Environmental Criteria for Cement Based Products

ECRICEM
Phase I: Ordinary Portland Cement
Phase II: Blended Cements and methodology for impact assessment

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Abstract

Regulations such as the European Construction Products Directive (CPD) or Drinking Water Directive (DWD) contain provisions to exclude or minimise adverse effects on environment or public hygiene through the use of construction materials.

The assessment of the "environmental quality" of construction products such as cement and cementitious products is usually based on the determination of their leaching characteristics, e.g. the potential release of constituents such as trace elements (heavy metals) or organic compounds to the environment when the products get in direct contact with water or soil.

The report on hand presents the results of a comprehensive study with the following main objectives:

- 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, e.g. as aggregates in new concrete, as fill materials in road construction, or others.
- To develop and propose an approach for establishing environmental quality criteria and control procedures for cements and cementitious products.

The study was carried out in two phases. Phase I of the project (van der Sloot et al, 2001) focused on the leaching behaviour of Ordinary Portland cements (OPC). For this seventeen commercial cements were collected from various worldwide sources, covering a wide range of trace element compositions. In addition, two special cements were produced in a special test facility using an industrial raw meal spiked with trace elements. Phase II of the project focused on the leaching behaviour of blended cements. In this case twenty-five commercial cements were collected worldwide.

After detailed chemical and physical characterisation of the test cements, nine Portland cements and one blended cement with limestone filler were selected for further testing (Phase I). In phase II six composite cements with slag only, six composite with fly ash, puzzolan and limestone as well as five composite cements with more than one component and three Portland cements were selected for further testing. A series of different leaching tests was applied on standard mortar samples made with the selected cements and the two special cement, in order to systematically characterise their leaching behaviour. Geochemical modeling supported the development of model predictions of the long term release of trace elements under various exposure scenarios. The main observations are summarized below:

- The pH dependence test is the test procedure best suited to characterize the generic leaching behaviour of trace elements in cementitious products.
- There are significant differences in the generic leaching characteristics of different trace elements.
- Elevated trace element contents in cements may lead to increased leaching for some elements (in particular oxyanions) in the characterisation tests.
- Elevated Zn contents in cements have no significant effect on the leaching in the characterization test.
- 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.
- Under certain environmental exposure scenarios, the leachability of trace elements from cementitious materials may be governed by solubility rather than by diffusion.
- In certain life cycle stages of concrete, carbonation may play an important role in the release of trace elements to the environment.

- Chromium and aluminium are critical elements with regard to their specific leaching characteristics and require more systematic investigations. Aluminium leachability can be important for concrete or mortar in drinking water systems.
- Rapid compliance tests have to be modified to allow predictions of the long-term leaching behaviour under different exposure scenarios.
- Compared to the Portland cements investigated in ECRICEM Phase I, the concentration ranges of metals are slightly extended for the blended cements
- Cementitious materials made of Portland cements and blended cements show a very systematic leaching behaviour
- Comparison of release in service life with regulatory criteria indicates compliance.
- Mortars produced with blast furnace slag containing cements or with chromate reduced cements show a significantly reduced Cr leachability
- Investigation of "historical" concretes gains new insight concerning the leaching behaviour and confirm modelling results
- Different stages of the life cycle of cementitious materials can be tested adequately with available standardised methods.
- Geochemical modelling can provide insight in factors controlling element behaviour
- Prediction of release from tank leaching test as basis for scenario modelling
- Leaching tests combined with geochemical modelling support the development of regulatory criteria

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 standard 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 test methods for soil and groundwater impact as part of the Essential Requirement No. 3 (ER 3) of the CPD.

Key words

Leaching, long term behaviour, concrete, mortar, Portland cement, blended cement, environmental impact, geochemical modelling, trace elements, life cycle.

