SLOVENSKI STANDARD
SIST-TP CEN/TR 16142:2011

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Cement - Študija značilnih lastnosti izluževanja strjenega betona za uporabo v naravnem okolju

Concrete - A study of the characteristic leaching behaviour of hardened concrete for use in the natural environment

Zement - Studie zum charakteristischen Auslaugverhalten von Festbetonen zur Verwendung in der natürlichen Umwelt

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91.100.10	Cement. Mavec. Apno. Malta	Cement. Gypsum. Lime. Mortar
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TECHNICAL REPORT

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English Version

Concrete - A study of the characteristic leaching behaviour of hardened concrete for use in the natural environment

Zement - Eine Untersuchung der bezeichnenden Auslaugungseigenschaften von ausgehärtetem Beton zur Verwendung in natürlichen Umgebungen

This Technical Report was approved by CEN on 20 December 2010. It has been drawn up by the Technical Committee CEN/TC 51.

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Contents

Page

Foreword

This document (CEN/TR 16142:2011) has been prepared by Technical Committee CEN/TC 51 “Cement and building limes”, the secretariat of which is held by NBN.

The work which the report refers to was developed by CEN/TC51-TC104 JWG12/TG6 in the period 1994-1999.

JWG12/TG6 has continued to work on this subject and has produced the CEN/TR 15678:2008 which is complementary to this TR.

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Summary

At the initiative of CEN/TC 51 (Cement and building limes) and CEN/TC 104 (Concrete and related products), a task group (TG 6) of TC 51/WG 12 was convened in order to accompany or follow research work being carried out within the EC research programme which has the objective of establishing the effects, if any, of concrete on the natural environment and the potential effects of cementitious materials on the quality of drinking water.

This Technical Report deals only with developments, as officially reported, by a consortium of Dutch/German Institutes, to the European Commission in EUR 17869 EN [1], leading to a performance test method for characterising the leaching behaviour of hardened concrete for use in contact with the natural environment.

NOTE The standardisation of test methods for the use of cementitious materials (possibly including concrete) in contact with drinking water, although not fundamentally different in principle, is being developed within an adhoc group of CEN/TC 164/WG 3 and will be reported elsewhere.

The protection of the natural environment and the public's health and safety are matters of major importance. Also of significant importance, however, is the efficient and sustainable use of natural and secondary materials/resources. Many of these may be used as constituents of concrete. The need to appropriately balance these two issues within the concept of sustainable construction, provided the motivation for the investigations considered in this Technical Report.

The prenormative research, underpinning this Technical Report, included a literature survey and three progressively staged interlaboratory studies (ILS). These led to the refinement of a characterisation (sequential leaching) test, comprising a tank (diffusion) test and a separate availability (maximum leaching) test. A single-extraction compliance test was not developed. A range of inorganic components/species (anionic and cationic) was targeted, some with a potential environmental significance, others of a more mechanistic relevance. Overall, a statistical and mechanistic evaluation of the results within EUR 17869 EN [1] and an environmental analysis undertaken in this Technical Report, has lead to the following conclusions.

- The leaching of major components/species, which have no environmental significance (e.g. Ca, Na, K and SO_4) from monolithic hardened concrete is diffusion controlled.

- Diffusion control could not be demonstrated, even after 14 days of leaching, for most environmentally relevant elements (e.g. As, Cd, Co and Cu) even from a relatively weak and porous concrete, since concentrations were at or below the limits of detections (DTL) of the sensitive instrumental techniques employed.

- Leached levels of components from monoliths are not related, in any simple or consistent manner, to the total concentrations of components present in concrete, and are, typically, orders of magnitude smaller.

- Leached levels of components from monolithic specimens are not related, in any simple or consistent manner, to amounts apparently available for leaching as indicated from a leaching test on finely ground concrete and the appropriateness of using such a test in attempting to characterise the leaching behaviour of hardened concrete is subject to continuing discussion.

- The concentration levels found in almost all leachates from the different tests were very low and often near the limit of the chemical analysis, indicating the good environmental quality of the concrete mixes tested.

