

**ACCREDITATION PROGRAMME BUILDING
MATERIALS DECREE**

SECTION: LEACHING INVESTIGATION

AP04 – U



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U1 Introduction

The Accreditation Programme "Building Materials Decree, section composition; soil" (hereafter called AP04-U) describes the tasks and the performance characteristics of those tasks that must be applied when carrying out a leaching investigation within the scope of the Building Materials Decree. Furthermore, the testing procedures for the determination of the performance characteristics and the corresponding criteria to which a task must comply have been defined.

The nationally and internationally standardised tasks that are applied in investigations within the scope of the Building Materials Decree are reference points for the Accreditation Programme AP04-U. All tasks in the field of leaching investigations "within the scope of the Building Materials Decree" must be performed as described in this Accreditation Programme; these are tasks determined by the method. For this reason, in this section (AP04-U) no equivalence criteria have been included.

In this document, the tasks relating to leaching investigation that fall within the scope of the Accreditation Programme are stated in Chapter U2. In Chapter U3, the concepts and parameters being used are defined and, in Chapter U4, the validation of a task through widely acknowledged procedures is provided. In Chapter U5, the first, second and third-line controls that must be applied at the very least during the execution of tasks that fall under the Building Materials Decree Accreditation Programme are described. The technical data for the tasks and the corresponding performance characteristics are given in Chapter U6.



U2 Overview of tasks

This section of the Accreditation Programme includes all the tasks that are required for the execution of leaching investigation within the scope of the "Building Materials Decree". For the specification of Leaching investigation, the tasks have been divided into two packages. These packages also include the relevant tasks relating to sample pre-treatment and analysis of eluates. Please refer to AP04-A.

In APO4-SG the following tasks are described:

In APO4-U, the following tasks are described:

- Determination of the availability for leaching of inorganic components
- Determination of the emission of inorganic components at $L/S = 10$, by means of the column test
- Determination of the emission of inorganic components by means of the diffusion test
- Determination of the pH in eluates
- Determination of the conductivity in eluates

Furthermore, in AP04-U two supporting activities are described:

- Preservation of eluates
- Coating of surfaces of moulded building materials for the diffusion test

For sample pre-treatment of soil and building materials for the leaching investigation, please refer to the relevant section of the Accreditation programme AP04-V.



U3 Concepts / parameters

Several concepts and terms regularly recur in the Accreditation Programme. In order to avoid confusion, the concepts and terms are defined below. Definitions and testing procedures are wherever possible in line with the following standards that are generally applied in the Netherlands: NEN 3114, ISO 3534-1, ISO 6879, ISO 8466-1, Draft-NEN-EN-ISO 9169, NEN 7777 and NEN 7778.

U3.1 Definitions of terms

In this section, the terms used in the definitions and testing procedures for performance characteristics in the chapters U4 and U5 are defined.

Leaching (NEN 7360)

The release of inorganic and/or organic components from materials through static or dynamic contact with a leaching liquid.

Explanation 1: *The factual leaching from a material is quantified by means of a leaching test.*

Emission

Leached quantity, calculated on the basis of the (measurement) results of a leaching test, expressed in mg/kg of dry matter or in mg/m² of the product surface.

Remark: *The concepts "leaching" and "emission" have much in common. The difference is that the leaching is determined (by means of the total task) and that the emission is calculated (in the calculation part of the task).*

Leaching liquid (NEN 7360)

Liquid to which the material is exposed during leaching tests.

Eluate (NEN 7360)

Leaching liquid in which the inorganic and/or organic components leached from the material have been absorbed.

LS-value (NEN 7360)

The quotient of the cumulative volume of leaching liquid and the mass of the material exposed to leaching (expressed in l/kg of dry matter).

L/V-value

The quotient of the volume of leaching liquid in the diffusion test and the volume of the test piece (product or monolith) to be investigated, expressed in l/l.

L/A-value

The quotient of the volume of leaching liquid in the diffusion test and the surface of the non-coated test piece (product or monolith) exposed to the leaching liquid, expressed in l/m².



Measurement value (NEN 3114, NEN 7777)

A value obtained by measuring.

Explanation 1: *The measurement value may be defined as the average value of multiple determinations.*

Explanation 2: *The 'measurement value' may be the result of a measurement followed by one or more processes, such as correction for 'procedure blank'.*

Explanation 3: *'Measurement value' is synonymous with the 'analysis result' (to be reported).*

Measuring method (NEN 3114, NEN 7777)

Manner in which measurements are performed under clearly defined circumstances.

Explanation: *"Measuring method" is synonymous with 'analysis method', 'determination method' or 'task'.*

Control sample

Homogeneous material which, in terms of leaching, composition and form, is accepted as being representative of the samples and which is intended for use in monitoring one or more performance characteristics of the measuring method.

Moulded materials / moulded building materials (NEN 7360)

Solid earthy and stony building materials and waste that are manufactured by the homogeneous mixing of one or more granular materials and, if necessary, one or more different additional materials (such as water), after which, in an moulding process, the base materials are bound in such a way that form, dimensions and qualities of the resulting product satisfy predetermined requirements.

Monolithic materials (NEN 7360)

Solid earthy and stony building materials and waste that are produced as a result of natural or industrial processes, worden gevormd zonder dat vorm en eigenschappen van het resulterende product aan vooraf gestelde requirements voldoen en waarvan de stukgrootte een kleinste dimensions heeft van ten minste 40 mm.

Standard deviation (s) (NEN 3114)

Square root of measured variance, where the variance is the sum of the squared measured accidental deviations divided by the number of measured values minus one.

$$s = \sqrt{\frac{\sum_{i=1}^n (x_i - \bar{x})^2}{n-1}}$$

Variation coefficient (vc) (NEN 3114)

Quotient of the standard deviation and the absolute value of the measurement prognosis.

The variation coefficient is related to the concentration. If the concentration may be assumed to be constant, it is defined as follows, with "percent" as the unit:

$$vc = 100 * \frac{s}{x}$$

In the event of duplicate determinations, in which the concentration is not constant, but where vc is assumed to be constant, the following formula is used:

$$vc = 100 * \sqrt{\sum_{i=1}^n \frac{(x_{i1} - x_{i2})^2}{0,5(x_{i1} + x_{i2})^2}}$$

z-score

$$z_i = \frac{x_i - x}{s}$$

Deviation of the measured value from the test value, relative to the standard deviation.

where:

x_i represents the measured value;

x represents the test value such as:

- an "assigned value" in an inter-laboratory investigation;
- an assigned value for a reference material;
- measurement value of a reference method.

s represents : standard deviation.

Explanation 1: In principle, in this document, testing is always performed according to the standard deviation required in the Performance Sheet.

Conformal (measurement) method

Measurement method in which the execution does not deviate in critical areas from the prescribed task (standard). A deviation in an area is seen as non-critical if the deviation has no demonstrable effect on the result.

U3.2 Definitions of performance characteristics

Detection limit (NEN 7777)

Lowest concentration of a sample component for which its presence can be determined with a certain degree of certainty.

Explanation 1: Detection limit is related to the quality criterion "presence".

Precision

Degree of conformity between measurement results in repeated measurements under prescribed conditions.

Explanation 1: 'Prescribed conditions' usually relate to differences in laboratories, executors and equipment.

Explanation 2: 'Precision' is an umbrella concept. It is quantified in the form of 'repeatability' and 'reproducibility'.

Explanation 3: In this document, reference is made to NEN 7777 for the determination of the detection limit. In this standard, the operational definition is used for the detection limit, which equates the detection limit with three times the standard deviation at this level. Therefore, the detection limit is the value of the measurement quantity, in which the variation coefficient by convention amounts to 33%.

Determination limit (NEN 7777, Appendix C)

Lowest concentration of the component in the sample, for which the presence can still be determined with a certain degree of certainty.

Explanation 1: Determination limit is related to the quality criterion "measurement value".

Explanation 2: The term determination limit is not used further in this document, the definition and the explanations have been included here only in order to illustrate the relation to the detection limit.

Explanation 3: In this document, reference is made to NEN 7777 for the determination of the detection limit. In latter standard, the operational definition is used for the determination limit, which equates the determination limit to ten times the standard deviation at the relevant level. Therefore, the determination limit is the value of the measurement quantity, in which the variation coefficient by convention amounts to 10%.

Repeatability (NEN 3114, NEN 7777)

Standard for the spread in measured values obtained using the same method in identical material under different conditions.

Explanation 1: 'Repeatability' is a form of 'precision' (see under "Precision").

Explanation 2: 'Repeatability' is quantified in practice as 'lack of repeatability'.

Explanation 3: The only remaining variable in practice is time.

Explanation 4: The maximum permitted variation coefficient for the repeatability ($VC_{r,requirement}$) is specified for each parameter in the Performance Sheets.

Reproducibility (NEN 7777)

Standard for the spread in measured values obtained using the same method in identical material under different conditions.

Explanation 1: Reproducibility is a form of precision.

Explanation 2: "Different conditions" may relate to "executor", "laboratory" (equipment, chemicals, standards), "environmental factors" (temperature, humidity), time.

Explanation 3: It is often useful to make a distinction between "intra-laboratory reproducibility and "inter-laboratory reproducibility"; in these cases, the "different conditions" relate to the variability within the laboratory or within a group of laboratories. If the group of laboratories is representative for all, then "inter-laboratory reproducibility" equals "reproducibility of the methods".

Explanation 4: The maximum permitted variation coefficient for the intra-laboratory reproducibility ($VC_{w,requirement}$) is specified for each parameter in the Performance Sheets.



U4 Validation of a task

An intra-laboratory validation investigation should be performed when introducing or modifying a task.

This validation investigation must demonstrate that the execution of the various tasks is conformity with the requirements of the relevant performance sheets (chapter U6) (in other words, that the performance characteristics can be fulfilled).

A validation investigation of leaching analysis concerns the performance characteristics intra-laboratory reproducibility and (in respect of some tasks) the repeatability.

In principle, the performance characteristics should apply to the entire task as described in the instructions, which includes e.g. the calculation of the emission. If this is not the case, the performance sheet of the validation investigation will explicitly state for which part of the task the performance characteristics apply.

In the section "leaching investigation", in principle only parameters are investigated that are determined by the method. This means that the method must be executed in conformity with the defined task.

The validation must be repeated if the standard on which the relevant task is based, has been changed. In this version (version 3) of AP04-U, new standards for leaching investigation have been included. This execution of the standards hardly departs from the standards stated in former versions. The leaching tests are executed with neutral water instead of with pH=4 water. However, the consequences of this change are negligible (*). The determination of the solubility behaviour in the diffusion test in NEN 7375 is different compared to NEN 7345. If by means of a second-line control (U5.2) it is demonstrated that the performances of the leaching investigation have remained the same, the validation does not need to be executed again.