Contents

List of tables

List of figures

1. Introduction

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, 1988). 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 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).**

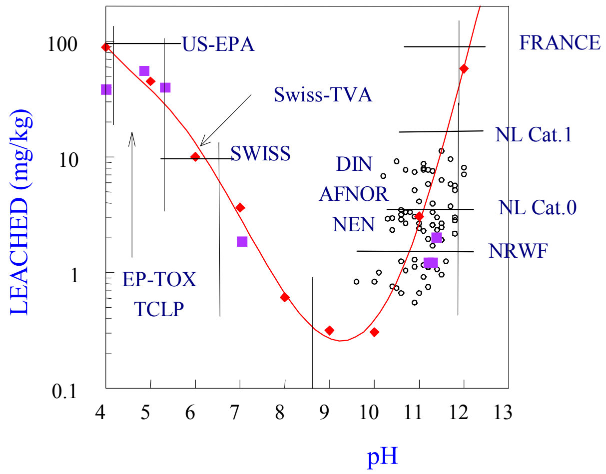
The trace element contents of commercial cements may vary broadly as a consequence of the use of various natural fuels and raw materials. Increasing concern has been raised with the use of ‘alternative’ (= waste derived) fuels and raw materials which may both increase or decrease the trace element content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

These studies have also shown that the release of constituents (trace elements) from cementitious 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 hold the key in defining environmentally sound trace element levels in clinker and cement.

A variety of laboratory leaching tests has been developed worldwide, 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.

1.1 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 cementitious 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 cementitious products.
- Development of a model scheme for the prediction of the potential short and long term release of trace elements from concrete under various exposure scenarios, based on laboratory tests and geochemical modelling.
- Verification of these (theoretical) predictions in selected field applications and studies.
- Development of a methodology for development of criteria for the acceptance of alternative fuels and raw materials in cement manufacturing, and for the assessment of the environmental impact of cementitious products during their complete life cycle.
- Development of a practical environmental quality control scheme (test procedures) in the manufacture and application of cements made with or without alternative fuels and raw materials.
- A more active role of the project team in the developments around the Construction Products Directive (CPD) should be taken in coordination with CEN TC's 51, 104, 164 and 351.

2. Experimental

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

- Collection of commercial OPC and blended cements worldwide
- Preparation of special clinkers with increased levels of heavy metals
- Determination of the chemical composition of the selected test cements
- Determination of the physical properties of the selected test cements
- Preparation of mortar samples for further testing
- Physical characterisation of the mortar samples
- Environmental characterisation (leaching tests)
- Interlaboratory comparison
- Geochemical reaction transport modelling
- Ecotoxicological characterisation (separately reported)
- Evaluation of criteria for environmental impact under different exposure scenarios
- Verification of against field data
- Evaluation of recycling and end of life aspects of concrete construction debris
- Recommendations for CEN, regulators and end-users

2.1 Cement Samples

In Phase I seventeen commercial cements in total were collected from various sources worldwide. Out of these seventeen commercial cements, ten samples were selected for further testing based on their detailed chemical composition, i.e. trace element contents. In addition, two cements (W1 and W2) were produced in a special test facility using an industrial raw meal spiked with trace elements (see Chapter 2.1.2). Test cement designation is given in Table 2.1.

Table 2.1 *Designation of test cements*

Sample Designation	**Cement Type**	**Cement Constituents**	**Clinker produced with Alternative Fuels**
Commercial Cements			
H1	CEM I	Clinker, gypsum, filler	Yes
N1	CEM I	Clinker, gypsum	Yes
H3	CEM I	Clinker, gypsum, filler	No
H5	CEM II/A-L	Clinker, gypsum, lime-stone (14 %)	No
H6	CEM I	Clinker, gypsum	Yes
D1	CEM I	Clinker, gypsum, filler	Yes
H7	CEM I	Clinker, gypsum, filler	No
N2	CEM I	Clinker, gypsum, filler	No
D2	CEM I	Clinker, gypsum, filler	Yes
H9	CEM I-HS	Clinker, gypsum	Yes
Special Cements			
W1	CEM I	Clinker, gypsum	No
W2	CEM I	Clinker, gypsum	No

2.1.1 Commercial Cements

Nine commercial Portland cements (type CEM I, according to the European cement standard EN 197, 2000)) and one blended cement with a limestone filler (type CEM II-L) were selected for further testing (see Table 2.1). One of the selected Portland cements was a sulphate resistant cement type CEM I-HS, i.e. with low aluminium (C_3A) content.

Out of the ten commercial cements, six were manufactured using alternative (waste) fuels such as tires, waste oil, impregnated saw dust, paper sludge, or solvents – up to a thermal substitution rate of 42 % at maximum. Four commercial cements were manufactured by using conventional fuels only (i.e. coal, oil).

