

ICS 13.030.01

English Version

Characterization of waste - Leaching behaviour tests - Influence of pH on leaching with continuous pH-control

Caractérisation des déchets - Essais de comportement à la lixiviation - Influence du pH sur la lixiviation avec contrôle continu du pH

Charakterisierung von Abfällen - Untersuchung des Auslaugungsverhaltens - Einfluss des pH-Wertes auf die Auslaugung bei kontinuierlicher pH-Wert-Kontrolle

This Technical Specification (CEN/TS) was approved by CEN on 9 October 2006 for provisional application.

The period of validity of this CEN/TS is limited initially to three years. After two years the members of CEN will be requested to submit their comments, particularly on the question whether the CEN/TS can be converted into a European Standard.

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EUROPEAN COMMITTEE FOR STANDARDIZATION
COMITÉ EUROPÉEN DE NORMALISATION
EUROPÄISCHES KOMITEE FÜR NORMUNG

Management Centre: rue de Stassart, 36 B-1050 Brussels

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Foreword

This document (CEN/TS 14997:2006) has been prepared by Technical Committee CEN/TC 292 "Characterization of waste", the secretariat of which is held by NEN.

This document has been prepared under a mandate given to CEN by the European Commission and the European Free Trade Association, and supports essential requirements of EU Directive(s).

For relationship with EU Directive(s), see informative Annex ZA, B, C or D, which is an integral part of this document.

According to the CEN/CENELEC Internal Regulations, the national standards organizations of the following countries are bound to announce this CEN Technical Specification: Austria, Belgium, Cyprus, Czech Republic, Denmark, Estonia, Finland, France, Germany, Greece, Hungary, Iceland, Ireland, Italy, Latvia, Lithuania, Luxembourg, Malta, Netherlands, Norway, Poland, Portugal, Romania, Slovakia, Slovenia, Spain, Sweden, Switzerland and United Kingdom.

Introduction

This document has been developed primarily to support the requirements for leaching behaviour testing within EU and EFTA countries. Tests to characterize the behaviour of waste materials can generally be divided into three categories. The relationship between these tests is summarized below:

- a) "Basic characterization" tests are used to obtain information on the short and long term leaching behaviour and characteristic properties of waste materials. Liquid/solid (*L/S*) ratios, leachant composition, factors controlling leachability such as pH, redox potential, complexing capacity, ageing of waste and physical parameters are addressed in these tests.
- b) "Compliance" tests are used to determine whether the waste complies with a specific behaviour or with specific reference values. The tests focus on key variables and leaching behaviour previously identified by basic characterization tests.
- c) "On-site verification" tests are used as a rapid check to confirm that the waste is the same as that which has been subjected to the compliance test(s). On-site verification tests are not necessarily leaching tests.

The test procedure specified in this document belongs to category (a): basic characterization tests.

In the test described in this standard an equilibrium condition is established as a result of continuous adjustment of pH. Size reduction is performed to accelerate reaching of equilibrium condition.

This test is different from the "Influence of pH on leaching with initial acid/base addition " (see CEN/TS 14429) in which the pH is controlled by addition of pre-determined amounts of acid or base to reach desired end pH values. The test is aiming at approaching equilibrium at the end of the procedure.

NOTE In Annex B specific uses of both the pH dependence test with initial acid/ base addition and the pH dependence test with continuous pH control are indicated.

1 Scope

This document specifies a test method for the determination of the influence of pH on the leachability of inorganic constituents from a waste material. Equilibrium condition as defined in the document is established by continuous adjustment of the pH by addition of acid or base to reach desired pH values. This test method produces eluates, which are subsequently characterized physically and chemically.

This document is a parameter specific test as specified in EN 12920. The application of this test method alone is not sufficient for the determination of the detailed leaching behaviour of a waste under specified conditions.

NOTE This generally requires the application of several test methods, behavioural modelling and model validation as specified in EN 12920.

2 Normative references

The following referenced documents are indispensable for the application of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

EN 12506, *Characterization of waste – Analysis of eluates - Determination of pH, As, Ba, Cd, Cl, Co, Cr, Cr VI, Cu, Mo, Ni, NO₂⁻, Pb, total S, SO₄²⁻, V and Zn*

EN 13370, *Characterization of waste – Analysis of eluates – Determination of Ammonium-N, AOX, conductivity, Hg, phenol index, TOC, CN_{easily liberable}, F*

EN 14346, *Characterization of waste – Calculation of dry matter by determination of dry residue or water content*

EN 14899, *Characterisation of waste – Sampling of waste materials – Framework for the preparation and application of a Sampling Plan*

EN 15002, *Characterization of waste – Preparation of test portions from the laboratory sample*

EN ISO 5667-3, *Water quality – Sampling – Part 3: Guidance on the preservation and handling of water samples (ISO 5667-3:2003)*

EN ISO 3696:1995 *Water for analytical laboratory use – Specification and test methods (ISO 3696:1987)*

3 Terms and definitions

For the purposes of this document, the following terms and definitions apply.

3.1

dry residue of the sample

W_{dr}

remaining mass fraction of a sample after a drying process at 105 °C

[EN 14346]

3.2

eluate

solution obtained by a laboratory leaching test

3.3 equilibrium condition
condition achieved when the acid or base consumption during a checking period at the last 4 h of the test is less than 2 % of the total acid or base consumption during the entire test

3.4 laboratory sample
sample or subsample(s) sent to or received by the laboratory

[IUPAC, 1997] [15]

3.5 liquid to solid-ratio
L/S
ratio between the amount of liquid (L) and of solid (S) in the test

NOTE *L/S* is expressed in l/kg dry matter.

3.6 leachant
liquid to be mixed with the test portion in the leaching procedure

3.7 suspension
mixture of leachant and test portion

3.8 test portion
amount or volume of the test sample taken for analysis, usually of known weight or volume

[IUPAC, 1997]

3.9 test sample
sample, prepared from the laboratory sample, from which test portions are removed for testing or for analysis

[IUPAC, 1997]

4 Symbols and abbreviations

ANC	acid neutralization capacity
BNC	base neutralization capacity
DOC	dissolved organic carbon
<i>L/S</i>	liquid to solid ratio
M_d	dried mass of the test portion
m_d	mass after drying
M_w	un-dried mass of the test portion
m_r	mass before drying
t_0	time at the start of the leaching test

$V_{A/B}$	volume of acid or base used in leachant
V_{demin}	volume of demineralised water used in leachant
w_{dr}	dry residue of the sample

5 Principle

Separate test portions are leached at a fixed L/S ratio with leachants where the pH is adjusted and controlled at pre-set pH-values. At least 8 final pH values are required, covering at the minimum the range pH 4 - pH 12 (both included i.e. the lowest value ≤ 4 and the highest value ≥ 12). The amounts of acid or base needed to cover the pH range can be derived from the results of a preliminary titration, from available experimental data on the material to be tested or from an arbitrary division of the predetermined maximum consumption of acid and base. The tests are carried out at a fixed contact time at the end of which equilibrium condition can be assumed to be reached for most constituents in most waste materials to be characterized. The equilibrium condition as defined in the standard is verified at the end of the leaching procedure.

