Environmental CRIteria for CEMent based products

ECRICEM

Phase I: Ordinary Portland Cements
Phase II: Blended Cements

EXECUTIVE SUMMARY

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EXTENDED ABSTRACT

1. Background

The protection of the immediate environment of structural works is one of the essential requirements of the European **C**onstruction **P**roducts **D**irective (CPD). According to the CPD, construction products can only be put on the market, if the structural works built with them fulfil the relevant requirements for hygiene, and the protection of health and the environment. These essential requirements in the respective standards are specified at the national level by the individual member states.

Cement and cementitious materials are considered to fulfil the fundamental requirements of the European Construction Products Directive and the corresponding national regulations. Therefore a technical regulation like the cement standard EN 197 in general does not cover separate requirements for determining compliance of cementitious materials with criteria on hygiene, health and environmental protection. Further regulations are laid down in cases where it appears necessary for constructive applications requiring a particular protection of water, soil and air.

In this context the assessment of the environmental quality of cement and cementitious products is usually based on leaching characteristics, i.e. the release of constituents such as trace elements or organic compounds when the materials are in contact with groundwater or soil. However, the relationship between release of substances like trace elements or organic components under specific laboratory test conditions and actual field situations may lead to some contradictions. Therefore, environmental testing has to be optimised such that a manageable and effective system of quality control can be designed. The findings of the project will be useful for the standardisation work taking place in CEN, for example in TC 51 ‘Cement’, TC 104 ‘Concrete’, TC 164 ‘Water supply’, and especially for TC 351 ‘Construction products: Assessment of release of dangerous substances’.

Emphasis in this project is mainly given to the following items:

- exposure of concrete structures in direct contact with groundwater, surface water or soil **(„primary“ applications or „service life“),**
- exposure of mortar or concrete to drinking water in distribution systems **(„primary“ application),**
- reuse of demolished and recycled concrete debris as aggregates in new concrete, in road construction, dam fill etc. **(„secondary“ applications),**
- landfilling of demolished concrete **(„end-of-life“ application).**

The trace element contents of commercial cements may vary broadly as a consequence of the use of various natural fuels and raw materials. Increasing concern has been raised with the use of ‘alternative’ (= waste derived) fuels and raw materials which may both increase or decrease the trace element content in cement.

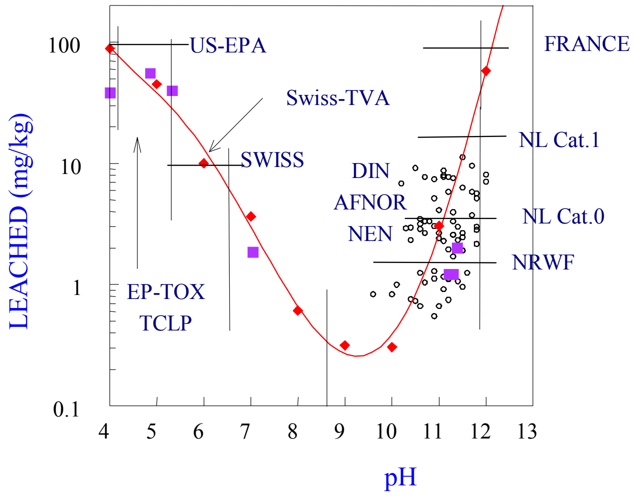
However, the findings of several studies have demonstrated that the chemical composition (i.e. the trace element content) of cement has no direct relation to the leaching characteristics and, thus, is not a good indicator for the environmental quality of cement based products.

These studies have also shown that the release of constituents (trace elements) from cement based products in contact with water during service life is mainly diffusion-controlled and affected by various physical and chemical retention mechanisms. The knowledge of these mechanisms, i.e.

- the physical retention of the potentially leachable fraction,
- the chemical retention of elements fixed in the hardened cement paste matrix (solubility limitation, sorption reactions, solid solutions), and
- the changes in conditions controlling trace element release such as the decrease of the pH value due to carbonation

holds the key in defining environmentally sound trace element levels in clinker and cement.

A variety of laboratory leaching tests has been developed world wide, of which a few are already used for regulatory control purposes. This is a major cause for confusion as the basis of reference is not the same, and different tests may lead to different results and different interpretations. As an example figure 1.1 shows the leachability of lead from **M**unicipal **S**olid **W**aste **I**ncinerator (MSWI) bottom ash as a function of the pH value in relation to various regulatory limits and standard tests.



Horizontal lines:	Limit values in various regulations.
Vertical lines:	*pH values applied in corresponding standard tests.*
Standard Tests:	
US-EPA:	*EP-TOX (predecessor of TCLP)*
Switzerland:	*TVA – Swiss CO2 test*
Germany:	*DIN – German batch leach test (S4)*
Netherlands:	NEN – Dutch column leaching test
France:	*AFNOR - French batch leaching test*

Figure 1.1 *Leachability of lead from MSWI bottom ash as a function of the pH value in relation to various regulatory limits*

For a sound understanding of the generic leaching behaviour of construction materials, so-called ‘characterisation’ tests focussing on the basic characteristics with regard to the long term leaching behaviour are needed. In addition, parameters influencing the principal leaching mechanisms have to be determined. The information generated can then be used for the evaluation of different exposure scenarios.

Once the principal leaching characteristics of a construction material have been established, strongly reduced testing will suffice to demonstrate that the material complies with the generic behaviour of this material category (as tested with a characterisation test), and/or complies with relevant regulations. For this purpose, so-called ‘compliance’ tests are available.

2. Project Organisation and Objectives

ECRICEM ('**E**nvironmental **Cri**teria for **Cem**ent-Based Products') is a comprehensive project set up by a consortium consisting of the following partners:

- Energy research Centre of the Netherlands (ECN)
- Holcim Group Support Ltd. (Holcim) and Holcim Belgium
- Verein Deutscher Zementwerke (VDZ)
- Norcem A.S., HEIDELBERGCEMENT Group

The following **main objectives** of the ECRICEM project have been identified by the partners:

- To describe the general leaching behaviour of cementitious materials produced with different cement types.
- To support and facilitate the environmentally sound use of alternative fuels and raw materials (derived from various waste streams) in cement and concrete production.
- To support the reuse/recycling of construction debris (demolished concrete) in construction projects, i.e. as aggregates in new concrete, as fill materials in road construction, etc.
- To develop and propose environmental quality criteria and control procedures for cements and cement-based products to both producers and regulators of construction materials.

The following **targets** have been defined:

- Establishment of an inventory of contents and leachability of trace elements in cements produced with different natural fuels and raw materials at various locations world-wide.
- Investigation of the influence of alternative fuels and raw materials on content and leachability of trace elements in cements.
- Increase of the fundamental knowledge about the incorporation of trace elements in clinker phases and about the leaching mechanisms prevalent in cement-based products.

3. Experimental Work ECRICEM Phase I: Ordinary Portland Cements

According to the work programme, the experimental section consisted of the following individual tasks:

- **Selection of test cements:**
  Ten commercial cements (nine regular Portland cements and one limestone filler cement) out of a total number of seventeen cements collected world wide were selected for further testing based on their detailed chemical composition, i. e. trace element content. Six of those cements were manufactured using alternative (waste) fuels up to a maximum thermal substitution rate of 42 %. Four commercial cements were manufactured by using conventional (fossil) fuels only.
  In addition, two cements with artificially high metals contents (special cements W1 and W2) were produced in a small pilot rotary cement kiln at a specific test facility. These test samples were prepared to evaluate the leaching behaviour of cements with trace element contents much higher than the common range of commercial cements.
- **Determination of the chemical composition of the selected test cements:**
  Major chemical composition and trace element contents were determined for all test cements. For comparison, selected trace element contents are given for commercial cements and 'special' cements in Table 3.1.