2.1.2 Special Cements

In order to evaluate the leaching characteristics of cements with trace element contents higher than the common range of commercial cements, two 'artificial' clinkers were produced in a small gas-fired rotary kiln at a specific test facility. A short description of the test facility (with a maximum capacity of 150 kg clinker per hour) is given elsewhere (van der Sloot et al, 2001).

The spiked clinkers were produced by artificially introducing elevated contents of trace elements ('spikes') to an industrial cement raw meal. The clinkers were prepared such as to arrive at approximately 2 times and 10 times the levels in clinker as specified in the Swiss Guidelines on the Use of Waste Materials in the Cement Industry (BUWAL Values, 1998, see Table 2.2).

Table 2.2 *BUWAL Values of trace elements in clinker (according to the Swiss guidelines on the use of waste in the cement industry, 1998), and target values of spiked clinkers(in mg/kg)*

	BUWAL Values		**Target Values**	
Trace Element	**Clinker**	**Portland Cement**	**Clinker for Cement W1**	**Clinker for Cement W2**
As	40	--	80	400
Sb	5	--	10	50
Be	5	--		
Pb	100	--	200	1000
Cd	1.5	1.5	3	15
Cr	150	--	300	1500
Co	50	--		
Cu	100	--		
Mo	--	--	80	400
Ni	100	--		
Hg	--	0.5		
Se	5	--		
Tl	2	2		
Zn	500	--	700	3500
Sn	25	--		

Two raw meal batches of 560 kg each were mixed with the metal 'spikes' at calculated proportions, and granulated to form pellets of 3 – 8 mm size. The pellets were fed to the test kiln at a rate of 30 – 35 kg per hour with a maximum burning temperature of 1450°C on average.

The two clinkers produced were ground in a laboratory mill and mixed with gypsum ('hemihydrate', $CaSO_4 \times 0.5\ H_2O$) to produce an ordinary Portland cement type CEM I at an SO_3 level of approximately 3 %. For comparative testing, a laboratory cement (designation 'D2', see Table 2.1) was prepared with industrial clinker produced from the same (non-spiked) raw meal in a full-scale commercial cement plant.

2.1.3 Blended Cements

In Phase II twenty five commercial cements in total were collected from various sources world-wide. Out of these twenty-five commercial cements, 20 samples were selected for further testing based on their detailed chemical composition, i.e. trace element contents. Test cement designation is given in Table 2.3.

Table 2.3 *Designation of blended cements tested.*

Sample Designation	**Cement Type**	**Cement Constituents**
Slag Cements		
HOL-1	CEM III/B	80% GBFS
HOL-2	CEM III/B	66% GBFS
HOL-3	CEM II/B-S	29% GBFS
HOL-4	CEM II/B-S	29% GBFS
HOL-5	CEM II/A-S	20% GBFS
HOL-6	CEM III/A	69% GBFS + 5% LS
VDZ-4	CEM II/A-S	
VDZ-5	CEM II/B-S	
Composite Cements (with one component)		
HOL-7	CEM II/B-V	33% FA
HOL-8	CEM II/A-V	10% FA
NOR-4	CEM II/A-V	with chromate reduction and 17 % FA
HOL-9	CEM II/B-Q	32% P
VDZ-1	CEM II/B-P	26 % Trass (P)
HOL-10	CEM II/B-L	28% LS
HOL-11	CEM II/A-L	13% LS
VDZ-3	CEM II/A-LL	13 % LS
Composite Cements (with more than one component)		
HOL-12	CEM V/A	32% GBFS+20% FA
HOL-13	CEM V/A	23% GBFS+22% FA
HOL-14	CEM II/B-M	33% GBFS+9% LS
HOL-15	CEM IV/A	15% FA+17% P
HOL-16	CEM II/B-M	14% GBFS+12% LS+5% FA
VDZ-2	CEM II/B-T	Burnt Oil Shale
Portland Cements		
NOR-1	CEM I	without LD slag in raw mix
NOR-2	CEM I	with LD slag in raw mix
NOR-3	CEM I	with chromate reduction

Six commercial composite cements with slag only (type CEM II and III according to the European cement standard EN 197, 2000)), six composite cements with one component other than slag (fly ash, puzzolan, limestone) (type CEM II), five composite cements with more than one component and three Portland cements were selected for further testing (light brown). Others were subjected to more limited testing (light purple).

