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Comparison of the characteristic leaching behavior of cements using standard (EN 196-1) cement mortar and an assessment of their long-term environmental behavior in construction products during service life and recycling

H.A. van der Sloot*

Soil and Waste Research, Netherlands Energy Research Foundation, P.O. Box 1, 1755 ZG Petten, The Netherlands

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Abstract

The uncertain environmental properties of cements, when used in construction materials, during these materials' service life and any "secondary life" (construction debris), have been raised as matters of concern due to the increasing use of alternative fuels and raw materials in the manufacture of cement clinker. A comparison of the leaching behavior of a range of traditional cement types, assessed in standard mortar prisms, with two non-traditional special cements, made using alternative fuels/raw materials, has shown that the leachability from these special cements does not exceed the leachability from the traditional cements. For relevant constituents, such as Cr, even a lower leachability is observed in spite of a higher total composition. This illustrates that an evaluation of cement based on total concentration of either the anhydrous cement or the cement-based product, in which it is used, is not a valid means of judging environmental impact. The emphasis in environmental evaluation has been on the properties during service life of cement-based products. This stage of life of a cement-based product has proved to be of limited concern. The emphasis should be focused on the "second life" of cement-based products. If construction debris is reused as aggregate in concrete, again leachability is of limited concern as the chemical environment dictated by the cement matrix ensures a low leachability. When construction debris are reused as hydraulically unbound aggregate, e.g., in road stabilization, environmental issues prove to be relevant as oxyanionic species (e.g., chromate, sulfate, molybdate, vanadate) may exceed critical limits according to Dutch regulations. With the possible exception of Cd, metals such as Pb and Zn are unlikely to become critical environmentally, even in the "second life" of cement-based products. When environmental criteria for cement-based products are developed they should be based on leachability of standard mortar and not on concentration to guarantee environmental compatibility during service life, "second life" and "end of life" scenarios.

Keywords: pH; Long-term performance; Modeling; Heavy metals; Leaching behavior

1. Introduction

For the production of cement, alternative fuels and raw materials are increasingly being used to produce clinker [1–3]. The uncertain environmental properties of the cements, when used in construction materials, during these materials' service life (primary application in intact structures) and any "second life" (construction debris used as aggregate in concrete or unbound in road construction), have been raised as matters for concern in relation to the increasing use of such alternative fuels and raw materials. An evaluation of the environmental properties of cement-based products cannot be based on total concentration of heavy metals as this has been shown for other matrices to be a poor predictor for release to the environment [4]. Since the release to the environment is the property of concern and release to the environment is controlled by transport through the water phase, leaching tests are the most appropriate means of assessing environmental impact from cement-based products. This is consistent with the European Commission's view regarding release of dangerous substances from construction products as stated in document CONSTRUCT 98/329 (1998). The choice of a test is however not unambiguous. Different tests are available each addressing a specific

* Tel.: +31-224-564-249; fax: +31-224-563-163.
E-mail address: vandersloot@ecn.nl (H.A. van der Sloot).

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aspect of leaching. In these studies carried out on the use of alternative fuels and raw materials to produce cement, tests working under acidic conditions [5,6] and tests working under prevalent alkaline conditions [7–9] have been applied. In both cases, the leachability observed reflects rather extreme exposure conditions, as in most normal applications (surface) carbonation will occur. It must be realized that in some cases concrete products are exposed to acidic soils. These situations require a separate evaluation of the exposure scenario.

In this study, a selection of relevant tests have been carried out on cements from different origin to judge the relative importance of different constituents in cement, the comparability of different tests, the relevance of the tests for the evaluation of material quality and material management. The cements tested cover cements produced from natural materials and special cements derived from alternative fuels and raw materials. A key question is how to evaluate long-term behavior both during the service life of intact cement-based products, in the recycling stage of construction debris and their ultimate "end of life" (disposal).

2. Experimental

2.1. Materials tested

Since cement powder as such is not used, the studies have been concentrated on cement mortars. To assess the final stage of cement-based materials, as construction debris, the mortars have been size reduced. The cement mortar samples for the study were prepared by Ciments d'Obourg according to EN 196-1 [10]. The mortars were wet cured in plastic bags. After 28 days, the mortars were subjected to testing. For some of the leaching tests the cement mortars were crushed in a jaw crusher to a size 95% <4 mm. For the availability test, the material was further size reduced to 95% <125 μm. The mortar samples were classified in three main groups: Portland cement (CEM I), different slag cements (CEM II to CEM V) and special cements based on alternative raw materials (non-Portland cements such as high-alumina cements excluded) (Table 1). SPCEM-11 and SPCEM-12 are based on artificial slag reprocessed from industrial and non-industrial slags and ashes.

2.2. Leaching tests

The leaching tests selected for the study are the following:

NEN 7341 availability test [5]: Dutch standard extraction test for assessment of maximum leachability (NNI, 1995c). The construction material is ground to <125 μm and extracted in two steps of L/S=50 l/kg each with demineralized water at pH=7 (first extraction) and pH=4 (second extraction), respectively. pH is kept constant by feed-back control and addition of HNO_3 or NaOH. The contact time in each extraction is 3 h. The two extracts are combined prior to analysis.

DEV S4 [8]: German standard batch leaching test developed to assess the leaching of sludges and sediments from water and wastewater treatment (DIN, 1984). The method is considered applicable to solids, pastes and sludges and does not simulate field conditions. The material to be tested should be <10 mm. Material is extracted at L/S=10 l/kg for 24 h with demineralized water under shaking or slow rotation. pH is not controlled in this test that is widely used for regulatory purposes in Germany and Austria.

pH static leach test [11]: This test provides information on the pH sensitivity of leaching behavior of the material. The test consists of a number of parallel extractions of a material at an L/S 10 during 24 h at a series of preset pH values. Since pH is one of the main leaching controlling parameters, the information can be used to evaluate the repeatability in testing (resulting from measurement at steep concentration–pH slopes) and to provide information on the sensitivity to pH in specific field scenarios. The acid neutralization capacity (ANC) derived from the test is a useful property in this respect. For material characterization this has been proven to be a very useful method [4,12,13]. The method is being standardized in two experimental modes by CEN TC 292 Working Group 6.

NEN 7345 tank leach test [9]: In this test, the specimen is subjected to leaching in a closed tank. The leachant is renewed after 8 h, 1, 2.25, 4, 9, 16, 36, 64 days at a leachant-to-product volume ratio (L/V) of approximately 5. The results are expressed in milligrams per square meter (mg/m^2). This test is a procedure to evaluate the release from monolithic material by predominantly diffusion control (e.g., exposure of structures to external influences). The distinction is necessary, as the transport limitations set by a

Table 1
Types of cement studied

Type and code	Remarks	Type and code	Remarks
CEM I-1		CEM II/B-6	natural pozzolanic materials
CEM I-2		CEM II/B-7	fly ash
CEM I-3		CEM V/A-8	20% fly ash and 20% slag
CEM I-4	C3A < 3%	CEM II/B-9	20% slag and 10% limestone
CEM I-5		CEM III/B-10	70% slag
SPCEM-11	100% artificial slag	SPCEM-12	100% artificial slag

solid form result in a significantly lower environmental impact than derived from crushed material. This condition is valid as long as the product retains its integrity. To assess the behavior after disintegration or demolition the information obtained in the pH dependence leach test is very relevant, as in this situation the pH is likely to change to more neutral conditions.

NFXP31-211 [7]: French experimental standard leaching test for monolithic material (AFNOR, 1995). The test has been derived from X-31-210 [14], which has been developed for granular materials. The release mechanism from monolithic materials has not been taken into account in the development of this method (arbitrary tool). The test consists of three leaching cycles of 16 h with 8 h in between, where the leaching is stopped. The dimensions of the specimen must be defined very precisely as results are presented in milligrams per kilogram (mg/kg).

ATA procedure: To assess the use of concrete for drinking water purposes the ATA procedure has been developed [15]. The material is pre-leached with mineralized water for 4 or more cycles of 24 h prior to the actual leaching to reduce the pH of the leachate below 9. This is followed by three consecutive leaching steps with mineralized water from a local source. The leaching cycles are 72 h each using water volume to surface area ratio of 5 cm^3/cm^2. The eluates resulting from this procedure are acidified and analyzed for trace metals. The results are expressed in milligrams per square decimeter (mg/dm^2) day.

2.3. Analysis

The total composition of the mortars is determined in the solution resulting from dissolution of the <125-m size reduced material in a mixture of HF, $HClO_4$ and HNO_3. The main elements were determined by X-ray fluorescence spectrometry (XRF) in the form of fused bead. Eluates obtained from the tests are filtered through 0.45-μm membrane filters and acidified to pH 2 prior to analysis. For a full screening of a wide range of elements in leachates induction-coupled plasma emission spectrometry (ICP) has been applied.