- (*) Evaluation of the consequences of modification of the pH of the leaching liquid in the leaching standards NEN 7343, 7345 and 7349
Sloot, H.A. van der; Rietra, R.P.J.J.; Mulder, E.
ECN Schoon Fossiel, Rapport no ECN-C--00-081

U4.1 Choice of materials and components for validation

The performance characteristics should preferably be determined for materials that are normally investigated in the laboratory concerned. On the other hand, it should also be observed, that measurable concentrations must be leached in order to be able to determine the performance characteristics. Materials for which this was found to generally apply, are (in respect of granular materials) AVI-fly ash, AVI-soil ash, (assorted) sieve sand and (sandy) soil. Regarding moulded or monolithic materials it is recommended to use fly ash /cement stabiliser, sand-lime bricks with E-central fly ash or yellow bricks. Both certified reference materials¹ and in-house materials may be chosen. The components to be analysed, from which a choice can be made, are divided into three categories, as stated in table U4.1. For the purpose of the validation investigation, a choice can be made from the components mentioned. The preconditions are:

- in total at least 4 components must be chosen;
- at least one component must be chosen from all three categories;



- the measured concentrations of the chosen elements in the eluates must preferably be at least on the level of 10 times the detection limit (AG).

Table U4.1 Components from which a choice can be made with regard to the validation investigation

Categories of components	Components from which a choice can be made
Main components	Na, K, Br, Cl, F, SO ₄
Heavy metals	Ba, Cd, Co, Cr, Cu, Hg, Ni, Pb, Sn, Zn
Amphoteric elements	As, Mo, Sb, Se, V, CN-tot, CN-vrij

The following are recommended material - component combinations:

AVI-fly ash	Na, Cl, SO ₄ , Pb, Zn, Mo, Sb
AVI-soil ash	Na, Cl, SO ₄ , Cu, Pb, Mo, Sb
(Assorted) sieve sand	Na, Cl, SO ₄ , Cr, Cu, Ni, Se,
(Sandy) soil	Na, Cl, Cu, Zn, As
Fly ash/cement-stabiliser	Na, Cl, SO ₄ , Ba, Mo, Se, V
Sand-lime brick with E-fly ash	Na, Cl, SO ₄ , Ni, Se, V
Brick	SO ₄ , Cr, As, Mo, V

U4.2 Test procedure and quantification of the performance characteristics

Leaching parameters are parameters that determine the method; the execution of the test, the method, determines how much of the different components will be leached. This also means that for tasks in this section (leaching investigation) it is more difficult to prove that the task is executed "correctly". The only performance characteristics that can be quantified, are the (intra-laboratory) reproducibility and, in some cases, the repeatability. The column test and the diffusion test take so long and consist of so many parts, that it is difficult to execute these under strict repeatability conditions. In this case, the repeatability and the intra-laboratory reproducibility approach each other so closely, that it is not useful to include both in the validation programme. In respect of the leaching tests, only the intra-laboratory reproducibility is included in this Accreditation programme as a performance characteristic. The repeatability applies only for the measurement of the pH and the conductivity.

Furthermore, leaching tests are somewhat complex tasks in the sense that they are multiple tasks. Leaching tests consist of at least three phases, viz. The execution of the test proper, the chemical analysis of the eluate or eluates and the calculation of the emission. The latter means that the calculating method must also be validated. The validation of the chemical analyses is specified in more detail in section Analysis of eluates (AP04-E).



U4.2.1 Determination of the repeatability standard deviation

Due to the tiny difference between repeatability and intra-laboratory reproducibility for leaching tests, **no** repeatability standard deviation needs to be determined for the **leaching tests**. Yet, for the **pH and the conductivity** the reproducibility standard deviation **must** be determined. For the latter variables, the measurements can be executed using either certified reference samples (eluates), or in-house samples.

The determination of the repeatability standard deviation is described in NEN 7777. This can be executed in two ways: either by duplicate analysis of different samples or by repeated analyses of the same laboratory sample. Both methods are permitted.

Criterion:

- The relative repeatability standard deviation must meet the requirement stated in the performance sheet.

U4.2.2 Determination of the (intra-laboratory) reproducibility standard deviation

A leaching test (and therefore also its intra-laboratory reproducibility) actually consists of three parts, viz. the execution of the leaching test itself, the chemical analysis of the eluates and the calculation of the emission (with or without the aid of a computer programme). In order to prevent the intra-laboratory reproducibility of the entire leaching test during the validation investigation from being influenced too much by inaccuracies in the chemical analysis, the concentration levels in the eluates must preferably be at least 10 times the detection limit. The leaching tests for determining the intra-laboratory reproducibility standard deviation are executed with certified reference materials or with in-house reference materials. This applies also for determining the intra-laboratory reproducibility standard deviation of the pH and the conductivity.

Execute at least 7, but preferably 10 leaching tests with like samples. Describe the reproducibility conditions in such a way, that they reflect their future application (representativity with respect to laboratories, executors, equipment, atmospheric conditions etc.). Execute the leaching tests in accordance with the relevant NEN standard. Analyse, in conformity with AP04-E, all eluates in one measurement series in respect of the components chosen from table U4.1 (at least four in all; at least one from all three categories). Calculate the emission on the basis of the measurement- and analysis data. Calculate for each of the four components the relative intra-laboratory reproducibility standard deviation of the total leaching test (i.e. including analysis and calculation), in conformity with ISO 5725-2. Calculate the intra-laboratory reproducibility also for the pH and the conductivity of the measurements executed.

Report, for each component, the individual leaching values (and the individual measurement values for the pH and the conductivity), the average and the intra-laboratory reproducibility.

Criteria:

- The intra-laboratory reproducibility standard deviations must meet the requirements stated in the performance sheet.

Remark: For the derivation of the requirements in respect of the intra-laboratory reproducibility stated in the performance sheets, the data from the validation report (U7.2.1) have been partially made avail of. In addition to this, the data available at IWACO and TNO have been used. Insofar as they have been adopted from the validation report, they are no intra-



laboratory reproducibilities, but repeatabilities, to which the analysis-inaccuracy has been added. For a more detailed account of the performance characteristics included, please refer to Attachment 1.

Explanation: *For the determination of the intra-laboratory reproducibility, the control sample from the second-line control may be used.*

U4.2.3 Validation of calculating methods

As the calculation of the emission, based on the measurement- and analysis results, form an essential part of the total task, it is important that this part is also validated. As a rule, computer calculating models are made avail of, so that it suffices to check, whether the calculations are carried out correctly.

For the benefit of this validation of calculating methods, for the tasks for which this is relevant, a set of fictitious measurement data have been included as appendix to the performance sheet. The tasks, for which the calculation method must be validated, are:

- the availability test (U-I);
- the column test (U-II);
- the diffusion test (U-III).

On the basis of the set of fictitious measurement data, it must be demonstrated for the relevant tasks that the emissions and other variables are calculated as stated in the attachment to the performance sheets.

The validation of a calculation method must be repeated after each change of calculation method in the standard and after each (substantive) change in the computer programme used for the calculation of the leaching (emission).

U4.3 Reporting of validation activities

A validation investigation should be concluded with a validation report. This validation report must also include a print-out of calculations, based on the fictitious measurement data. The conclusions of the investigation must be relevant in connection with the validation scheme.

Complete documentation of all validation investigations carried out should be available during the accreditation assessment.



U5 Quality assurance of a task

The quality assurance of a task is subdivided as follows:

- First-line control - Performance check by the executors themselves.
- Second-line control - A check within the institute's organisation, but independent of the executors.
- Third-line control - Independent external check, ring tests.

Explanation: *When this version of AP04-U was published, it was not possible to carry out quality assurance by means of third-line control due to the lack of ring test and certified reference materials. As long as this is situation persists, third-line control is not required.*

The quality assurance of the institute must be laid down in first-, second- and third-line documents that should cover the following aspects:

- statistical supervision of the quality assurance;
- resolution of out-of-control situations;
- use or preparation of the samples;
- responsibilities of officials.

The defined first-, second- and third-line controls do not represent an additional quality assurance, but rather the minimum quality assurance that must be applied.

The quality assurance described in this chapter concentrates on the (standard) leaching tests in particular. For several other tasks (within this section leaching investigation) different or additional quality assurance points apply. These are specified further in chapter U6, in which the tasks and the related quality assurance are described in more detail.



U5.1 First-line control

During a leaching investigation, the first-line control is limited to a quality check during the execution of a task.

U5.1.1 Temperature control in the laboratory

During the execution of leaching tests, the temperature is a parameter which influences the outcome of the test. Therefore it is important that the temperature in the laboratory does not differ from the "standard"-temperature of 20 ± 2 °C. For this reason, the temperature must be measured and recorded regularly (at least 4 times a day), but preferably continuously.

Criterion:

- The temperature of the laboratory should not differ from the course of 18 - 22 °C for more than maximally 10% of the execution time of the test.

U5.1.2 Checking the percolation speed (column test)

During the execution of the column test, the percolation speed must be checked regularly, at least once every two days (or, if a weekend falls in between, on Friday and Monday).

Explanation: *In order to guarantee a proper contact between the solid and the liquid, the percolation speed must be less than the maximum value given below. Furthermore, the percolation speed may increase or decrease in course of time, due to reactions in or with the sample material. This needs to be corrected, first and foremost, if the percolation speed increases. See also the relevant standard for this.*

Criterion:

- The flow-rate of the pump (expressed in l/h) must be smaller than 0,025 times the mass of the sample in the column (expressed in kg dry matter).

U5.1.3 Quality control of demineralised water

The purity of the demineralised water must be determined, if it is to be used as leaching liquid. The required purity of the demineralised water to be used (in terms of conductivity) is stated in the performance sheets.

Remark: Om achteraf deviationen te kunnen verifiëren is het aan te bevelen om van de te gebruiken leaching liquidfen, per aan te maken hoeveelheid, samples (blanco's) te nemen en deze te analyseren op koper en enkele andere, ten behoeve van het betreffende onderzoek te analyseren components.

U5.2 Second-line control

The laboratory must regularly check the performance of all leaching tests and related tasks, as frequently as is stated in the performance sheets (at least twice a year). This regular performance check is carried out by means of a second-line control sample, which is presented to the executor(s) in unrecognisable form, if possible.

During the second-line control, materials should be used preferably that are investigated in the laboratory concerned on a regular basis. On the other hand, however, the concentrations to be leached must be measurable, in order that the performance characteristics can be determined. Materials for which this is generally the case, are (in respect of granular materials) AVI-fly ash, AVI-soil-ash, (assorted) sieve-sand and (sandy) soil. Regarding moulded or monolithic materials it is recommended to use fly ash/cement-stabiliser, sand-lime bricks with E-central fly ash or yellow bricks. For the second-line control, either certified reference materials¹ or in-house materials may be used. When in-house materials are produced, the material must be dried (at 40 °C), in order to prevent the leaching characteristics of the material from changing in course of time. When a new "in-house" material is used, the "in-house" new average value must be determined again according to U4.2.2.

The components to be analysed, from which can be chosen, are divided into three categories, as shown in table U5.1. For the second-line control, a choice can be made from the components listed in table U5.1. The preconditions are:

- in all, 4 components must be chosen;
- at least one component must be chosen from all three categories;
- the concentrations measured in the eluates of the chosen elements must preferably be on a level of at least 10 times the detection limit (AG).