2.2 Chemical Composition

Major Oxides

In the test cements, major oxides were determined by means of X-ray fluorescence spectrometry (XRF) applying fused bead preparation technique. Alkalis were measured by means of atomic absorption spectrometry (AAS). Total sulfur – expressed as SO_3 – was determined using a sulfur analyzer with selective infrared detection.

Chlorides were analyzed by means of potentiometric titration after sample pre-treatment with nitric acid. Free lime was determined complexometrically using an ethylene glycol extraction procedure.

Trace Elements
Determination of trace elements was carried out in duplicate by means of ICP-MS (inductively coupled plasma mass spectrometry), after microwave digestion using a mix of nitric and fluoric acid. In some cases, the results obtained were cross-checked by means of AAS techniques.
Hexavalent (water - soluble) chromium was determined by means of ICP-AES (inductively coupled plasma atomic emission spectrometry) after extraction with demineralised water at a water-cement ratio of 5 to 1 for about 30 minutes.

2.3 Particle Size Distribution

The particle size distribution of the test cements was determined with a laser granulometer type CILAS 715.

2.4 Mortar Samples

2.4.1 Preparation and Physical Tests

Mortar samples were prepared from the test cements in accordance with the European standard EN 196-1 (‘Methods of testing cement – Determination of strength’, 2005). After demoulding at the age of 24 hours, the mortar samples for the leaching tests were cured at 20 ºC and 95 % relative humidity for another 27 days in plastic bags to prevent pre-leaching. Test samples were dispatched to the partners after 10 days of curing at minimum.

Characteristic physical properties of the standard cement and mortar samples – i.e. setting time, water demand, soundness, and compressive strength at 1, 2, 7 and 28 days – were determined according to the European cement standard EN 196-1 and 196-3, respectively (see Table 2.4). In addition, microscopic investigations (porosity, microstructure) were carried out.

Table 2.4 *Physical and structural tests*

Test	**Method**
Compressive strength (1,2,7,28 d)	EN 196-1
Setting time	EN 196-3
Soundness	EN 196-3
Structure and porosity	Optical microscopy (thin sections)
Structure/morphology	Scanning electron microscopy

2.4.2 Structural Investigations

Structural investigations were carried out on standard mortar samples made of the test cement by means of optical microscopy. Structural properties such as air void content and capillary porosity may have an influence on physical properties (compressive strength etc.) and on leaching characteristics.

Scanning Electron Microscopy(SEM)
Microstructural investigations were carried out by means of SEM equipped with a backscatter detector on polished mortar samples coated with a thin layer of gold. Only two samples (H1 and N1) were investigated, because little additional information was obtained to that of optical microscopy.

Scanning electron microscopy investigation was not performed on the samples from ECRICEM phase II. Such investigation on the mortar samples of ECRICEM phaset I (van der Sloot et al, 2001) showed that little additional information was obtained to that of optical microscopy.

In general the structural investigations were performed to control the quality of the casting and to support the evaluation of the leaching test data.

Optical Microscopy
Microscopical investigations were carried out on thin sections in transmitted light. Capillary porosity is measured with a spotlight meter on samples impregnated with a fluorescent resin. The intensity of the fluorescence light is proportional to the water/ cement ratio. A standard concrete serves as reference sample for the assessment.

The contents of cement paste, aggregates and air voids were determined by means of point counting (2000 points in total).

The results of the optical microscopy demonstrate the homogeneity and porosity of the hardened mortar/cement paste, the air void content and size of pores, and eventual development of micro-cracks.

2.5 Leaching Tests

2.5.1 Test Procedures

A series of leaching tests (NEN 7341, 1994; NEN 7345, 1994; van der Sloot et al, 1994; CEN/TS14429, 2005) was carried out on the standard mortar samples addressing various aspects of leaching. The test conditions are described in Table 2.5. In addition pore water was obtained by pressing water out of hardened mortar bars with special equipment and a powerful press (van der Sloot et al, 2001).