2.4. Geochemical modeling

The geochemical code MINTEQA2 [16] has been applied for the modeling of the chemical speciation in leachates from crushed cement mortars using data from the pH dependence experiments. Davies equation is applied to

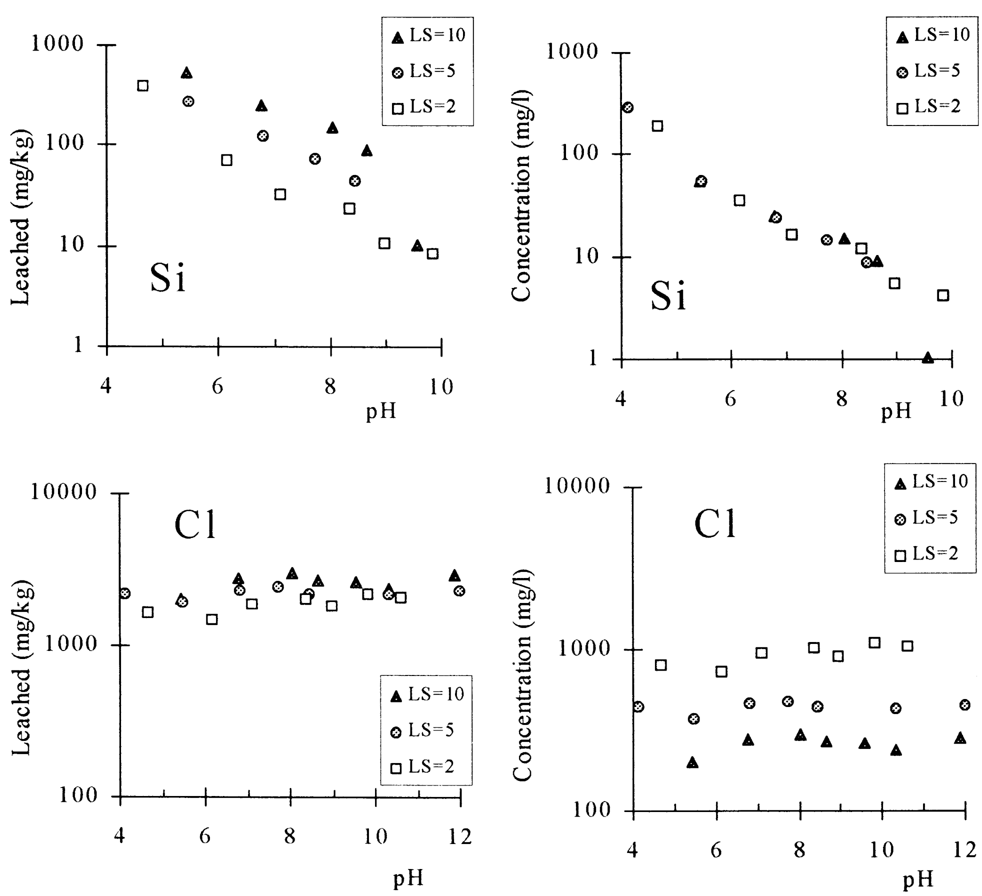


Fig. 1. Distinction between solubility control (Si) and availability control (Cl) in MSWI bottom ash [11].

correct for ionic strength effects. For most pH values at the L/S values used, this correction is usually adequate. The saturation indices for the different chemical phases are calculated under the conditions as measured in the leachate. The possible leachability controlling phases for the respective elements will be discussed. The substitution of oxyanions (e.g., MoO_4^-, AsO_4^{3-}, CrO_4^-) in ettringite cannot be described by a stability constant [17–22], because a proper model description is at present not available. This limits the possibility of quantifying the effects of incorporation of oxyanionic species, e.g., Cr, Mo, V, As in ettringite phases in the pH domain pH>10.

2.5. General aspects of data interpretation

A general aspect of data interpretation is related to the behavior of elements in terms of availability or solubility control of leaching [13]. Leaching test results can be expressed either as leachate concentration (mg/l) or as constituent release (mg/kg residue). The basis selected for expressing leaching results should be the type of data comparison that is desired.

Results expressed as leachate concentrations (mg/l) permit a comparison of constituent solubility that reflects the chemical speciation of the elements and leaching solution conditions (e.g., pH). Transformation of measured concentrations into release is necessary for comparison of the data obtained at different liquid-to-solid (L/S) ratios and for determination of availability. Regulatory test results are most often expressed in milligrams per kilogram (mg/kg) for comparison to limit values, but do not consider the underlying basis for release phenomena that are observed. Release is defined as the mass of a constituent dissolved divided by the mass of residue leached. In Fig. 1 the leaching of Cl is given as an example representing the leachability of an availability-controlled species. Data from tests at different L/S expressed in milligrams per liter (mg/l) lead to apparent differences, while data presented in milligrams per kilogram (mg/kg) show that in all cases the fraction available for leaching is released. At L/S>2 all Cl is leached from the material studied. The element Si represents a solubility-controlled constituent. Here presentation in milligrams per kilogram (mg/kg) leads to differences, whereas data represented in milligrams per liter (mg/l) show the solubility control in the pH region 4–10.

3. Results

3.1. Basis for comparison of different types of cement

To control the environmental quality of cements judgements have been made based on either total concentration of the cement or on leachability of the actual construction product. According to the Swiss approach (Buwal Liste [24]), the total concentration is used to control cement quality for environmental purposes. In the Dutch Building Materials Decree [25], the release of constituents from the actual construction product to the soil in a period of 100

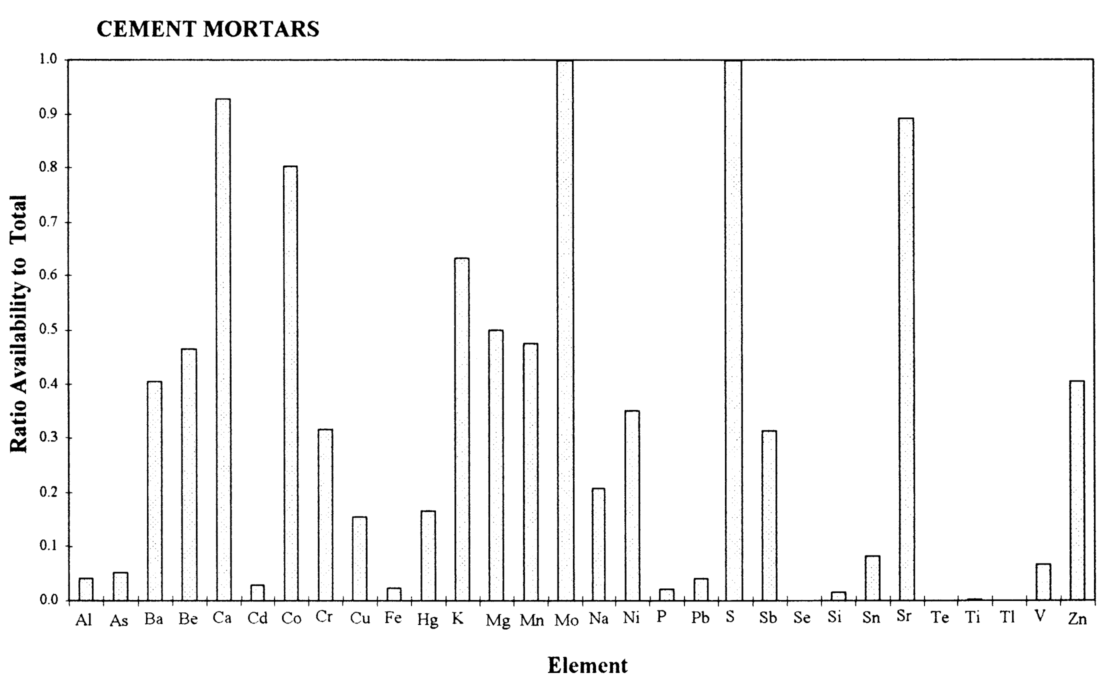


Fig. 2. Fraction of the total concentration, which is potentially leachable under worst case conditions (availability test — NEN 7341) for different elements in the different cement mortars.