Remark: The concentrations in the eluates of the diffusion test often show an increase (due to the replacements times chosen and because the leaching process sometimes starts a bit slowly). The results of diffusion tests can

¹ At the moment, only few building materials are available as reference material. In the near future, amongst others. The "Nederlands Meet Instituut" (Dutch Measurement Institute) will work on this. Sand-lime brick with E-fly ash is not being produced (any more) at the moment; therefore it is not advisable to use this material for the second-line control.



be used for second-line controls, if the concentrations measured in the last four fractions are higher than 10 times the detection limit.

Table U5.1 Components from which can be chosen for the quality assurance

Categories of components	Components from which a choice can be made
Main components	Na, K, Br, Cl, F, SO ₄
Heavy metals	Ba, Cd, Co, Cr, Cu, Hg, Ni, Pb, Sn, Zn
Amphoteric elements	As, Mo, Sb, Se, V, CN-tot, CN-vrij

Recommended material - component combinations are:

AVI-fly ash	Na, Cl, SO ₄ , Pb, Zn, Mo, Sb
AVI-soil ash	Na, Cl, SO ₄ , Cu, Pb, Mo, Sb
(Assorted) sieve-sand	Na, Cl, SO ₄ , Cr, Cu, Ni, Se,
(Sandy) soil	Na, Cl, Cu, Zn, As
Fly ash/cement-stabiliser	Na, Cl, SO ₄ , Ba, Mo, Se, V
Sand-lime bricks with E-fly ash	Na, Cl, SO ₄ , Ni, Se, V
Bricks	SO ₄ , Cr, As, Mo, V

During the second-line control, the v_{cW} is tested. A control chart is used for this. During each check, the performance is tested against the validation data of the institution. Additionally, once every 10 checks, during the closing of a control chart the performance is tested against the requirements set in the performance sheets. If the second-line control is not consistent with the validation data and/or the requirements set in the performance sheets, the institution must take corrective measures

The second-line control is specified in more detail in the following point.

U5.2.1 Starting a control chart

A control chart is started by executing the task under intra-laboratory reproducibility conditions at least ten times. For this, the results of the validation investigation can be used (see Chapter U4.2.2.). If the performance characteristics obtained do not meet the requirement set for the intra-laboratory reproducibility variation coefficient, for the first 10 observations an outlier test is carried out. In order to identify the outliers, the Grubbs test is executed twice at most. When the outliers have been removed, the average and the standard deviation are calculated again and the outliers test is repeated. This is performed, until no outliers are observed any more.

At least 8 observations should remain, in order that the remaining observations can be used for starting a control chart. On the basis of these experiments, the average and the 2s- and 3s-limit are calculated.

Grubbs-test:

$$G_p = \frac{|x_p - \bar{x}|}{s}, \text{ in which: } x_p \text{ is the individual observation being tested}$$

if $G_p >$ critical value, then the value is an outlier.

If $n=10$ $G_p = 2,482$

$n=9$ $G_p = 2,387$

$n=8$ $G_p = 2,274$

For each component to be analysed (for each type of leaching test at least 4 components) the average, the 2s- and 3s-limits are indicated on a separate control chart.



U5.2.2 Filling in a control chart (NPR 6603)

Once in every 20 determinations, but minimally twice a year and maximally 6 times a year for the availability- and column test, and 3 times a year for the diffusion test, the task is executed singularly, under reproducibility conditions, on a second-line control sample. The eluate or eluates are analysed in respect of the chosen components (at least 4). Subsequently, the emissions are calculated in the usual manner. The calculated value of each test determination (not the average value of several determinations) is registered on a control chart (a separate chart for each component).

U5.2.3 Checking by using a control chart

During each leaching test, the check within the scope of the second-line control is carried out for at least 4 components. In order to observe 'out-of-control'-situations, all components are assessed collectively. In the following cases, the quality is uncontrolled ('out-of-control'):

- if the 2s-limit is exceeded in respect of 3 components;
- if the 3s-limit is exceeded in respect of 1 component;
- if the 2s-limit is exceeded twice consecutively on the same side of the average in respect of 2 components;
- if the calculated value is on the same side of the average for the sixth consecutive time in respect of 2 components.

In case the quality is uncontrolled ('out-of-control'), the following measures must be taken respectively:

- 1) an investigation is set up into the cause of this (all three steps in the execution of a leaching test must be included);
 - the execution of the leaching test itself;
 - the chemical analyses of the eluates;
 - the calculation of emissions;
- 2) when the cause of the errors has been removed, the clients of the leaching tests that have been executed since the last second-line control, must be contacted in any event, as the investigation or parts of it might have to be performed again. For the rest, one should act according to the circumstances.
- 3) if uncontrolled quality is established as a result of 2 components for which the calculated 6 observations lie on one side of the average, the cause of the shift must be examined immediately. If the problem cannot be solved (no cause known or the cause cannot be removed), the control is closed immediately and the charts are joined together. The new chart starts with $n=0$, $\sum x=0$ and $\sum x_i^2=0$. When the new control chart is closed, however, the (cumulative) standard deviation determined during the previous periods is made avail of. During the investigation into the cause of the shift, it is allowed to analyse and report samples. In order to prevent a situation of uncontrolled quality, the results of the second-line control samples must comply with the characteristics of the last control chart.

Remark: It is advisable to let the second-line control of the leaching tests coincide with the first- or the second-line control of the eluate analyses, in order to in this way gain an insight into the degree in which the inaccuracy in the leaching test is caused by an inaccuracy in the chemical analysis of the eluates.

U5.2.4 Closing and evaluating a control chart

Close a control chart after 10 test determinations and calculate the average value and the standard deviation in respect of these 10 determinations.



- When calculating the average and the standard deviation of a control chart, the uncontrolled results caused by exceeding the 3s-limits are not taken into account.
- When closing a control chart, the average and standard deviation are checked in respect of the historical data of previous charts and the requirements set for accuracy (recovery) and the intra-laboratory reproducibility in the performance sheets.
- It is stated in NPR 6603, how the check must be executed in respect of the historical data of previous charts for the standard deviation, but not for the average. The average must be checked with the t-test:

$$t = \frac{|X_1 - X_2|}{\sqrt{(A+B)}}$$

Where: X_1 and X_2 are the averages of the previous chart(s) and the present control chart respectively

$$A = \frac{s_1^2}{n_1} \quad \text{and} \quad B = \frac{s_2^2}{n_2}$$

where: s_1 and s_2 are the standard deviations of the previous control chart(s) and the present control chart respectively

The number of measures of freedom is
$$v = \frac{(A+B)^2}{\frac{A^2}{(n_1+1)} + \frac{B^2}{(n_2+1)}} - 2$$

Subsequently, the testing value of $t(0,95;v)$ can be determined.

- If it is not permitted to combine the average and/or the standard deviation, the cause must immediately be investigated. If the quality of the analysis has improved (recovery closer to 100% or a smaller standard deviation), the cause does not have to be investigated further. If the standard deviation has increased, or the recovery has deteriorated, yet the requirements set in the performance sheet are still being met, the cause needs not be investigated and the charts may be joined. In latter case, it may be considered to calculate a new average or standard deviation.

If there is no improvement in quality or if the recovery or standard deviation does not meet the requirements of the performance sheet, a further investigation must be carried out. Should this fail to solve the problem (no cause known or the cause cannot be removed), the relevant performance characteristics must be determined and tested again against the criteria laid down in the performance sheets. In case of a deviation from the average, the accuracy/recovery must be determined again and in case of a deviation from the standard deviation, the intra-laboratory reproducibility standard deviation must be tested again. The chart is closed and the charts are joined. The new chart starts with $n=0$, $\sum x=0$ and $\sum x_i^2=0$. During the determination of the relevant performance characteristics samples may nevertheless be analysed and reported. In order to avoid a situation in which the quality is uncontrolled, the results of the first-line-control samples must comply with the characteristics of the last control chart.

After it has been established that no cause can be found, the performance characteristics of the new control chart must be determined within 10 measuring days. In latter case, the additional requirement is that these 10 measuring days must fall within a period of 3 months.



- In order to make sure that during the joining together of the control chart data the last data still have a sufficient influence on the values, during the joining together, maximally the last four charts are used (approximately 120 observations). During the start-up of a new chart, the average and the standard deviation of the previous five charts are employed to fill in the average and the 1s, 2s and 3s limits.

U5.3 Third-line control

For each accredited task, the institution should, if possible, participate in at least one ring test a year. The calculation of the analysis results should be part of such a ring test.

The results of a ring test are evaluated as follows.

For each parameter, the z-score is calculated according to:

$$z_i = \frac{x_i - x_{ref}}{s}$$

where:

- x_i the found value
- x_{ref} the assigned value (exclusive of outliers; in accordance with ISO 5725-2 and, for instance, a Grubbs test)

If the number of participants in a ring test is larger than 6, the standard deviation, s , is determined according to:

- If $s_{W,requirement} > s_{ring}$ then $s = s_{W,requirement}$
- If $s_{W,requirement} < s_{ring}$ then $s = s_{ring}$

where:

- $s_{W,requirement}$ the requirement in terms of the intra-laboratory reproducibility standard deviation;
- s_{ring} the standard deviation in the assigned value across the ring test.
- n number of laboratories that participated in the ring test.

If the number of participants is less than 6, the standard deviation, s , is equal to

$s_{W,requirement}$.

The z values are only calculated and evaluated for components with a level higher than five-times the determined AG. The result for a component, or group of components, is significantly different from the assigned value, if:

- The absolute value of the z-score of one the observations is larger than 3 ($|z| > 3$).
- In a ring test consisting of 1 or 2 samples of the same matrix, the absolute values of the z-scores of one specific component is larger than 2 and lies on the same side of the mean for more than 2 samples in the most recent two ring tests, or for 2 samples within the most recent ring test.
- In a ring test consisting of 3 samples of the same matrix, the absolute values of the z-scores of one specific component is larger than 2 and lies on the same side of the mean for more than 2 samples within the most recent two ring tests or within one of these ring tests.
- In a ring test consisting of 4 samples of the same matrix, the absolute values of

the z-scores of one specific component is larger than 2 and lies on the same side of the mean for more than 3 samples within the most recent two ring tests or within one of these ring tests.

In the table below, by way of illustration, the borderline cases have been entered. Firstly, an examination is performed of the latest ring test. Here, the maximum number of exceedances must be lower than that given in Column 2 and Column 3. If no significant deviation is found within the latest ring test or the previous one, then the most recent two investigations are tested against the requirements given in Columns 2 and 3.

The order given in the table is arbitrary and is of no significance in testing a significant deviation. The evaluation only concerns the number of exceedances and their type (II or III).