Except for the leaching tests on monolithic samples, the mortars were crushed to different particles sizes according to the standards specified in table 2.5 respectively of 95 % < 4 mm (pH dependence leaching test, 2005, EN 12457-3, 2001 and concise test, 1994). For the availability tests (NEN 7341, 1994), the material was further ground to a particle size of 95 % < 125 µm.

Currently, the test methods applied here are being standardised at European level for construction products in CEN/TC351 (Construction Products - Assessment of release of dangerous substances) (TS-2, 2010; TS-3, 2010). In the mean time the same methods (Draft EPA methods 1313, 1414 and 1315, 2009 have been adopted by US EPA for inclusion in SW 846 (EPA handbook of standards).

All leaching tests are conventions, by which leaching is examined under the specific conditions of the individual test. For example compliance tests provide short-term testing of monolithic or granular samples. Full characterisation tests provide longer-term information on granular materials under various pH conditions or release as a function of L/S or time. The different tests can individually and complementarily contribute to the overall understanding of the leaching behaviour. At the end only through modelling it will be possible to describe this leaching behaviour under certain environmental exposure conditions. A single test, however, can give useful information, if the general leaching behaviour of a trace element is known. Therefore, it is important to know, how the different test results are related to each other. A summary of standardised test methods is given in table 2.5.

Table 2.5 *Leaching test conditions*

Test name:	**NEN 7341** Availability test	**TS 14429** pH dependence test	**TS14405** Percolation test	**NEN 7345** Diffusion Test	**NEN 7345** Diffusion Test	**WI 292010** Compliance test for monolithic material	**EN 12457-3** Compliance test for granular materials	**Concise test** (van der Sloot et al, 1994)	**EN 12457-4** Compliance test for granular materials
Type of test:	Batch extraction	Batch tests at specified conditions	Column leaching test	Tank leaching test	Tank leaching test modified pH	Tank leaching test	Batch test	Batch test with two L/S values and two controlled pH conditions	
Country:	Netherlands	CEN TC 292 WG6	CEN TC 292 WG6	Netherlands	Netherlands	EU CEN TC292	EU CEN TC292	WASCON 1997	EU CEN TC292
Particle size:	95%< 125 µm	< 2 mm	<4 mm	> 40 mm	> 40 mm	> 40 mm	< 4 mm (95%)	< 2 mm	< 10 mm (95%)
Leachant:	DMW at fixed pH=7 and pH=4, using HNO_3	DMW with pH control using HNO_3 or NaOH (pH 3-12)	DMW	DMW initially acidified to pH=4 with HNO_3	DMW flushed with air or air with increased CO_2 to maintain pH = 7.5 – 8 in eluate	DMW	DMW	DMW without and with pH control using HNO_3 or NaOH (pH 4 –7)	DMW
Amount of solid:	16 g	100 g	0.5-0.7 liter	> 100 g	> 100 g	> 100 g	100 ± 5 g	100 g	100 ± 5 g
L/S (l/kg) per step:	50	10	cum.L/S: 0.1, 0.2, 0.5,1,2,5,10	L/V = 5 l/l	L/V = 5 l/l	L/V = 1.5 l/l	2 in 1st step 8 in 2nd step	2 and 10	10
Maximum accumulated:	100	10	10	Not applicable	Not applicable	Not applicable	10	10	10
Number of steps:	2	8	7	8	8	3	2	4	1
Contact time per step:	3 hours	48 hours	total: max 3 weeks	Varies (64 days for all 8 steps)	Varies (64 days for all 8 steps)	Varies (2 h up to 48 h)	6 h for 1st step and 18 h for 2nd step	48 hours	24 hours
Renewal of leachant or solid:	New leachant	not applicable	Not applicable	New leachant	New leachant	New leachant	New leachant	not applicable	
Method of agitation:	magnetic stirrer	ANC mode: End over end rotation, 5 - 10 rpm. pH stat mode: magnetic stirrer	Not applicable	No agitation	No agitation	Mild stirring	End over end or roller-table rotation (10 rpm)	ANC mode: End over end rotation, 5 - 10 rpm pH stat mode: magnetic stirrer	End over end or roller-table rotation (10 rpm)
Filtration/filter size:	0.45 µm	0.45 µm	0.45 µm	0.45 µm	0.45 µm	0.45 µm	0.45 µm	0.45 µm	0.45 µm
Comments:						Some details not yet fixed		[19]; Own pH same as EN 12457-3	Same as DEV-S4

