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Waste Materials in Construction: Putting Theory into Practice

# Development of a Leaching Protocol for Concrete

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## Abstract

Based on two pre-validation studies and a final validation study a characterisation test for the determination of the leaching behaviour of concrete has been developed. The test protocol includes a tank test and an availability test. Generally, the emissions from the concrete specimen investigated were very low and often close to or well below the detection limits. Therefore, the development of a short-time characterisation test proved to be difficult. From the leaching results it could be deduced, that the leaching from concrete is in principle diffusion controlled. The results from both the tank leaching test and the availability tests indicated that the precision in terms of repeatability of the tests is good and the reproducibility is acceptable.

## 1 Introduction

For cement-based materials, a main aspect in respect to environmental compatibility is the leaching of heavy metals and salts /1/. Up to now, no uniform and accepted leaching test exists to evaluate the leaching of environmentally relevant compounds from concrete, either with and without the application of industrial by-products.

In this paper, the development of a procedure for the basic characterisation of the leaching behaviour of inorganic species from concrete is described. The protocol thus developed aims to be a tool that enables the assessment of the environmental quality of concrete. The paper summarises the research work carried out during a research project funded by the European commission under the Measurement and Testing Programme /2/.

The experimental work was carried out in three stages. The first stage was implemented as a small interlaboratory study, together with the investigation of several relevant variables in a leaching test. Although only a validating interlaboratory study was planned after this first stage, it was decided to organise a second interlaboratory study, that served as a pre-validation of the test procedure. The final stage in experimental work was the validation of the test procedure by means of an interlaboratory study.

## 2 Materials and sample preparation

For the preparation of the concretes for the first and second interlaboratory study an ordinary Portland cement (PC1) in compliance with the requirements of European standard ENV 197

***Table 1:*** *Total contents of some minor elements of the Portland cement and of the fly ashes used in the investigations /2/*

| Component | | Composition (mg/kg) | | |
|---|---|---|---|---|
| | | PC1 | FA1 | FA2 |
| Antimony, | Sb | 2 | 6.7 | 21 |
| Arsenic, | As | 8.9 | 27 | 471 |
| Barium, | Ba | 317 | 803 | 1330 |
| Cadmium, | Cd | 0.3 | 0.65 | 11 |
| Cobalt, | Co | 7.7 | 51 | 74 |
| Chromium, | Cr | 86 | 118 | 360 |
| Copper, | Cu | 28 | 118 | 178 |
| Nickel, | Ni | 32 | 111 | 238 |
| Lead, | Pb | 22 | 142 | 1870 |
| Zinc, | Zn | 311 | 334 | 2190 |
| Vanadium, | V | 61 | 244 | 269 |

has been selected. For the validation study a Portland cement with higher alkali content (PC2) was used, since it was assumed it would lead to a somewhat higher leachability. Two types of bituminous coal fly ashes were chosen as concrete additions. FA1 was from a conventional dry bottom boiler and FA2 from a wet bottom boiler. FA2 showed considerably higher concentrations of some relevant minor elements than FA1. Sand and gravel from the river Rhine were used as aggregate. The total contents of minor elements of the cement and the fly ashes are reported in table 1 (the element contents of PC2 are assumed to be in the same range as for PC1) /1/.

The composition of the concrete mixture for the first interlaboratory study (C1) can be taken from table 3. The water-binder ratio (w/(c+0.4f)) was 0.55.

The concentration levels of most of the species in the leachates obtained from the concrete samples of the first interlaboratory study were too low to be suitable for a validation of the test procedure. Therefore, a second interlaboratory study was performed with a concrete of higher water-binder ratio (higher permeability) and addition of FA2 (with higher element concentrations). The composition of this concrete mixture is given in table 3. The water-binder ratio (w/(c+0.4f)) was 0.75.