The results are expressed in mg/l of constituents for each final pH value. For each final pH value also the quantity of acid that is added is expressed in mol H^+ /kg dry matter and the quantity of base that is added is expressed as mol OH^- /kg dry matter (-mol H^+ /kg dry matter).

NOTE 1 Other expression of results is possible (including mg leached /kg dry matter). Since this test is aiming at equilibrium condition i.e. solubility controlled, the results alone cannot be used to quantify the soluble mass fraction.

The ANC or BNC of the waste is also determined. The ANC or BNC is defined as the amount of acid or base (+/- mol H^+ /kg dry matter) needed to reach a given user-defined end-pH. It is graphically [2] or numerically derived from a curve representing each end-pH obtained as a function of the amounts of acid or base added

NOTE 2 The pH range covered by the test may be restricted to a pH range relevant for the specific material and the considered problem (see 8.2).

6 Reagents and laboratory devices

6.1 Reagents

6.1.1 Distilled water, demineralised water or water of equivalent purity with a conductivity < 0,1 mS/m [ISO 3696].

6.1.2 Nitric acid (pro analysis), 0,1 mol/l to 5 mol/l.

6.1.3 Sodium hydroxide, NaOH, 0,1 mol/l to 5 mol/l.

NOTE NaOH is unstable due to possible uptake of CO_2 . Therefore it is recommended to prepare a fresh solution.

6.2 Laboratory devices

6.2.1 Analytical balance (accurate to 0,1 g).

6.2.2 Bottles or vessels equipped with a lid.

Use bottles or vessels (250 ml for the test portions of 15 g of dry mass, 500 ml for test portions of 30 g dry mass and 1 l for test portions of 60 g dry mass) made of polypropylene (PP), polyethylene (PE) or PTFE. In the bottles or the lid of the vessels an opening must be present for the pH-electrodes and for input of acid and/or base and a small outlet for gas. The bottles have to be as close as possible to prevent CO_2 uptake.

NOTE At high pH values it is recommended to perform the test under nitrogen to prevent CO_2 intake .

6.2.3 Crushing equipment, e.g. a jaw crusher.

NOTE Crushing is prescribed in 7 to avoid unnecessary grinding to very fine particle sizes, such as takes place in a rotary swing mill, ball mill or similar device.

6.2.4 Stirring device.

The parts in contact with sample and eluate shall be made of materials not affecting the outcome of the test like glass, PTFE.

6.2.5 Membrane filters for the filtration device.

Use filters or a filter device, fabricated from inert material, which is compatible with the waste and has a pore size of 0,45 µm. Filter must be pre-washed with demineralized water or similarly clean in order to remove DOC.

6.2.6 pH meter.

Use a pH meter with a measurement accuracy of at least $\pm 0,05$ pH units.

NOTE At high pH values the use of specific electrodes is recommended.

6.2.7 Sample splitters for a minimum test portion size equivalent of 15 g of dry mass.

6.2.8 Sieving equipment with sieve of 1 mm nominal screen sizes.

NOTE Due to crushing and sieving, contamination of the sample may occur to an extent, which may affect the leached amounts of some constituents of concern, e.g. Co and W from tungsten carbide crushing equipment or Cr, Ni, Mo and V from stainless steel equipment.

6.2.9 Device for continuous pH control with a precision of 0,2 pH units through acid/base addition.

NOTE The pH-control of the suspension is achieved by continuous addition of acid/base by measuring the pH of the solution in case of a deviation from the desired pH a continuous dosing of acid or base is required.

6.2.10 Vacuum filtration device or pressure filtration device.

7 Sampling

7.1 Laboratory sample

Perform sampling in accordance with EN 14899 in order to obtain a representative laboratory sample.

The laboratory sample shall consist of a mass equivalent of at least 1 kg of dry mass.

7.2 Test sample

The tests shall be made on material with a grain size of 95 % less than 1 mm. In order to ensure that the test sample consists in 95 % mass of particles less than 1 mm in diameter, it shall be sieved, using the sieving equipment, to separate the oversized particles. If oversized material exceeds 5 % (mass) the entire oversized fraction shall be crushed. Any non-crushable material (e.g. metallic parts such as nuts, bolts, scrap) shall be separated from the oversized fraction and the weight and nature of the non-crushable material shall be recorded. Crushed and uncrushed material shall be mixed to constitute the test sample.

Moist material that is not possible to sieve needs to be dried prior to sieving and/or crushing. The drying temperature shall not exceed 40 °C.

NOTE 1 The crushed material can change upon storage due to ageing of fresh surfaces. It is therefore recommended to test the material as soon as possible after crushing.

NOTE 2 It is recommended that materials with a high natural pH should be crushed under nitrogen in order to avoid contact with air leading to carbonation.

7.3 Determination of dry residue of the sample

The whole test sample, complying with the size criteria in 7.2 shall not be further dried. The dry residue (w_{dr}) of the test sample shall be determined on a separate test portion.

The dry residue of the sample shall be determined at $105\text{ °C} \pm 5\text{ °C}$ according to EN 14346. The dry residue expressed as a percentage of the mass fraction is calculated as follows:

$$w_{dr} = 100 \times \frac{m_d}{m_r} \quad (1)$$

where

w_{dr} is the dry residue of the sample expressed as percentage (%);

m_d is the mass after drying expressed in grams (g);

m_r is the mass before drying expressed in grams (g).

7.4 Test portion

Prepare at least 8 test portions by the use of a sample splitter or by coning and quartering in accordance with EN 15002. Based on sample heterogeneity and eluate volume requirement for analysis, test portion size shall be either $M_d = 15\text{ g}$, 30 g or 60 g (with a tolerance of $\pm 10\%$).

Calculate the undried mass of the test portion M_w in grams to be used for the test in accordance with Equation 2:

$$M_w = \frac{M_d}{w_{dr}} \times 100 \quad (2)$$

where

M_w is the total mass of the test portion expressed in grams (g);

M_d is the dry mass of the test portion expressed in grams (g).

8 Test procedure

8.1 Contact time

The leaching procedure consists of two defined stages:

- Period A (equilibration period) from t_0 up to $t_0 + 44\text{ h}$ for equilibration at continuously controlled pH;
- Period B (verification period) from $t_{0+44\text{ h}}$ up to $t_0 + 48\text{ h}$ for verification of equilibrium condition at continuously controlled pH.

The amount of acid or base added is recorded after each of these periods.

The pH in the liquid is recorded after each of these periods.

The total contact period (A+B) is 48 h.

8.2 pH range

The test shall cover the range pH 4 to pH 12 (both included i.e. the lowest value ≤ 4 and the highest value ≥ 12) with at least 8 pH values tested including the natural pH (without acid or base addition). The maximum difference between two consecutive pH values shall not exceed 1,5 pH units.

NOTE The pH range covered by the test may be restricted to a pH range relevant for the specific material and the considered problem. The pH range to be covered may depend on the specific properties of the waste material, the available information on this material and the questions to be answered by performing the test. The number of pH levels considered can be reduced, correspondingly.