2.5.2 Test Use

Confusion results when objectives for tests are mixed and that has happened a number of times in recent years. For an understanding of material leaching behaviour more elaborate tests are needed that can take into account aspects that relate to practice. As the best test is a test, that allows to explain the situation in the field application as close as possible. Both for a regulator, who has to set criteria for a material as well as a producer of such a (new) material need to know what the environmental consequences in the application can be. A characterisation leaching test is suited for that purpose. When this question is answered satisfactorily, then verification of compliance comes in and on a regular basis (if needed) a test must be carried out to check compliance. For quality improvement of materials (for instance when they do not comply with criteria) the more elaborate tests are most suitable to verify improvement of modifications. In many cases it has been shown that making improvements based on too simple compliance type tests leads to high expenses and limited guarantees that the modification holds in practice. In figure 2.1 the relationship between characterisation and compliance and their uses is illustrated.

A combination of characterisation of material behaviour, with more simplified testing (compliance testing) for verification and quality control purposes, can provide the necessary understanding and at the same time, limits the need for testing when the level of knowledge is sufficient and/or the variability in quality needs to be assessed (Kosson et al., 2002).

The tiered framework of testing methods (EN12920, 1996), developed in CEN TC 292, has proven its applicability for a wide variety of alternative and waste materials to provide the necessary insight.

Characterization tests are tests primarily used for basic characterization of the release behaviour of the material. This data allows for the assessment of materials by categories based on common controlling characteristics and therefore reduces the number of materials within a category that require characterization. The data can be used for:

- Judgement if a material in a certain application scenario fulfils criteria.
- Insight in the release *mechanisms* under a variety of environmental conditions and application scenarios.
- Characterisation of potential *variability* in measured values, by repeating tests on a certain (type of) material. Knowledge of the chemical and physical factors (chapter 2) may provide insight in the cause of spreading in measurements (relevant for producers).
- Characterisation of the *expected range* (maximum and minimum) release under "field" conditions (in a certain application scenario).
- Characterisation with the purpose of *quality improvement* of the product. Characterisation tests, in combination with insight in release mechanisms, provide knowledge with which specific properties of the material can be altered/improved.
- Characterisation of the relation between characterisation tests and compliance tests (see below).

Compliance tests have the purpose to "check" whether a material (still) complies with the behaviour of a reference material (tested with a characterization test) and/or comply with regulations. Because of its simplicity, compliance testing has practical and financial advantages. Once the leaching behaviour has been investigated by a characterization test, a single measurement is often sufficient to check whether the material still complies with this behaviour or that the behaviour has undergone significant changes.

On-site verification/Quality control tests have the purpose to determine quickly (within a short time) if a material (or conditions) complies with earlier determined or expected behaviour in its practical application. In general, only administrative checks will be done and visual control. Quick test methods for on-site verification can only give an impression on some specific points. For a real confident chemical check for on-site verification, in general at least a full compliance test should be done.