***Table 3:*** *Composition of the concretes for the two interlaboratory studies and the validation study*

| component | unit | concrete | | |
|---|---|---|---|---|
| | | C1 | C2 | C3 |
| Portland cement, PC1 | $kg/m^3$ | 302 | 200 | - |
| Portland cement, PC2 | | - | - | 270 |
| Fly ash, FA1 | | 60.5 | - | 60 |
| Fly ash, FA2 | | - | 100 | - |
| water | | 181 | 180 | - |
| solution of heavy metals (see table 2) | | - | - | 162 |
| aggregate (grading curve A/B 16) | | 1799 | 1819 | 1730 |

***Table 2:*** *Amounts of compounds added as spike to the concrete mixture*

| Substance | Amount |
|---|---|
| | g/ℓ mixing water |
| $Na_2HAsO_4 \cdot 7H_2O$ | 6.25 (=2.5 g As/ℓ) |
| $Cd(NO_3)_2 \cdot 4H_2O$ | 2.74 (=1.0 g Cd/ℓ) |
| $K_2Cr_2O_7$ | 4.24 (=1.5 g Cr/ℓ) |
| $NH_4VO_3$ | 4.69 (=2.0 g V/ℓ) |

The composition of the concrete of the validation study (C3) is reported in table 3. This concrete resembled very closely that of the first interlaboratory study. In order to guarantee reasonable element concentrations in the leachates, the concrete was spiked with As-, Cd-, Cr-, and V-compounds. These metal compounds have been introduced into the samples by the mixing water (see table 2).

***Table 4:** Curing of the concrete cubes for the two interlaboratory studies and the validation study*

| Concrete | C1 | C2 | C3 |
|---|---|---|---|
| curing | duration in days | | |
| in the mould | 1 | 1 | 1 |
| fog room 20°C/100% rel. humidity | 6 | 6 | 6 |
| climate chamber 20°C/65% rel. humidity | 56 | 42 | 56 |
| age of the samples at the beginning of the tank test | 69 | 52 | 75 |

From each concrete mixture concrete cubes (0.1 m by 0.1 m by 0.1 m) were produced. The curing of the concrete samples as well as the age at the beginning of the leaching tests is given in table 4. Some of the concrete cubes were grounded for the availability tests. The total element concentrations of the three concretes are summarised in table 9.

## 3 First interlaboratory study

### 3.1 General

From literature it followed, that the leaching of environmentally relevant compounds from concrete samples is mainly a diffusion controlled process /1/. Therefore, a standard leaching procedure should include a diffusion test (tank test). For further characterisation of the samples and to be able to determine effective diffusion coefficients (in order to assess long-term leaching behaviour), it is necessary to determine the amount that is available for leaching (availability) /1, 2/. As a result, following leaching tests were selected for the first interlaboratory study:

- Availability tests:
  - leaching test according to Dutch NEN-ISO 7341 /3/ (first step at constant pH=7 and second step constant at pH=4; test A),
  - leaching test similar to Dutch NEN-ISO 7341 (first step without pH-control and second step at constant pH = 4; test B),
  - leaching test according to DIN 38 414 T4 (DEV-S4) /4/, with demineralised water (test C).
- Diffusion test (tank test):

  The tank test procedure developed adopts the principles of the Dutch standard NEN 7345 /5/. For application of the leaching test in the construction producing industry, it was felt that the time necessary for obtaining the results was too long. A protocol was developed that implements the following conditions (test D):

| | |
|---|---|
| – Samples: | concrete cubes, 0.1 m by 0.1 m by 0.1 m |
| – leachant: | demineralised water |
| – L/S (V/V): | 5 : 1 |
| – leaching periods: | 6, 24, 54, 96, 168 hours |
| – temperature: | 20°C |
| – leachant refreshments: | 5 |
| – stirring action: | no stirring |

The influence of various parameters was investigated, in addition to the intercomparison tests in order to be able to find suitable parameters for the leaching of concrete. The following variations of the standard conditions were selected: flow of $CO_2$/air (test E), test duration: 14 days (test F); L/S (V/V): 2.5, 25 (test G); stirring during the test (test H); sea water as leachant (test I).

Five laboratories were involved in the first interlaboratory study. The concrete cubes from the mixture C1 (see table 1) were used for the leaching tests.

### 3.2 Data evaluation

The interlaboratory studies in this project have been evaluated in accordance to ISO 5725-2:1994. According to the NEN-ISO standard 5725 the precision is determined using two parameters, repeatability and reproducibility:

- repeatability: precision under conditions where independent test results are obtained with the same method on identical test material in the same laboratory by the same operator using the same equipment within short intervals of time.
- reproducibility: precision under conditions where independent test results are obtained with the same method on identical test material in different laboratories with different operators using different equipment.