- Concrete, containing a bituminous coal fly ash constituent specifically selected for its relatively high content of trace/heavy metals, and designed to represent a worst case within EN 206-1 [2] in terms of permeability, did not show significant leaching of trace/heavy metals. Most components were at concentrations below the analytical limits of detection.

- The anomalous leaching behaviour shown by specimens where the mixing water was spiked with aqueous solutions of the very mobile oxyanions of As, Cr, Cd and V, indicates that they were not representative of real concretes, as acknowledged by the research investigators.

- The disproportionate effect observed in the investigations, between the relatively large amounts of trace/heavy metals added as spikes to fresh concrete and apparently available for leaching, versus the minimal amounts actually leached, suggests that substituting standardized recycled or more marginal, but standardized, novel materials for the traditional constituents of concrete, would not significantly affect concrete's environmental compatibility.

- Subjecting the solid constituents of concrete to test, in isolation, either on the basis of their total elemental composition, or their response to an availability test, or their individual performance in a compliance test, will give no indication of their potential performance (either relative or absolute) when chemically and physically bound in hardened concrete.

- The characterisation leaching method, reproduced in Part II of this Technical Report, demonstrates such poor reproducibility (R approximately 76 % at 14d for trace metals As/Cd/Cr/V) that without much further investigation and development, it should not proceed to CEN/TS status or become the precursor to a draft compliance test or be used for any regulatory purpose.

- Concretes within the envelope of compositions permitted in the EN 206-1 [2] will have an insignificant impact upon the natural environment under conditions of natural exposure.

1 Introduction

Traditionally, hardened concrete has not been perceived to be a material which has contributed emissions adversely affecting the quality of the natural environment. Indeed, concrete construction in contact with the natural environment constitutes the bedrock of infrastructure and the built environment. Additionally, hardened concrete has never been shown to be responsible for any incidence of environmental pollution. Accordingly, within the range of traditional compositions used in the EU Member States, concrete's environmental service record can be taken to be unblemished.

Concrete, unlike most other construction materials, is an active material; its chemical and physical microstructure develops in a continuous process as it ages. These changes give rise to a densification of the matrix, with attendant reductions in porosity/permeability and a more efficient/effective binding of chemical species within the hydrate structures. It would be expected that concrete's leaching behaviour would also be subject to age-related changes and that this would be dissimilar to many other materials. Much research indicates that this is the case and so calls into question whether protocols, derived as in this study, from those developed for testing inert materials, are at all appropriate for concrete.

Concrete is, however, in common with other construction materials, subject to continual product development. Its compositional complexity is increasing, as constituent materials, formerly considered to be marginal, are either now in use or being considered for use. In the absence of quantitative information, some of the more marginal materials (e.g. where a total analysis reveals an apparently high heavy metal content) can give rise to concerns about their potential emission levels.

In addition, environmental regulatory activity, although at different points in the cycle in different EU Member States, is more and more subject to centralised direction via instruments such as EU Directives and mandates, and is generally increasing in its pace and scope.

Within this operational framework, standardised leaching tests, whether national or international, have taken a range of forms:

- characterisation;
- compliance;
- verification;

each of which can be used to evaluate the environmental performance/compatibility of hardened concrete, under different specified conditions using different assessment criteria. Characterisation leaching tests consist of an availability (granular or pulverized specimen) procedure and a sequential/periodic tank (monolithic specimen) procedure which together provide the means for discriminating between the several transport processes such as:

- dissolution;
- wash-off;
- diffusion;

and for predicting the rate of leaching and long term behaviour of a material.

In addition, physical characteristics such as tortuosity, which is a measure of the prolonged path along which leached components have to travel, can be calculated.

Compliance leaching tests consist of single extractions of short duration, generally without agitation, and which permit a direct comparison with regulatory limits for individual analytical components. Such tests use the prior output from characterisation tests to establish and optimise their parameters.

Verification leaching tests are essentially second order compliance tests, modified for operation in the field and used to identify/assess changes in established performance of batches of a material.

A final, and desirable, element in any authoritative procedure designed to evaluate environmental performance would be the preparation and maintenance of a certified reference material (CRM), for example, a certified reference concrete, preferably used within the context of a proficiency testing scheme (PTS), in order to monitor the performance of a laboratory and validate the accuracy of its procedures. In the case of concrete, the preparation and robust certification of a CRM is unlikely to be either attempted or to be feasible given the continuous changes in microstructure to be expected, with the likelihood of associated changes in its leaching characteristics.