8.3 Leaching test

8.3.1 General

The following procedure applies for each of the chosen pH values to be tested. Testing at natural pH is described in 8.4.

8.3.2 Preparation of leachant

Identify the acid or base consumption for reaching the relevant pH values as A (mol H⁺/kg dry matter) or B (mol OH⁻/kg dry matter).

NOTE 1 The acid or base consumption for the considered pH values may be derived from available information, from the preliminary procedures in Annex C or from information in Annex D.

The volume (V) of liquid consists of the water content of the test sample and the amount of leachant (V_L). Calculate the volume (V) of liquid to establish $L/S = (10 \pm 0.2)$ l/kg for the actual size of test portion M_d (see 7.4) including the volume of acid or base in accordance with Equation 3.

$$V = 10 \times M_d \quad (3)$$

where

V is the total volume of liquid in the test expressed in millilitres (ml);

M_d is the dry mass of the test portion expressed in grams (g) (see 7.4).

NOTE 2 In relation to L/S -ratio, V in this equation is equivalent with the "L" and M_d is equivalent to the "S".

Calculate the amount of leachant (V_L) to be added to the actual size of test portion and compensate for the moisture content in the test portion, in accordance with Equation 4:

$$V_L = V - \left(\frac{100}{w_{dr}} - 1 \right) \times M_d \quad (4)$$

where

V_L is the volume of added leachant expressed in millilitres (ml).

V is the total volume of liquid in the test expressed in millilitres (ml);

w_{dr} is the dry residue of the waste expressed as percentage of total weight (%) (see 7.3);

M_d is the dry mass of the test portion expressed in grams (g) (see 7.4).

The volume of acid or base added shall not exceed a volume corresponding to M_d 1 ($V_{L/S 1}$). This volume is calculated in accordance with Equation 5:

$$V_{L/S 1} = 1 \times M_d \quad (5)$$

where

$V_{L/S 1}$ is the volume of liquid corresponding to L/S 1 in the test expressed in millilitres(ml);

M_d is the dry mass of the test portion expressed in grams (g) (see 7.4)

Calculate the minimum concentration of acid (C_A) or base (C_B) to be used as follows, with Equation 6 or 7.

$$C_A = \frac{A \times M_d}{V_A} \quad (6)$$

or

$$C_B = \frac{-B \times M_d}{V_B} \quad (7)$$

where

V_A is the volume of acid needed expressed in millilitres (ml);

V_B is the volume of base needed expressed in millilitres (ml);

A is the acid consumption for the pH (mol H^+ /kg dry matter);

B is the base consumption for the pH (mol OH^- /kg dry matter, expressed as $-mol H^+$ /kg dry matter);

C_A is the minimum concentration of the acid expressed in mole per litre (mol/l) (see 6.1.2);

C_B is the minimum concentration of the base expressed in mole per litre (mol/l) (see 6.1.4).

NOTE 3 The concentration of the acid or base can be estimated from a preliminary titration (Annex C) or previous results from similar materials (Annex D)

Choose a convenient concentration of the acid (c_A) or base (c_B), which is stronger than the calculated minimum concentration.

Calculate the volume V_{demin} of demineralised water (see 6.1.1) to be added initially to the test portion as follows:

$$V_{demin} = V_L - \frac{A \times M_d}{c_A} \quad (8)$$

or

$$V_{demin} = V_L - \frac{-B \times M_d}{c_B} \quad (9)$$

where

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V_{demin} is the volume of demineralised water used expressed in millilitres (ml);

V_L is the volume of prepared leachant expressed in millilitres (ml);

A is the acid consumption for the pH (mol H^+ /kg dry matter);

B is the base consumption for the pH (mol OH^- /kg dry matter, expressed as $-\text{mol H}^+$ /kg dry matter);

c_A is the chosen concentration of the acid expressed in mole per litre (mol/l) (see 6.1.2);

c_B is the chosen concentration of the base expressed in mole per litre (mol/l) (see 6.1.4);

M_d is the dry mass of the test portion expressed in grams (g) (see 7.4).

Prepare the pH control device (see 6.2.9) with the chosen concentration of acid or base.

8.3.3 Leaching procedure

Carry out the test at a temperature of $20\text{ }^\circ\text{C} \pm 5\text{ }^\circ\text{C}$.

Select the appropriate bottle size according to the test portion size. For $M_d = 15\text{ g}$, 30 g and 60 g , this means respectively bottle sizes of 250 ml, 500 ml and 1000 ml.

Clean the bottle before use by filling it with 1 mol/l nitric acid (see 6.1.3), leaving it for at least 24 h and then flushing it out with demineralised water (see 6.1.1).

Place one of the test portions in the rinsed bottle.

Add the volume of demineralised water V_{demin} .

Connect the bottle to the pH control device (6.2.9) and insert the pH electrode.

The suspension is stirred for $15\text{ min} \pm 5\text{ min}$ before acid or base addition and the starting pH is recorded.

To ensure proper suspension of waste particles mixing of the solution is applied throughout the procedure.

Start pH control at the preset pH value with a tolerance of $\pm 0,2$ pH unit at t_0 and continue until $t = t_0 + 48\text{h}$.

Measure and record the pH at $t_{0+4\text{h}}$.

NOTE 1 The pH measurement may be done over a 5 min interval to avoid incidental deviation due measurement shortly after acid or base addition. If the added acid or base disturbs the pH-measurements the acid or base addition can be stopped during the measurement of the pH.

The pH at $t_{0+4\text{h}}$ shall not deviate more than 0,3 pH unit from the preset pH value. If this requirement is not met, this leaching procedure shall be aborted and restarted with another acid or base strength.

Measure and record the acid or base consumption and the pH at $t_{0+44\text{h}}$ and $t_{0+48\text{h}}$.

The pH value measured before filtration at $t_{0+48\text{h}}$ will be the one associated to the analysis of the eluate.

NOTE 2 pH is measured directly in the bottle at $t_{0+48\text{h}}$ since filtration may change pH in the eluate.

The test aims at a final L/S ratio of 10 after acid or base addition. The ultimate L/S shall not deviate more than 10 % from $L/S = 10\text{ l/kg}$. If the L/S exceeds 11 because of high acid or base consumption of the material at the specific pH value, this condition shall be repeated using a stronger acid or base for pH adjustment.

NOTE 3 For some waste materials gas formation may occur (e.g. CO₂, H₂, etc.). Pay attention when opening the bottles to release the pressure (preferably in a fume hood).

Report and check the acid or base consumption up to t_{0+44h} and between t_{0+44h} and t_{0+48h} .

Report the pH deviation at t_{0+4h} , t_{0+44h} and t_{0+48h} from the preset value. The acid or base addition between t_{0+44h} and t_{0+48h} shall not exceed 2 % of the total acid or base consumption (mol/kg) between t_0 and t_{0+48h} . This is the limit for achieving equilibrium condition (see 3.3). A special note shall be made in the report if this requirement is not met.

Allow the suspended solids to settle for 15 min ± 5 min.