The precision can be expressed as the standard deviation of the test results obtained under repeatability or reproducibility conditions, indicated by '$S_r$' and '$S_R$' respectively. It should be noted that the precision does not relate to the true value of test result, but depends only on the distribution of random errors.

### 3.3 Results and Discussion

### 3.3.1 Availability tests

The average results from the three availability tests are summarised in table 9. Some results from the two availability tests performed similar to NEN-ISO 7341 (test A and test B) are presented in Fig. 1.

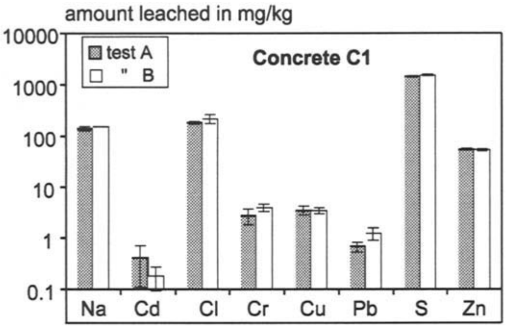

*Fig. 1: Comparison of two pH regimes in the availability test (test A: 1st step at pH=7, 2nd step at pH=4; test B: 1st step without control, 2nd step at pH=4)*

No significant difference is found between results from test A and B. The leached amounts of the concrete samples yielded with the DEV-S4-procedure (test C) are generally lower than with test A and B. Most concentrations in the leachates were below the detection limits (see table 9).

The presented results show, that the availability test according to NEN 7341 is suited for an estimation of the leaching potential needed for calculation of effective diffusion coefficients. For concrete, no major influence is found when using a pH higher than 7 for one of the pH-static leaching steps. Using the DEV-S4 procedure, the potential is not correctly estimated (the leachable amounts would be estimated too low).

### 3.3.2 Tank test

Evaluating the tank leaching test data according to NEN 7345, the results shown in table 5 were obtained. In this table the $pD_e$-values (negative logarithm of effective diffusion coefficient) are combined for those elements, for which results indicate that the leaching is controlled by diffusion. The $pD_e$-value is a measure of the mobility of the elements (the lower the $pD_e$-value, the higher the mobility).

***Table 5:*** *Results of tank leaching tests for concrete C1 evaluated according to NEN-ISO 7345 /2/*

| laboratory | Na | | As | | Cl | | Cr | | Cu | | S | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $pD_e$ | $\sigma$ | $pD_e$ | $\sigma$ | $pD_e$ | $\sigma$ | $pD_e$ | $\sigma$ | $pD_e$ | $\sigma$ | $pD_e$ | $\sigma$ |
| 2 | n.d. | - | *DTL* | - | *DTL* | - | *DTL* | - | *DTL* | - | *DTL* | - |
| | n.d. | - | *DTL* | - | *DTL* | - | *DTL* | - | *DTL* | - | *DTL* | - |
| 3 | n.d. | - | *DTL* | - | n.d. | - | 14.0 | 0.33 | *DTL* | - | *DTL* | - |
| | n.d. | - | *DTL* | - | n.d. | - | 13.4 | 0.26 | *DTL* | - | *DTL* | - |
| 4 | n.d. | - | 13.8 | 0.11 | 12.6 | 0.16 | 13.8 | 0.21 | 14.5 | 0.50 | n.d. | - |
| | n.d. | - | 13.8 | 0.10 | 12.6 | 0.06 | 14.5 | 0.19 | 14.6 | 0.16 | 16.1 | 0.24 |
| 5 | 11.9 | - | *DTL* | - | 13.3 | 0.6 | 14.5 | 0.08 | *DTL* | - | n.d. | - |
| | n.d. | - | *DTL* | - | 13.6 | 0.4 | 14.2 | 0.12 | *DTL* | - | 16.4 | 0.19 |

*$pD_e$*: negative logarithm of the effective diffusion coefficient
*DTL*: only detection limit values measured
n.d.: no diffusion control found