Accepting that a concrete CRM is unlikely to be developed, then the preparation of a standard leachate, again for use within a PTS, would be the minimum expected for validation of laboratory performance.

It should be understood that the complete analysis of a concrete (or any of its constituents) in order to give a total elemental composition, is generally acknowledged to be of little environmental value and would be rarely undertaken in testing given that the greater proportion of most analytical components, whether environmentally significant or not, is known to be insoluble under naturally occurring exposure conditions.

Part I

2 Scope of the study

2.1 Summary of three interlaboratory studies (ILS)

As reported in EUR 17869 EN [1], the Dutch/German Project Team (see 6.2) carried out its investigations in three stages, each stage leading to an interlaboratory study (ILS); the final ILS involved European participation much broader than the Project Team's membership.

The starting point for each stage was that a method of short duration, for the basic characterisation of leaching of inorganic components, should be developed and finally, validated.

A literature survey had indicated that the main transport process from monolithic concrete should be diffusion controlled and that a diffusion (tank) test, together with a maximum leachability (availability) test would be required in order to derive effective coefficients of diffusion, in order to be able to predict long-term leaching behaviour of concrete in the field

2.1.1 First interlaboratory study and its evaluation (ILS #1)

2.1.1.1 Objective

The objective of the first ILS was to assess the effect(s) on the leaching of a range of inorganic components from concrete, made to a single mix design, of varying the major parameters within several different, nationally and internationally (ISO) standardised, availability and tank leaching methods; the work being carried out in up to five laboratories.

2.1.1.2 Concrete used in the first ILS

Table 1 a — Mix design

Constituent	Content (kg/m^3)
Portland cement (Class 42,5)	302
Coal fly ash	60,5
Water (demineralised)	181
W/(c + 0,4f) [a]	0,55
Gravel 16 mm – 8 mm	573
Gravel 8 mm – 2 mm	743
Sand < 2 mm	483

Table 1 b — Miscellaneous

Strength at 28 days (mean)	48 MPa (N/mm^2)
Specimen type	100 mm cube
Curing regime Fog room: Climate chamber:	Demould : 1 day 20 °C/100 % RH : 6 days 20 °C/65 % RH : 56 days
Age at start of test	69 days

[a] k-value concept for additions in EN 206-1 [2]; where c = Portland cement content, k = 0,4 for Class 42,5 Portland and f = coal fly ash content

2.1.1.3 Test procedures and data analysis

For the analytical (instrumental) techniques used, the leaching tests investigated and the statistical/mechanistic data analysis, see 6.2.2, 6.2.3 and 6.2.4, respectively, in EUR 17689 EN [1].

2.1.1.4 Results

2.1.1.4.1 General

The results of the first ILS did not contribute to an understanding of the mechanisms involved in leaching or in establishing the influence of varying the test conditions on the performance of the tests. The reason for this shortcoming is given in [1] by the investigators. They observe that the concentration levels found in almost all leachates from the different tests were quite low and often near the limit of detection of the chemical analysis, indicating the good environmental quality of the concrete tested.

The mean results of the first ILS, as obtained from the test procedures which were selected for all the subsequent work, are given in Table 2 a for total contents, available contents and amounts leached over 7 d and over 64 d (calculated). In Table 2 b comparisons are presented, where data permits, between amounts leached at 7 d and 64 d and available amounts and total contents, in order to place the degree of leaching, for individual components, in perspective.

2.1.1.4.2 Environmental analysis and discussion of the results

a) Introduction

Although these investigations did not set out to assess the environmental performance/compatibility of the concretes under test, much useful information can be obtained from an environmental analysis of the results obtained at each stage in the development of the research.

In this first ILS, points of particular significance are reported and discussed, below:

- A large amount of potential data is missing from Tables 2 a and 2 b much of it for components generally agreed to have an environmental significance. These omissions usually result from concentrations being at or below the limits of detection after 7 d of cumulative leaching during the tank test.