Rinse the part of filtration device (see 6.2.10), which is in contact with the eluate with nitric acid (see 6.1.3), and flush with ultra pure water (see 6.1.1). before any use.

Filter the suspension through a 0,45 µm membrane filter (see 6.2.5) using the filtration device (see 6.2.10).

Proceed immediately with the eluate treatment as specified in Clause 9.

If too many experimental points deviate (more than 3 amongst 8) during the checking period, the conclusion is that this test is not applicable to this material.

NOTE 4 When equilibrium condition is strictly compulsory for specific use but not fulfilled in the test, it is possible to continue the test to maximum 7 days for all the 8 experimental points in order to avoid association of results at 48 h with those at longer leaching time. In this case, the checking period relates to the last 24 h (between 6th and 7th day). The experimental point(s), which do not conform to these new conditions, will not be exploited and this fact shall be mentioned in the report. This specific procedure is not part of this document.

8.4 Natural pH

Repeat 8.3 for a test portion but without acid or base addition.

Measure pH at t_{0+4h} , t_{0+44h} and t_{0+48h} as in 8.3.

The pH value measured before filtration at t_{0+48h} will be the one associated to the analysis of the eluate.

NOTE A very low conductivity in the eluate at natural pH may increase generation of colloids, which may clog filters and increase analysed concentrations. To avoid this it is recommended to add, especially for waste being soil and soil like material, 0,001 M CaCl₂ in the leachant at a concentration comparable to the concentration of acid or base in the closest pH values tested. The use of CaCl₂ (amount and concentration) should be reported.

9 Eluate treatment, storage and analysis

Divide the eluate into an appropriate number of sub-samples for different chemical analysis and store them in accordance with the requirements in EN ISO 5667-3.

Determine the concentrations of constituents of interest using the standardized methods of eluate analysis according to EN 12506 and EN 13370

10 Blank tests

The contribution of the leachant, devices and membrane filters to the result shall be determined by running a blank test periodically in order to check how the whole procedure is performed.

Obtain three different blank tests by carrying out the procedure according to 8.3 and 9 without the solid material with the addition of:

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- a) both the maximum amounts of acid and base to the leachant of similar volume as used in the tests;
- b) acid to obtain pH 4;
- c) base to obtain pH 12.

The eluates of the blank tests shall fulfill the minimum requirement that the concentration of each considered element shall be less than 10 % of the concentration in the eluate. If the concentration of an element is below the detection limit for the analytical method applied, the blank test requirements will be fulfilled if the blank test is below the same limit of detection. If this requirement is not fulfilled it is necessary to reduce contamination.

Blank test results must be available upon request.

Do not subtract the results of the blank test determination from the test results.

NOTE The test is aiming at equilibrium condition in which the contribution from the equipment is included. Subtraction of the blank test results will therefore lead to an incorrect equilibrium concentration.

11 Performance characteristics

The performance of the test regarding repeatability and reproducibility is dependent on the tested waste material and also on the testing conditions. When the document was adopted by CEN, the test specified in this document was not validated and no data were available on robustness, repeatability and reproducibility.

12 Test report

In order to conform to this document the test report shall contain at least the following data:

- a) reference to the present document;
- b) date of receipt of the laboratory sample;
- c) sampling report according to paragraph 7.1;
- d) date of the test (beginning and end);
- e) a complete identification of the laboratory sample (including dry residue);
- f) pre-treatment (e.g. method of size-reduction, drying, sub-division) and storage conditions;
- g) temperature range during the performance of the test;
- h) selected pH interval and number of test portions tested (N) within this interval;
- i) deviations from the preset pH values;
- j) dry mass of the test portion expressed in grams (g);
- k) added acid volumes (ml) and concentrations (mol/l), base volumes (ml) and concentrations (mol/l) and the corresponding amounts of H_3O^+ or OH^- (mol/kg dry matter);
- l) leachant volume (ml) and the resulting *L/S* (l/kg);
- m) pH values at $t_{0+4\text{h}}$, $t_{0+44\text{h}}$ and $t_{0+48\text{h}}$;
- n) concentrations of each analyzed substance (mg/l);

- o) any deviation from the test method and the reason of this deviation together with all circumstances that have influenced the results;
- p) record the data for the test results on a data sheet.

NOTE An example of a data sheet is given in Table A.1.

Annex A (informative)

Example of a data sheet

Table A.1 — An example of a data sheet for the recording of test results

	Unit	Bottle no.							
		1	2	3	4	5	6	7	8
Dry mass of the test portion	g								
Acid concentration	M								
Acid volume t_{0+44h}	ml								
Acid volume t_{0+48h}	ml								
Base concentration	M								
Base volume t_{0+44h}	ml								
Base volume t_{0+48h}	ml								
H_3O^+ or OH^- $t_{0+44 h}$	mol/kg DM								
H_3O^+ or OH^- $t_{0+48 h}$	mol/kg DM								
Total leachant volume (V)	ml								
Resulting L/S	l/kg								
pH at t_{0+44h}									
pH at t_{0+48h}									
Constituent 1 :	mg/l								
Constituent 2 :	mg/l								
Constituent 3 :	mg/l								

etc

Annex B (informative)

Operation and uses of the test: influence of pH on the leaching behaviour

B.1 Clarification of the two modes of operation of the test: influence of pH on the leaching behaviour