Table Criteria for the evaluation of ring tests¹

Number of samples to be evaluated	One ring test	
	Allowed ²	Not allowed ³
1	II	III
2	I, II	II, II
		I, III
3	I, II, II	II, II, II
		I, I, III
4	I, I, II, II	I, II, II, II
		I, I, I, III
5	I, I, I, II, II	I, I, II, II, II
		I, I, I, I, III
6	I, I, I, I, II, II	I, I, I, II, II, II
		I, I, I, I, I, III
7	I, I, I, I, I, II, II, II	I, I, I, I, II, II, II, II
		I, I, I, I, I, I, III
8	I, I, I, I, I, II, II, II	I, I, I, I, II, II, II, II
		I, I, I, I, I, I, I, III

¹) **I** = $|z| < 2$ sigma (content lies within the 95% reliability range), **II** = $2 \text{ sigma} < |z| < 3 \text{ sigma}$ (content lies outside the 95% reliability range) and **III** = $|z| > 3 \text{ sigma}$ (an exceedance, determine the cause); ²) z-scores for each parameter that are allowed within a single ring test; ³) z-scores for each parameter from which the cause of the deviation must be determined.

When evaluating the table and determining whether the laboratory has undertaken timely action, the reporting time of the ring tests should be taken into account. It may be that the results of ring test n are only reported after the results of ring test n+1 have already been submitted. In this situation, it can only be determined whether the results of a given component in both ring test n and ring test n+1 contained deviations after the submission of ring test n+2 results. It is possible that the same deviation will also occur in ring test n+2 but, in the situation described, without the laboratory being at fault for not undertaking timely action.



By way of an illustration, the following diagram shows this graphically.

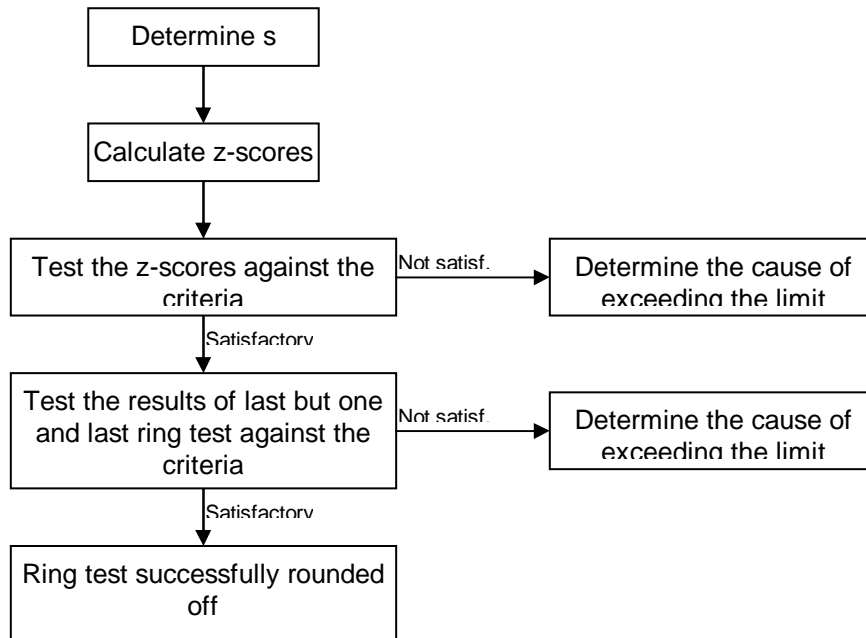


Figure Diagram of assessing ring test results

If a result deviates significantly, then the laboratory needs to investigate the possible cause.

During this investigation, the following actions should be undertaken:

- analysis of the quality problem, based on the results of the most recent successful ring tests, internal data on quality assurance and the relevant measurements;
- draw up a plan for corrective actions;
- record the performance of the corrective action(s);
- check if the corrective action has been successful.



U6 Technical description and quality assurance of the tasks

U6.1 Matrix of tasks and groups of materials

The execution of certain combinations of leaching tests (tasks) and materials may be problematic. In this paragraph, this is examined in more detail.

In paragraph U6.2, the performance sheets are listed for the tasks from the section Leaching investigation of the Accreditation Programme Building Materials Decree. These are:

- determination of the availability of inorganic components;
- determination of the emission of inorganic components by means of the column test;
- determination of the emission of inorganic components by means of the diffusion test;
- measuring the pH in eluates;
- measuring the conductivity in eluates;

Instruction sheets are included for the following supportive activities:

- preservation of eluates.
- the coating of thin, sawn or glazed test pieces, in accordance with the informative Appendix C of NEN 7375;

In respect of the column test, not the standard test (in accordance with NEN 7373) has been included, but the most utilised, shortened version derived thereof, in accordance with NEN 7383. The eluate fractions are in this case not all 7 collected and analysed separately (as NEN 7373 prescribes). The eluate is collected in two fractions (to and including $L/S = 1$ and from $L/S = 1$ to and including $L/S = 10$). These both fractions are preserved separately. Both fractions can be analysed separately or they are analysed together, on the basis of the L/S -ratio.

In the performance sheet, it is left free to analyse both eluate fractions separately. For the purpose of the characterisation investigation, it is of course also possible, to collect and analyse all seven fractions separately (in accordance with NEN 7373). In these cases, the calculation scheme must be adapted to this.

The material groups, upon which the tasks can be executed, can be divided as follows:

- sludges (inclusive of dredgings);
- hardened powders and gypsums;
- other powders and fine- and coarse-grained materials;
- "neat" products and monoliths;
- other products and monoliths (these can be: thin products, glazed products, products that are sawn, and monoliths with a partially irregular surface (in short, all products that must be coated for the purpose of the diffusion test)).

Problems often occur with sludges and hardening powders and gypsums during the execution of the leaching tests and during filtrations of the eluates. In the temporary exemption regulation Building Materials Decree 2004, an exemption of the emission requirements has been included for poorly permeable materials, if the column test has not reached $L/S=2$ within 28 days. If it appears from the extrapolation of the flow that $L/S=2$ cannot be achieved, then the laboratory reports, that the test cannot be finished



off within the period of 28 days. If after 28 days the L/S-ratio lies between 2 and 10, then, in accordance with this exemption regulation, the determined emission must be extrapolated to emission value for L/S=10.

For products and monoliths with irregular surfaces, it is often hard to determine the geometrical surface unambiguously. In that case, the choice can be made to coat part of the surface and to subject only the most regular surfaces to the diffusion test.

On the basis of what has been stated above, a tasks/material groups-matrix has been drawn up and rendered as table U6.1. During the formulation of the matrix, problem cases in respect of the leaching of specific components or groups of components have not been taken into account. This, namely, "only" relates to specific cases.

Table U6.1 Tasks/ matrix of material groups

	Sludges	Hardening powders and gypsums	Other powders and fine- and coarse-grained materials	"Neat" products and monoliths	Other products and monoliths
Measuring pH in eluates	O	O	O	O	O
Measuring conductivity in eluates	O	O	O	O	O
Preserving of eluates	O	O	O	O	O
Availabilitysproef	!	O	O	O	O
Column test	!	X	O	-	-
Diffusion test	-	-	-	O	!
Diff.test; coating of surfaces	-	-	-	-	!

- = Is not applicable.

O = Can be executed by "standard" laboratory without problems.

! = Requires specific expertise or skill.

X = Execution of the test is technically not possible.



U6.2 Performance sheets

Performance sheet U.I Determination of the emission of inorganic components by means of the column test

Principle

The aim of the column test (in accordance with NEN 7383) is to stimulate the leaching of inorganic components from powdery and granular materials in an aerobic environment, as a function of the LS-value, over a section ranging from 0.1 to 10 litres per kg dry matter. In this Accreditation Programme, a column test has been included which is derived from this, which only determines the cumulative leaching for an L/S of 10 l/kg.

A quantity of reduced material (95% \leq 4 mm) is inserted into a vertically placed column. Demineralised water is flown through this column from underneath at a low speed for approx. three weeks. The eluate is collected in two fractions, each with a specific volume. Immediately after the separate eluate fractions have been collected, they are filtered, the pH and the conductivity are measured (in accordance with U-IV and U-V respectively) and the eluates are preserved (in accordance with U-VI). Then, the eluates are combined **in the right volume proportions** and this mixed eluate is analysed in respect of the desired components.

Remark: It is also permitted to analyse the eluate fractions (when L/S = 1 and L/S = 10) separately. Furthermore, it is permitted (e.g. for the purpose of characterisation assessment) to collect and analyse all 7 eluate fractions separately (in accordance with NEN 7373). In both cases, the calculation scheme must be adapted to this.

On the basis of the measurement- and analysis results, the cumulatively leached quantity (emission) of each analysed component is calculated (in mg/kg dry matter). For the calculations, the computational formulas mentioned in NEN 7383 are used.

Conformity with the standard

The execution based on this performance sheet is completely in line with the standard as stated here under 'Method'. If the work is performed in accordance with the performance sheet, conformity with the standard may be claimed.

Field of application

Within the framework of this Accreditation Programme, sludges, hardening powders and gypsums excluded from the field of application of these tasks. (The hardening powders and gypsums cannot be investigated by means of the column test, whereas in the case of sludges, problems may occur during the execution of the test by means of filtration, see U6.1). Apart from this, problems may also occur with clays in connection with a poor permeability of the material.

During the validation of this task, the following materials are used: AVI-fly ash, E-soil ash and AVI-soil ash.

Variables to be determined / calculated

- The pH and the conductivity of the eluate-fractions.
- For each component, the calculated cumulatively leached quantity (cumulative emission for L/S = 10), in mg/kg of dry matter.



Method and quality assurance

METHOD

Sampling

Sample pretreatment

Sample size

Particle size

Task

Measurements of column

Eluate sampling

Storage period of eluates

Measuring the pH

Measuring the conductivity

Preservation of eluates

Combining eluates

(after preservation)

Transfer of eluates

Building material / soil

AP04-M, VKB-protocols

AP04-V

± 0,5 litre (when using a column of a diameter of 5 cm and a height of 20 cm)

95% ≤ 4 mm

NEN 7383 (alternatively NEN 7373)

Diameter 5 cm and height ≥ 20 cm

When $LS_{\text{dry matter}} = 1,0$ and $10,0$ l/kg¹⁾

SIKB-protocol 3001

See U-IV

See U-V

See U-VI

In proportion to tot 1 mixture eluate ($L/S = 10$)²⁾

See NEN 5861

FIRST-LINE CONTROL

Standard quality assurance points (See Ch. U5.1)

Temperature laboratory

Between 18 and 22 °C

Conductivity demi-water

< 1 µS/cm

Percolation speed

Check regularly if the speed is right (pumping flow rate (in l/h) < 0,025 * mass in column (in kg dry matter), see U5.1.2

Points of attention

Regular check of the accuracy (< 1%) of scales and top-pan balances

If cyanide is also to be determined in the eluates, the eluate must be collected in brown bottles (in order to prevent the cyanide from disintegrating by UV-radiation).