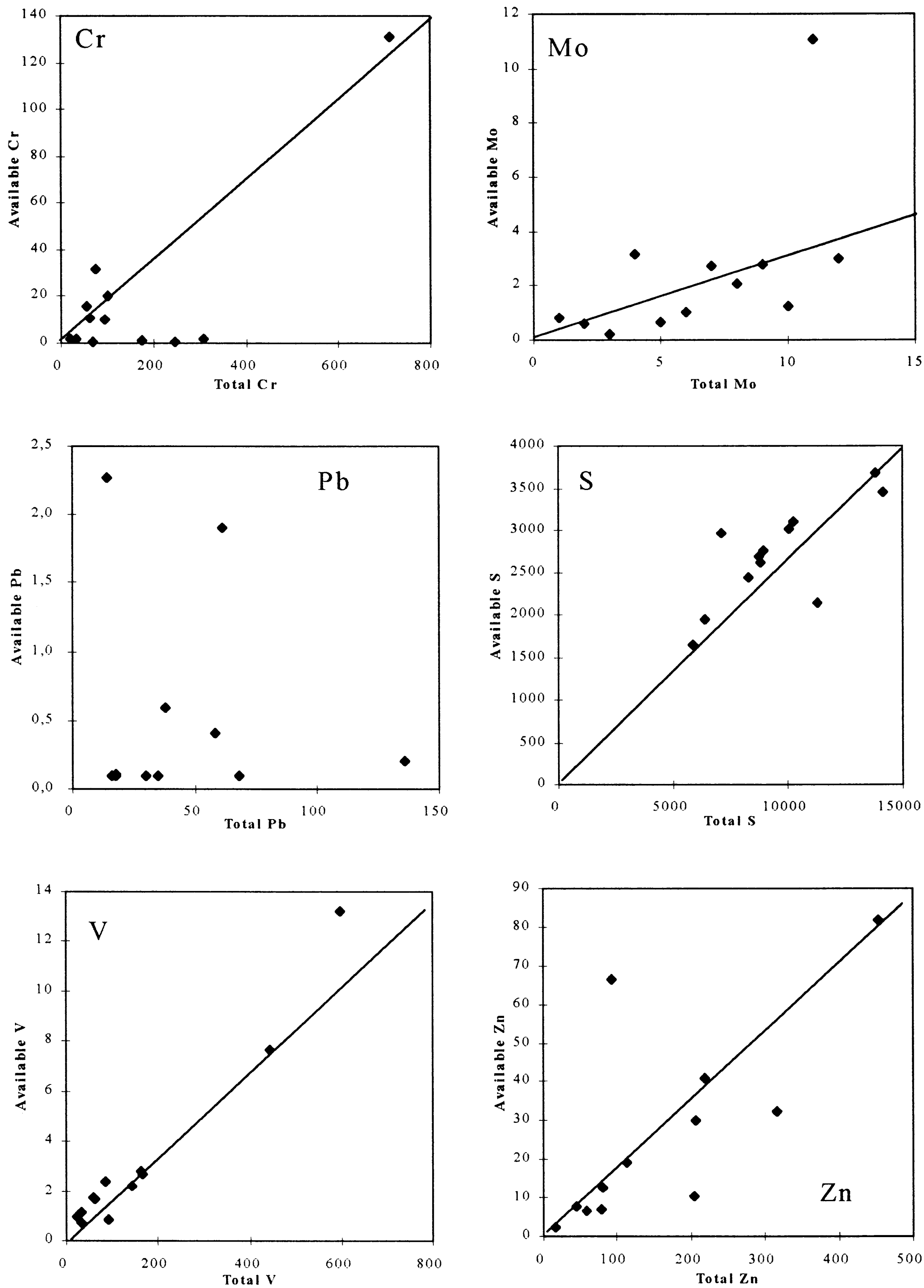


Fig. 3. Correlation between total and availability for Cr, Mo, Pb,S, V, and Zn on all cements (mg/kg).

years is taken as the basis of reference. A marginal increase in soil burdening has been considered acceptable and has been quantified in relation to leaching tests assessing the release from granular or monolithic materials. The use of either of these approaches is discussed below based on results of the individual tests.

Table 2
Total concentration, availability, and leachability of Cr under specified conditions (mg/kg)

Code	Total	Availability	Maximum in pH-stat	pH at maximum	Leached at pH 12.5
SPCEM-11	89	1.98	2.5	4	0.18
SPCEM-12	67	0.68	2.69	10	0.72
CEM I-1	27	10.94	10.7	10	2.26
CEM IIB-6	14	2.04	2.07	10	0.49
CEM IIB-9	18	1.81	2.12	8	0.67
CEM I-2	181	131	142	6	34
CEM VA-8	25	15.9	15.75	10	3.05
CEM IIIB-10	22	0.52	1.30	10	1.32
CEM I-5	31	20	31	7	5
CEM IIB-7	29	10.1	7.52	9	3.3
CEM I-3	21	1.10	1.41	10	0.6
CEM I-4	47	31.8	25.8	8	7.3

3.1.1. *Total concentration versus availability for leaching (potential leachability)*

By controlling the quality of cement through its total concentration, it is implied that only a fraction of the total is environmentally relevant. For, if the total concentration had to be considered as potentially available for leaching, the release would be unacceptably high. Leaching tests on hydrated samples form a refining of the evaluation by focusing on the fraction that may be leached under specified circumstances. In this context, the availability test (hydrated product, subsequently crushed) can be considered as a worst case approach. Leaching tests of intact monolithic products and leaching at a controlled pH provide a basis for release under more specific exposure conditions. As can be seen from Fig. 2, the fraction of the total that is potentially leachable under worst case conditions varies widely between elements. In Fig. 3 the poor correlation between total and potentially leachable (availability according to NEN 7341) is illustrated for Cr, Pb, Mo, S, and Zn. Only for V, is a reasonably linear correlation observed between total and potentially leachable. The Cr availability is quite low for the special cements investigated. This is probably related to the oxidation state of the clinker at the end of the kiln.

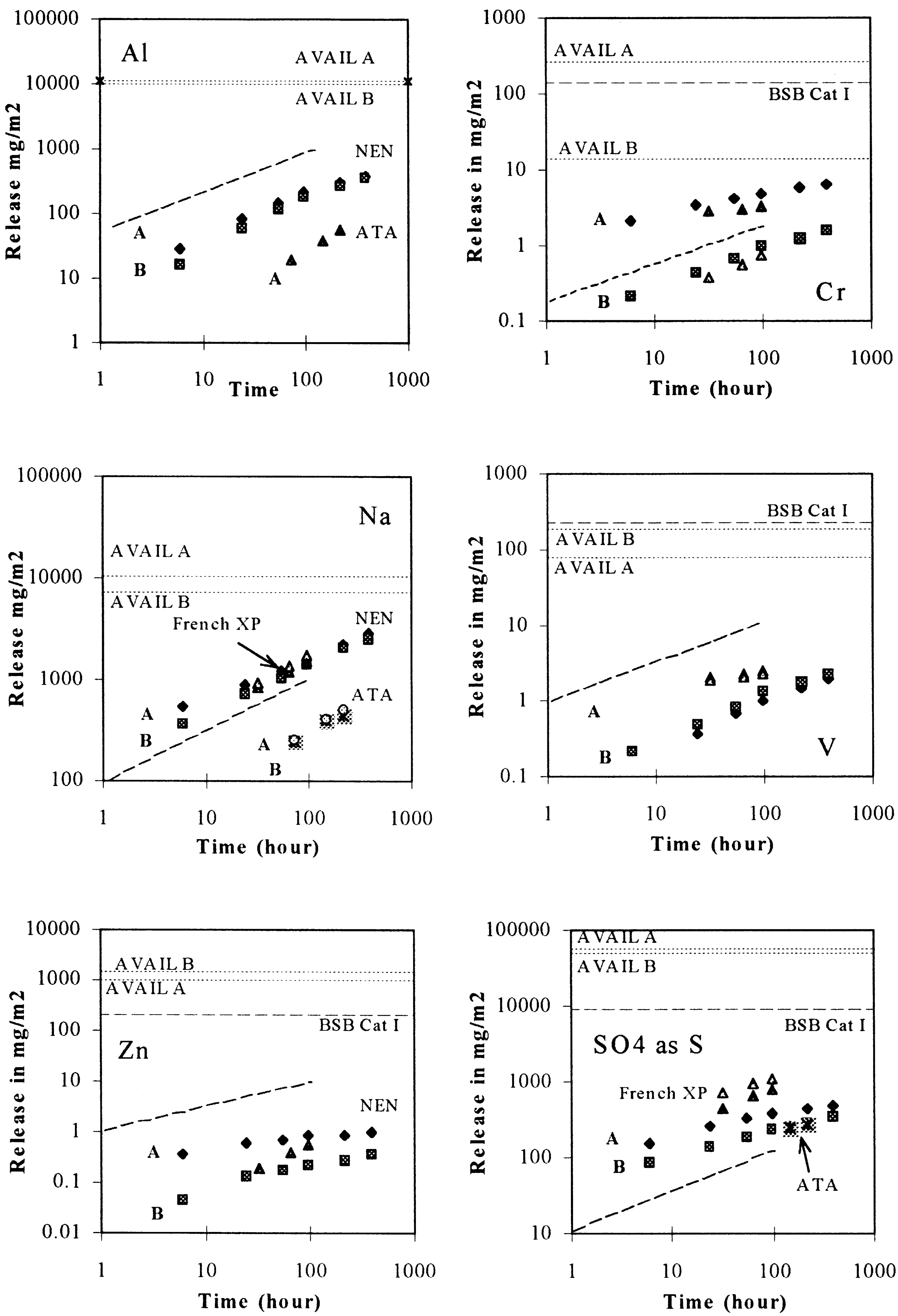
In Table 2, a comparison of total concentration (mortar), availability for leaching (crushed cement mortar) and the leaching under specified conditions is given for Cr (crushed mortar, pH adjusted). The comparison illustrates the lack of correlation between leachability and total concentration. Since the availability for leaching is a more realistic parameter from an environmental point of view than total composition [4], the lack of correlation between availability and total concentration would favor the use of availability as a control parameter over total concentration, if a choice between the two has to be made.

3.2. *Tests to assess cement-based products during their service life*

The test methods — NFX31-211, ATA and tank leach test (NEN 7345) — aim to assess the release from intact products. The results are converted to the same release units (mg/m^2) to allow data comparison. In Fig. 4, the relation between the test methods is graphically shown. The data obtained for the ATA procedure are relatively unreliable for elements of concern due to subtraction of two large numbers of about equal size, namely the eluate and the mineral water composition.