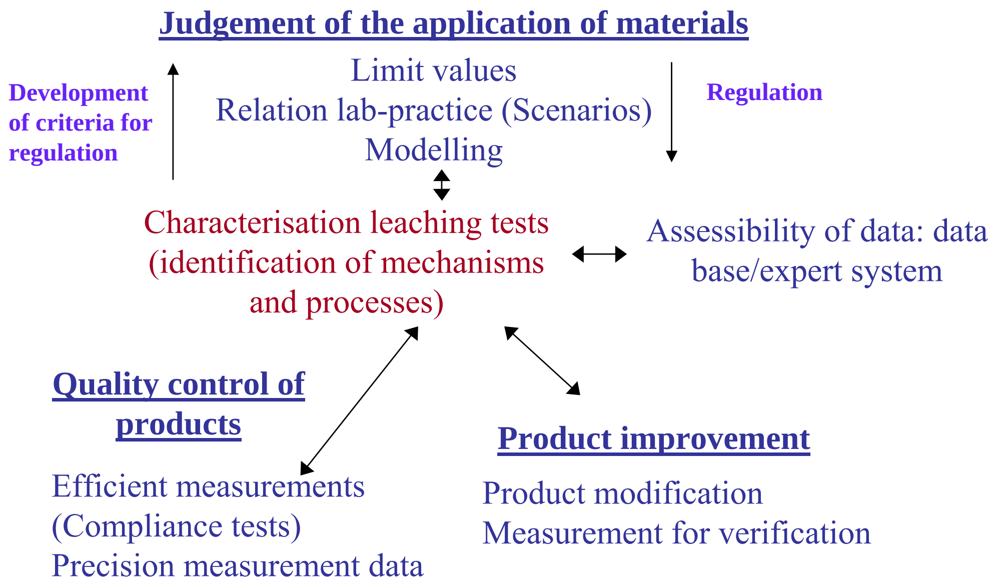


Figure 2.1 *Characterisation leaching tests as basis for criteria development, as reference for compliance testing, quality control and product improvement*

2.5.3 Compliance Test (Monolith)

Example of the use of simplified monolith leach test to illustrate the tiered approach indicated before. In Figure 2.2 tank leaching test measurements on monolithic samples at own pH are given. The figures show 64 day release for barium (left) and chromium (right). In the figures the measured results of the long term (64 days) tank leaching test are compared with calculated 64 day values, the latter values were extrapolated from the short term monolith compliance (2 days) tank leaching test by assuming diffusion controlled (√t) behaviour. As can be seen, these extrapolated data give a quite good indication of the actual release after 64 days. However, an accurate long-term release can only be derived from the full 64 day test. Thus, when reducing the test time significantly educated guess of the long-term behaviour can only be made once the general leaching behaviour of the specific elements are known.

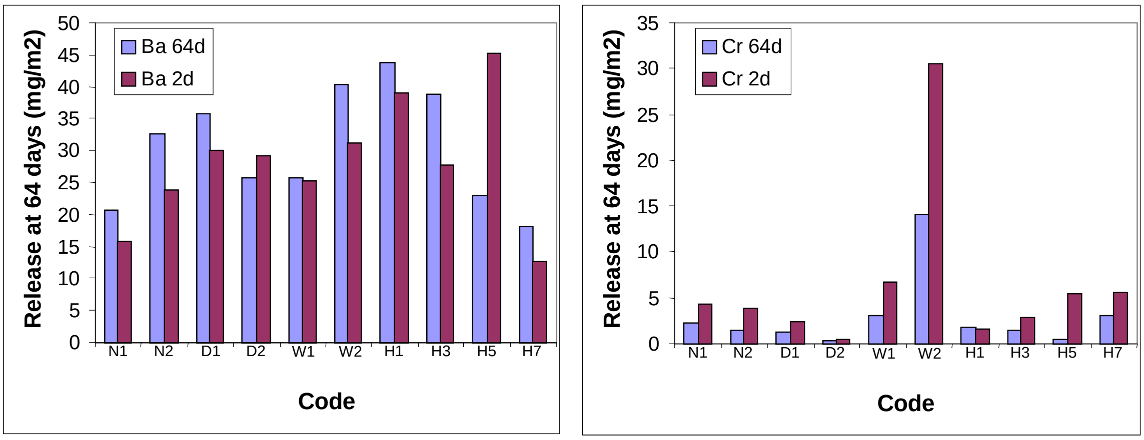


Figure 2.2 *Long term release (64 days, own pH) for barium (left) and chromium (right). The calculated data are extrapolated from a short compliance (2 days) leaching test assuming diffusion controlled behaviour*

2.5.4 Analytical Methods

The following methods were applied in the analysis of the leachates:

Table 2.6 *Analytical methods.*

Component	**Analytical Method**
Metals/ Non-metals	ICP-AES, ICP-MS, AAS
Anions (halogens, sulfate)	Ion chromatography

2.5.5 Data Presentation and Interpretation

Leaching test results may be expressed either as:

- Leachate concentration in [mg/l].
- Constituent release in [mg/kg of material] for granular materials.
- Constituent release in mg/m^2 for monolithic materials.

Leach test results are frequently expressed as eluate concentration, as this is the form in which results become available after eluate analysis. Subsequent data conversion may be necessary for different purposes. The eluate concentration as measured is used for geochemical modelling. Some regulations use concentrations expressed in mg/l. Others use leached quantities (mg/kg dry matter) or other derived units, such as mg/m^2.