SECOND-LINE CONTROL

Frequency

1 * for every 20 determinations (with a minimum of 2 * per year and a maximum of 6 * per year)

Control sample

Granular, inorganic material (see Ch. U5.2)

Analytes

Choice of 4 components (concentrations > 10 * AG), see Ch. U5.2

Requirement for the relative intra-laboratory reproducibility variation coefficient vc_w ³⁾

Main components

< 12 %

heavy metals

< 19 %

amphoteric elements

< 23 %

¹⁾ it is also permitted to sample all seven eluate fractions separately (in accordance with NEN 7373)

²⁾ it is also permitted to analyse both eluate fractions separately

³⁾ the values given are inclusive of the chemical analysis of the component concerned.



THIRD-LINE CONTROL

Frequency At least 1 * a year

Ring tests

Reporting limit 3*AG
 Organising company institution accredited for ring tests

Ring test **inclusive of** analysis of the eluates and performance of the calculations, **unless** these tasks are checked separately, yet simultaneously, by means of ring tests.

Reference materials

Samples of Bureau Communautaire de Reference (BCR),
 National Bureau of Standards (NBS),
 Nederlands Bureau van Reference materials (NMI-NBR),
 National Institute of Standards and Technology (NIST),
 Samples with a conventional true value

Set of fictitious measurement data and the calculation results based on these

Measurement data

Mass ingewogen sample (not dried) 0,44 kg

Moisture content of sample (determined at 105 °C) 10,0 %

Volume collected fraction 1 0,40 l

Volume collected fraction 2 3,60 l

Element 1
 Measured concentration in mixture eluate (µg/l) 78

Element 2
 < 15

Calculation results

L/S-ratio fraction 1 1,01 l/kg

L/S-ratio fraction 2 9,09 l/kg

Cumulative L/S-ratio of total test 10,1 l/kg

Element 1
 Cumulative emission (mg/kg of dry matter) 0,79

Element 2
 0 - 0,15



Performance sheet U.II Determination of the emission of inorganic components by means of the diffusion test

Principle

The aim of the diffusion test (in accordance with NEN 7375) is to stimulate the leaching of inorganic components from moulded and monolithic materials, as a function of the time. In the test, an intact product of monolith is put into demineralised water in an L/V-ratio of 2 to 5 l/l product volume² for 64 days. The demineralised water changed according to a fixed changing scheme (0.25; 1; 2.25; 4; 9; 16 and 36 days after the start of the test). After 64 days, the test is terminated.

After filtration, the pH and the conductivity of the eluates are measured (in accordance with U-IV and U-V respectively), and the eluates are preserved (in accordance with U-VI). Then, the eluates are analysed op de gewenste componentsgeanalyseerd.

After 64 days, for each component an emission is calculated from the measurement values and analysis results, expressed in mg component per m², on the basis of a leaching determined by diffusion. If the product as such does leach according to the diffusion mechanism, but the leaching of specific components is not determined by diffusion, an upper assessment limit of the emission must be given, depending on the side effects that occur. The procedure for this is given in this performance sheet under "Set of fictitious measurement data and the calculation results based on these". If the behaviour of the material of the test piece (according to paragraph 9.3.3 of NEN 7375) shows solution behaviour, no assessment on the basis of the Building Materials Decree may occur with the diffusion test.

Conformity with the standard

The execution based on this performance sheet is completely in line with the standard as stated here under 'Method'. If the work is performed in accordance with the performance sheet, conformity with the standard may be claimed.

Field of application

The field of application of this task relates to materials that do not dissolve during the execution of the test. In NEN 7375, paragraph 9.3.3, criteria are given for this.

² For coated products and monoliths, the quantity of leaching liquid is determined by means of the surface of the test piece to be investigated (not by the volume of the test piece). The surface to be investigated is the non-coated part of the surface of the test piece. The liquid/surface (= L/A-) ratio is 50 to 200 litre per m² non-coated product surface. During the execution of the calculations, the non-covered surface of the product (not the total surface of the product) must always be filled in for A.



Variables to be determined / calculated

- The pH and the conductivity of the eluate fractions.
- The slope with related standard deviations of all (four) trajectories in the emission/time diagram.
- Leaching mechanism of the test piece.
- The calculated cumulative emission over a period of 64 days of those components of which the emission has been diffusion controlled, expressed in mg/m² of the non-coated product surface.
- For components of which the leaching is not diffusion determined, the following variables must be calculated:
 - the measured cumulative emission over a period of 64 days, expressed in mg/m² of the (non-coated) product surface;
 - the cause of the impossibility to determine a diffusion determined leaching (see "Set of fictitious measurement data and calculation results based on these" in this performance sheet);
 - the period over which the upper limit for leaching is calculated (e.g. 64 days or 100 years (for the benefit of the Building Materials Decree));
 - the calculated upper limit of the emission.

If the availability test is also carried out, its effective diffusion coefficients (expressed in m²/s) and its negative logarithm must also be calculated and (in as far as the components display a diffusion-controlled emission).

Method and quality assurance

METHOD

Sampling

Sample pretreatment

Sample size

Dimensions of the product

Task

L/V-value

Eluate sampling

Storage period of eluates

Measuring the pH

Measuring the conductivity

Preservation of eluates

Transfer of eluates

FIRST-LINE CONTROL

Standard quality assurance points

(See Ch. U5.1)

Temperature laboratory

Conductivity demi-water

Points of attention

Regular check of the accuracy of scales and top-pan balances (< 1%)

If cyanide is also to be determined in the eluates, the arrangement of the test must be protected as much as possible against incident rays of (sun)light (in order to prevent cyanide from disintegrating by UV-radiation). In this case, the eluates must be preserved as soon as possible.

Building material / monolith

AP04-M, VKB-protocols

AP04-V

Preferably 2 products / monoliths

minimal dimensions of 4 x 4 x 4 cm (if this is not the case, the product and/or monolith must be partially coated, see U-VII)

NEN 7375

5 l leaching liquid / l sample

0,25; 1,0; 2,25; 4; 9; 16; 36 and 64 days after starting the test

SIKB-protocol 3001

See U-IV

See U-V

See U-VI

See NEN 5861

Between 18 and 22 °C

< 1 µS/cm



SECOND-LINE CONTROL

Frequency

1 * in every 20 determinations (minimally 2 * a year and maximally 6 * a year)

Control sample

Analytes Moulded inorganic building material (see Ch. U5.2)
Choice of 4 components (concentrations > 10 * AG), see Ch. U5.2

Requirement for the relative intra-laboratory reproducibility variation coefficient vc_w ¹⁾

Main components < 12 %
Heavy metals < 18 %
Amphoteric elements < 17 %

THIRD-LINE CONTROL

Frequency

At least 1 * a year

Ring tests

Reporting limit

3*AG

Organising company

institution accredited for ring tests

Ring test **inclusive of** analysis of the eluates and performance of the calculations, **unless** these tasks are checked separately, yet simultaneously, by means of ring tests.

Reference materials

Samples of

Bureau Communautaire de Reference (BCR),
National Bureau of Standards (NBS),
Nederlands Instituut voor Referentiematerialen (NMI-NBR),
National Institute of Standards and Technology (NIST),
Samples with a conventional true value

¹⁾ the values given include the chemical analysis of the component concerned.

Method for calculating the upper limit of the emission

The method described hereafter is applicable for situations in which it is determined (in accordance with NEN 7375) that the product as such does leach according to the diffusion mechanism, yet for which it cannot be ascertained that it is diffusion-determined. The fact that it cannot be proven that the leaching of this component is diffusion-determined may have, amongst others, the following causes:

- 1 The concentrations measured are too low, as a result of which the concentration factor is smaller than 1.5.
- 2 At the start of the procedure, the component concerned is rinsed off, whereupon the concentrations measured are too low to determine diffusion-controlled behaviour. This behaviour is characterised by a relatively high concentration factor (≥ 1.5 and $rc < 0.35$) at the start of the procedure (fractions 1 - 4) and a low concentration factor (< 1.5) in the end of the procedure (fractions 5 - 8).
- 3 There is an apparent exhaustion as a result of the presence of several chemical forms (speciations). This behaviour is characterised by a low slope ($rc < 0.35$ and $CF \geq 1.5$) in at least two of the procedures 2-5 and/or 3-6 and/or 4-7 and/or 5-8.
- 4 The component concerned starts to dissolve. This is the case if the slope is high (> 0.65) during the whole procedure (fractions 2 - 7).
- 5 There is a spread in measurement results, as a result of which the standard deviation in the slope for the sub-procedures 3-6, 4-7 and 5-8 is larger than 0.5.



The following procedure must be adopted for calculating an upper assessment threshold of the emission:

The calculations are performed on the basis of the measured cumulative leaching over a period of 64 days (for all 8 fractions). This is indicated by ϵ_8^* in NEN 7375, paragraph 9.2.1, in which the 8 indicates cumulation across 8 fractions, and the * means that it relates to measured values (as opposed to calculated values). ϵ_8^* is determined according to 9.1 and 9.2.1 (of NEN 7375), in which, in 9.1, formula (3) is filled in for c_i . c_i = reporting limit, if the concentration of a component in a certain fraction is lower than the reporting limit.

For the different situations, the calculation of the upper limit for leaching over a certain period of T days (ϵ_T) is carried out through of the formulas given in the table below. In this table, the various criteria are stated. They are described in paragraph 9.6 of NEN 7375. The criteria must be checked in the order shown.

Description of the situation	Criteria:	Formula for calculating ϵ_T :
1. Measured concentrations too low	$CF_{1-8} < 1,5$	$\epsilon_T = \epsilon_{1-8}^* \times \sqrt{(T/64)}$
2. Rinsing off in first two steps, thereafter measured concentrations too low	$CF \geq 1,5$ and $rc < 0,35$ for first procedure (1 - 4) + $CF < 1,5$ for procedure (5 - 8)	$\epsilon_T = \epsilon_{1-2f}^* + \epsilon_{3-8}^* \times ((\sqrt{T}-\sqrt{1})/(\sqrt{64}-\sqrt{1}))$
3. Apparent exhaustion or different chemical forms	$rc < 0,35$ and $CF \geq 1,5$ for at least two of the procedures 2-5 and/or 3-6 and/or 4-7 and/or 5-8	$\epsilon_T = \epsilon_{1-2}^* + \epsilon_{3-8}^* \times ((\sqrt{T}-\sqrt{1})/(\sqrt{64}-\sqrt{1}))$
4. Dilute over the procedures 2-7	$rc > 0,65$ for procedure 2 - 7	$\epsilon_T = 2 \times \epsilon_{1-8}^* \times \sqrt{(T/64)}$
5. Large spread in all sub-procedures	$sd_{rc} > 0,5$ for subprocedure 3-6, 4-7 and 5-8	$\epsilon_T = 5 \times \epsilon_{1-8}^* \times \sqrt{(T/64)}$

Remark: In general, it can be stated that the emission at the point in time T cannot be higher than the maximum emission on the basis of the availability test (ϵ_b). This emission is calculated according to the following formula:

$$\epsilon_b = U_{bes} \times \rho \times d$$

where:

- ϵ_b is the amount of a component available for leaching in the object to be assessed, in mg dry matter per m^2 ;
- U_{bes} is the amount of a component available for leaching, in mg/kg dry matter, according to NEN 7371;
- ρ the volumic mass of the test piece, in Kg dry matter per m^3 ;
- d the thickness of the building material to be assessed, in the intended application, in m.