From all elements for the ATA method, only four three elements (Na, K, S and Al, K not shown in figure) remain with significantly distinct data. All other values are too unreliable to report. In comparison with the tank leach tests, all values fall well below the tank leach tests data due to the pre-leach in the ATA procedure. The data from the ATA procedure cannot be used for further data evaluation in spite of the presentation as a flux. The method applied is mainly aimed at preventing release of constituents at an initially high pH, which is indeed not representative of the actual condition in drinking water pipes. A simpler approach to reach the same goal — one that allows realistic measurement of constituents and one that does allow long-term release calculations to be carried out — is carrying out the NEN 7345 under slightly modified conditions. These conditions would be to control the pH of the leachant during testing at pH 8 by bubbling air through the solution [26]. This leads momentarily to a lower initial pH than otherwise would be obtained with mortar and consequently to a lower release of constituents of concern (Pb, Zn, etc.). This option has been verified in an EU study of cement-stabilized MSWI fly ash [12]. By using demineralized water instead of mineralized water, the concentrations of several constituents are measur-

Fig. 4. Comparison of release as obtained from NEN 7345 (8–564 h), ATA (72–216 h) and NFX31-211 (24–96 h). (A) Traditional cement CEM IIB-7 and (B) special cement SPCEM-12. Availability data are included for both cements. BSB category I is the regulatory limit value as specified in the Dutch Building Materials Decree [21]. The broken line represents slope 0.5 for diffusion control.


Al
AVAIL A
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A
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Release mg/m2
Time
100000
10000
1000
100
10
1
1
10
100
1000
AVAIL A
BSB Cat I
AVAIL B
Cr
A
B
Release in mg/m2
Time (hour)
1000
100
10
1
0.1
Na
AVAIL A
AVAIL B
French XP
NEN
ATA
Release mg/m2
Time (hour)
BSB Cat I
AVAIL B
AVAIL A
V
Release in mg/m2
Time (hour)
AVAIL B
AVAIL A
BSB Cat I
Zn
NEN
Release in mg/m2
Time (hour)
10000
0.1
0.01
AVAIL A
AVAIL B
BSB Cat I
SO4 as S
French XP
ATA
Release in mg/m2
Time (hour)

able and can be quantified. The data obtained with the French test are for several elements systematically lower in release due to the principle of the test in which a few periods of no leaching are incorporated (three cycles of 16 h leaching and 8 h standing in moist condition). The French test is also more susceptible to variations resulting from pH change upon carbonation during the 8-h contact with the atmosphere. The cumulative release curve shows changes in pH over the subsequent leaching cycles in case very sharp changes occur in leaching as a function of pH (Zn, S). The test most consistent with the release mechanism from monolithic materials is the NEN 7345. The data from this test are also more consistent. The number of steps is not limiting as an option exists to run the test with less samples for analysis (this aspect is addressed further in the section on quality control).

3.3. Evaluation of the time dependent release from cement-based products (service life)

During the service life of cement-based products and concrete the material must be judged as a monolith. This implies that release is limited due to transport constraints. Diffusion from the interior of the matrix is slow due to the tortuous path that the diffusing ions have to follow. The test applied to address this leaching condition is the tank leach test NEN 7345. The release can be modeled in a first approach by a one-dimensional diffusion model to assess release over longer time-scales than the duration of the leaching test. Parameters for the extrapolation are derived from the tank leach test. In Table 3, the release after 100 years is given for a monolith of 1 m^3 exposed to leaching. These results can be compared with regulatory limit values as specified in the Dutch Building Materials Decree [25].

The comparison is conservative as no correction for ambient temperature or for wet/dry periods has been made. All elements meet the limits even without this correction. The results of projected release at 100 years can also be used to derive the release from a concrete slab or pile exposed continuously to water (pillar in groundwater), intermittently (surface structure exposed to rain) or exposed to neutral pH water (pillar in a freshwater body).

Table 3
Release projection at 100-year exposure during service life

Element	Release predicted from test data (mg/m^2 in 100 years, 20°C, saturated)	Regulatory limits (category I) at 100 year (mg/m^2)
S	7900	40000
Zn	29	2100
V	92	2400
Mo	72	150
Pb	138	1275
Cr	209	1500
Ba	2004	6300

In the latter case, the release is dictated by the external pH of the concrete (almost neutral). This reduces the release of metals, but increases the release of oxyanions. In any case, the release falls within the specifications of a category I material (Mo and sulfate are the most critical elements). If temperature effects and wet/dry cycles are taken into account the predicted release at 100 years reduces for Mo from 72 to around 19 mg/m^2 [25].

For an evaluation of cement-based products and concrete during its service life, the tank leach test provides a good indication of the release behavior of different elements. A scenario approach [27] can give a more detailed estimate of projected release under different utilization conditions, as the conditions of application are not all the same. Clearly, an evaluation based on total concentration of anhydrous cement will not allow the level of control as provided with the leaching test methods. Total concentration can only be used for quality control when all three levels of evaluation — total, availability and actual leachability are correlated. This is not the case and thus use of total concentration would lead to unnecessary restrictions.

The tank leach test according to NEN 7345 (closed system) does not give the proper information for all situations. In case the material is exposed to a significant level of water refreshment like in flowing water and/or in case of exposure to the atmosphere (drinking water pipes), a tank leach test with externally controlled pH by flushing air through the external solution to reach a constant pH of around 8 provides a better representation of the actual release [26]. Under these circumstances other solubility controlling phases dominate the release from monolithic specimen, which is what will occur also in practice. For metals, this will generally lead to lower leachability. By applying air the carbonate level will not be so excessively high as to cause significant bicarbonate levels in solution, which would not be representative of normal exposure conditions. The pH-stat data can be used to provide an estimate of the difference in release between the two scenarios and thus allows a decision on the need to carry out such an additional test.

3.4. Comparison of tests used to assess the release from cement-based products in their second life

In the second life of cement-based products some degree of size reduction will take place either by mechanical demolition or by degradation. The material may either be used as a bound aggregate in new concrete or as an unbound aggregate. When the material is reused in a bound application, such as an aggregate in concrete, the leachability of the new product needs to be assessed, which will be similar to the data presented before on intact specimens. Tests that have been used to assess the long-term properties of cement-based products in their second life in unbound form are the availability test, DEV S4 and pH dependence leach test. The availability test results and the DEV S4 data correspond well with the data obtained with the pH dependence procedure at the respective pH values as can been seen in Fig. 5 for Ca, Mg, Cr, V, Ni, and Zn. For metals and earth alkali elements, the availability data correspond well with the plateau in leachability at pH < 4, whereas the availability data for anionic species correspond well with the data for the pH dependence test in the neutral to light alkaline pH domain. This implies that pH dependence test results can be used as a general basis for data comparison of cements as has been demonstrated before for other matrices [4]. In other work it has been shown that data obtained with other tests, such as TCLP and TVA can be placed in perspective in the same way [12].