- Of the components for which 7 d leaching data is presented, Cl (chloride ion), Na (sodium ion) and S (sulfate anion) are naturally present in almost all soils and groundwaters and have no environmental significance; accordingly they can be disregarded in any environmental analysis of the results.

- For a small number of components, for example B (boron) and Cd (cadmium) in Table 2 a, the mean results recorded for amounts available for leaching, as deduced from a test on pulverized concrete, are greatly in excess of the total amounts determined to be present in the concrete. The most likely causes of such anomalies are the analytical difficulties of working at concentrations near to the limits of detection of the analytical techniques. Such results, however, can readily give rise to false conclusions.

In this ILS this leaves As, (arsenic), Cd (cadmium), Co (cobalt), Cr (chromium), Cu (copper), Pb (lead), Tl (thallium) and Zn (zinc) for further environmental consideration.

Simple inspection of the data reported in Tables 2 a and 2 b indicates that responses to the different leaching regimes, i.e. availability test or tank test, are component-specific; this is consistent with the body of research evidence in this area. An analysis of the data for each individual component could tend to obscure rather than illuminate any general trends. The discussion section, which follows, addresses characteristics of the data which have a broad significance for the assessment of the environmental compatibility of concrete with its environment.

b) Discussion

From Tables 2 a and 2 b some reasonably general points can be observed.

- Only a small proportion of the total amount of a trace/heavy metal has been leached during the sequential extractions (over either 7 d or as extrapolated to 64 d). The total amount, therefore, does not give the potential amount for leaching and gives no indication of what proportion of a component would be leached under either standard or field exposure conditions.

Table 2 a — Mean results from first ILS

Component	Total content		Available		Leached 7 d (measured)		Leached 64 d (calculated)	
	(measured) (mg/kg)	(calcula-ted) (mg/m^2)	Lmax (mg/kg)	Emax (mg/m^2)	L7d (mg/kg)	E7d (mg/m^2)	L64d (mg/kg)	E64d (mg/m^2)
Al	9 755	-	71,4	-	-	n.d.	-	-
As	5,15	202	0,15	5,9	< 0,1	< 1,67	0,13	< 5,1
B	1,5	-	20,9	-	-	DTL	-	-
Ba	174,3	-	50,3	-	-	DTL	-	-
Br	n.d.	-	< 2,07	-	-	DTL	-	-
Ca	52 954	-	52 427	-	-	n.d.	-	-
Cd	0,16	6,3	0,44	17,3	< 0,01	< 0,1	< 0,01	< 0,3
Cl	103,5	4 068	103	4 048	9,8	383,3	25,1	987,6
Co	4,89	192	1,17	46	< 0,01	< 0,8	< 0,1	< 2,5
Cr	483,2	18 990	2,51	98,6	0,15	< 5,8	0,5	< 17,7
Cu	10,6	417	3,56	139,9	< 0,01	1,2	< 0,1	< 3,36
F	99,00	-	62,7	-	-	DTL	-	-
Fe	6 776	-	413,3	-	-	n.d.	-	-
Hg	n.d.	-	<0,022	-	-	DTL	-	-
K	3 046	-	853	-	-	n.d.	-	-
Li	n.d.	-	4,76	-	-	DTL	-	-

Table 2 b — Comparisons from first ILS: % leached vs. available/total

% leached (measured or calculated)				
7 d (measured) vs. available	7 d (measured) vs. total	64 d (calcula-ted) vs. available	64 d (calculated) vs. total	Available vs. total
-	-	-	-	0,7
28,3	1,9	< 86,0	2,5	2,9
-	-	-	-	?
-	-	-	-	28,9
-	-	-	-	-
-	-	-	-	99
0,5	1,6	1,6	4,8	100
9,5	9,5	24,4	24,4	100
1,8	< 0,2	< 5,5	2	23,9
5,9	< 0,1	< 18,0	0,1	0,5
0,9	< 0,1	< 2,4	<1	33,6
-	-	-	-	63,3
-	-	-	-	6,1
-	-	-	-	-
-	-	-	-	28
-	-	-	-	-