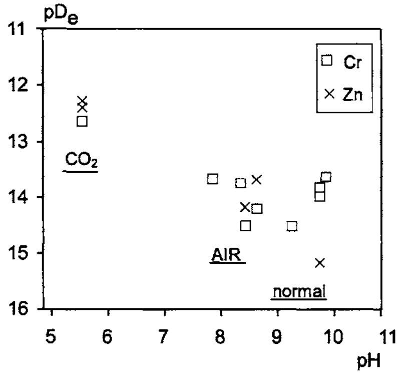

***Fig. 2:*** *Relation between mobility (expressed as the negative logarithm of the diffusion coefficient) and pH*

<u>*Influence of the flow of air or $CO_2$ during tank leaching (test E)*</u>

The influence of the flow of air or $CO_2$ (test F) could be translated into a pH effect. This is summarised in Fig. 2 for some metals. The mobility, expressed as $pD_e$ (negative logarithm of the diffusion coefficient) changes as function of pH corresponding with the solubility curves for the metals. Strictly speaking this effect can be interpreted by differences in availability with one *constant* $pD_e$ or one availability value with *different* $pD_e$ values.

<u>*Influence of the tank leaching period (test F)*</u>

No significant influence was found from the difference in total leaching time (7 and 14 days) on the leaching rates. Each of the five leaching periods was doubled in the 14 days leaching test compared to the 7 days test. This results in a theoretical increase in the concentrations by a factor of 1.4 if the leaching is diffusion controlled. This factor is generally too small for a significant improvement of the possibilities for interpretation.

*Influence of liquid/solid ratio during tank leaching (test G)*

Larger leachant volumes (test G, L/S (V/V) = 25) have had only the effect that the fractions were extra diluted so the measured concentration levels were even lower. The interpretation of the effect of the smaller leachant volume (L/S (V/V) = 2.5) was limited because concentration levels were still near DTL.

*Influence of stirring during tank leaching (test H)*

The diffusion model used assumes virtually zero concentration levels in the leachate. If this model is correct stirring of the leachant during the experiment should not influence the concentration levels in the leachates. In the experiments H no influence was found although interpretation was hampered by low concentration levels.

*Usage of sea water as leachant during tank leaching (test I)*

Due to the low concentration levels in the leachates and the presence of, relative to these levels, rather high concentrations in sea water for several elements, only general indications for differences in leaching could be identified. Leaching levels from sea water seemed to be somewhat lower for the elements Cr and Zn /2/.

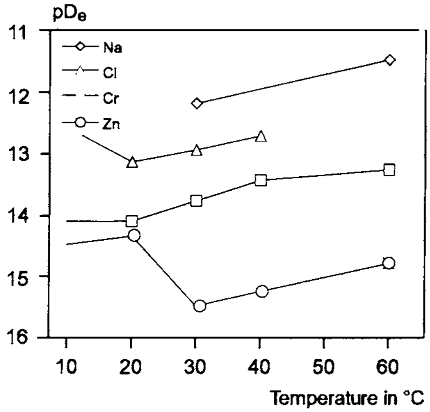

*Fig. 3: Relation between mobility (expressed as the negative logarithm of the diffusion coefficient) and temperature.*

*Influence of temperature during tank leaching (test J)*

The temperature is expected to influence the leaching behaviour (higher temperature causes higher concentration levels in the leachates) /6/. For some elements, whose concentrations in the leachates were at reasonable levels, the mobility ($pD_e$) is plotted in Fig. 3 against the temperature. The results indicate that for temperatures higher than 20 °C indeed the mobility increases with temperature. At lower temperature (< 20 °C) the concentration levels in the leachates become too low to give a reliable result.

### 3.3.3 Conclusions

Although the majority of the factors investigated has an influence on the test results, the concentration levels obtained during the tank leaching test were very low, often well below the detection limits. None of the variations on the test protocol led to a relevant increase in concentration levels measured, so it was decided to keep the tank test procedure as simple as possible. For the further evaluation of the leaching protocol for concrete the availability test according to Dutch standard NEN 7341 and a modified diffusion test similar to Dutch standard NEN 7345 were adopted.

## 4 Second interlaboratory study

### 4.1 Generals

Due to the fact, that the concentration levels obtained in the first interlaboratory study were too low to be suitable for a proper validation of the test protocol, an additional pre-validation study was necessary. In this second interlaboratory study specimen from concrete mixture C2 (see table 1) with higher water-binder ratio (higher permeability) and addition of a fly ash with higher concentrations of relevant elements (FA2) were investigated.