Table 3.1 *Trace element contents of the test cements (in mg/kg)*

	Commercial Portland cements		Special cements	
	Range		W 1	W 2
Element	Min	Max		
As*	2	23	102	340
Be	0.5	3	0.8	0.9
Cd*	<0.1	1	0.3	1.2
Co	6	22	7	14
Cr tot.*	29	580	335	1400
Cr VI	2	94	7	39
Cu	14	54	23	22
Hg	<0.02	0.1	0.03	0.08
Mo*	<1	8	46	202
Ni	14	75	14	42
Pb*	6	106	50	13
Sb*	<1	5	8	31
Sn	<1	14	< 1	3
V	22	230	25	27
Zn*	30	380	502	2030

** Spiked in the pilot cement kiln*

- **Determination of the physical properties of the selected test cements:**
  Setting time, soundness, and compressive strength at 1, 2, 7 and 28 days were determined according to the European cement standard EN 196.
- **Preparation of mortar samples:**
  Standard mortar samples were prepared from all test cements (according to EN 196) for further testing, i.e. the leaching tests. The structural characteristics of the mortar were examined microscopically.

- **Environmental characterisation (leaching tests):**
  Various leaching tests were carried out on intact ('monolithic') and on crushed mortar samples according to established (Dutch) or proposed European standard procedures. The tests were selected to evaluate generic leaching characteristics of trace elements and to cover different exposure scenarios in primary, secondary and end-of-life applications.
- **Geochemical modelling:**
  Geochemical modelling was carried out to identify mineral phases controlling the release of trace elements under specific environmental exposure scenarios.
- **Prediction of long-term release of metals:**
  Based on the results of the leaching tests, model estimates were made on the long-term release of trace elements under different exposure scenarios in the application of cementitious construction materials.

Table 3.2 *Main exposure scenarios for cementitious construction materials*

APPLICATION	EXPOSURE SCENARIO	EXAMPLES
Primary ('Service Life') applications	Utilisation of concrete in direct contact with drinking water	Concrete pipes and basins
	Utilisation of concrete in structures exposed to fresh surface water	Pillars for bridges, quays, breakwaters, locks
	Utilisation of concrete in the marine environment	Breakwaters, oil rigs, embankments, etc
	Utilisation of concrete in contact with ground water	Pilings, shafts, etc
	Utilisation of concrete in surface structures	All forms of building on land
Secondary ('Recycling') applications	Recycling of concrete construction debris in new concrete as aggregates	New concrete
	Reuse of construction debris as unbound aggregates	Road construction, dams, etc.
'End of life' applications	Landfilling of fines from construction debris and multiple recycled material not meeting criteria for reuse	Landfill

- **Inter-comparison test:**
  To check the analytical performance and to assure a good comparison of the analytical results among the project partners, inter-laboratory tests were carried out on a standard leachate sample and on a monolith leaching test with subsequent leachate analysis.

3.1 The pH dependence test is the test procedure best suited to characterize the generic leaching behaviour of trace elements in cement based products

The leaching characteristics of trace elements in cement mortars have been determined by examining the leaching concentrations as a function of the pH value in the range pH 2 to 13 (pH dependence test, CEN/TS14429). These tests have revealed consistent and systematic leaching patterns for all cements tested. The broad pH range is relevant to understand the behaviour of cementitious materials under different exposure scenarios. In practical applications, the pH domain ranging from 7.5 to 12.5 is relevant.

The pH dependence test results form a basis for evaluating the results obtained from various 'compliance' tests commonly used in the assessment of the leaching behaviour of cement based products under different exposure scenarios. The strong influence of the pH value in these scenarios is clearly demonstrated.

3.2 There are significant differences in the generic leaching characteristics of different trace elements

Confirming the results from previous studies, three different categories of elements can be identified with regard to their generic leaching behaviour (see Fig. 3.1):

- 'Regular' metals, such as Pb, Cu, Cd, Ni, and Zn, showing a minimum leachability in the pH range 8 – 11.
- Elements occurring as 'oxyanions', such as Cr, Mo, As, Sb, and V (i.e. chromate CrO_4^-, arsenate AsO_4^{3-} or molybdate MoO_4^-) featuring a maximum leachability at neutral to slightly alkaline pH.
- Soluble salts showing no relationship with pH at all. Only a few constituents behave like this in cement based systems.

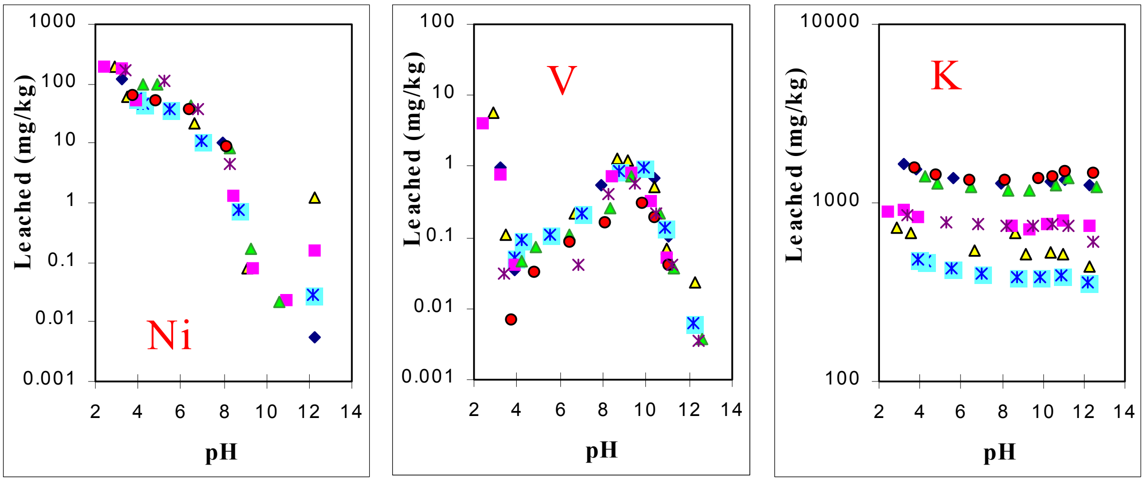


Figure 3.1 *Generic leaching behaviour of 'regular' metals, oxyanions and soluble salts (obtained from pH dependence tests on different crushed cement mortars)*

3.3 Elevated trace element contents in cements may lead to increased leaching for some metals in the characterisation tests

The special ('spiked') cements with artificially increased total concentrations of selected trace elements show very similar generic leaching characteristics compared to the commercial Portland cements with common trace element levels. 'Regular' metals (such as Zn and Cd) show only slight increase in the leached amounts in the pH range relevant for common concrete applications.

However, the leaching of 'oxyanions' such as Cr, Mo, As, and Sb is increased in the characterisation (pH dependence) tests. For Cr, Sb and Mo, the increase in leaching is roughly proportional to the increase in the total concentration in cement. For As, a more than 10 and 30 fold increase of the total concentration in the 'spiked' cements leads to a 2 and 5 fold increase of the leached concentrations only.

3.4 Elevated Zn contents in cements have no significant effect on the leaching in the characterization test.

Elevated levels of Zn in the special cements have an effect on the leaching concentrations at low pH value (pH < 7) only (see figure 3.2). At a pH value of > 8, no significant increase of the leachability was observed. This implies that even a Zn content as high as 0.2 % in cement would hardly have an effect on the long-term release of Zn through leaching in size reduced concrete rubble, i.e. in recycling or landfill applications.