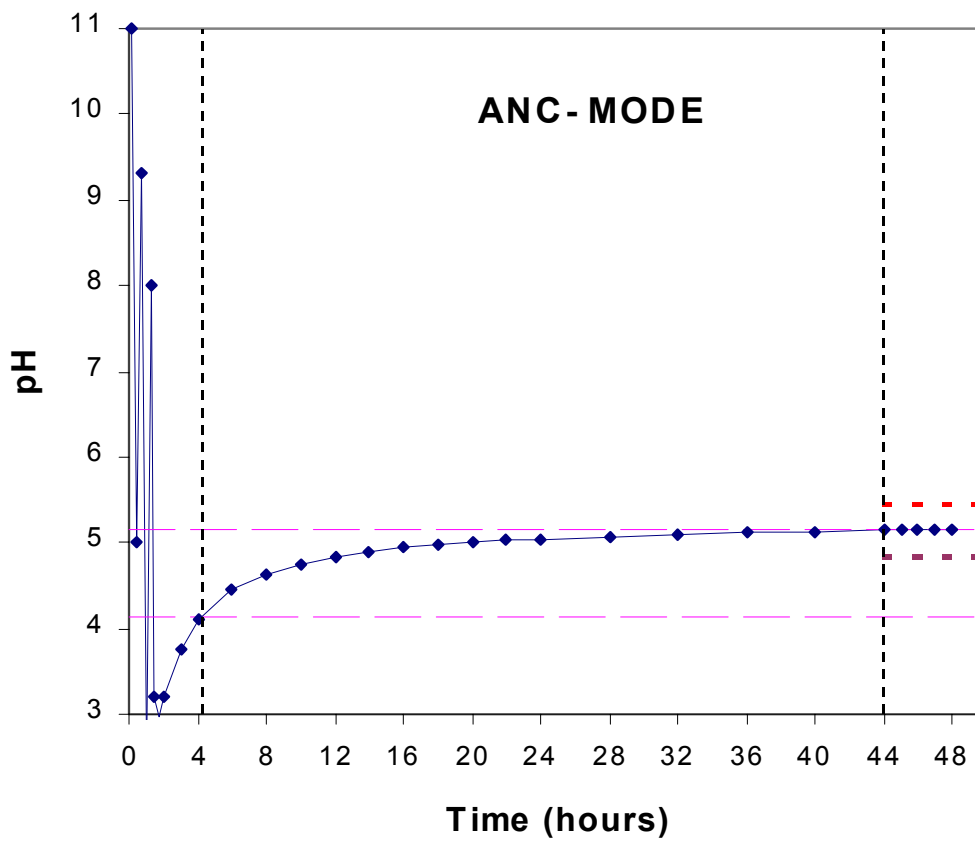
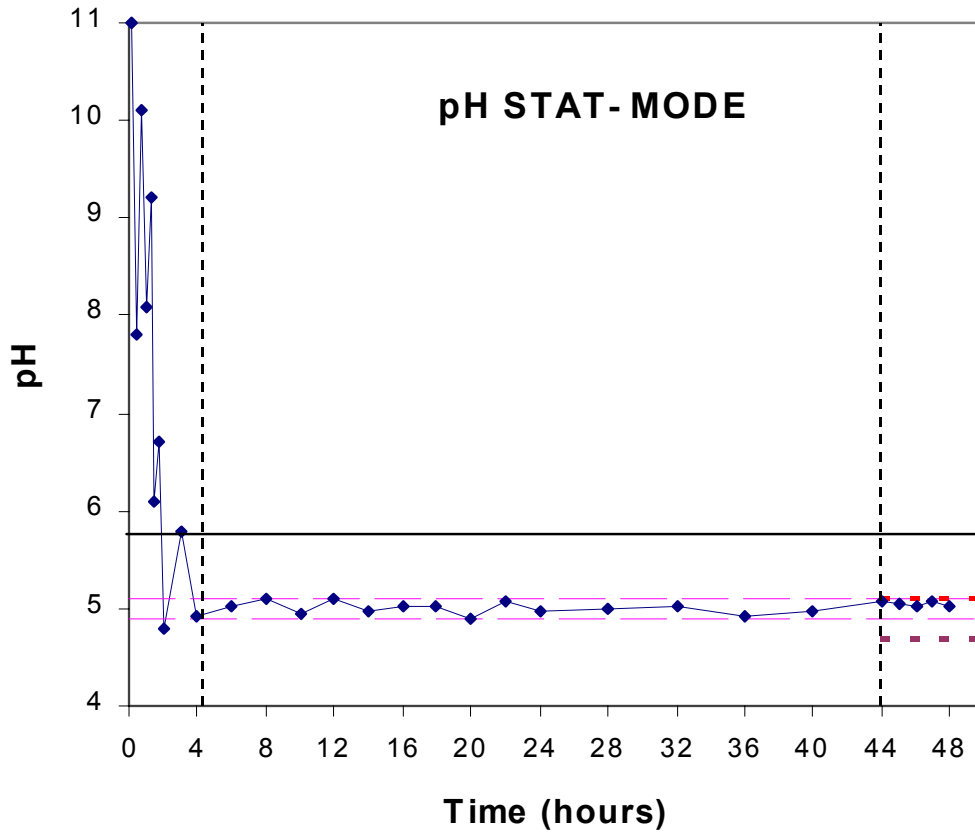
Two standards are aiming at determining the influence of pH on the release of the inorganic constituents from a waste material.

In the test described in CEN/TS 14429, an equilibrium condition is established at different pH-values as a result of the reaction between pre-selected amounts of acid or base and test portions of the waste material. Size reduction is performed to accelerate reaching of equilibrium condition. In the test described in this document (characterization of waste – leaching behaviour test – Influence of pH on leaching with continuous pH control) an equilibrium condition is established as a result of continuous adjustment of pH.

Figure B.1 illustrates the typical pH variations of these two modes.

In addition to the pH influence on leaching, the test addressing the influence of pH on leaching by continuous pH control is suitable for solubility control at a precisely specified pH. The test addressing the influence of pH on leaching by continuous pH control can be particularly suitable when materials are tested which have a very low buffer capacity or in the case of measurement of pH influence on leaching at a pH where a small pH change leads to strong change in release.

Figure B.1 — Typical pH variations during the two modes of the tests for determining the influence of pH on the leaching behaviour of an alkaline material at a final pH around 5.



B.2 Expression of results

Three graphical presentations of the results can be obtained. They provide a visual representation of the test results as a trend (see B.3):

- 1) pH at t_{0+48} h (see 8.3.2) versus the amounts of acid/base added (ANC and BNC curve) expressed in mol H^+/OH^- added per kg of dry matter;
- 2) concentration of each analysed constituent in eluates in log scale in mg/l versus pH at t_{0+48h} ;
- 3) concentration of each analysed constituent in eluates in linear scale in mg/l versus the amounts of acid or base added (mmol of H^+/OH^- /kg dry matter).

NOTE In the third visual representation, pH at t_{0+48} h can also be added as a second ordinate.

In case when the leached amounts (U_x) (mg/kg dry waste material) are needed, they can be directly calculated by multiplying the concentrations in mg/l by the L/S value (normally $L/S = 10$ l/kg dry material).

B.3 Scope and limits of the application field of the test

This test provides information on the influence of pH on leaching under the experimental conditions specified in this standard. It does not directly take the effects of other parameters such as influence of other acids and bases than the nitric acid/sodium hydroxide used in the test, dissolved organic carbon, complexation, redox conditions into account.

This test method is a parameter specific test as specified in EN 12920. The application of this test method alone is not sufficient for the determination of the detailed leaching behaviour of a waste under specific conditions.

NOTE This generally requires the application of several test methods, behavioural modelling and model validation as specified in the EN.

Therefore, provided that the nitric acid/sodium hydroxide used in the test as well as the other experimental conditions are relevant for the considered scenario, this test is useful to:

- qualify and quantify the material resistance to acid-basic attack through the concentration measured, as a function of pH and the acid/base amount needed to reach a given final pH;
- identify the chemical behaviour trends and the availability levels of components at different pH values under the experimental conditions specified in this test. These values can be used as input to modelling of chemical behaviour using geochemical speciation models (e.g. MINTEQA2, GEOCHEM WORKBENCH, PHREEQC, ECOSAT, ORCHESTRA, CHESS, SPEC, etc.). In many cases, it also provides insight in the relevance of particular solubility controls and release mechanisms (e.g. formulate hypothesis on the dissolution mechanisms);
- provide a basis of reference for different leaching tests, as it has been shown that pH is one of the major controlling factors distinguishing tests from one another;
- compare leaching behaviour, with respect to pH, of the same parameter from different wastes or different material classes to be able to demonstrate similarities in solubility controlling conditions irrespective of material matrix;
- provide data to feed dynamic behavioural models, for instance under the following relationship: solubilisation = f (pH or meq H^+/g) in the physico-chemical context linked with the presence of the other compounds in the material. This is not always possible with available literature data.