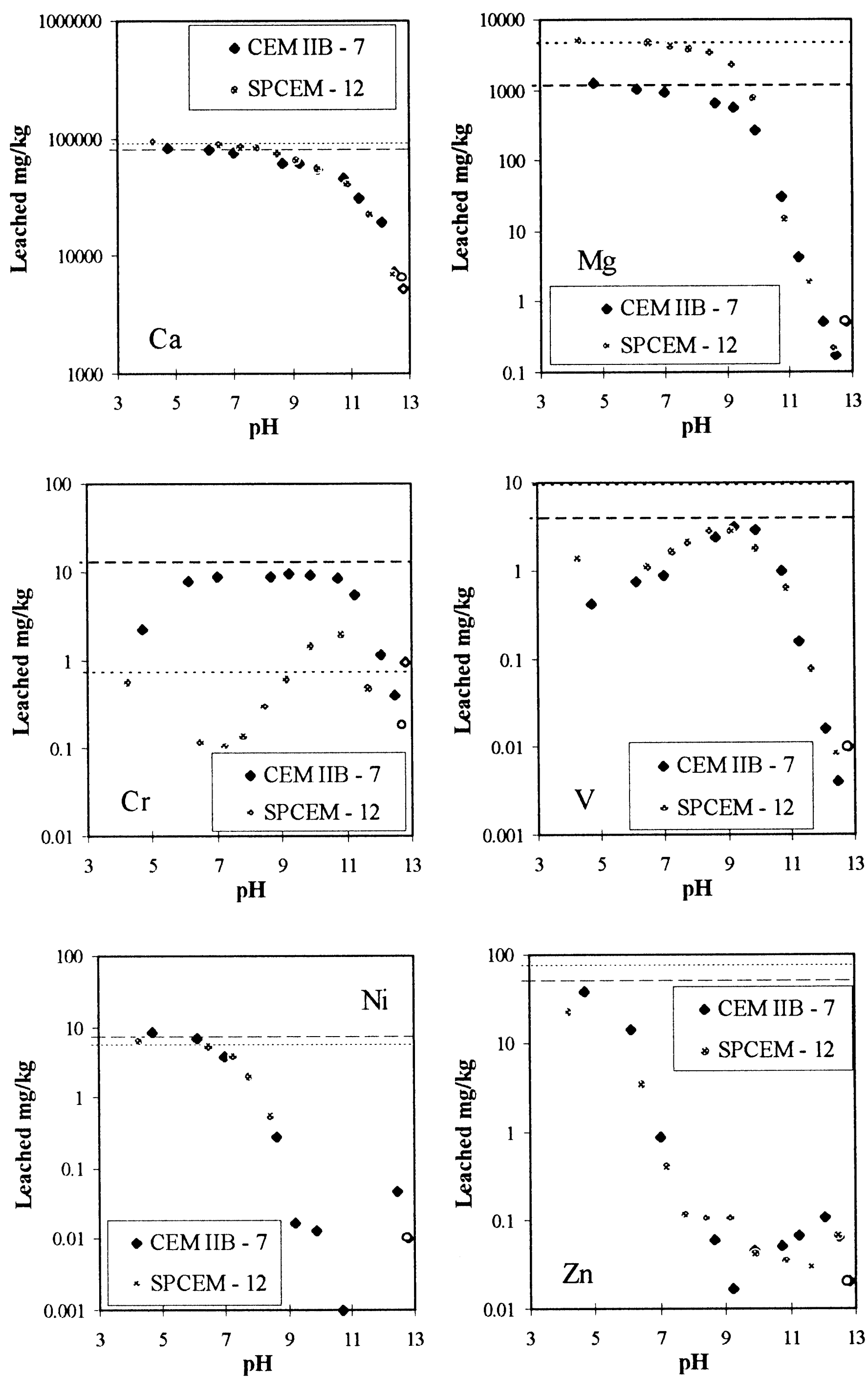

Fig. 5. Comparison of availability test data (NEN 7341, broken line CEM IIB; dotted line SPCEM-12) and DEV S4 data (closed circle SPCEM-12 and closed diamond CEM IIB) with pH dependence data for two cement mortars.

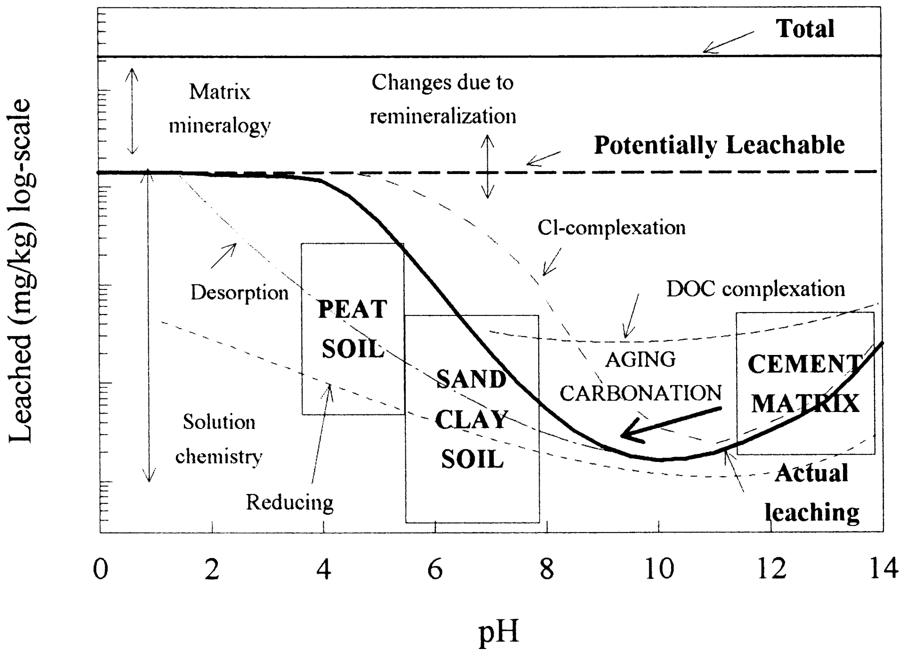

Fig. 6. Factors controlling leaching from cement products in different chemical environments (example for metals).

In addition, the leaching behavior as a function of pH covers a wide range of environmentally relevant conditions and as such forms a good basis for evaluation of environmental impact (see Fig. 6). The relevant pH domain for cement products may range from pH 4 (peat soils) to neutral conditions (most natural soils) extending to alkaline conditions in situations where very limited water transport occurs (e.g., concrete pilings in virtually stagnant groundwater).

Owing to the higher sensitivity and its relevance from an environmental point of view, the availability test will provide a better tool to assess a worst case condition than the total concentration.

3.5. Comparison and correlation between leaching tests

Leaching information for Cr is illustrated in Fig. 7 showing that the total concentration has no relation with

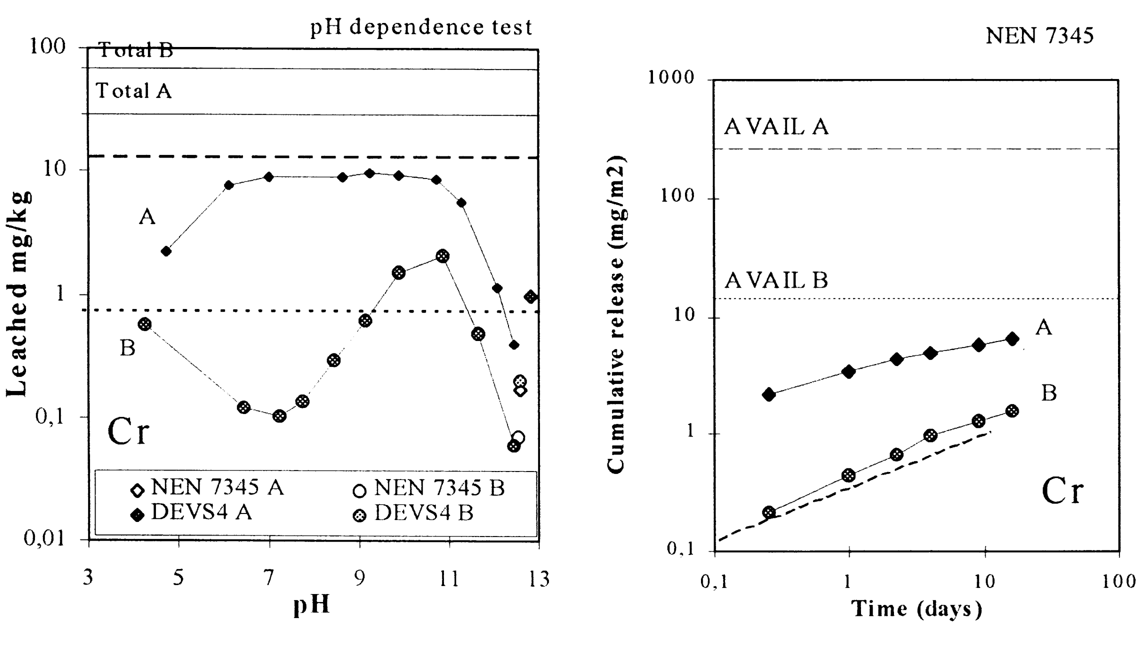

Fig. 7. Comparison and interrelations between leaching tests for Cr from cement mortars.

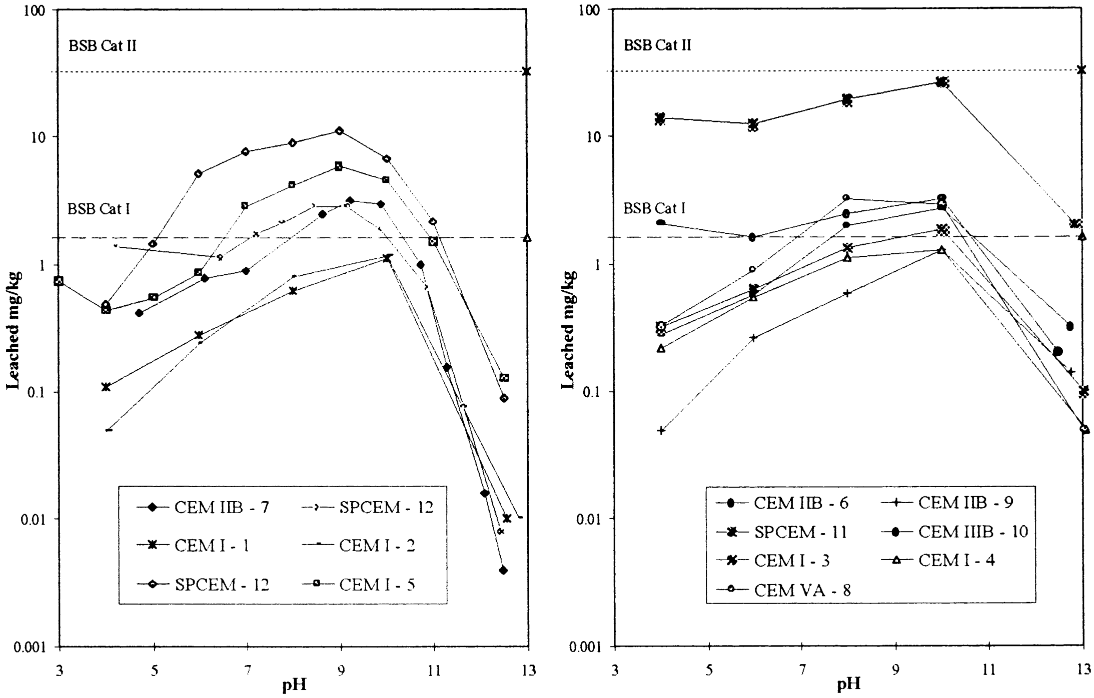

Fig. 8. Consistent leachability of vanadium from 12 cement mortars as a function of pH (after crushing to <2 mm; L/S = 10; 24 h). BSB categories I and II are regulatory limits according to the Building Materials Decree.

leaching as cement B with the highest total Cr content leaches less that cement A. In addition, the leaching behavior of the two cements as obtained from a pH dependence measurement show a markedly different behavior, which can be related to solubility controlling phases in the respective cement matrices. The relationship between the dynamic tank leach test (NEN 7345), the availability test and the pH dependence test is also indicated. The availability corresponds with the maximum in the pH dependence release curve. The level of release for the two cements in the NEN 7345 test is consistent with the pH curve (for the two cements the concentration points in the pH plot obtained at the end of the test match well with the general shape of the curve).