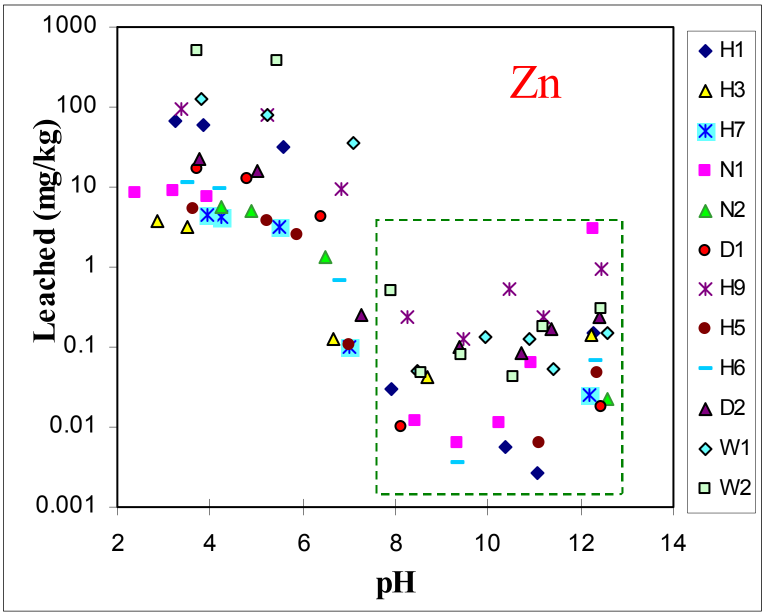


Figure 3.2 *pH dependence test data for the release of Zn from various cement mortars. The box indicates the relevant pH range for most cement-based applications*

Due to the fact that the total contents of Pb and Cd could not be increased considerably in the special cements, it is not possible to draw similar conclusions for these metals. However, results from additional tests with Pb/Zn slag and pure metal oxide added to cement mortar indicate that a similar conclusion may be drawn for Pb.

3.5 There is no systematic correlation between the total content of trace elements in cement mortar and the leaching from mortar even under worst case conditions

Table 3.3 shows the ratios between the maximum ‘available’ trace element content (as obtained from the ‘availability’ test on crushed mortar) and the ‘total’ trace element contents (calculated for mortar), expressed as a percentage of the total for all investigated ECRICEM Phase I cements. The ratio between the leached amount for the batch test at neutral pH relative to the total content is given in a similar manner. For exposure conditions as specified in table 3.3 the amount released from a monolithic slab in 100 years is also expressed as a percentage of the total content. The table demonstrates that there is no systematic trend or correlation in the ratios for the trace elements investigated.

The total content of trace elements in cement may exceed the release of trace elements as observed in leaching tests by orders of magnitude and in the ‘availability’ test by significant factors. Thus it is confirmed that the total content of trace elements in cements is, from a scientific point of view, not a good indicator for the release,. The elements Be, Hg, Tl and Sn are not considered in the table due to very limited data or data below the limit of detection.

Table 3.3 *Relationships between 'available' trace element concentrations (pH = 4 at particle size < 125 μm), leached quantity in batch test (L/S=10, pH 8 control), and the average release of tank test data on all cement mortars investigated in ECRICEM Phase I. All trace element concentrations are given as percentage of the total*

Element	Availability	Batch (neutral pH)	Tank leach test (100 y)*
	Average	Average	Average
As	1.0	0.66	0.002
Ba	14	9.4	0.22
Cd	14	2.5	0.03
Co	21	3.4	0.03
Cr	16	15	0.01
Cu	19	0.29	0.03
Mn	16	2.0	0.0002
Mo	9.0	10	0.02
Ni	90	40	0.02
Pb	7.2	0.92	0.002
Sb	3.7	3.9	0.02
Sn	15	7.8	0.31
Sr	25	22	NA
V	2.7	1.1	0.004
Zn	23	1.3	0.005

* Conditions: Block 100x100x20 cm, 10 ˚C, one side exposed, intermitted wetted (10% of time wet), own pH, 100 years exposure.

3.6 Under certain environmental exposure scenarios, the leachability of trace elements from cement based materials may be governed by solubility rather than by diffusion

Diffusion is the dominant leaching mechanism in the highly alkaline system of the bulk cement matrix. At the surface of concrete structures exposed to water or air however (at neutral or slightly alkaline conditions), release of trace elements may be controlled by solubility of minerals other than the hydration phases of the bulk hardened cement paste.

Leaching experiments under controlled pH conditions indicate that this distinction is important for the prediction of long-term release of trace elements from concrete. Thus, the interpretation of laboratory leaching test data have to be carefully adapted to the exposure scenario under evaluation.

In geochemical modelling experiments, several solubility controlling mineral phases have been identified. For Cr, a solid solution of $BaSO_4$-$BaCrO_4$ and substitution in ettringite seems to control the release of this trace element.

3.7 In certain life cycle stages of concrete, carbonation may play an important role in the release of trace elements to the environment

Due to its high alkalinity, the cement/concrete system has a significant buffering capacity (expressed as 'acid neutralization capacity', ANC) maintaining a stable chemical system upon exposure under varying conditions. Only in a rather acidic environment, this chemical buffer may not be sufficient to maintain stable conditions over a long time scale.

During the ‘service life’ of concrete, carbonation (i.e. the conversion from calcium hydroxide to calcium carbonate with buffering at pH 7.5 - 8) is limited. In recycling stages (as unbound concrete debris) or in disposal scenarios however, carbonation effects may be quite significant. During carbonation, trace elements incorporated in hydration phases such as ettringite may be released due to the decrease in alkalinity.

In recycling or disposal scenarios, the fine particle size fraction of concrete debris (i.e. sieve sands) may be carbonated to a large degree and may therefore, contribute considerably to the release of trace elements. Coarser particles will largely maintain their original alkaline system.

Significant differences between small and coarse graded material have been observed in the leaching experiments. Model predictions of the release of trace elements under recycling/disposal scenarios have to consider both effects (particle size and carbonation).

3.8 Chromium and aluminium are critical elements with regard to their specific leaching characteristics and require more systematic investigations

In the assessment of the long-term release from concrete debris, chromium features amongst the trace elements with the highest leachability in the experiments.

However, the generic leaching behaviour of Cr was not consistent for all cements in the experiments (see Fig. 3.3). The reason for the deviating behaviour of two test cements (with very low Cr leachability) could not be clearly identified so far, but is certainly related to the different chemical oxidation states of Cr (hexavalent versus trivalent Cr). The leaching characteristics of these two cements are comparable to the behaviour of slag type blended cements (see ECRICEM Phase II).

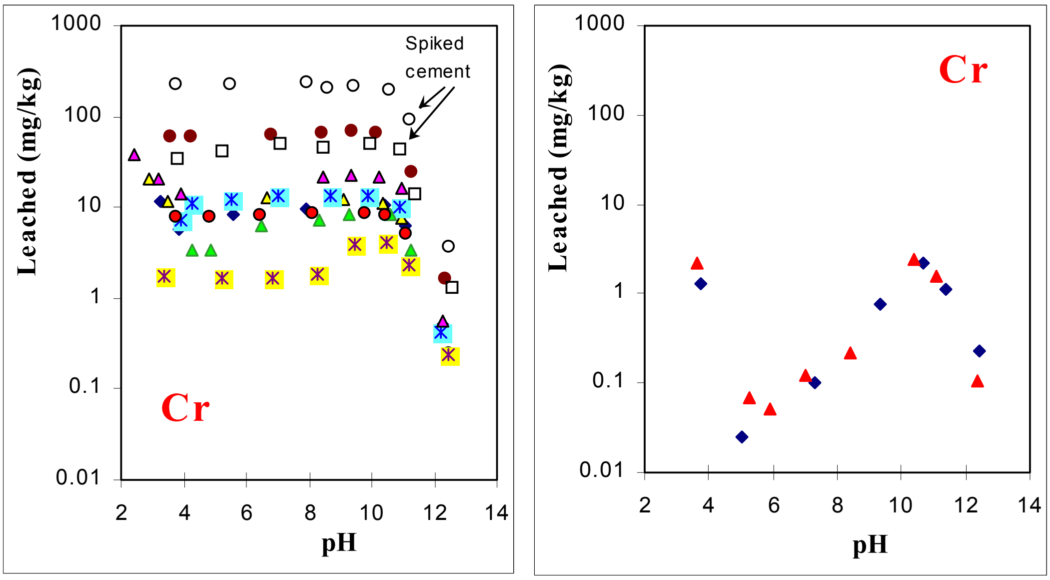


Figure 3.3 *Different characteristics of Cr leachability from various cement mortars (The deviating behaviour of two test cements is related to the different oxidation states of Cr)*

The leachability of aluminium is of importance in application of concrete or mortar in drinking water systems. At high pH conditions, which may develop in case water is stagnant for relative long time, the pH-values and leaching rates of Al from cementitious materials can exceed the drinking water limits. Conditioning (i.e. artificial carbonation) is therefore required to reduce the pH-values and leachability of Al.