Mg	1 064	-	777,9	-	-	n.d.	-	-	-	-	-	-	73,1
Mn	101,8	-	47,4	-	-	DTL	-	-	-	-	-	-	46,6
Mo	6,2	-	0,55	-	-	DTL	-	-	-	-	-	-	8,9
Na	397,9	15 638	156,8	6 162	10,4	408,3	22	862,9	6,6	2,6	14	5,5	39,4
Ni	121,3	-	11,5	-	-	DTL	-	-	-	-	-	-	9,5
P	201,5	-	1,16	-	-	DTL	-	-	-	-	-	-	0,6
Pb	13,6	535	0,65	25,5	0,25	9,85	0,81	31,7	38,6	1,8	100	6	4,8
S [a]	1 217	47 828	1 341	52 701	5,7	222,3	-	-	0,4	0,5	-	-	100
Sb	< 1,96	-	0,2	-	-	DTL	-	-	-	-	-	-	10,2
Se	0,36	-	0,094	-	-	DTL	-	-	-	-	-	-	26,1
Si	371 224	-	3 093	-	-	DTL	-	-	-	-	-	-	0,8
Sn	n.d.	-	3	-	-	DTL	-	-	-	-	-	-	-
Ti	704,3	-	< 0,21	-	-	DTL	-	-	-	-	-	-	< 0,1
Tl	< 1,22	48	0,085	3,3	< 0,1	< 1,67	0,13	< 5,1	49,9	< 8	100	10,7	7
V	18	-	0,16	-	-	DTL	-	-	-	-	-	-	0,9
Zn	80,9	3 179	55	2 162	0,21	< 8,3	0,64	25,3	0,4	0,3	1,2	0,8	68

[a] S is sulfate anion (SO_4)

NOTE 1 Lmax, in mg/kg is the maximum amount available for leaching.

NOTE 2 Emax, in mg/m^2 is Lmax. × 39,3; 39,3 is a geometrical factor for the 100 mm cube specimens, used to convert mass specific leaching into an equivalent value per unit area.

NOTE 3 E7d, is the measured cumulative release in the tank test, in mg/m^2, (L7d is calculated from E7d by dividing it by 39,3)

NOTE 4 E64d is a calculated extrapolation using the 7 d data.

NOTE 5 DTL means at or below the limit of detection.

NOTE 6 The amount available is determined on a sample of finely ground concrete (90 % < 125 µm) extracted consecutively in demineralised water at pH 7 then at pH 4.

- Much larger proportions of the available amount of the trace/heavy metals have been leached during the sequential extractions as extrapolated to 64 d. The actual proportion is component-specific but in the case of As, Pb and Tl it constitutes almost all of the available quantity.

On the evidence above, the available amount can give a good indication of the potential amount for leaching for some components (As, Pb, Tl) but is much less informative for other trace/heavy metals, being a particularly poor indicator of the potential amount for leaching for Cd, Cu and Zn.

- It can also be observed that there is no single, simple relationship between the amount of a trace/heavy metal, defined as available for leaching, and the total quantity in the concrete. The amount available as a proportion of the total ranges from < 0,1 % for Ti to 100 % for Cd.

- Most importantly, in terms of the environmental impact of this particular, but reasonably typical, concrete, the absolute amounts of the trace/heavy metals which gave measurable concentrations when leached over 7 d (or as extrapolated to 64 d), were in the sub-ppm (< 1 mg/kg) range; as recorded in Table 2 a.

2.1.2 Second interlaboratory study and its evaluation (ILS #2)

2.1.2.1 Objective

The objective of the second ILS was to validate the appropriateness of the test protocols (availability and tank) selected from those investigated in the first ILS for characterising leaching from concrete.

In the first ILS, the leaching behaviour of some environmentally insignificant components e.g. chloride ion, had suggested that transport could be diffusion controlled. The validation exercise was designed to try to establish whether or not diffusion control also applied to trace/heavy metals; this could not be established from the results of the first study because leached levels were too low.

Concrete of a different mix design (see Table 3 a) was prepared in order to give, what was considered would be, a worst case, within the scope of EN 206-1 [2], in terms of its potential leaching performance. The design included the use of a bituminous coal fly ash, specifically selected for its relatively high content of trace/heavy metals, in order to increase the intrinsic level in the concrete, together with a relatively high water/binder ratio in order to give a more porous/permeable, and hence potentially leachable, microstructure.