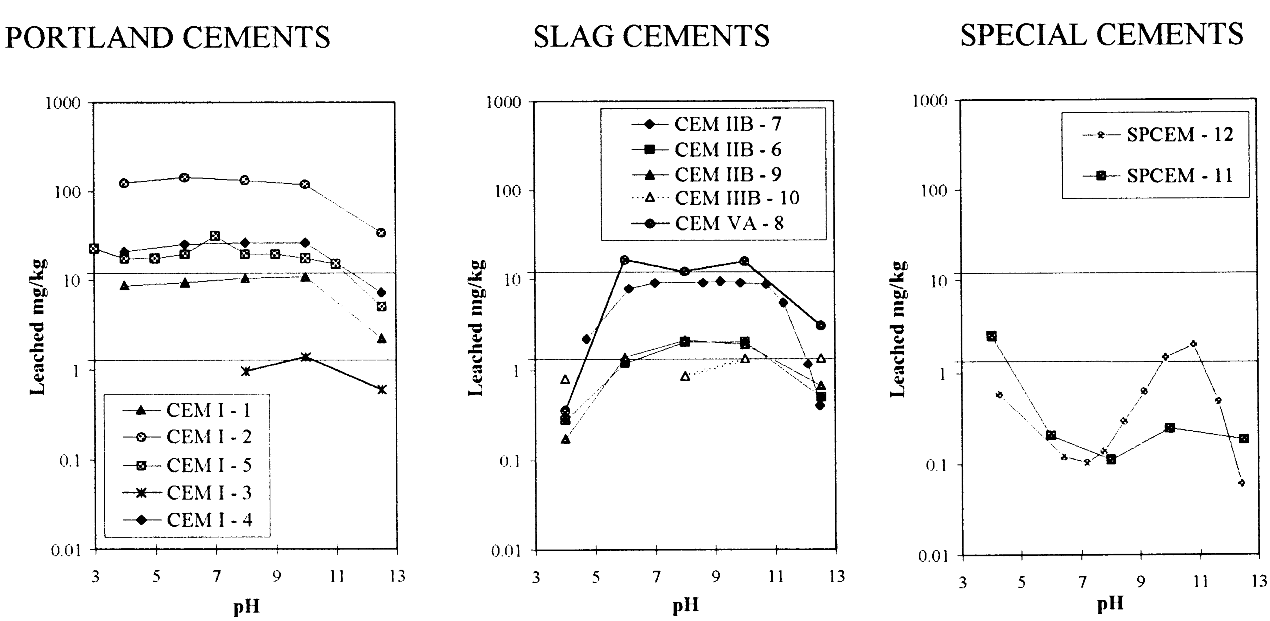

Fig. 9. Consistent leachability of chromium from 12 cement mortars as a function of pH (after crushing to <2 mm; L/S = 10; 24 h). BSB categories I and II are regulatory limits according to the Dutch Building Materials Decree.

3.6. Solubility control in cement leaching

The pH dependence leach test provides a basis to assess the solubility controlling phases of a cement matrix. In several other studies [17–21], the emphasis has been on the high pH domain (pH > 11). Here the focus is on the entire pH range from 4 up to 13. From Fig. 5, the leaching behavior of elements from a cement matrix as a function of pH proves to be very consistent for different cements. This is further illustrated for vanadium leaching from 12 cements (Fig. 8). For Cr, three groups with different leaching behavior can be identified (Fig. 9) as a result of different chemical speciation. The different behavior of Cr leaching corresponds to the classification in three types of cement: Portland cement, slag cements and special cements. Clearly, the traditional Portland cements feature the highest Cr leachability, whereas the special cements show low Cr leachability. The distribution between CrO_4^{2-} and Cr^{3+} forms is a likely cause for the

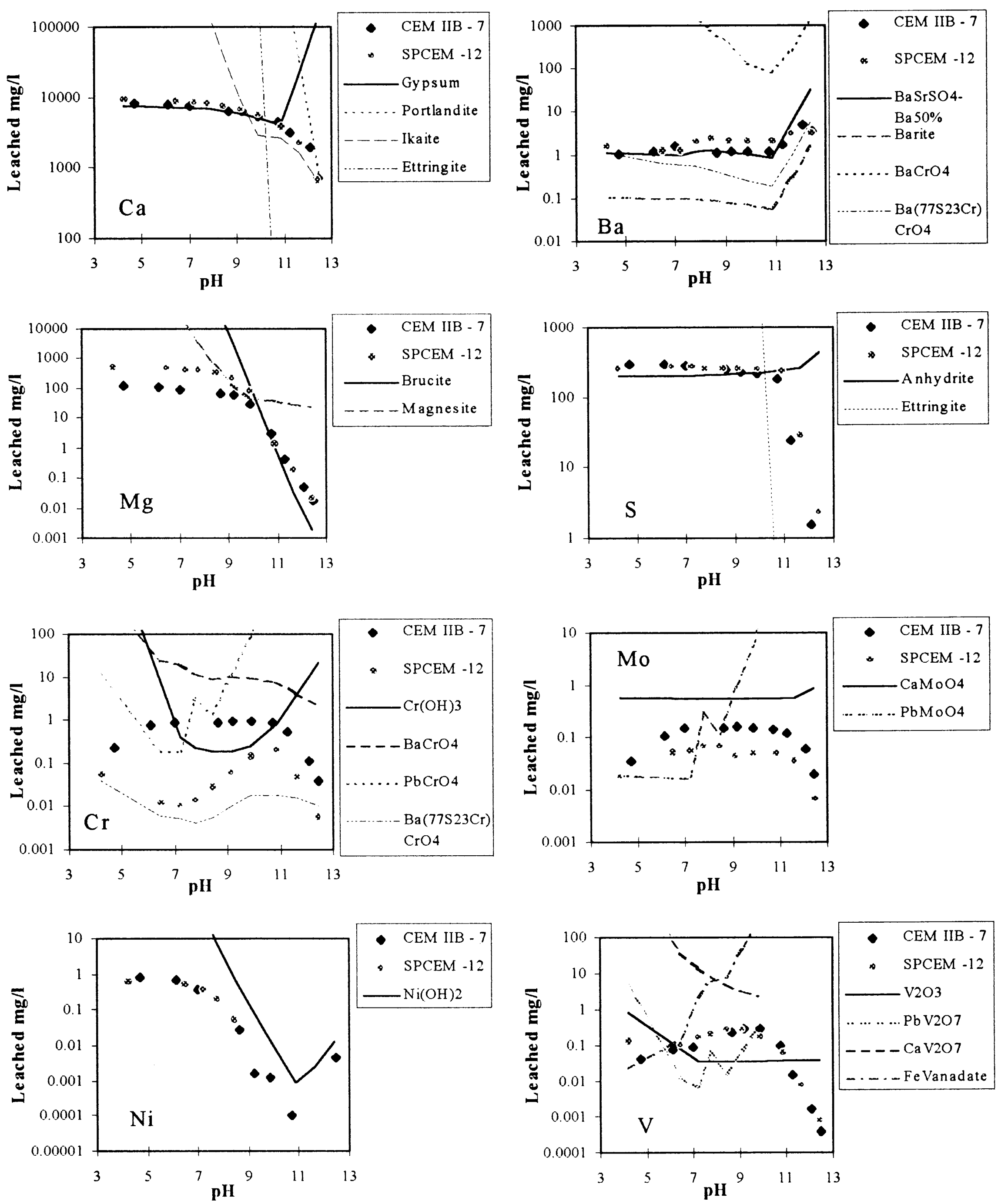

Fig. 10. Geochemical modeling of crushed cement mortars using MINTEQA2.

difference in Cr leaching behavior between the different cements, as it is known that blast furnace slag cements feature lower Cr leachability as a consequence of reducing properties of blast furnace slag [22].

The data from pH dependence leaching tests are used to carry out modeling of the geochemical speciation in leachates obtained from extraction of crushed cement mortars. In Fig. 10, results of the modeling are specified for Ca, Ba, Mg, S, Cr, Ni, Mo, and V. The sulfate in ettringite can be partly substituted for oxyanions (e.g., CrO_4^{2-}, MoO_4^{-}, AsO_4^{3-}, VO_4^{3-}), metals and earth alkali elements (e.g., Ba, Pb, Cd, Zn, Ni) can partly substitute for Ca, whereas trivalent elements (e.g., Fe, Mn, Co) can substitute for Al [18,22]. Proper information to model incorporation in ettringite phases is still lacking. The information available in the literature [18–23] on incorporation of metals and, particularly, oxyanions in ettringite cannot be directly converted to stability constants that can be used in the MINTEQA2 database as the incorporation of metals and anions in the ettringite matrix cannot be described by a straightforward stability constant. This aspect of metal and anion incorporation, which is mainly relevant at pH above 10 is underdeveloped at this point and needs to be addressed in more detail in future work.