Generally, the experiments have demonstrated that the leaching of aluminium responds very sensitively on any change in the pH conditions of the test procedure.

3.9 Rapid compliance tests have to be modified to allow predictions of the long-term leaching behaviour under different exposure scenarios.

Extrapolation of the results of shorter ‘compliance’ tank tests (2 days instead of 64 days) are in good agreement with the standard tank test for some trace elements, but not for all. Long-term predictions for some trace elements such as cadmium can only be made by running the full-time test.

4. Experimental Work ECRICEM Phase II: Blended Cements

According to the work programme, the experimental section consisted of the following individual tasks:

- **Selection of test cements:**
  Twenty commercial cements out of a total number of twenty five cements collected world wide were selected for further testing based on their detailed chemical composition, i. e. trace element content. Three of those cements were Portland cements (one cement with LD slag in the raw mix), six cements were manufactured using blast furnace slag as main constituent, six cements were manufactured with fly ash, pozzolana, limestone or burnt shale as main constituent and five cements were manufactured with more than one main constituent besides clinker.
- **Determination of the chemical composition of the selected test cements:**
  Major chemical composition and trace element contents were determined for all test cements. For comparison, selected trace element contents are given for the cements in Table 4.1.

Table 4.1 *Trace element contents of the test cements (in mg/kg)*

	Portland cements (n=3)		Cements with blast furnace slag (n=6)		Cements with fly ash, pozzolana, limestone or burnt shale (n=6)		Cements with more than one main constituent besides clinker (n=5)	
Element	Range		Range		Range		Range	
	Min	Max	Min	Max	Min	Max	Min	Max
As	5.4	12.6	1.3	6.1	2.7	12.6	4.2	46.6
Be	0.6	1.3	1.1	6.2	0.4	1.9	1.1	4.4
Cd	0.2	0.4	0.1	1.4	0.1	0.9	0.1	1.9
Co	13.3	16.3	2.3	9.5	3.8	23.1	6.3	15.8
Cr tot.	79.7	151.0	32.0	94.1	25.9	122.0	49.5	155.0
Cr VI	0.5	2.9	1.4	11.7	0.4	7.8	3.5	15.1
Cu	17.8	82.1	5.5	49.6	11.8	144.0	8.1	80.4
Hg	<0.02	0.1	<0.02	0.1	<0.02	0.1	<0.02	0.1
Mo	2.3	10.2	1.5	3.2	1.5	4.0	2.9	14.2
Ni	31.6	117.0	11.5	40.1	9.9	53.5	26.6	67.6
Pb	12.6	23.0	2.7	40.3	8.7	43.3	4.6	169.0
Sb	2.3	5.7	1.1	19.4	2.6	23.1	1.6	3.7
Sn	4.2	5.6	1.0	3.2	1.6	6.0	1.2	7.0
V	31.7	774.0	38.7	212.0	24.5	139.0	69.4	138.0
Zn	53.5	115.0	15.9	318.0	26.0	170.0	26.8	372.0

- **Further investigations on the selected test cements**
  Physical and structural tests, mortar sample preparation, and leaching tests were carried out in accordance to the test program of ECRICEM Phase I.
- **Field samples**
  In order to check and verify the results of the experimental leaching tests and the modelling work, samples were taken from three “historical” concrete structures long-term exposed to different field conditions (concrete test specimen exposed at a test site for 50 years, samples from a 200 year old fort and core samples from a cooling channel of a reactor with 25 years of exposure to surface water. These samples were subject to various leaching experiments and chemical modelling.

4.1 Compared to the Portland cements investigated in ECRICEM Phase I, the concentration ranges of metals are slightly extended for the blended cements

The individual data show elevated contents of metals such as arsenic, beryllium, nickel, lead, antimony, vanadium and molybdenum in the blended cements. In many cases, these elevated contents reflect the presence of other main constituents such as blast furnace slag (example: beryllium) or coal fly ash (example: nickel) in the cement. In one case, the use of a LD slag in the raw mix for clinker production obviously leads to higher metal contents in this Portland cement.

4.2 Cementitious materials made of Portland cements and blended cements show a very systematic leaching behaviour

All mortars produced with OPC and blended cements have a very systematic and consistent leaching behaviour, which largely falls within the ranges as observed for the previously studied Portland cement mortars (ECRICEM Phase I). In figure 4.1 data for Zn leachability from all mortars are shown from pH dependence leaching test (CEN/TS14429) and tank test (NEN 7345). Also results are given for carbonated material. For all mortars produced with cements from world wide sources, independently of the use of alternative fuels or raw materials, the range for the release in the tank leaching test is, for several constituents, narrow and not more than a factor of 2 to 2.5 above and below the average (figure 4.2). However, a few elements show a considerable range (e.g. Cr).

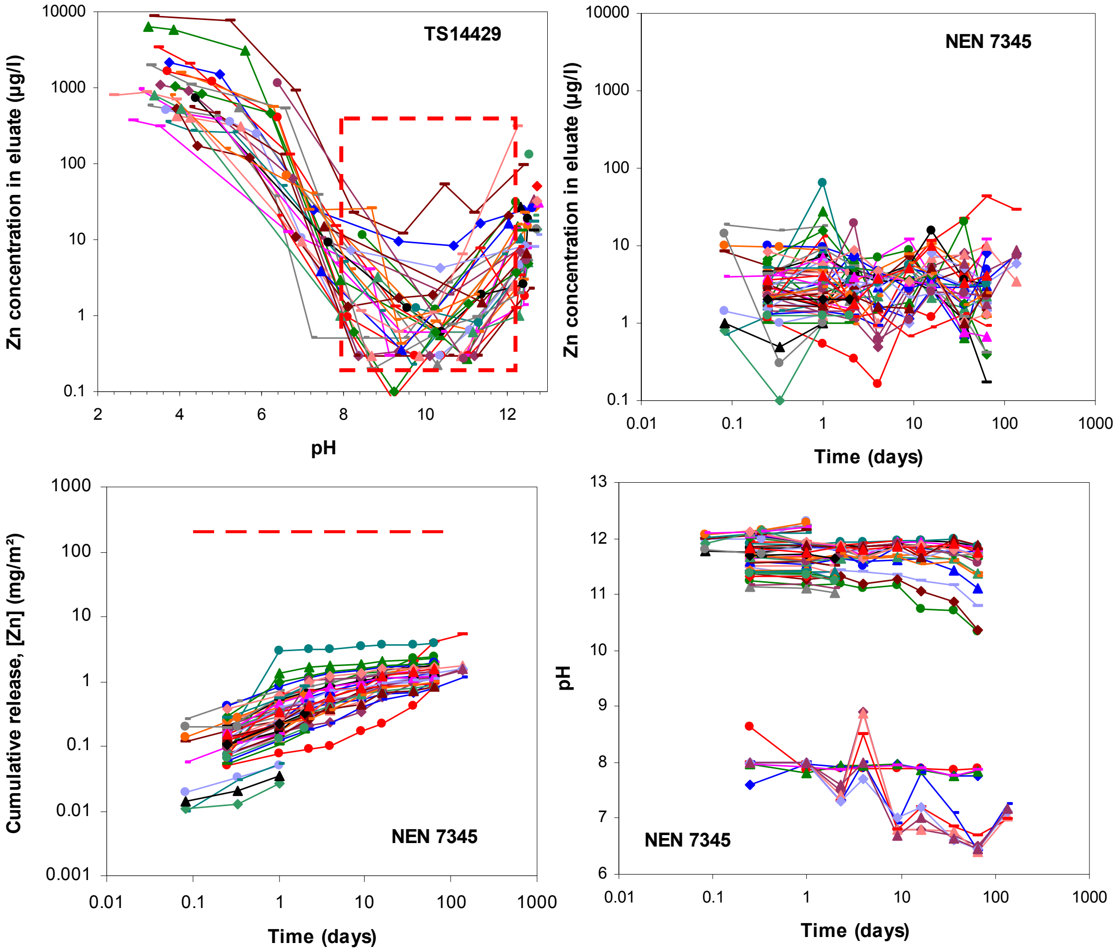


Figure 4.1 *Characterisation of cement mortar with pH dependence test and tank test. Data presentation as function of pH and as function of time allows several conclusions to be drawn (data consistency of world wide cement mortars, comparison with regulatory criteria – BMD 1995, effect of carbonation on release)*