The experimental conditions for the tank leaching test read as follows:

| | |
|---|---|
| – leachant: | demineralised water |
| – L/S (V/V): | 5:1 |
| – leaching periods: | 6, 24, 78, 168, 336 hours |
| – stirring action: | no stirring |
| – temperature: | 20°C |

The only difference in experimental conditions with the preliminary experiment was the time intervals. The parameters to be analysed were sodium, arsenic, calcium, chloride, chromium, copper, potassium, and sulphate.

### 4.2 Availability test

The results of the availability test are summarised in table 9. The total concentration and the availability of C1 and C2 are represented for some examples in Fig. 4. The results illustrate the fact that using a fly ash with higher element concentrations does not necessarily results in higher leaching levels.

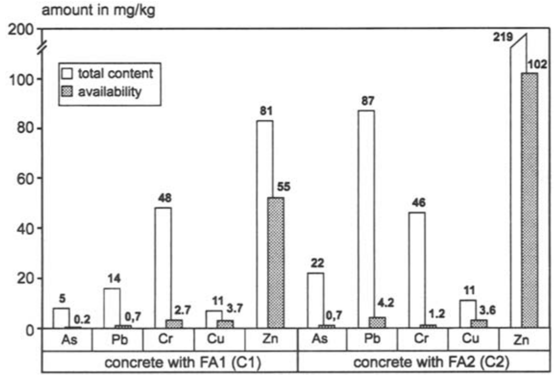

*Fig. 4: Comparison of concrete C1 and C2 in respect to total element contents and availabilty*

### 4.3 Diffusion test

Although the fly ash used for the second round of experiments generally had a higher content of heavy metals and the tortuosity of the concrete produced with this fly ash was about 3 times lower /2/ than that for concrete C1, the leached amounts of heavy metals from this concrete were again very low.

The results of the tank test from the second interlaboratory study are summarised in table 6. Note the limited number of results for which diffusion control was found according to NEN 7345 procedure. Most measured concentrations were at DTL-levels. This presents a problem for the evaluation of the leaching test itself concerning these elements. The levels for Na and K were high enough for adequate analysis, but the leaching mechanism could not be deduced successfully from the leaching data, due to S-shaped release curves /2/.

***Table 6:*** *Results of the tank test from the second interlaboratory study*

| Lab | Na | | As | | Ca | | Cl | | Cr | | Cu | | K | | S | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | pDe | $\sigma$ | pDe | $\sigma$ | pDe | $\sigma$ | pDe | $\sigma$ | pDe | $\sigma$ | pDe | $\sigma$ | pDe | $\sigma$ | pDe | $\sigma$ |
| 1 | - | | *DTL* | | - | | *DTL* | | > 13.5 | | > 14.5 | | - | | 15.39 | 0.21 |
| | - | | *DTL* | | - | | *DTL* | | > 13.35 | | *DTL* | | - | | 15.34 | 0.14 |
| 2 | - | | - | | - | | *DTL* | | > 13.24 | | *DTL* | | - | | *DTL* | |
| | - | | - | | - | | *DTL* | | - | | *DTL* | | - | | *DTL* | |
| 3 | - | | - | | 15.85 | 0.13 | 10.62 | 0.07 | > 13.58 | | *DTL* | | 10.91 | 0.16 | > 14.71 | *0.15* |
| | - | | - | | 17.59 | 0.22 | - | | > 13.32 | | *DTL* | | - | | > 14.88 | *0.16* |
| 4 | - | | - | | - | | - | | - | | - | | - | | 15.76 | 0.15 |
| | - | | - | | - | | 13.92 | 0.29 | > 13.45 | | >14.55 | | - | | 15.60 | 0.17 |
| 5 | 12.13 | 0.28 | *DTL* | | *DTL* | | 10.07 | 0.23 | 14.26 | 0.56 | *DTL* | | 11.13 | 0.18 | - | |
| | - | | - | | - | | - | | 13.58 | 0.16 | - | | 10.90 | 0.08 | - | |
| 6 | - | | *DTL* | | - | | - | | *DTL* | | *DTL* | | - | | *DTL* | |
| | - | | *DTL* | | - | | 11.68 | 0.29 | *DTL* | | *DTL* | | - | | *DTL* | |

DTL: concentration levels below detection limit

$pD_e$: effective diffusion coefficient; values with >: concentration levels close to detection limit

- : not determined

The results indicated that a validation study with concrete specimen used in the second interlaboratory study was not useful. There seemed to be no alternative than to use 'spiked concrete' for this evaluation. The spiking of a concrete with additional amounts of several elements seemed to present a suitable option to measure concentrations distinctly above the DTL and thereby to be able to validate the leaching test procedure.