Based on the modeling the following controlling phases have been identified:

Barium: For Ba, barite is apparently not a controlling phase, whereas the solid mixed mineral phase $BaSrSO_4$ (50% Ba) reflects the leaching behavior of Ba and Sr quite well. $BaCrO_4$ solubility is not a controlling phase, but a solid solution of $Ba(S,Cr)O_4$ (77% S and 23% Cr) appears to be a good candidate as it reasonably matches the leaching behavior.

Calcium: At high pH, portlandite is the most likely solubility controlling phase. The solubility control by gypsum corresponds with a large section of the pH range.

Chromium: Chromium appears to be controlled by $BaCrO_4$ in the case of CEM IIB-7. Or more likely a solid solution of $Ba(S,Cr)O_4$. In case of SPCEM-12, solubility control by $PbCrO_4$ is possible, but a solid solution of $Ba(S,Cr)O_4$ (77% S and 23% Cr) matches very well with the observed concentration pH curve. The leaching behavior of SPCEM-12 is quite characteristic. $Cr(OH)_3$ may play a role as a controlling phase at low pH. If the solubility control by $BaCrO_4$ phases is active in mortar additional Ba will help reduce the release of chromate. In future studies the role of Ba concentration in controlling Cr needs to be studied in more detail by increasing the Ba and Cr levels in a cement clinker and verifying the consequences for the leachability. The present data point at an upper limit for Cr solubility in cement mortar of 10 mg/l.

Magnesium: Magnesium is controlled by brucite and possibly in part by magnesite. At pH < 9 magnesium is limited by the availability of leachable Mg in the cement matrix.

Molybdenum: Calcium molybdate is an important controlling phase in mortar. This implies that Mo release from mortar is kept in check by the abundant amount of Ca. Artificial increase of Mo can provide a verification of this condition. Possibly ettringite is important in the high pH domain, as CEM I-4 has a low C_3A content and thus is expected to be low in ettringite. This sample shows a relatively high Mo leaching. On the basis of $CaMoO_4$ solubility, the present data point at an upper limit for Mo solubility in cement mortar of 2 mg/l.

Nickel: The nickel leachability is probably controlled by $Ni(OH)_2$.

Sulfate: The mortar leachate is controlled by anhydrite solubility. At high pH ettringite is likely to become a major controlling phase.

Vanadium: In the pH domain of pH 5 to 8 Fe-vanadate appears to be important, while at pH > 9 calcium vanadate may play an important role. The combination of these phases could very well explain the observed leaching curve with a maximum at pH 9. The role of ettringite for V needs to be verified in further work. The present data point at an upper limit for V solubility in cement mortar of 2.5 mg/l.

The geochemical modeling has provided some very interesting solubility controlling phases. If these prove to hold up, there appears to be an inherent limiting factor for release from cement. Even the option of increasing one element slightly to keep leachability of a more critical element in check is of interest. Clearly, leachability from cement is not at all related to its total concentration, but depends on other factors. The differences in chemical speciation in cements produced from different source materials are relevant for environmental quality control of cement production. Such information is lost when environmental quality is only verified on the basis of total concentration. The level of understanding of the processes

Table 4
Comparison of "end of life" concrete with utilization criteria

Element	Building materials decree (mg/m^2 in 100 years) category I	Minimum release	Maximum release
As	435	54	*1034*
Ba	6300	*9460*	*56400*
Cd	12	5.4	11.9
Cr	1500	116	*143660 (28000)*[a]
Co	300	11	*11600*
Cu	540	54	*2080*
Hg	4.5	2.7	2.7[b]
Pb	1275	54	370
Mo	150	55	*20500*
Ni	525	54	*3900*
Se	15	54	54[b]
Sb	39	*108*	*705*
Sn	300	54	*3226*
V	2400	620	*28600*
Zn	2100	54	1200
S	33300	*1360000*	*4940000*

[a] Between brackets, the value is given after removal of one extreme value.

[b] Insufficient sensitivity of analysis.

controlling release from cement-based products has increased to a level that more sophisticated, yet straightforward, environmental quality control can be achieved.

3.7. Long-term leaching behavior from cement-based products ("second life" as construction debris)

The evaluation of cement-based products after their service life in unbound form should be based on size reduced material, which due to the enhanced exposure to the atmosphere is more strongly carbonated and as such has a lower pH than normal cement mortar or concrete. The changes brought about by this combination of effects is covered largely by the pH dependence leach test results. The range of leachability conditions that construction debris can cover in their "second life" are reflected by the leachability behavior going from pH 13 (porewater pH of cement) to neutral conditions pH 8.3 (calcite-controlled system). This has already been illustrated in Fig. 6.

The size range of construction debris can range from very coarse material (to be judged rather as a monolith) to fine material, which is best judged as a granular material. Here the latter is chosen, which is a worst case approach.

3.8. Evaluation of concrete in its "end of life status"

For the evaluation of the "end of life" leaching behavior of concrete and cement-based products, which

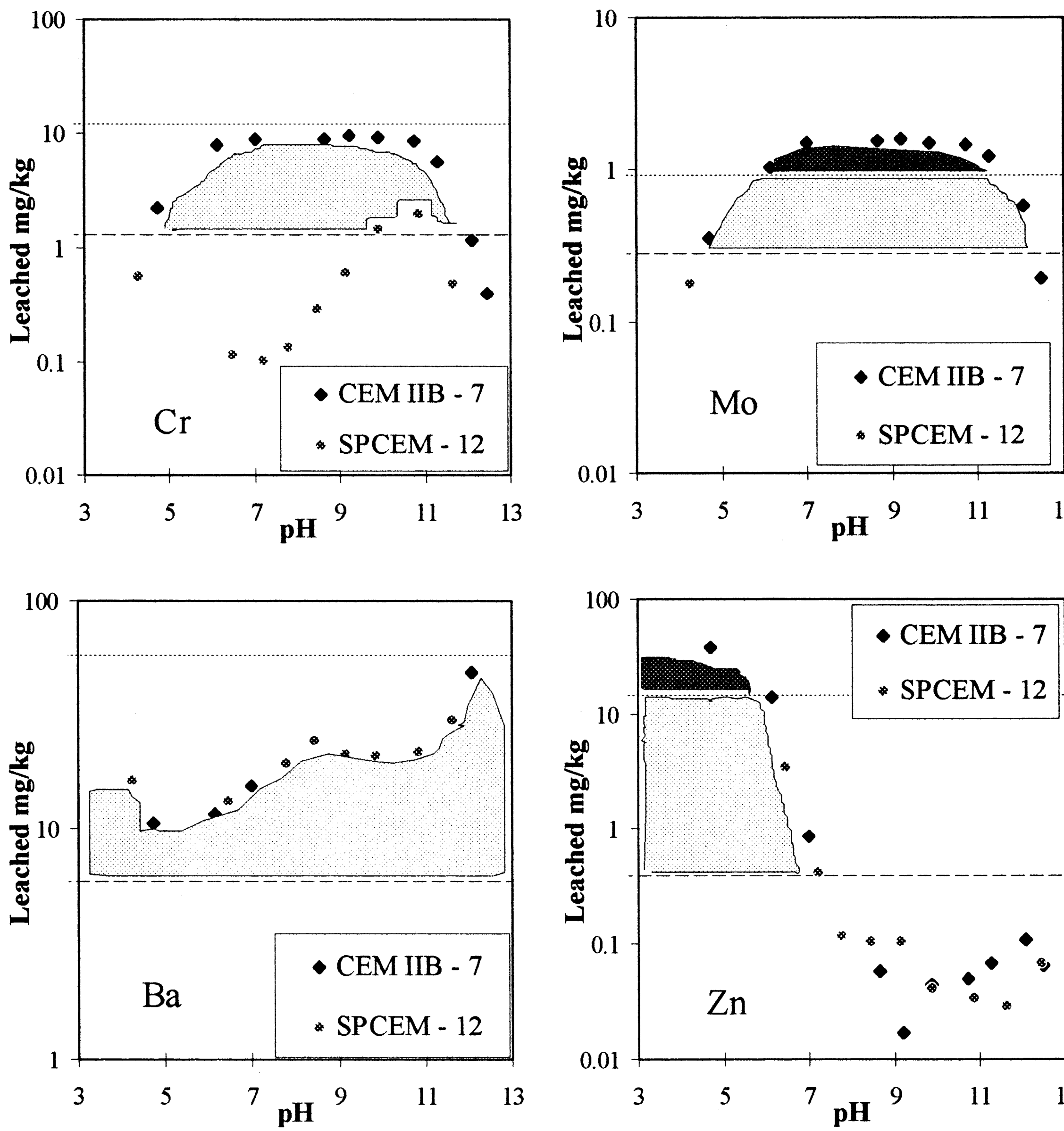

Fig. 11. pH domains for which cement mortars leached in granular form are not in compliance with the Building Materials Decree. The fields indicate non-compliance with the two critical levels.

are to be either used or disposed of in an unbound form, the material can be judged in its granular form. Since the material can be assumed to be largely carbonated, the best end point condition for construction debris is a final pH of around 8. The pH dependence information obtained at this pH can be related to the criteria for the application of granular materials as specified in the Building Materials Decree [25], which is based on a leaching test at L/S = 10. This is a conservative approach, as the particle's size is assumed to be smaller than will actually occur in practice. The release to the soil at 100-year exposure (expressed as mg/m^2 soil surface area) is obtained from the release at L/S = 10 (expressed as mg/kg) as follows:

$$E_{100\ \mathrm{years}} = E_{\mathrm{L/S=10}} dh$$

with d as the average density of the material in kilogram per cubic meter (kg/m^3) and h as the height of a perceived application in meters. Here we have chosen $d = 1550\ kg/m^3$ (average density used in the Building Materials Decree) and $h = 0.7$ m.