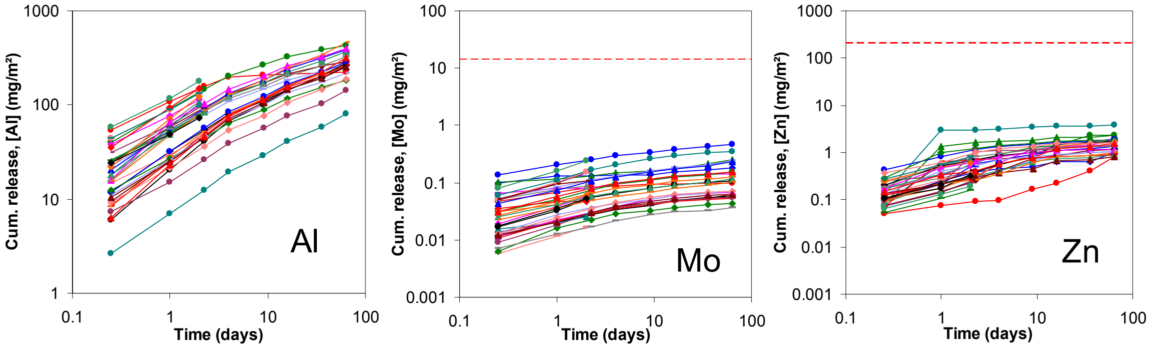


Figure 4.2 *Leaching results for monolith leach test (NEN 7345) illustrating the limited bandwidth for world wide cement mortars. Al: at t=4 days factor 2.1 above and below the average of 78 mg/m2 ; Mo: at t=4 days factor 2.45 above and below the average of 0.14 mg/m2; Zn: at t=4 days factor 1.98 above and below the average of 0.76 mg/m2*

4.3 There is no systematic correlation between the total content of trace elements in cement mortar and the leaching from mortar even under worst case conditions

Table 4.2 shows the ratios between the maximum ‘available’ trace element content (as obtained from the ‘availability’ test on crushed mortar) and the ‘total’ trace element contents (calculated for mortar), expressed as a percentage of the total for all investigated ECRICEM Phase II composite cements. The ratio between the leached amount for the batch test at neutral pH relative to the total content is given in a similar manner. For exposure conditions as specified in table 3.3 the amount released from a monolithic slab in 100 years is also expressed as a percentage of the total content. The percentage leached from a monolith depends very much on specimen dimensions used and thus one must handle the percent leached with caution. The release expressed in mg/m^2 at a specified time is within bounds independent of dimensions and is given in section 4.4.

Table 4.2 *Relationships between ‘available’ trace element concentrations (pH = 4 at particle size < 125 μm) and leached quantity in batch test (L/S=10, pH 8 control), and the average release from tank test data on all cement mortars investigated in ECRICEM Phase II. All trace element concentrations are given as percentage of the total*

Element	Availability	Batch (neutral pH)	Tank leach test (100 y)*
	Average	Average	Average
As	2.0	0.60	0.01
Ba	14	4.2	0.10
Cd	8.7	0.94	0.16
Co	90	2.0	0.02
Cr	5.1	2.5	0.04
Cu	8.1	0.03	0.02
Hg	10	4.8	< 0.02
Mn	10	0.74	0.0003
Mo	70	3.2	0.05
Ni	20	2.1	0.02
Pb	2.9	0.60	0.01
Sb	8.6	1.3	0.04
Sn	2.9	1.1	0.15
Sr	22	17	0.04
V	1.0	0.43	0.006
Zn	15	0.05	0.02

* Conditions: Block 100x100x100 cm, 10 ˚C, 1 side exposed, intermitted wetted (10% of time wet), own pH, 100 years exposure

The table confirms the findings of ECRICEM Phase I (compare point 3.5), that there is no systematic trend or correlation in the ratios for the trace elements investigated. (See for exception Cr in Portland cement in section 4.5)

4.4 Comparison of release in service life with regulatory criteria

In table 4.3 the results from the tank leach test (intact product) are compared with regulatory criteria by taking the upper 95 % confidence interval of release at 64 days (mg/m^2) from all cement mortars studied in ECRICEM Phase I and II. The values are compared with the Building Materials Decree (BMD) category I limit values for unrestricted use. The results for the wider range of cement mortars studied in Phase II confirms that all mortars studied fall within the regulatory criteria for unrestricted use.

Table 4.3 *Comparison of release in mg/m2 observed in tank leach test at 64 days for all investigated ECRICEM Phase I and Phase II cements mortars with BMD criteria for unrestricted use*

Element	Tank leach test (64d) 95% confidence interval (mg/m^2 at 64 days)	BMD (1995) Category I (mg/m^2 at 64 days)
As	0.75	41
Ba	129	600
Cd	0.044	1.1
Co	0.54	29
Cr	7.4	140
Cu	2.8	51
Hg	< 0.3	0.43
Mo	0.45	14
Ni	2.6	50
Pb	1.8	120
S	1500	27000
Sb	0.45	3.7
Se	n d	1.4
Sn	0.93	29
V	7.2	230
Zn	3.1	200

4.5 Mortars produced with blast furnace slag containing cements or with chromate reduced cements show a significantly reduced Cr leachability

All mortars produced with blast furnace slag containing cements show a significantly reduced Cr leachability due to reducing conditions imposed on the cement by the sulphide in the slag (reduction of chromate to Cr III, see also Fig 3.3, right graph). This phenomenon is already quite marked at 10 % slag addition. The mortars produced with chromate reduced cements using Fe II salts show also reduced Cr leachability as expected due to the reducing chemical applied (Figure 4.3).

Figure 4.4 shows the total Cr content for the investigated commercial cements (ECRICEM Phase I and II) versus the leachable Cr (pH dependence test: pH 10 at L/S = 10) for mortars produced with these cements. For OPC a direct correlation between leachable Cr (CrVI) and total Cr can be found, which is indicative of production process based Cr VI formation.