Consequently, this does explicitly not concern the mass and the surface of the test piece or product investigated with the leaching test, but the mass and the surface of the application to be assessed in practice.



Set of fictitious measurement data and calculation results based on these.

Measurement data

Dimensions of test piece 155 * 155 * 150 mm
Mass of test piece 5,000 kg
Moisture content of sample (determined at 105 °C) 11,0 %

Calculation results

Surface of test piece 0,141 m²
Density of test piece (on basis of dry matter) 1387,7 kg/m³
Volume of leaching liquid 18 litre

Determinating whether the matrix dissolves

Gegevens voor criterion I en II

Procedure numbers	Time of sampling (d)	pH	EC (µS/cm)
1	0,25	7,60	200
2	1,00	7,56	210
3	2,25	7,60	250
4	4,00	7,65	240
5	9,00	7,80	510
6	16,0	7,64	525
7	36,0	7,84	1120
8	64,0	7,95	1210

Criterion I

$$S_{7-8} > 1,5 * V_p/V + 10^{(pH_{7-8}-11,75)} + 10^{(2,5-pH_{7-8})}$$

$$S_{7-8} = 1,17$$

$$1,5 * V_p/V + 10^{(pH_{7-8}-11,75)} + 10^{(2,5-pH_{7-8})} = 0,30$$

Satisfactory, go to criterion 2

Criterion II

$$S_{7-8} > 2 * S_{5-6}$$

$$S_{7-8} = 1,17$$

$$2 * S_{5-6} = 1,04$$

Satisfactory, analyse Cl and SO₄, go to criterion III



Data for criterion III

Procedure numbers	Time of sampling (d)	Concentrations measured, in µg/l		
		Ca	Cl	SO ₄
1	0,25	880	1100	190
2	1,00	200	300	220
3	2,25	260	300	210
4	4,00	160	610	200
5	9,00	570	1300	300
6	16,0	520	1400	300
7	36,0	600	2400	300
8	64,0	370	2200	300
Lower determination limit		15	15	15

Criterion III

For at least 2 of 3 components (Ca, Cl, SO₄):
 CF₅₋₈ > 3,0 and rc₅₋₈ > 0,8

	Ca	Cl	SO ₄
CF ₅₋₈	34,3	121,7	20,0
CF ₅₋₈ > 3,0	ja	ja	ja
rc ₅₋₈	-0,089	0,400	0,073
rc ₅₋₈ > 0,8	no	no	no
CF ₅₋₈ > 3,0 and rc ₅₋₈ > 0,8	no	no	no

Does not satisfy, matrix does not dissolve.



Fraction	Time of sampling (d)	Concentrations measured, in µg/l						
		elem. 1 ¹⁾	elem. 2 ¹⁾	elem. 3 ¹⁾	elem. 4	elem. 5	elem. 6	elem. 7
1	0,25	880	1100	190	800	930	250	1,0
2	1,00	200	300	220	980	980	450	0,60
3	2,25	260	300	210	1200	1200	400	0,60
4	4,00	160	610	200	1200	1200	430	0,71
5	9,00	570	1300	300	2200	2200	650	1,5
6	16,0	520	1400	300	1800	10000	650	2,0
7	36,0	600	2400	300	2500	10000	1000	1,3
8	64,0	370	2200	300	2000	10000	1200	1,4

reporting limit		15	15	15	500	15	10	0,1
Availability (in mg/kg)		28	300	53	7500	7500	140	3,4

Fraction	Time of sampling (d)	Concentrations measured, in µg/l				
		elem. 8	elem. 9	elem. 10	elem. 11	elem. 12
1	0,25	0,60	3,0	10	800	0,10
2	1,00	0,41	0,3	30	980	0,20
3	2,25	0,41	< 0,1	50	1500	0,10
4	4,00	0,41	< 0,1	50	2000	2,0
5	9,00	0,41	< 0,1	40	4000	0,20
6	16,0	0,41	< 0,1	15	10000	2,0
7	36,0	0,80	< 0,1	16	10000	0,20
8	64,0	0,70	< 0,1	18	5000	1,0

reporting limit		0,40	0,1	15	500	0,10
Availability (in mg/kg)		5,2	3,2	3,2	28	7500



	elem. 1 ¹⁾	elem. 2 ¹⁾	elem. 3 ¹⁾	elem. 4	elem. 5	elem. 6	elem. 7
Concentration factor	30	80	17	3,2	304	63	11
Slope procedure 2-7	0,47	0,74	0,23	0,37	0,85	0,34	0,43
Standard deviation r.c. tr. 2-7	0,10	0,09	0,07	0,07	0,17	0,03	0,14
Slope procedure 5-8	-0,09	0,40	0,07	0,09	0,73	0,42	-0,03
Standard deviation r.c. tr. 5-8	0,10	0,05	0,13	0,01	0,48	0,08	0,25
Slope procedure 4-7	0,46	0,50	0,08	0,20	0,98	0,27	0,20
Standard deviation r.c. tr. 4-7	0,25	0,05	0,12	0,06	0,42	0,04	0,30
Slope procedure 3-6	0,60	0,88	0,30	0,36	1,11	0,36	0,73
Standard deviation r.c. tr. 3-6	0,20	0,17	0,05	0,05	0,41	0,06	0,06
Slope procedure 2-5	0,60	0,91	0,33	0,55	0,55	0,37	0,61
Standard deviation r.c. tr. 2-5	0,19	0,15	0,06	0,06	0,06	0,06	0,04
Slope procedure 1-4	-0,07	0,22	0,52	0,66	0,60	0,69	0,36
Standard deviation r.c. tr. 1-4	0,20	0,31	0,03	0,02	0,03	0,09	0,10
Procedure for calculating diff.coeff.	2-7	5-8	1-4	2-7	2-5	5-8	2-7

Cum. Measured load 64 d (mg/m ²)	454	1227	258	1619	4661	642	1,16
Cum. Calculated load 64 d (mg/m ²)	434	1271	418	1997	2280	609	1,29
Rinsing off (mg/m ²)	83,6	19,8	-	-	-	-	0,043
pD _e (-)	10,8	11,9	11,3	14,3	14,2	15,3	14,0

¹⁾ These three are used to check if the does not show dilution behaviour (criterion 3 paragraph 9.3.3 NEN 7375).

	elem. 8	elem. 9	elem. 10	elem. 11	elem. 12
Concentration factor	1,3	4,9	1,9	8,6	7,3
Slope procedure 2-7	0,24	-0,12	-0,17	0,83	0,33
Standard deviation r.c. tr. 2-7	0,07	0,08	0,20	0,12	0,55
Slope procedure 5-8	0,43	0,07	-0,26	0,17	0,36
Standard deviation r.c. tr. 5-8	0,03	0,13	0,26	0,41	1,05
Slope procedure 4-7	0,19	-0,09	-0,69	0,70	-0,81
Standard deviation r.c. tr. 4-7	0,16	0,11	0,12	0,30	0,98
Slope procedure 3-6	0,07	0,07	-0,49	1,02	0,96
Standaardafw. r.c. tr. 3-6	0,13	0,13	0,23	0,21	1,23
Slope procedure 2-5	0,20	-0,26	0,33	0,84	0,54
Standard deviation r.c. tr. 2-5	0,16	0,17	0,32	0,10	1,08
Slope procedure 1-4	0,36	-0,80	1,11	0,83	1,29
Standard deviation r.c. tr. 1-4	0,05	0,22	0,10	0,07	0,62
Procedure for calculating diff.coeff.	none ²⁾	none ²⁾	none ²⁾	none ²⁾	none ²⁾

Measured cumulative load 64 d (mg/m ²)	0,53	0,50	29,2	4376	0,74
Measured cumulative load of fractions 1 - 2 (mg/m ²)	-	-	-	-	-
Measured cumulative load of fractions 3 - 8 (mg/m ²)	-	-	-	-	-
Reason for non-diffusion-determined behaviour	concentr. too low	Rinsing off	Apparant exhaustion	dissolving	Large spread
Calcul. of upper limit for leaching 64 d (mg/m ²)	0,53	0,50	29,2	8752	70,7
Calcul. of upper limit for leaching 100 y (mg/m ²)	12,7	2,50	660	209017	88,4

²⁾ The leaching of the components 8 to and including 12 is not diffusion-determined. For these components an upper limit assessed, in accordance with "Method for calculating the upper limit of the emission" in this performance sheet, for the cumulative load after 64 days and after 100 years.



Performance sheet U.III Determination of the availability of inorganic components for leaching

Principle

Availability for leaching (in accordance with NEN 7371) is determined by extracting a sample of ground down material twice successively with water in a proportion between liquid and solid matter (LS-value) of 50 litre per kg dry matter, at a pH of 7 and 4 respectively with the aid of nitric acid (or a lower pH-value, if the material itself makes the pH lower).

The reduced material (95 % \leq 125 μ m) is brought into contact with demineralised water. Subsequently, after 1 and after 10 minutes, the pH of the suspension is measured. The pH is kept at 7 ± 0.5 (or lower, if the material itself makes the pH lower) for three hours, after which the suspension is filtered. After filtration, the damp material is again brought into contact with a similar amount of demineralised water. The pH is kept at 4 ± 0.5 (or lower, if the material itself makes the pH lower) for three hours. After filtration, the compound (or both individual eluates) must be analysed in respect of the desired components, after having been preserved (according to U-VI). The availability, in mg component per kg of dry material, as well as the acid neutralising capacity, is calculated from the measurement- and analysis results by means of the calculation formulas from NEN 7371.

Conformity with the standard

The execution based on this performance sheet is completely in line with the standard as stated here under 'Method'. If the work is performed in accordance with the performance sheet, conformity with the standard may be claimed.

Field of application

Within the framework of the Building Materials Decree, the availability test is only prescribed for moulded building materials. The test is, however, very well performable for granular materials, with the exception of sludges. (The test as such is suitable for this type of material, but during the execution, problems may occur with regard to filtration.) As far as is known, all other (secondary) building materials can be tested by means of the availability test. However, during the execution of the test, oxidation may occur in reducing materials. To what extent this will happen, cannot be predicted in advance.

During the validation of the test, the granular materials AVI-fly ash, E-soil ash and AVI-soil ash and the moulded materials Fly ash/cement-stabilisation, Sand-lime bricks with coal-dust fly ash and Brick have been used.