On the contrary, this test is not meant for:

- quantifying a maximum removable fraction as the concentrations obtained correspond to steady state situation close to chemical equilibrium. For example, the values obtained for the lowest pH and at high pH can only be considered as approaching the maximum removable fraction of respectively metals and oxyanions;
- simulating actual situations in specific scenarios, as in addition at least information on low L/S will be needed.

B.4 Example: Identification of the sensitivity of leaching to pH over the environmentally relevant pH range

The test provides insight in the sensitivity of leaching of components from a specific material to pH (see Figure B.2). This factor has been found to be a major release controlling parameter in virtually all materials. Obviously, the relevant pH range for a given application may be limited. However, for characterisation purposes the full pH range from at least 4 to 12 is important as different uses of the information relate to different pH domains. In Figure B.2 the leaching behaviour under the influence of pH is illustrated for Cd from heavily sewage sludge amended soil [6]. An indication of the repeatability of the method can be obtained from the duplicate test data. The test was performed with initial acid/base addition. This Figure B.2 indicates also pH ranges typical of some waste – conditions of scenarios combinations.

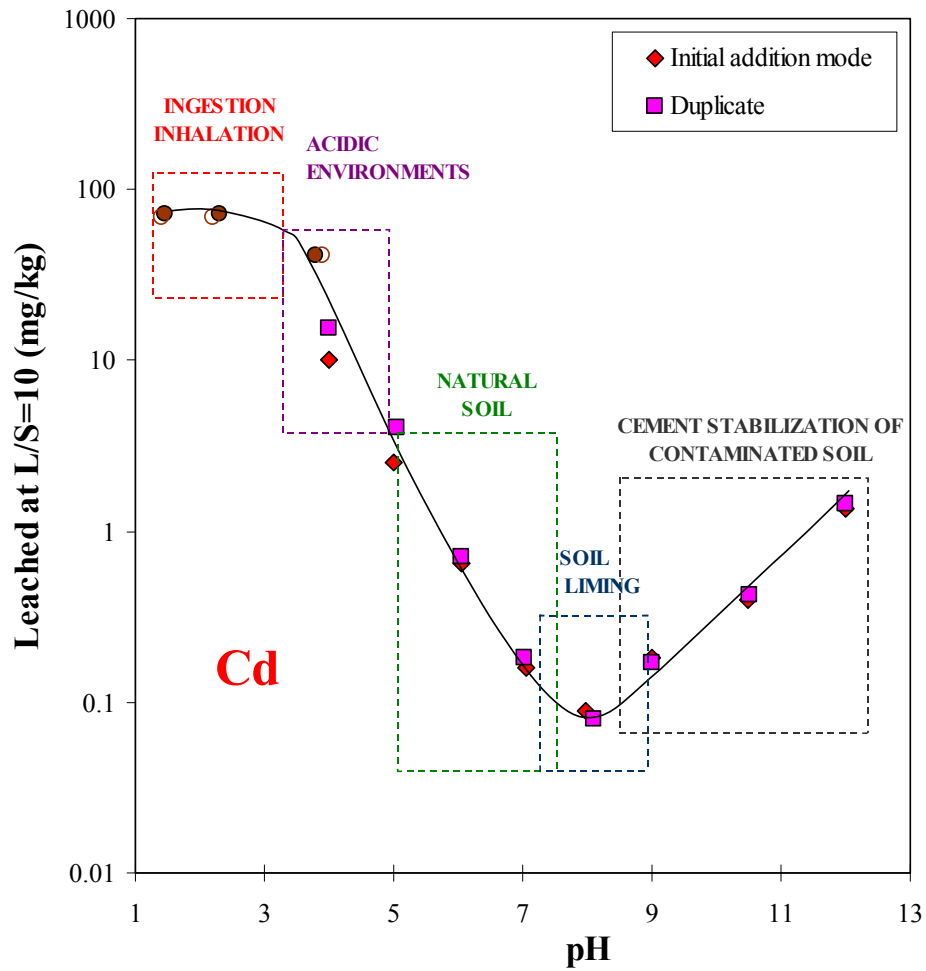


Figure B.2 — Illustration of the influence of pH on the leaching behaviour of a heavily sewage sludge amended soil as obtained in a pH range 4-12 (test performed with initial acid/base addition) its use in relation to different scenarios for the same material

Annex C (informative)

Preliminary determination of the acid/base consumption

C.1 General

In order to determine the amount and concentration of acid/base two methods are possible:

- 1) a titration procedure to estimate the ANC and the BNC;
- 2) an arbitrary division of the maximum acid/base consumption for the extreme pH values.

C.2 Titration procedure to estimate the ANC and the BNC

C.2.1 Reagents and laboratory devices

- a) Bottles made of polypropylene (PP), PTFE or polyethylene (PE);
- b) Stirring or agitation device. This is a magnetic stirring device, using a polytetrafluorethylene (PTFE) coated magnetic stirring rod, or a mechanical stirring device, made of glass or PTFE;
- c) Nitric acid (pro analysis), 1 mol/l;
- d) Sodium hydroxide, NaOH, 1 mol/l;
- e) Distilled water, demineralised water or water of equivalent purity ($5 < \text{pH} < 7$) with a conductivity $< 0,5$ mS/m;
- f) pH control device (optional).

C.2.2 Test portion

Test portions are prepared in accordance with the procedure in Clause 7. Based on sample heterogeneity, test portion size shall be either $M_d = 15$ g, 30 g or 60 g (dry weight) (with a tolerance of ± 10 %).

C.2.3 Procedure

C.2.3.1 Preparation

Place the test portions in two rinsed bottles, one for acid titration and the other for alkaline titration. The test aims at a final L/S ratio of 10 after acid or base addition. If the L/S exceeds 11 because of the high acid or base consumption of the material at the specific pH value a stronger acid or base should be used for pH adjustment.

Add an amount V of demineralised water in the bottles establishing a liquid to solid ratio (L/S) about 9. Calculate the volume V as follows assuming the density of water to be 1 g/ml:

$$V = 9 \times M_d - (M_w - M_d) \quad (\text{C.1})$$

where

V is the amount of demineralised water added in the bottles expressed in millilitres (ml);

M_w is the undried mass of the test portion expressed in grams (g);

M_d is the dried mass of the test portion expressed in grams (g).

Record the amount V of water added.

NOTE If information is available on the material concerning a particularly strong ANC or BNC another initial L/S can be used to allow the final L/S to remain ≤ 11 .

C.2.3.2 Natural pH

Put the two filled bottles on the agitation device. Agitate or stir for 1 h. Determine the pH of the eluate directly in the bottles after settling for 10 min.

C.2.3.3 Acid titration

Add a portion of acid (C.2.1.c), manually or by use of the pH control device, into one of the bottles from C.2.3.2 and determine the pH directly in the bottle after 30 min agitation or stirring. Record the amount and concentration of acid added, and the pH obtained.