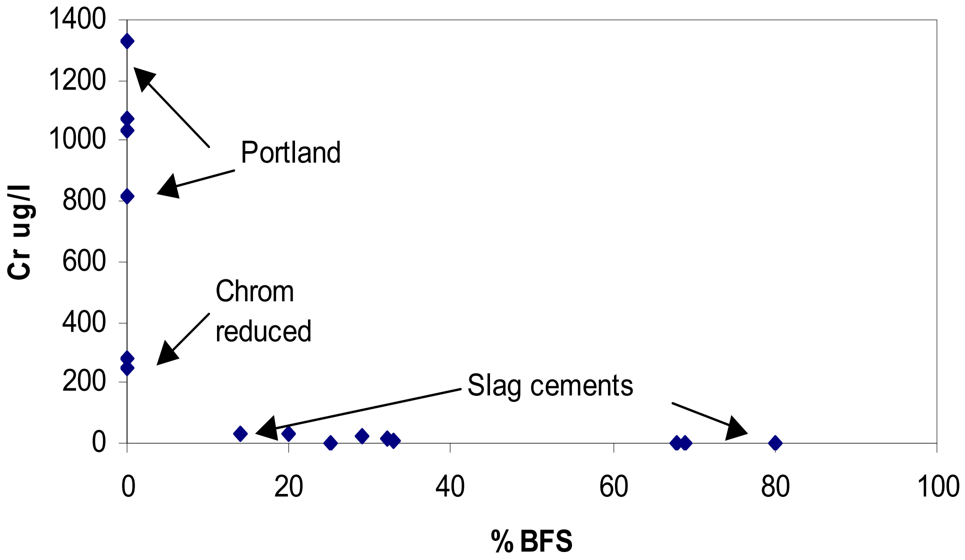


Figure 4.3 *Cr leaching from mortars as a function of blast furnace slag content (pH dependence test: pH 10 at L/S = 10)*

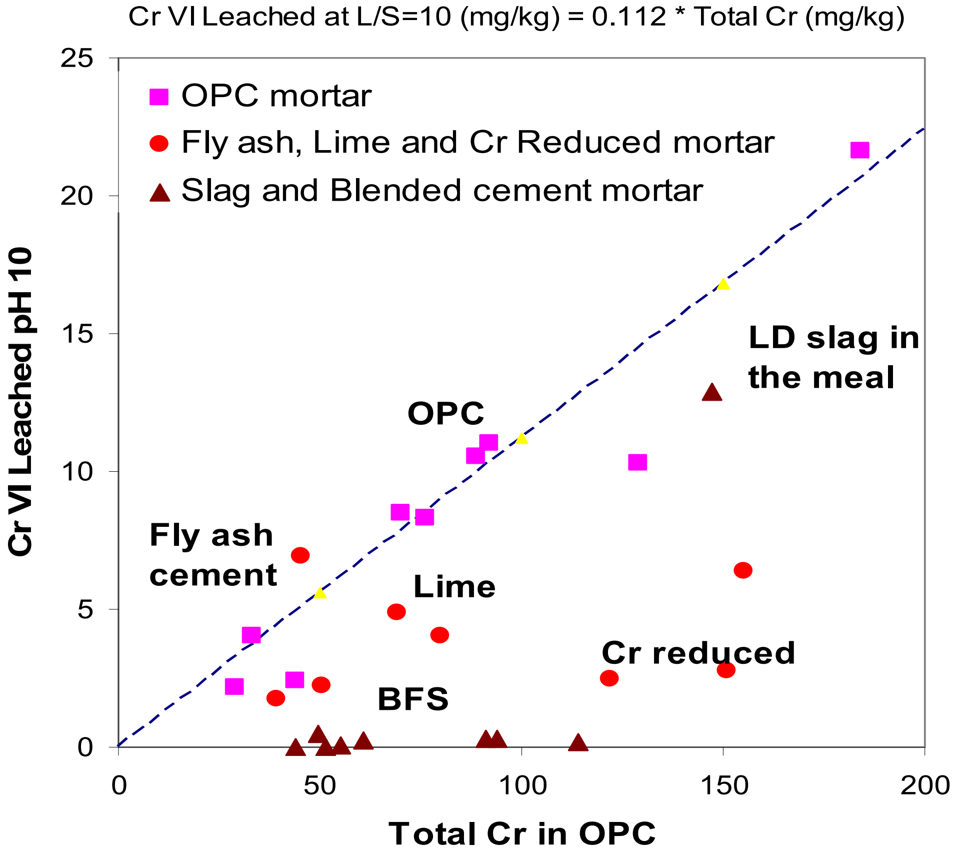


Figure 4.4 *Total Cr content for the investigated commercial cements (ECRICEM Phase I and II) versus the leachable Cr (pH dependence test: pH 10 at L/S = 10) for mortars produced with these cements*

4.6 Investigation of “historical” concretes gains new insight concerning the leaching behaviour and confirm modelling results

Concrete slabs that have been exposed for 50 years to leaching being half-submersed in water have been investigated. For the tests, mortar was isolated from coarse aggregates. The concentration profiles within the slabs as obtained by leaching the mortar (L/S =10 at own pH) from different slab-depths have shown that the general notion that transport of elements is limited to the carbonation depth is a misconception. Mobile species can be depleted from concrete to much greater depth below the carbonation zone, when exposed to continuous leaching (Na, K, and to a lesser extent Li, SO_4 and Cr).

A significant reduction appears to have taken place in the Cr leachability of the 50-years old specimen. Modelling and data interpretation have shown that chemical conversion of Cr VI to Cr III is occurring in the non-carbonated part of the specimen. In the carbonated layer depletion of leachable chromate has obviously taken place. This also provides a means of assessing release of oxyanions, when the progression of the carbonation front is known.

4.7 Different stages of the life cycle of cementitious materials can be tested adequately with available standardised methods

For monolithic cementitious materials the combination of the pH dependence test and the tank leaching test provide basic information that allows a chemical fingerprint for the material to be established. Since the speciation at L/S=10 does not necessarily reflect the speciation in the pores of the product, the first fraction(s) of a column test on size reduced concrete provides very useful information for modelling, as phases that are completely dissolved at L/S=10 may still be present at L/S = 0.2 – 0.3.

For the recycling of aggregates from demolished concrete in bound application (aggregates in new concrete structures) the same approach can be followed as for primary concrete. For recycling of demolished concrete in unbound applications (aggregates in road construction etc.) the combination of the pH dependence test and the percolation test is recommended. The modelling tools for the release prediction and the development of criteria for the recycling of demolished concrete as unbound aggregate are now available (see below).

5. Modelling

For the characterisation of the environmental behaviour of construction products leaching tests alone are not sufficient as the test results need to be linked to an impact assessment typically addressing regulatory criteria. This implies that such results should provide the necessary information to describe a source term for impact modelling, as a coupled chemical reaction and transport modelling is the only option available to provide insight into the long term behaviour of materials under changing exposure conditions in the field.

In this work the modelling framework ORCHESTRA (Objects Representing CHEmical Speciation and TRAnsport models) embedded in LeachXS (LEACHing database/eXpert System) was used to identify solubility controlling phases relevant for cementitious materials.