## 5 Validation study

### 5.1 Generals

The test conditions for the tank tests in the validation study were the same as during the second interlaboratory study. A spiked concrete mixture (C3, see table 1) was used as a test sample.

In the validation study 18 laboratories from the following countries participated: the Netherlands, Germany, Belgium, France, United Kingdom, Sweden, Poland, Hungary, Portugal, and Austria.

In CEN TC51/WG12/TG6 a discussion had taken place whether demineralised or mineralised water should be used as a leachant for cement-based materials. The main reason for this discussion is that the use of demineralised water may lead to dissolution of the surface of concrete. On this background, in this validation study, the use of a mineralised (low hardness water) was included.

### 5.2 Availability

The average results of the availability test and the result of the determination of precision is shown in table 7.

***Table 7** : Average results and precision of the availability test*

| Element | Availability | $S_r$ | $S_R$ | $N_r/N_R$ | Rejected laboratories |
|---|---|---|---|---|---|
| | mg/kg | % | % | - | |
| Na | 307.3 | 7.2 | 28.4 | 3/4 | - |
| As | 9.7 | *24.2* | *64.2* | 14/15 | - |
| Cl | 779.7 | *27.6* | *104.9* | 11/12 | 1 |
| Cr | 75.7 | 11.9 | 23.3 | 14/15 | 1 |
| K | 1820.0 | 6.4 | 16.7 | 14/15 | 1 |
| S | 1507.0 | 3.0 | 18.8 | 13/14 | 2 |
| V | 20.6 | 14.4 | 29.7 | 11/12 | 3 |

The very limited precision for As and Cl can be explained by a higher analytical error caused by relatively low concentration levels relative to DTL. When 10 times DTL as the minimum concentration level is used, the average level of precision expressed as $S_r$ and $S_R$ is 8.6% and 23.4%, respectively. The average value of $S_R$ is relatively high.

## 5.3 Diffusion test

The precision results are listed in table 8 for two types of leachants, demineralised (standard) and mineralised water. The precision is lower at concentration levels below 10 times DTL.

### Demineralised water

The evaluation of the leaching data is done by determining $E_{64d}$ (emission after 64 days, assuming diffusion as dominating mechanism) from the experiments with demineralised water according to NEN 7345.

Using only values larger than 10 times DTL, the average values of $S_r$ and $S_R$ are 14% and 28% respectively. These values are about the same as for the precision values found for the measured release with demineralised water in 14 days ($E_{14d}$-measured), 12% and 22% respectively. In the $E_{14d}$-measured values, data for elements are included for which diffusion control according to NEN 7345 could not be identified. The rather low values for $N_r$ and $N_R$ in table 8 (maximal value is 16 which is the number of laboratories that performed the test) were therefore not caused by rejected values in the outlier procedure but by the result of the evaluation procedure in the leaching test protocol that no diffusion control could be established. Consequently no diffusion coefficient could be determined for these elements and therefore the test result $E_{64}$, which is calculated from this diffusion coefficient, could not be obtained.

### Mineralised water as a leachant

In order to investigate the influence of the usage of the so-called 'low hardness' water on the leaching behaviour of concrete, water with 0.25mM $CaCl_2 \cdot 2H_2O$ + 0.5mM $NaHCO_3$ was also used as a leachant. The initial concentrations in the leachate for Na, Ca and Cl are a factor 4 to 10 higher than the amount leached from the test piece. These elements can therefore not be used for the comparison. For all elements measured (see table 8) except for Na and Cl, no significant difference in leaching was found.