Variables to be determined / calculated

- pH of the material after 1 and after 10 minutes
- Availability per component (in mg/kg dry matter)
- Acid neutralising capacity



Method and quality assurance

METHOD

Sampling

Sample pre-treatment

Sample size

Particle size

Task

L/S

pH first step

pH second step

Acid for maintaining pH

Storage period of eluates

Preservation of eluates

Transfer of eluates

Building material / waste matter

AP04-M, VKB-protocols

AP04-V

16 ± 2 g

95% ≤ 125 µm

NEN 7371

50 l/kg (twicel)

7 ± 0,5 (see U-IV)

4 ± 0,5 (see U-IV)

0,2 M and 1,0 M nitric acid

SIKB-protocol 3001

See U-VI

See NEN 5861

FIRST-LINE CONTROL

Standard quality assurance points (See Ch. U5.1)

Temperature of laboratory

Between 18 and 22 °C

Conductivity demi-water

< 1 µS/cm

Points of attention

Regular check of accuracy of scales and top-pan balances (< 1%)

If the availability of cyanide is also to be determined, the arrangement of the test must be protected as much as possible against incident rays of (sun) light (in order to prevent cyanide from disintegrating by UV-radiation). In this case, the eluates must be preserved as soon as possible.

SECOND-LINE CONTROL

Frequency

1 * every 20 determinations (minimally 2 * a year and maximally 6 * a year)

Control sample

Analytes

anorganic material

Choice of 4 components (concentrations > 10 * AG), see Ch. U5.2

Requirement for the relative intra-laboratory reproducibility variation coefficient vc_w ¹⁾

main components

< 10 %

heavy metals

< 13 %

amphoteric elements

< 17 %

THIRD-LINE CONTROL

Frequency

At least 1 * a year

Ring tests

Reporting limit

3*AG

Organising company

institution accredited for ring tests

Ring test **inclusive of** analysis of the eluates and performance of the calculations, **unless** these tasks are checked separately, yet simultaneously, by means of ring tests.

Reference materials

Samples of

Bureau Communautaire de Reference (BCR),
National Bureau of Standards (NBS),
Nederlands Bureau van Referentiematerialen (NMI-NBR),
National Institute of Standards and Technology (NIST),
Samples with a conventional true value.

1) the values given include the chemical analysis of the component concerned



Set of fictitious measurement data and calculation results based on these

Measurement data

Ingewogen solid substance (not dried)	17,7 gram
Moisture content at 105 °C	10,0 %
Added quantity of demineralised water 1st and 2nd step	2 * 800 ml
Added quantity of acid (1,00 N) 1st step	10 ml
Added quantity of acid (1,00 N) 2nd step	20 ml

Concentration of element 1 measured in mixed eluate	220 µg/l
Concentration of element 2 measured in mixed eluate	< 1 µg/l

Calculation results

L/S-ratio of total test	102 l/kg
Acid-neutralising capacity	1,88 mol/kg
Availability element 1 (per kg dry matter)	23 mg/kg
Availability element 2 (per kg dry matter)	< 0,10 mg/kg



Performance sheet U.IV Determination of the pH in eluates

Principle

The pH is measured (according to NEN 6411) either with an indication electrode in combination with a reference electrode, or with a combined electrode, in which the indication- and the reference electrodes have been put together. The indication electrode consists of a glass electrode, whereas the reference electrode usually consists of a kalomel electrode. The kalomel electrode is filled with a concentrated potassium chloride solution.

Conformity with the standard

The execution based on this performance sheet is completely in line with the standard as stated here under 'Method'. If the work is performed in accordance with the performance sheet, conformity with the standard may be claimed.

Field of application

The application field of this task encompasses all eluates released during the execution of a leaching test. This task relates in particular to the measurement of the pH of eluates that are released during one of the tasks U-I, U-II or U-III.

Method and quality assurance

	Eluate Column test	Eluate Diffusion test	Eluate Availability test
METHOD			
Sampling	see U-I	see U-II	see U-III
Storage period	SIKB-protocol 3001	SIKB-protocol 3001	SIKB-protocol 3001
Task	NEN 6411	NEN 6411	NEN 6411
Range	7 < pH < 12	7 < pH < 12	4 < pH < 7
Parameter is determined by the method			

FIRST-LINE CONTROL

Standard quality assurance points

	Eluate from leaching test	Eluate from leaching test	Eluate from leaching test
Daily calibration (if pH-meter is used)	when pH = 7 and pH = 12	when pH = 7 and pH = 12	when pH = 4 and pH = 7
Calibration check with control sample	after calibration	after calibration	after calibration
Control sample	Eluate from leaching test	Eluate from leaching test	Eluate from leaching test
pH-range	7 < pH < 12	7 < pH < 12	4 < pH < 7

Requirement for the repeatability standard deviation s_r

In the acid range pH < 8	< 0,10	< 0,10	< 0,10
In the alkaline range pH > 8	< 0,20	< 0,20	

Requirement for the intra-laboratory reproducibility standard deviation s_w

In the acid range pH < 8	< 0,10	< 0,10	< 0,10
In the alkaline range pH > 8	< 0,20	< 0,20	

Remark: *In the above performance sheet, the pH-range of the eluates was chosen as the basis for each test; this means a range of 4 - 7 for the availability test and a range of 7 to 11 or 12 for the column- and diffusion tests. Besides this however, in the availability test the pH of the material is also determined (which can rise to 12). This means that in practically all cases, more than one pH-meter must be used, or that 3-punts-calibrations must be performed. For the calibrations, such calibration buffers must be used, that the measurement range falls within them.*



SECOND-LINE CONTROL

Frequency

equal to the frequency of the second-line control of the leaching test

Control sample

(Synthetic) eluate buffered, in usual pH-range

THIRD-LINE CONTROL

Frequency

At least 1 * a year

Ring tests

Reporting limit

n/a

Organising company

institution accredited for ring tests

Reference materials

Samples of

Bureau Communautaire de Reference (BCR),
National Bureau of Standards (NBS),
Nederlands Bureau van Referentiematerialen (NMI-NBR),
National Institute of Standards and Technology (NIST),
Samples with a conventional true value



Performance sheet U.V Determination of the conductivity in eluates

Principle

The electric conductivity of eluates is measured with a conductivity cell. A conductivity cell consists of platinum squares that are platinised. The measurement range is usually adjustable.

Conformity with the standard

The execution based on this performance sheet is completely in line with the standard as stated here under 'Method'. If the work is performed in accordance with the performance sheet, conformity with the standard may be claimed.

Field of application

This task applies to all eluates that are released during the execution of a leaching test. This task specifically relates to the measurement of the conductivity of eluates, released in one of the tasks U-I, U-II or U-III.

Procedure and quality assurance

Eluate	Availability test Column test Diffusion test
PROCEDURE	
Sampling	see U-I, U-II and U-III
Storage period	SIKB-protocol 3001
Task	NEN-ISO 7888
Range	0,1 $\mu\text{S}/\text{cm}$ - 100 mS/cm
Parameter is determined by the method	

FIRST-LINE CONTROL

Standard quality assurance points

Daily calibration (if conductivity meter is used).

Attune conductivity meter to cell constant of electrode

Check calibration with a control sample

Control sample Eluate from leaching test
range conductivity 200 $\mu\text{S}/\text{cm}$ < conductivity < 20.000 $\mu\text{S}/\text{cm}$

Requirement for the relative reproducibility variation coefficient vc_r

< 2000 $\mu\text{S}/\text{cm}$ < 20 %

> 2000 $\mu\text{S}/\text{cm}$ < 15 %

Requirement for the relative intra-laboratory reproducibility variation coefficient vc_w

< 2000 $\mu\text{S}/\text{cm}$ < 25 %

> 2000 $\mu\text{S}/\text{cm}$ < 15 %

SECOND-LINE CONTROL

Frequency equal to the frequency of the second-line control of the leaching test

Control sample (Synthetic) eluate
range 200 $\mu\text{S}/\text{cm}$ < conductivity < 20.000 $\mu\text{S}/\text{cm}$



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THIRD-LINE CONTROL

Frequency

At least 1 * a year

Ring tests

Reporting limit

n/a

Organising company

institution accredited for ring tests

Reference materials

Samples of

Bureau Communautaire de Reference (BCR),
National Bureau of Standards (NBS),
Nederlands Bureau van Reference materials (NMI-NBR),
National Institute of Standards and Technology (NIST),
Samples with a conventional true value.



Instruction sheet U.VI Preservation of eluates

Principle and field of application

During the execution of the tasks U-I, U-II and U-III eluates are released. Depending on the components to be analysed, the (partial) eluates must be preserved. In principle, the eluates should be divided and preserved as soon as possible (in any case within 3 days) after the execution of the leaching test.

Chemicals

All chemicals used for the preservation must be at least of pro-analysis quality.

Procedure and quality assurance

Before the preservation, the conductivity of the eluate must be checked. If the conductivity is more than 75 mS/cm, the eluate must be diluted with demineralised water, until the conductivity is smaller than 75 mS/cm. During the calculation of the results, the analysis result found must be multiplied by the dilution factor in order to obtain the actual concentration in the eluate.

In conformity with SIKB-protocol 3001, the task is executed according to the table below.

Analysis for	Size of partial eluate (material of bottle)	Procedure
Metals ¹⁾	250 ml (P ³⁾ or (borosilicate) glass)	Bring pH to 1 - 2 with nitric acid For Tin, hydrochloric acid is also permitted
Anions ²⁾	250 ml (P ³⁾ or glass)	-
Fluoride	250 ml (P ³⁾ , not PTFE)	-
Mercury	100 ml (P ³⁾ or (borosilicate) glass)	Bring pH to 1 - 2 with nitric acid and add 0,2 g/l potassium dichromate
Cyanide	100 ml (brown glass ⁴⁾)	Bring pH to > 12 with caustic soda

- ¹⁾ Metals: Arsenic, Barium, Cadmium, Cobalt, Chromium, Copper, Molybdenum, Nickel, Lead, Antimony, Selenium, Tin, Vanadium and Zinc
- ²⁾ Anions: Bromide, Chloride, Sulfate.
- ³⁾ P: Synthetic material (the suitability of which is previously checked), namely: polyethylene (PE), polypropylene (PP), polycarbonate (PC) or polytetrafluorethylene (PTFE).
- ⁴⁾ Cyanide: the material of the bottle must be coloured, in connection with the requirements set in SIKB-protocol 3001 to store the sample in the dark.



Instruction sheet U.VII Coating of surfaces of moulded building materials for the purpose of the diffusion test

Principle

In a number of cases it is necessary or desirable that, in the diffusion test, one or more sides of a moulded building material do not come into contact with the leaching liquid (see also "Field of application" in this Instruction sheet). In those cases, the sides concerned are fitted with a coating. This coating should possess the following properties:

- it should be chemically inert (no components are absorbed and/or emitted);
- it should adhere well to the building material;
- it does not let water through;

The application of either acrylate resin or paraffin wax has proven to provide an appropriate coating for the leaching investigation of inorganic components by means of the diffusion test.

Field of application

Moulded building materials must preferably be subjected to the diffusion test, in the same form and in the same manner that they will be used in practice. In order to achieve this, it is necessary or desirable that one or more sides of the test piece are coated. The following four groups of materials can be distinguished:

- Thin products

The precondition for moulded building materials to be subjected to the diffusion test is that all their dimensions must be larger than 4 cm. This condition will prevent fast-leaching components from exhaustion during the 64 days the tests lasts (as a result of which the first-order-diffusion model does not apply anymore). Certain products, roofing tiles for instance, do not meet this requirement; they are only 2 cm thick. But by coating these products on one side, only one-sided leaching can occur, so that the set requirement is still being met.