The amount of acid needed to get a decrease in pH varies between materials and the initial portions need to be small in order to see the magnitude of the first response by the material.

NOTE In case of high acid demand manual addition of strong acid in the beginning of the determination is practical and a shorter response time than 30 min may be used.

Continue to add portions of acid and to measure pH after 30 min stirring or agitation after each portion added. Repeat until the entire pH interval from the initial pH (C.2.3.2) to pH 4 or below is obtained and the distance between the obtained pH values is smaller than 1,5 pH values. Record the amounts and concentrations of acid added, and the pH values obtained.

C.2.3.4 Base addition

Add a portion of base (C.2.1.d) into the other of the bottles from C.2.3.2, and determine the pH directly in the bottle after 30 min agitation or stirring. Record the added amount and concentration of base, and the obtained pH.

NOTE 1 In case of high base demand manual addition of strong base in the beginning of the determination is practical and a shorter response time than 30 min may be used.

Continue to add portions of base and to measure pH after 30 min stirring or agitation after each portion added. Repeat until the entire pH interval from the initial pH (C.2.3.2) to pH 12 or above is obtained and the distance between the obtained pH values is smaller than 1,5 pH value.

NOTE 2 In order not to underestimate the ANC or the BNC it is recommended to wait 24 h for pH 4 in case of very alkaline materials or pH 12 for materials with a high buffer capacity.

C.2.4 Expression of results

Make a curve of pH versus amounts of acid and base expressed in mol H^+ /kg and mol OH^- /kg.

C.3 Arbitrary division of the maximum acid/base consumption for the extreme pH values

C.3.1 General

For waste materials with a very strong acid-base capacity, manual titration may lead to excessive experimental duration when the maximum acid and base consumption in order to reach respectively pH 4 and pH 12 is unknown. In this procedure the natural pH and acid and base consumption at pH 4 and pH 12 respectively is estimated.

C.3.2 Reagents and laboratory devices

- a) Bottles made of polypropylene (PP), PTFE or polyethylene (PE);
- b) Stirring or agitation device. This is a magnetic stirring device, using a polytetrafluorethylene (PTFE) coated magnetic stirring rod, or a mechanical stirring device, made of glass or PTFE;
- c) PH control device;
- d) Nitric acid (pro analysis), 1 mol/l;
- e) Sodium hydroxide, NaOH, 1 mol/l;
- f) Distilled water, demineralised water or water of equivalent purity ($5 < \text{pH} < 7$) with a conductivity $< 0,5 \text{ mS/m}$.

C.3.3 Test portion

Test portions are prepared in accordance with the procedure in section 7. Based on sample heterogeneity, test portion size shall be either $M_d = 15 \text{ g}$, 30 g or 60 g (dry weight) (with a tolerance of $\pm 10 \%$).

C.3.4 Procedure

C.3.4.1 Preparation

Place two of the test portions in rinsed bottles, one for acid titration and the other for alkaline titration. The test aims at a final L/S ratio of 10 after acid or base addition. If the L/S exceeds 11 because of the high acid or base consumption of the material at the specific pH value, a stronger acid or base should be used for pH adjustment.

Add an amount V of demineralised water in the bottles establishing a liquid to solid ratio (L/S) about 9. Calculate the volume V as follows assuming the density of water to be 1 g/ml :

$$V = 9 \times M_d - (M_w - M_d) \quad (\text{C.2})$$

where

V is the amount of demineralised water added in the bottles expressed in millilitres (ml);

M_w is the undried mass of the test portion expressed in grams (g);

M_d is the dried mass of the test portion expressed in grams (g).

Record the amount V of water added.

NOTE If information is available on the material concerning a particularly strong ANC or BNC another initial L/S can be used to allow the final L/S to remain ≤ 11 .

C.3.4.2 Natural pH

Put the two filled bottles on the agitation device. Agitate or stir for 1 h. Determine the pH of the eluate directly in the bottles after settling for 10 min.

C.3.4.3 Acid titration

Titrate one of the bottles in C.3.4.2 with acid (C.3.2.d) in the titration equipment set at pH 4. Confirm the acid consumption over a titration period of 24 h. Record the added amount and concentration of acid, and the obtained pH.

NOTE 1 If the time taken to complete this last point needs to be reduced, samples may be size reduced to below 0,5 mm (as no analysis is foreseen).

NOTE 2 If this equipment is not available, manual titration may be carried out with the objective of achieving pH 4 as soon as possible including an overnight waiting period to validate the last measurement points.

C.3.4.4 Base addition

Titrate the other of the bottles in C.3.4.2 with base (C.3.2.e) in the titration equipment set at pH 12. Confirm the base consumption over a titration period of 24 h. Record the added amount and concentration of base, and the obtained pH.

NOTE 1 If this equipment is not available, manual titration may be carried out with the objective of achieving pH 12 as soon as possible including an overnight waiting period to validate the last measurement points.

NOTE 2 If the time taken to complete this last point needs to be reduced, samples may be size reduced to below 0,5 mm (as no analysis is foreseen).

C.3.5 Expression of results

The acid consumption to reach pH 4 and the base consumption to reach pH 12 is recorded together with the natural pH.

Divide the amount of acid by double the number of pH values intended to be tested within the acid pH range (pH range as a result of acid addition).

Divide the amount of base by double the number of pH values intended to be tested within the alkaline pH range (pH range as a result of base addition).

NOTE 1 If e.g. between the natural pH and pH 4, 5 pH values are sought and if the maximum acid consumption is 5 mol H⁺/kg, prepare 10 different acid solutions from 50 mmolH⁺/l to 500 mmolH⁺/l at evenly-spaced intervals.

NOTE 2 This method allows to limit the misevaluation of the ANC and BNC and the selection of the 7 solutions to be analyzed after reaching the stationary pH. This allows also to choose solutions leading to the same pH, i.e. along a potential pH plateau corresponding to the buffer capacity of the material (e.g. carbonates) of high interest in term of behaviour.

NOTE 3 Due to buffering of the matrix equally spaced portions generally will not lead to proper final pH values. Doubling the number of bottles is no guarantee for obtaining properly spaced final pH values. Through interpolation, it will be possible to estimate the proper amounts needed from the curve of final pH against acid/base consumption.

Annex D (informative)

Examples of acid and base neutralisation capacities for waste, soil, sediment and construction materials

D.1 Examples of acid and base neutralisation capacities

From previous work [2,3,4,6,7,8,9] data on acid - and base neutralisation capacity data have been obtained for a wide range of materials. This implies that this previous knowledge can be used in 8.3.1 of the pH dependence test. The information provided may not be entirely accurate for a sample under consideration. However, the variation within one material class is generally not very large.

In Figure D.1 acid neutralisation and base neutralisation capacities for waste, soil and construction materials are given, which can be used as starting point to carry out a pH dependence test. This information allows the selection of the relevant acid or base strength as well as the approximate amount of acid or base needed for a given sample weight to reach a certain desired end pH. This information can come in the place of the pre-titration as described in Annex C of the standard.