***Table 8**: Precision of diffusion test for demineralised and mineralised water as leachant*

| Leachant | Element | Value mg/m$^2$ | $S_r$ % | $S_R$ % | $N_r/N_R$ | rejected laboratories |
|---|---|---|---|---|---|---|
| Demineralised water | *$E_{64}$ acc.to NEN 7345* | **release 64 d** | | | - | |
| | Na | 3139 | 17.8 | 26.8 | 6/6 | - |
| | As | 13 | 11.3 | 25 | 5/10 | - |
| | Cl | 455 | 11.8 | 50.4 | 3/8 | - |
| | Cr | 339 | - | - | - | - |
| | K | 31505 | 14.1 | 32.0 | 14/15 | - |
| Mineralised water | *$E_{64}$ acc.to NEN 7345* | **release 64 d** | | | | |
| | K | 34795 | 14.1 | 16 | 13/13 | - |
| | As | 11 | 10.2 | 18.8 | 3/5 | - |
| Demineralised water | *$E_{14}$ measured* | **release 14 d** | | | | |
| | Na | 1489 | 9.1 | 24.8 | 8/9 | - |
| | As | 8.5 | 9.7 | 26.8 | 13/13 | - |
| | Cd | 0.05 | 15.8 | 41 | 2/2 | - |
| | Cl | 211 | 11.3 | 56 | 10/10 | - |
| | Cr | 113 | 15.3 | 20.7 | 16/16 | - |
| | K | 13442 | 11.9 | 21.7 | 16/16 | - |
| | V | 78 | 7.6 | 19.6 | 15/15 | - |
| | S | 1012 | 17.1 | 17.4 | 15/15 | 1 |
| Mineralised water | *$E_{14}$ measured* | **release 14 d** | | | | |
| | Na[1] | *4944* | 3.6 | 34.8 | 9/9 | 1 |
| | As | 7.6 | 13.9 | 24.5 | 9/9 | - |
| | Cd | 0.02 | - | - | 1 | - |
| | Cl[1] | *5366* | 4.1 | 57.9 | 8/8 | - |
| | Cr | 111 | 12.8 | 16.7 | 12/13 | - |
| | K | 14068 | 6.5 | 14.3 | - | - |
| | V | 75 | 9.6 | 15.7 | 12/12 | - |
| | S | 1030 | 26.8 | 29.9 | 13/13 | 1 |

[1] present in blank

<u>Effect of spiking</u>

To create larger concentration levels in the leachates, which were needed to validate the leaching procedure, the concrete was spiked with As, Cd, Cr and V. The use of a spike was only successful to a certain extent. The concentration levels obtained in the leachates were increased, but the emission behaviour of the spiked elements differed from elements that were present in the constituents of the concrete. As a result, diffusion control could be clearly demonstrated for the matrix using major elements but only for a limited number of minor elements due to low leaching levels and the spiking artefact /2/.

## 6 Conclusions

The aim of this research project was the development of a leaching standard for the determination of the environmental quality of concrete. The test procedure should be a short time characterisation test.

Generally, the emissions from the investigated concrete specimen were very low and often close to or well below the detection limits. From the results of the three interlaboratory studies it could be deduced, that following major elements are suitable to identify diffusion control during leaching from concrete: *K, As, Cr and Cl.* If these elements show diffusion control, it can be concluded, that the leaching from the matrix is in principle diffusion controlled.

The results from both the tank leaching test and the availability tests indicated that the precision in terms of repeatability and reproducibility of the tests is good. No significant differences were observed between the tank leaching test with demineralised water and mineralised water. The test protocol with demineralised water has following advantages: demineralised water is easily to harmonise and the problem that species that are used to 'mineralise' the water cannot be included in the evaluation of the tank leaching test does not occur.

The development of a short time characterisation test procedure for standardised concrete with usual constituents was difficult. The results show that the two types of concrete that were tested in this project do not have significant leaching of environmentally relevant elements. The concentrations of released environmentally relevant elements were mostly below the DTL. This is consistent with results in literature regarding the leaching behaviour of concrete with usual ingredients /1, 6/. This could indicate that further testing with a characterisation test is unnecessary for concrete with usual ingredients with known leaching behaviour. However the leaching procedure described is useful for the determination of the leaching behaviour of concrete with unknown ingredients.