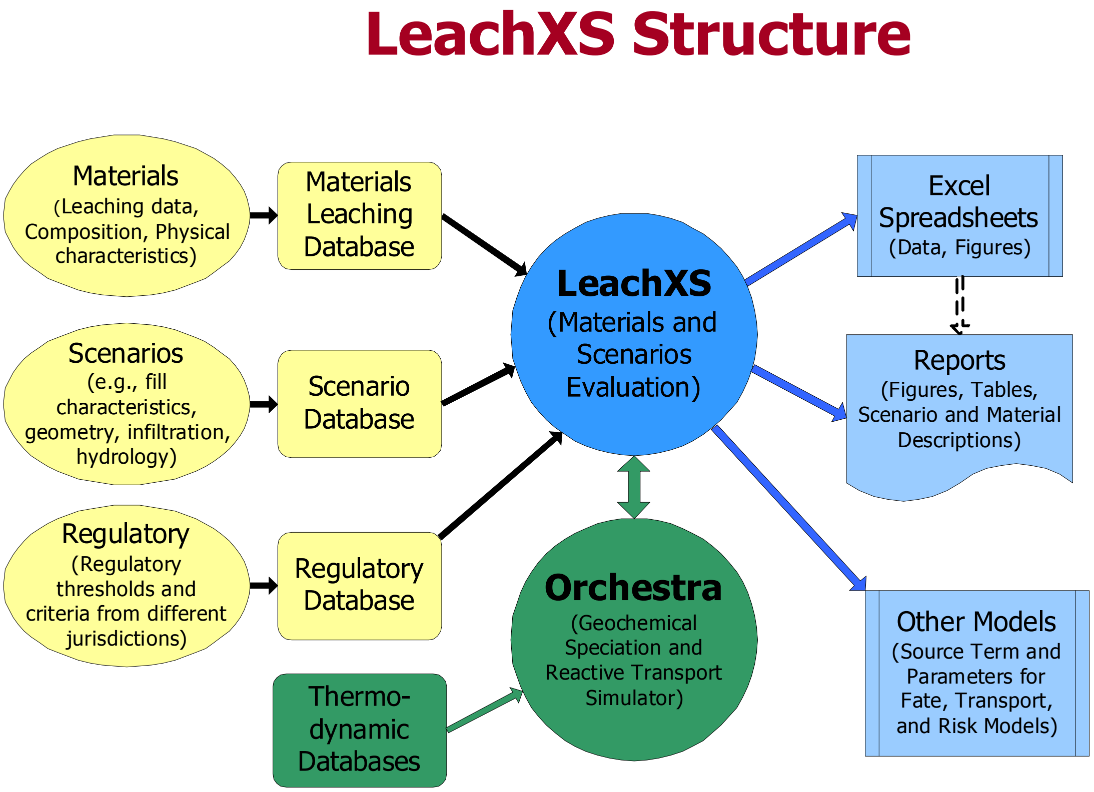


Figure 5.1 *Schematical representation of the database/expert system LeachXS*

LeachXS forms an integrated approach that allows linking various aspects together, like selection and definition of testing protocol, geochemical speciation evaluation, source term models, reference database of leaching characteristics for previously evaluated materials etc. Figure 5.1 gives an overview about the structure of LeachXS.

The present version of ORCHESTRA – embedded in LeachXS – allows partitioning of elements between dissolved and particulate phases both in the pH dependence test as well as in percolation or diffusion scenarios. As output the model provides concentration profiles in the pore water as a function of depth in the product for specific time intervals over the entire duration of the test. This allows visualisation of the concentration development in the pore water as a function of depth and, simultaneously, precipitation reactions at the interface (e. g. pore sealing by carbonation).

5.1 Geochemical modelling provides additional insights and allows to optimize and reduce necessary testing

Geochemical modelling capabilities of the leaching of cementitious materials have greatly expanded. It now allows far more detailed prediction of leaching test data using solubility controlling mineral phases, solid solutions (ettringite) and sorption processes (oxide surfaces and organic matter, when present).

The present model adequately predicts pH dependence results for more than 30 major, minor and trace elements and their partitioning over dissolved and solid phases simultaneously. A basic set of typical cement minerals adequately describes the leaching behaviour of all major and minor elements (figure 5.3).

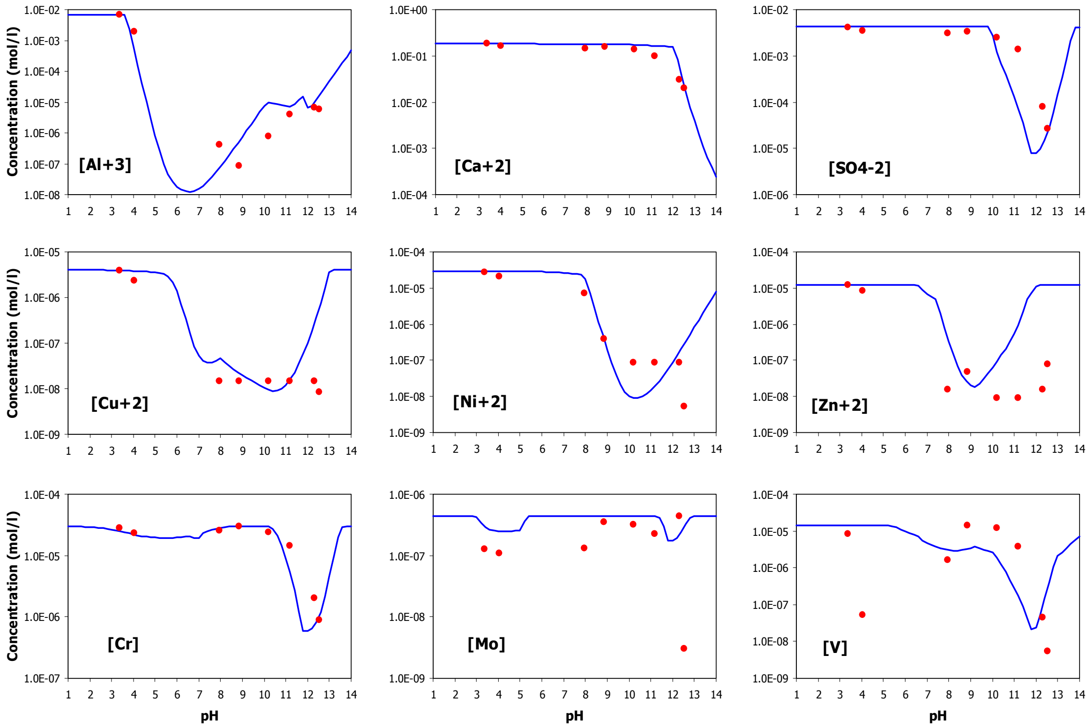


Figure 5.2 *LeachXS-Orchestra prediction (using TS 14429) as basis for transport modelling in intended use scenarios. Test specimen: CEM I cement*

The chemical speciation fingerprint (CSF) obtained this way can be used in subsequent chemical reaction-transport modelling. For some trace constituents additional mineral phases have to be considered. This means that very limited testing can provide a wealth of relevant information through the combination with modelling.

Chromium is one of the important elements in concrete, due to the presence of part of the chromium as Cr VI. The partitioning of Cr in mortars is of importance to find ways to reduce the Cr VI content. Mixing of OPC with blast furnace slag substantially reduces the Cr VI level. Cr substitution in ettringite is an important binding mechanism in mortars, however, as pH drops due to carbonation ettringite is converted to other phases and Cr is released as chromate.

5.2 Prediction of release from tank leaching test as basis for scenario modelling

The prediction of release of substances from monolithic specimen using the before mentioned fingerprint already is a major step, as all complexity of interface reactions needs to be taken along for a proper description. In figure 5.4 the current status of modelling is depicted. The next step to model release under field conditions requires the implementation of wet/dry cycles and carbonation through exposure to CO_2 from the atmosphere. Model descriptions are available. ORCHESTRA allows the modeling of the concentration of the relevant elements in soil or groundwater for any distance from the application (Point of Compliance, POC) for the different exposure scenarios listed in Table 3.2 in a relatively quick and meaningful manner.