The selection of the acid strength is based on the buffer capacity of the material. In case of low buffer capacity in materials such as soil, metallurgical slag, sintered brick and sintered aggregates, the lowest acid/base strength specified in the standard should be used.

For the pH dependence test using continuous pH control, which is aimed at reaching a fixed and pre-determined pH, the acid strength is the most crucial parameter. For the pH dependence test with fixed initial acid/base addition, the proper amounts of acid/ base to be added needs to be determined. Generally more bottles are prepared in this latter test mode, from which the proper end pH values are selected for further analysis. For the acid neutralisation it does not make a difference which test is used.

To calculate the amount of acid or base needed from the ANC/BNC expressed in mol/kg the following formula applies:

$$A_{\text{pHX}} = 1000 \times \text{ANC}_{\text{pHX}} \times \frac{M}{N_{\text{pHX}}} \quad (\text{D.1})$$

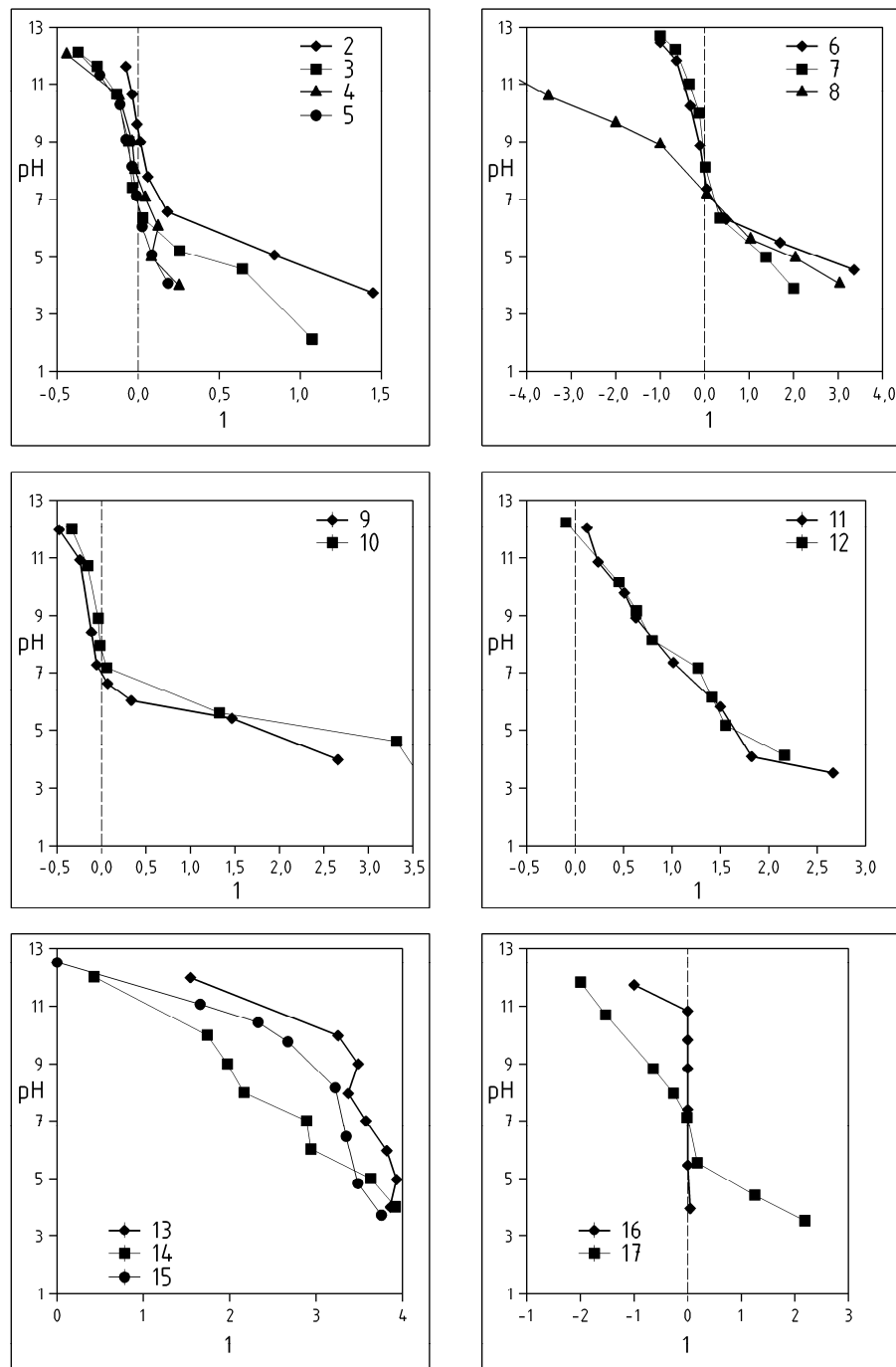
where

A_{pHX} is the amount of acid needed in ml to reach pH = X for sample of weight M ;

ANC_{pHX} is the acid neutralization capacity in Mol/kg from figure 1 at pH = X;

N_{pHX} is the acid normality selected based on the buffer capacity around pH = X in mol/l;

M is the sample weight in kg.



Key

- | | | |
|---------------------------------|--------------------------------------|-------------------------------------|
| 1 ANC/BNC (mol/Kg) | 7 CW5 Compost from Source separation | 13 Fly ash Cement - CIFA |
| 2 Contaminated Soil – A | 8 Sewage sludge (rural) – SEW1 | 14 Blast Furnace Slag Cement – C2FA |
| 3 Contaminated Soil – B | 9 Cont. River sediment – SED3 | 15 Portland Cement |
| 4 Eurosoil 4(SMT4–CT96–2066) | 10 Lake sediment – SED1 | 16 Metallurgical Slag |
| 5 Eurosoil 6(SMT4–CT96–2066) | 11 MSWI Bottom Ash | 17 Ni - Sludge |
| 6 CW1 Compost from Integral MSW | 12 MSWI BA (SMT4-CT96-2066) | |

NOTE The base addition is given as negative values – [6,8,9]

Figure D.1 — Acid/base neutralization curves for a wide range of materials

D.2 Use of acid and base neutralisation capacity data

These ANC/BNC characterisation test data can be used to assess the amount of acid (as H^+) or base (as OH^-) needed to reach a given final pH in a waste. This property can be used also to determine the final pH of mixed waste in a landfill by summing the buffer capacities. (provided that there is no chemical interaction between the different wastes) The data can also be used to assess the effect of external influences, such as carbonation and oxidation (acid production resulting from sulphide oxidation) on the pH of a waste. (as a first approximation, only considering the H^+ providing, without taking into account the specific effect of carbonation or sulphate in solution on the solubility of the different elements.). It can be used also to assess the development of a pH front with potential consequences for changes in leaching behaviour or durability of cement-based materials (carbonation may lead to loss of structural integrity of cement stabilised waste). The external influences need to be calculated in the same units to allow comparison, so carbonation would have to be assessed through volume of gas, concentration of CO_2 , conversion to corresponding moles of H^+ neutralising capacity.

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