***Table 9:*** *Element contents and availability results of the concretes investigated /2/*

| concrete | C1 | | | | | | | | C2 | | | | C3 1) | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| addition | FA1 | | | | | | | | FA2 | | | | FA1 | | | |
| method | total content | | availability; A | | availability; B | | availability; C | | total content | | availability; A | | total content | | availability; A | |
| parameter | mg/kg | | | | | | | | | | | | | | | |
| | *mean* | *N* | *mean* | *N* | *mean* | *N* | *mean* | *N* | *mean* | *N* | *mean* | *N* | *mean* | *N* | *mean* | *N* |
| Arsenic, As | 5.2 | 7 | 0.16 | 10 | < 0.1 | 8 | < 0.01 | 9 | 22 | 1 | < 0.9 | 12 | 95 | 1 | 12.3 | 30 |
| Cadmium, Cd | 0.2 | 7 | 0.48 | 9 | 0.2 | 8 | < 0.01 | 9 | 1.3 | 1 | 0.4 | 1 | 63 | 1 | 42 | 6 |
| Chloride, Cl | 104 | 5 | 95 | 7 | 142 | 5 | < 35 | 9 | 108 | 1 | 73 | 8 | n. a. | 1 | 985 | 26 |
| Chromium, Cr | 48 | 7 | 2.7 | 10 | 4.1 | 8 | 0.12 | 8 | 46 | 1 | 1.2 | 12 | 124 | 1 | 82 | 32 |
| Cobalt, Co | 4 | 7 | 1.2 | 8 | 1.7 | 8 | < 0.03 | 7 | 3 | 1 | n. a. | | 7 | 1 | n. a. | - |
| Copper, Cu | 11 | 7 | 3.7 | 9 | 3.6 | 8 | < 0.03 | 9 | 11 | 1 | 3.6 | 12 | 12 | 1 | n. a. | - |
| Lead, Pb | 14 | 7 | 0.7 | 9 | 1.3 | 8 | < 0.04 | 9 | 87 | 1 | 4.2 | 1 | 24 | 1 | n. a. | - |
| Mercury, Hg | n. a. | - | < 0.1 | 8 | < 0.1 | 8 | < 0.01 | 9 | 0.03 | 1 | n. a. | - | n. a. | 1 | n. a. | - |
| Nickel, Ni | 121 | 3 | 12 | 2 | n. a. | - | n. a. | - | 17 | 1 | n. a. | - | 26 | 1 | n. a. | - |
| Potassium, K | 3046 | 2 | 835 | 4 | 890 | 2 | 666 | 2 | 4080 | 1 | 1047 | 12 | n.a. | 1 | 2085 | 32 |
| Sodium, Na | 398 | 7 | 154 | 10 | 161 | 8 | 76 | 9 | 760 | 1 | 199 | 12 | n.a. | 1 | 312 | 8 |
| Sulphur, S | 1217 | 7 | 1206 | 9 | 1115 | 7 | 308 | 9 | 1112 | 1 | 1141 | 10 | n.a. | 1 | 1543 | 10 |
| Thallium, Tl | < 1.2 | 6 | 0.1 | 8 | 0.1 | 8 | < 0.01 | 9 | 0.4 | 1 | 0.11 | 1 | n.a. | 1 | n. a. | |
| Vanadium, V | 18 | 4 | n. a. | 2 | n. a. | - | n. a. | - | 16 | 1 | n. a. | - | 114 | 1 | 29.9 | 30 |
| Zinc, Zn | 81 | 7 | 55 | 9 | 52 | 8 | < 0.8 | 9 | 219 | 1 | 102 | 1 | 80 | 1 | n. a. | - |

1): this concrete was spiked with arsenic, cadmium, chromium and vanadium (see tables 3, 2)

A: procedure according to NEN-ISO 7341; 1st step 3 h constant pH = 7, 2nd step 3 h constant pH = 4

B: procedure similar to NEN-ISO 7341; 1st step 3 h without pH-control, 2nd step 3 h constant pH = 4

C: procedure according to DIN 38414 Teil 4 (DEV-S4-procedure)

n. a.: not analysed

Characterisation of the leaching mechanism of elements that leach in sufficiently high concentrations can be hampered by initial effects like surface wash-off and an S-shaped curve as occurred for most spiked elements. In order to be able to calculate the long-term leaching behaviour of concrete for these elements accurately the leaching time intervals of the tested leaching procedure have to be prolonged. But this would turn the 'short time' characterisation test that was aimed at in this project back into the standardised Dutch leaching test procedure NEN 7345.

## 7 References

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