In Table 4, the range of release values from granular material at L/S = 10 (in mg/kg) in the relevant pH domain (pH 7–11) are converted to milligrams/square meter (mg/m^2) for comparison with the regulatory values. This choice is justified by the fact that cementitious materials, when fully carbonated, will be buffered around pH 8 and are not likely to fall below 7. Concrete construction debris in fine granular form should not be applied in a peat environment or in acidic soils.

Following this conservative approach, several elements can become critical relative to the Dutch Building Materials Decree, when the material is applied as a fine granular material fully exposed to leaching. This situation is equally relevant for cements produced from natural materials as for cements produced with alternative fuels and raw materials. Since Cd, Hg, Pb, and Zn are not critical following this conservative approach, these elements are not very relevant from an environmental perspective. Elements of more concern are: As, Cr, Cu, Mo, Ni, Sb, Sn, V, and sulfate. For Se, the analytical sensitivity has been insufficient to decide, whether it is critical or not as the detection limit leads to exceeding the limit.

A quick assessment of the critical nature of elements relative to regulatory limit values is given in Fig. 11. Here the levels in release expressed in milligrams per kilogram (mg/kg) for categories I and II (Building Materials Decree [25]) are inserted showing the pH domains where an element can become critical. In Figs. 8 and 9, the relation to the limit values is illustrated for V and Cr for the full range of cement mortars tested. In case of V, the demolition debris always meets the criteria for category II (restricted use). For Cr in a few cases even category II is exceeded.

A more realistic evaluation is to take a normal particle size distribution for building debris into account instead of all material smaller than 2 mm. This will lead to a substantially lower release as transport resistance (by diffusion) comes into play. This calculation requires a more sophisticated model to take depletion into account. During the service life a proportion of the elements may have been leached. By assessing different exposure scenarios through modeling the critical nature of elements in the "end of life" of cement-based products can be quantified more precisely and management scenarios for the "end of life" based on these findings can be provided.

3.9. Tests appropriate for the environmental quality control of cement-based products during their life

In the evaluation of leaching behavior of materials, three levels are distinguished: characterization test for leaching behavior, compliance tests and quick on-site verification tests [28]. This is a practical distinction as the leaching behavior of industrially produced materials has been shown to be very consistent [13,29]. This implies that once the leaching behavior has been sufficiently characterized, simpler tests can be used to verify compliance with criteria to be met for regulatory purposes. Different characterization tests are used for different purposes and to assess different scenarios [27]. In Table 5, an indication of the use of

Table 5
Tests to be used to assess cement-based products

Scenario	Characterization test	Compliance test
Utilization in service life (contact with the atmosphere)	NEN 7345 modified to pH control at pH = 8	short tank test 24 h with pH control
Utilization in service life (isolated from the atmosphere)	NEN 7345 or equivalent	short tank test 24 h.
Construction debris — second life of cement-based products — used as aggregate in cement product	same as service life	same as service life
Construction debris — second life as unbound aggregate	pH dependence test, Column test NEN 7343 or equivalent	concise test, 24 h [30,31]
Extreme exposure conditions (e.g., low pH) and waste stage	pH dependence test	concise test, 24 h [30,31]

different tests is given with the associated short test for quick evaluation. Further work is needed to determine the appropriate test for the different scenarios.

In several cases, a good correlation exists between availability and actual leachability at controlled pH. In such cases both availability and actual leachability can be used for environmental quality control purposes. A cost effective environmental quality control system can be developed, that uses the present characterization background as reference.

4. Conclusions

The leaching characteristics of standard (EN-196-1) cement mortars have been determined, in monolithic (prism) and granular form, by examining the leaching behavior as a function of pH in the pH range 4–13, which has revealed very consistent and systematic leaching patterns. Since leachability in the pH range 7 to 11 is most relevant from an environmental point of view, the total concentration is of very limited relevance in protecting the environment. Only in case a direct relationship between total concentration, availability and leachability can be found will it be possible to use total concentration as a criterion.

For most elements there is no relationship or a rather poor one between total concentration and availability for leaching.

Significant differences in generic leaching behavior as a function of pH are noted for metals, oxyanions and salts. Metals generally show a minimum leachability at neutral pH. Oxyanions feature a maximum leachability at neutral to mild alkaline pH and salts show no relation with pH.

From a measurement point of view the ATA method is a poor test due to the subtraction of concentrations (extract and blank of mineral water) that are often in the same order of magnitude. The data generated are mostly below the detection limits, which is a waste of analytical effort. A more meaningful alternative may be a tank test with externally controlled pH at neutral conditions by air flushing. This option meets the requirement that the pH should not increase too much in the extract, thus preventing unrealistic metal release. The advantage of such an approach would be that results can be related to observations in other fields and that results can be used for model predictions.

This option would imply a modification of NEN 7345 to comply with specific utilization scenarios, in which the external conditions to which materials are exposed are dominated by the external medium. This is the case in, for instance, concrete applications in freshwater systems. Except for the controlled air flushing, all other aspects of the test remain the same.

Similar to the situation in other fields, the pH dependence leach test forms a solid basis for mutual comparison of cement, in standard mortar prisms, as it has the possibility to make distinction between cements based on chemical speciation aspects. In addition, it allows the placing of other commonly used tests in perspective. Leachability as a function of pH has revealed differences in cement mortar leaching behavior not identified before. By comparing pH dependence leach test information with availability data and total concentration, it is immediately clear that relationships between these properties are very dependent on the pH at which the comparison is made.

Based on the pH dependence leach test information geochemical modeling has been carried out, in which interesting solubility controlling phases have been identified. It can be noted that also in cement mortar bars leachability is to a large extent dictated by solubility control. In the case of Cr, Mo, and V, Ba, Ca, and Pb provide possible solubility limiting phases. By modifying clinker concentration, this control is worth verifying in future work in order to investigate possible scenarios to reduce the leachability of specific elements in the long-term and "end of life" scenarios.

Over the entire pH range, different phases may control solubility in particular pH domains. The information at the high pH range is still rather limited. Here phases such as ettringite and C-S-H phases play a role and can possibly explain the observed decrease in leachability of metals and oxyanions at pH values > 10.

In the comparison with regulatory limits (only present in the Netherlands at this stage), the service life of concrete generally does not seem to pose a problem. All elements specified in the regulation are well below the threshold for category I applications for the cement-based products tested in this study. An aspect that has not been addressed sufficiently is to find if under neutral pH exposure conditions leachability of oxyanions is, or is not increased above critical limits during service life.

In case of cement-based products considered in granular form as construction debris, the situation is more complex as some elements — As, Cr, Cu, Mo, Ni, Sb, Sn, V, and sulfate — can be critical, when a conservative approach is used for evaluation of compliance. Oxyanions, such as those of Mo, Cr, V, are more crucial for an environmental evaluation of long-term behavior of cement products than metals such as Pb, Zn, and Cd. In particular, Pb is a non-issue in leaching from cement-based products. From a leaching point of view, the tolerance for Pb in cement is well beyond the normal levels found in cement. In this conservative approach, the particle size is assumed to be rather small for all the material. A further evaluation is needed to verify the "second life" and "end of life status." The aspect of aging is not covered. Generally, aged material will have more stable phases resistant to leaching. The degree to which this occurs in cement-based products needs to be verified. When the material is reused as aggregate in concrete, there is no environmental problem perceived as the same low levels of release will be observed as for the monolithic primary material.

An environmental benefit of the economy-driven use of alternative fuels and raw materials in the manufacture of cement is the reduction of the potential leaching of Cr. This could be an additional incentive to encourage this route. This reduction is obviously reflected in the actual leachability under field exposure conditions in service life, "secondary" life and "end of life," scenarios. Several cements produced from natural materials do not meet the "end of life" criteria for different elements according to the Dutch regulatory system. In the case of Cr, this is probably related to the oxidation state of Cr in the clinker at the end of the kiln (more conversion by oxidation to the more leachable chromate).

In case of V, there is direct relation between input and leachability. Reducing the input of V has a direct effect on the ultimate leachability in this case. In further work, the level of V and Mo should be increased in the clinker to verify the proportionality among leachability, availability and total concentration. At the same time, other controls of leachability can be verified.

In view of the increased understanding of the leaching behavior of cements from different origin, where large differences in release exist in spite of marginal differences in total concentration, the use of total concentration as a criterion for quality control of cement is unnecessary limiting. By using leaching tests instead of total concentration one can focus on the key issues in relation to the reuse or disposal of the material in its "second life" or "end of life" disposal stage.

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