- Products fitted with a top layer

The structure of certain building materials is not homogeneous. Especially ceramic products are often fitted with a layer of glaze or another top layer. In these cases, it is more practical to subject only the side(s) of the object to the leaching test that is/are also exposed to the environment in practice. The other sides should then be coated.

- Sawn or cored test pieces

Other building materials are too big to subject them to a leaching test in the form in which they are applied. Usually, manageable pieces are sawn off from or cored out of these building materials, in order to subject them to the diffusion test. But the sawn or cored surfaces (saw-cuts) may have another structure than the surfaces that are normally exposed to the environment. If such is the case, these saw-cuts are coated, so that only the "original" surfaces are tested.

- Materials with a (partially) irregular surface

Finally, there is a category of materials (slags in particular) of which it is difficult to determine the size of the leaching surface. In those cases, it may be desirable to coat "awkward" parts of the surface and to expose only well-quantifiable surfaces to the leaching test.



Building material / monolith

PROCEDURE

Sampling

AP04-M, VKB-protocols

Sample pretreatment

AP04-V

Sample size

preferably 2 products / monoliths

Task

NEN 7375, paragraph 8.3.2 and Appendix B

Put the sample in a clean and dust free room (e.g. fume cupboard), possibly fitted with a (point-) suction unit. Prepare the cover material for application.

Apply the cover material to the surfaces to be covered with a brush.

Leave the cover material to be exposed/to dry (preferably for one night).

In order to be on the safe side, apply a second layer of cover material and leave this to dry again.

FIRST-LINE CONTROL

Standard quality assurance points

Equipment

clean

Facilities

clean, dust free, preferably fitted with a point suction unit

SECOND-LINE CONTROL

Frequency

Twice a year

Control sample

Relatively porous, moulded inorganic building material
(e.g. a brick or roofing tile)

Method

Two identical control samples are used for the second-line control. One of the two is coated on all sides, according to the method described; the other one is not coated. Put both samples, in 2 different trays, in demineralised water which is previously made acid with nitric acid to pH = 4, in an L/V-ratio of 5 l/l. Take a blank from the acidified demineralised water. Leave both samples for one week in the acidified demineralised water. Analyse both eluates and the blank in respect of one of the main components sodium or calcium.

Criteria

The coating has been applied well if the concentration of the main component in the eluate of the coated sample is not higher than the concentration of the same component in the blank + 5% of the concentration of the relevant component in the eluate of the non-coated sample.

THIRD-LINE CONTROL

Ring tests

If ring tests are organised for this task, the institution must participate in them at least once a year.



U7 Literature

NEN 3114	1990	Nauwkeurigheid van metingen - "Termen en definities".
ISO 3534-1	1993	Statistics - Vocabulary and symbols - Part 1: Probability and general statistical terms.
ISO 5725-2	1994	Nauwkeurigheid (juistheid en precisie) van meetmethoden en resultaten - Deel 2: Basismethode voor de bepaling van herhaalbaarheid en reproduceerbaarheid van een standaard meetmethode.
NEN 5861	1997	Procedures voor monsteroverdracht (concept versie van februari 1997).
NEN 6411	1981	Water - Bepaling van de pH
NPR 6603	1988	Nederlandse Praktijkrichtlijn - Water en slib - Richtlijnen voor interne kwaliteitsbeheersing met controlekaarten bij chemische analyses.
ISO 6879	1995	Air Quality - Performance characteristics and related concepts for air quality measuring methods.
NEN 7371	2004	Vaste grond- en steenachtige bouw- en reststoffen - Uitloogkarakteristieken - Bepaling van de beschikbaarheid voor uitloging van anorganische componenten.
NEN 7373	2004	Vaste grond- en steenachtige bouw- en reststoffen - Uitloogkarakteristieken - Bepaling van de uitloging van anorganische componenten uit poeder- en korrelvormige materialen met een kolomproef.
NEN 7375	2004	Uitloogkarakteristieken - Bepaling van de uitloging van anorganische componenten uit vormgegeven en monolithische materialen met een diffusieproef - Vaste grond- en steenachtige materialen.
NEN 7383	2004	Uitloogkarakteristieken - Bepaling van de cumulatieve uitloging van anorganische componenten uit poeder- en korrelvormige materialen met een vereenvoudigde procedure voor de kolomproef.- Vaste grond- en steenachtige materialen.
NEN 7777	2003	Milieu – Prestatiekenmerken van meetmethoden.
NEN 7778	2003	Milieu – Gelijkwaardigheid van meetmethoden.
NEN-ISO 7888	1994	Water - Bepaling van het elektrische geleidingsvermogen.
ISO 8466-1	1990	Water Quality - Calibration and evaluation of analytical methods and estimation of performance characteristics. Part 1: Statistical evaluation of the linear calibration function.



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ISO 9169 1994 Air Quality - Determination of performance characteristics of measurement methods.



Appendices

Appendix U1 Statistical foundation of the performance characteristics for leaching tests

In Chapter U4 it has already been stated that in respect of the leaching investigation, for reproducibility, only statistical indicators have been deduced. Due to the long run time of especially the column test and the diffusion test (3 weeks and 64 days respectively) these tests are in effect carried out under reproducibility conditions (and their execution under reproducibility conditions is almost impossible). In order to assess all leaching tests in the same manner, for the availability, too, no performance characteristics have been deduced in respect of the reproducibility.

For the deduction of the intra-laboratory reproducibility, **no** measurement values have been used that relate to (inter-laboratory) reproducibility, because in this respect, too, relatively large differences between the laboratories have been allowed for. Instead, parallel measurements (measurement pairs) have been used, that (for example in the validation investigation) have been made avail of for the calculation of the reproducibility. It has already been mentioned above that during leaching tests, the intra-laboratory reproducibility conditions are more or less similar to the reproducibility conditions.

Moreover, not only the leaching test as such, but also the analysis of the eluates has been included in the consideration (whereas, in the validation investigation, the performances of the leaching tests only have been scrutinised).

Column test

For the determination of the statistical indicators for the column test, the data of the validation investigation as well as data from TNO and IWACO have been used. All results of the validation investigation with an analysis error larger than 5% have been discarded. During the validation investigation, approx. 100 paired measurements (3 materials, 10 laboratories, several parameters) have been statistically incorporated. The sets of data from TNO and IWACO included approx. 450 paired measurements with cumulative emissions above the set criterion of either 3 times the determination limit (BG), or 10 times the detection limit (AG).

In table 1 below, the results of both populations are given. The results of both series correspond reasonably to well.

Table 1: Statistical indicators of the column test

	validation investigation	IWACO + TNO
Average v_{cw} (%)	16	16
Median	14,7	9,0
Number of observations	± 100	441

The above data show, that the average values are comparable indeed, yet the median values are quite different. It also appears that both populations are not spread in a normal way. The relatively big difference between the average and the median value of the TNO-IWACO-population is in particular caused by a number of outliers in the upper region. As opposed to the correction made for this in the validation investigation, in this case, no correction has been made.

Subsequently, the emission results of IWACO and TNO have been divided into three

categories. In table 2, the parameters are given for each category. A distinction has been made between the emission figures of the macro parameters (Na, Cl, Br, F and SO₄), the heavy metals (Ba, Cd, Cu, Co, Cr, Hg, Pb, Ni, Sn and Zn) and the amphoteric elements that show a characteristic leaching behaviour with peak leaching (Se, Sb, As, Mo, V and CN). The number of measurements per category is sufficient to make a statistical statement.

Table 2: Statistical indicators of the column test, per category of components

category	1	2	3
parameters	Na, K, Cl, SO ₄	Ba, Cd, Cr, Cu, Ni, Pb, Zn	As, Mo, Sb, Se, V
average v_{Cw} (%)	12	19	23
median	6	14	12
Number of observations	119	206	116

For the time being, the average value has been chosen as the requirement for the relative intra-laboratory reproducibility standard deviation. The precondition for admission in the performance sheets is, that the requirement for the relative reproducibility standard deviation for the whole leaching test may not be stricter than the most flexible requirement for the relative reproducibility standard deviation included in the section Analyses of Eluates with regard to the chemical analysis of the eluates, i.e. the requirement for "heavy matrices". The latter requirement is 10% for (part of) the main elements, 13% for (most of the) heavy metals and 17% for most amphoteric elements.

It may be concluded that the average values mentioned in table 2 for the execution of the column test (inclusive of analyses) are higher than the requirements set for the eluate analysis. The requirement for the intra-laboratory reproducibility standard deviation (v_{Cw}) for the column test ultimately included in the performance sheets consequently is:

- 12% for the main components (category 1)
- 19% for the heavy metals (category 2)
- 23% for the amphoteric components (category 3)

Availability test

For the indicators of the availability test, only the results of the validation investigation have been used. The average standard deviation of the intra-laboratory reproducibility (v_{Cw}) is 7.4%. In table 3, a subdivision is made for each category of components.

Table 3: Statistical indicators of the availability test, for each category of components

category	1	2	3
parameters	Na, K, Cl, SO ₄	Ba, Cd, Cr, Cu, Ni, Pb, Zn	As, Mo, Sb, Se, V
average v_{Cw} (%)	5	11	8
median	4	11	7
Number of observations	± 130	± 80	± 60



Here, the indicators deduced for the leaching test (including the chemical analysis of the eluate) are **lower** than the performance characteristics included in the Accreditation Programme, section analyses of eluates. This is presumably caused by the relatively high concentration level in the eluates of the availability test, as a result of which the measurements can be made with a higher degree of precision. The requirement for the relative intra-laboratory reproducibility standard deviation (v_{cW}) for the availability test ultimately included in the performance sheets is therefore equal to the requirement for the chemical analysis, and amounts to:

- 10% for the main components (category 1)
- 13% for the heavy metals (category 2)
- 17% for the amphoteric components (category 3)

Diffusion test

For the indicators of the diffusion test, too, only the results of the validation investigation have been used. This means, that the number of observations (measurement values) are relatively low, especially with regard to the trace elements. The average standard deviation of the intra-laboratory reproducibility (v_{cW}) for the **calculated** ϵ_{64} is 15%. In table 4, a subdivision is made for each category of components.

Table 4: Statistical indicators of the diffusion test, for each category of components

Category	1	2	3
Parameters	Na, K, Cl, SO ₄	Ba, Cd, Cr, Cu, Ni, Pb, Zn	As, Mo, Sb, Se, V
Average v_{cW} (%)	12	18	16
Median	11	18	16
Number of observations	30	8	41



The indicators, deduced (in total) for the diffusion test, are higher than the performance characteristics included in the Accreditation Programme, section eluates. The requirement for the relative intra-laboratory reproducibility standard deviation (v_{cW}) for the diffusion test, ultimately included in the performance sheets, amounts to:

- 12% for the main components (category 1)
- 18% for the heavy metals (category 2)
- 17% for the amphoteric components (category 3)