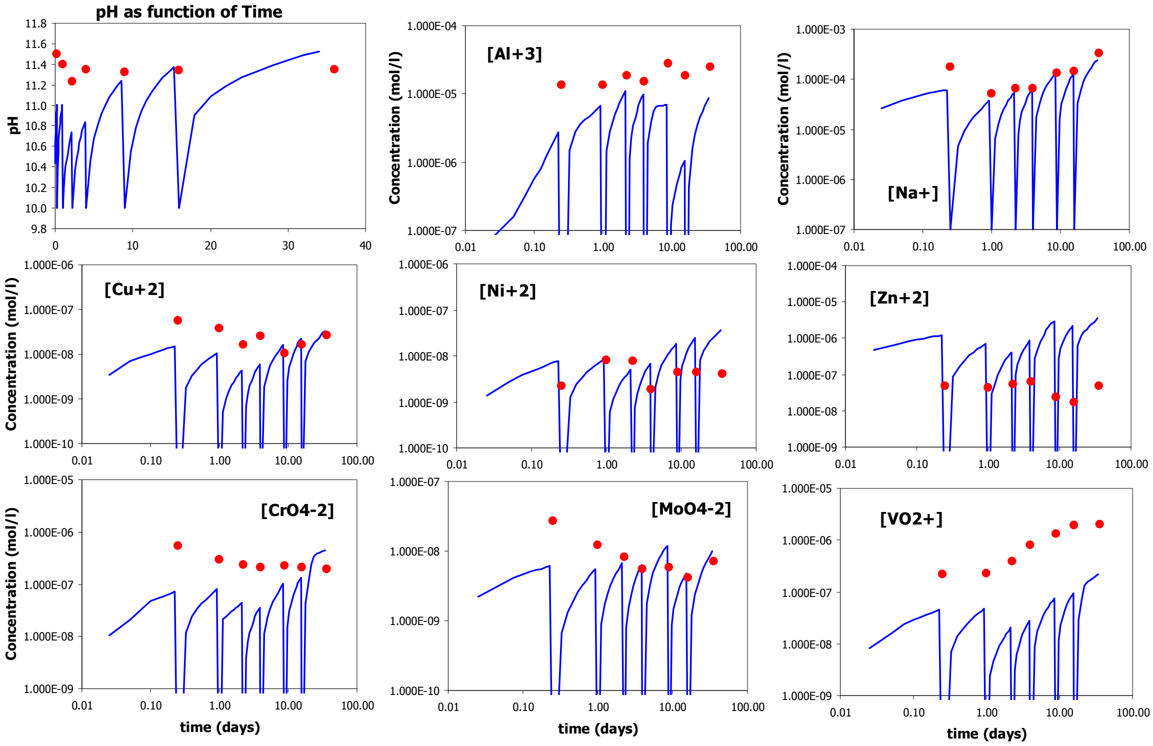


Figure 5.3 *LeachXS-Orchestra prediction of release of substances from cement mortar according to EN 197 in a tank leach test with leachant renewal illustrating the match between measurement (NEN 7345) and model output*

5.3 Investigations of historical concretes verify the modelling results

The concentration profiles as obtained by leaching the mortar parts (L/S = 10 at own pH) from different slab-depths of a 50 year exposed concrete slab half-submersed in water (compare point 4.6) have been modelled quite satisfactorily. This type of modelling in combination with data interpretation of the leaching experiments is also able to explain the chromium profile in the concrete sample. It appears that during service life initially present Cr VI is slowly converted to Cr III. Another observation is that leaching of substances is not limited to the carbonated zone, but for mobile constituents can extend far beyond that layer.

5.4 Leaching tests combined with geochemical modelling support the development of regulatory criteria

The combination of pH dependence test and tank test provides a database for principal characterisation which – in combination with geochemical modelling – is able to deliver a sound basis for understanding the release behaviour of constituents that can be used as a basis to decide about (regulatory) criteria.

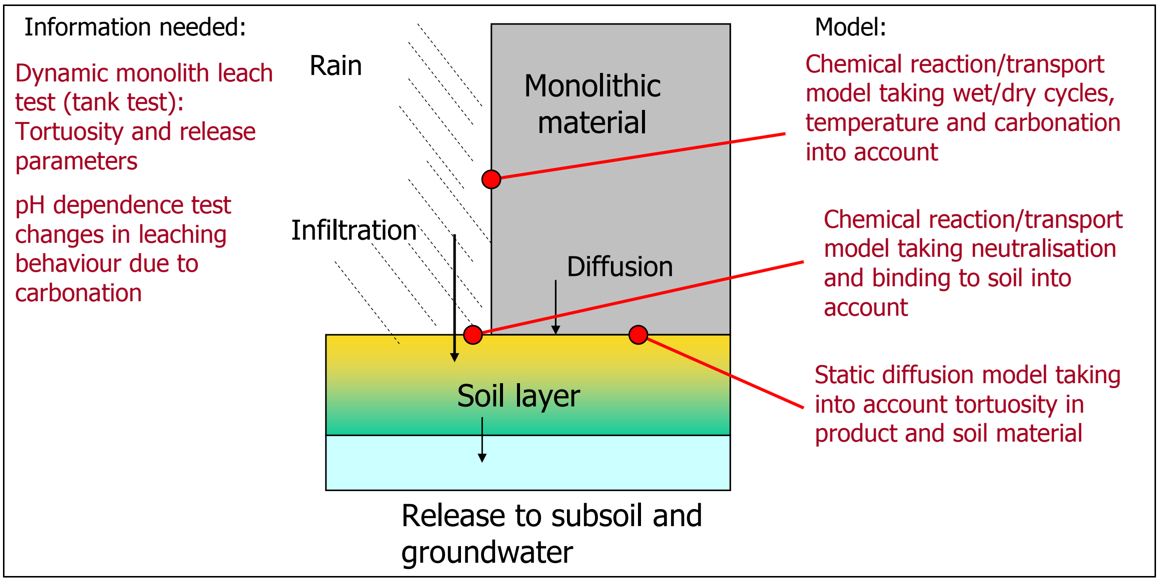


Figure 5.4 *Schematic release scenario with information needs and model description to assess release to soil and groundwater*

With this, geochemical modelling can support the development of a regulatory approach using environmental criteria at a defined target under different scenarios (i.e. soil, soil/groundwater interface, groundwater, surface or drinking water).

Based on the current understanding of the release processes, quality control or compliance/conformity testing can be targeted to relevant parameters thus avoiding unnecessary testing.

6. Conclusions

The release of trace elements from monolithic materials like cementitious materials is very complex as it is very much determined by changes in a very thin surface layer of the product. However, all investigated mortars produced with cements collected from world wide sources (ECRICEM Phase I and Phase II) and with considerably different trace element contents show a very systematic and consistent leaching behaviour. For example, the observed range for the release in the tank leaching test is not more than a factor of 2 to 2.5 above and below the average for several constituents of all mortars tested. For some elements with significant changes in leachability in the pH range 11 to 12.5, substantially wider ranges may be found (e.g. Pb, Mo, Cr, sulphate). Upon carbonation, this range can become larger due to further changes in leachability as a function of pH.

In comparison with regulatory limits (e. g., the Dutch Decree on Building Materials), the 'service life' of concrete generally does not pose a problem as observed in the standard tank leaching tests carried out at the inherent high pH values typical for cement based systems. If the same tank leach test is carried out at (imposed) neutral conditions, trace elements such as Mo, Se or Sb may occasionally exceed the Dutch limits, when present at elevated concentrations (as in the special cements). This observation is important for the evaluation of cement based materials in exposure scenarios where neutral or slightly alkaline environmental conditions prevail. These conditions are more frequent in practical applications than highly alkaline conditions.

For the characterisation of the environmental behaviour of construction products leaching tests alone are not sufficient as the results need to be linked to an impact assessment. However, for monolithic cementitious materials the combination of the pH dependence test and the tank leaching test provide basic information that allows a chemical fingerprint for the material to be established. Together with additional information such as tortuosity, dimensions, exposure scenario etc. the chemical fingerprint can be used to describe a source term for a detailed impact modelling (including coupled chemical reaction and transport modelling). Simulation of field behaviour under laboratory conditions is not feasible. Therefore testing provides the basis for modelling of impact under conditions relevant to the various field exposure conditions of concrete and mortar.

Using the Orchestra software for chemical reaction and transport modelling embedded in the leaching expert system LeachXS, it is possible to predict the release of constituents from cementitious materials to the water phase under a wide range of exposure conditions (continuous wet or intermittent wetting, flowing or stagnant water, atmospheric exposure, seawater exposure etc.). Moreover, the concentration of environmental relevant elements at a defined target (underlying soil, soil/groundwater interface, groundwater adjacent to the application, surface water or drinking water) can be modelled in a relatively quick and meaningful manner. Spin off from this modelling work will be a more detailed chemical evaluation of processes like carbonation (pore sealing) and processes causing concrete deterioration resulting from salt intrusion (Cl^- and SO_4^{2-}).

According to the Mandate M/366 "Development of horizontal standardized assessment methods for harmonised approaches relating to dangerous substances under the Construction Products Directive (CPD)" the future CEN product standards will have to provide information on the release/emission of regulated dangerous substances related to various release scenarios. The experimental and modelling results obtained in ECRICEM Phase I and Phase II will for cementitious materials contribute significantly to the work of CEN/TC 351 'Construction products: Assessment of release of dangerous substances' in the development of criteria for soil and groundwater impact as part of the Essential Requirement No. 3 (ER 3) of the CPD.