximal pH in normal environments, where application on/in soil or disposal is considered.

The pH in the monolith test is not controlled as the material is allowed to dictate the pH conditions in the surrounding extractant solution. The main criterion for the proper performance of the test is to maintain the maximum gradient between the pore water composition in the interior of the specimen and the external solution. In practice, protective coatings may form on/in the specimen and diffusion may slow down in stagnant situations. These aspects have to be dealt with in the interpretation / translation of the laboratory test results to actual field situations.

The uptake of CO_2 from the air is kept limited to avoid a substantial precipitation of $CaCO_3$ in the tank and a subsequent decrease in pH associated with it. It may hamper the interpretation of the results. At the same time the uptake of oxygen is minimized to avoid oxidation of the material during the diffusion experiment.