Conversion of measured leachate concentrations into constituent release is necessary for the comparison of data obtained in different leaching tests at different liquid to solid (L/S) ratios.

Conversion formula:
Constituent release [mg/kg] = leachate concentration [mg/l] x L/S ratio [l/kg]

However, in comparing results from different leaching tests it is important to take other aspects that control release of constituents into account (e. g. pH value, L/S ratio)

Presentation of data as measured eluate concentrations or as constituent release also can be necessary for the determination of the general leaching mechanism (see Figure 2.3). Examples:

- Chlorine (Cl) represents an availability controlled element. Data from tests at different L/S ratios expressed in [mg/l] lead to apparent differences, while data presented in [mg/kg] show that in all cases the whole fraction available for leaching is released.
- Silicon (Si) represents a solubility controlled element. Here, presentation of leaching data in [mg/kg] leads to differences, whereas data presented in [mg/l] show the solubility control in the pH region of 3 to 8 (constant concentration irrespective of L/S).

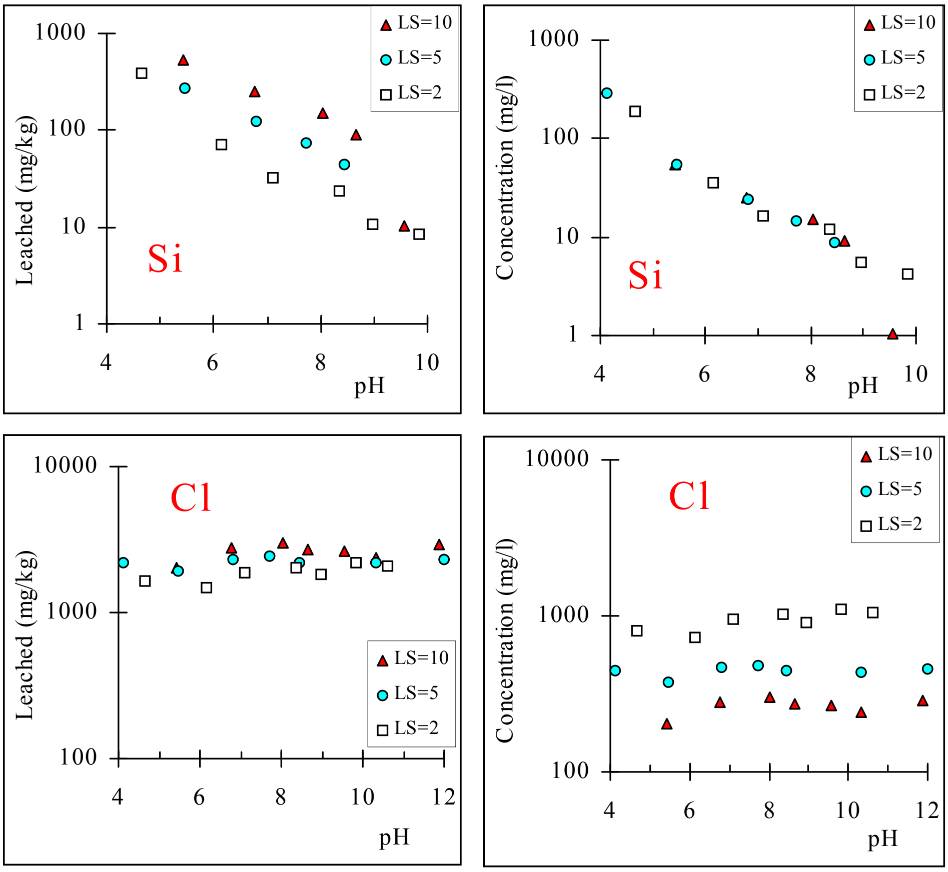


Figure 2.3 *Distinction between solubility control (Si) and availability control (Cl) in the presentation of leaching test results*

For monolithic materials data presentation of results in terms of mg/m^2 allows direct comparison of release from products with different dimensions provided depletion of relatively mobile species has not occurred.

Explanation of release

The characterisation of the leaching behaviour of monolithic materials like cement mortars, concrete and cement stabilised waste is best carried out by a combination of the pH dependence leaching test (TS14429, 2005), a monolith leach test (CEN TS 15863 - DMLT-PLR dynamic monolith leach test with periodic leachant renewal, 2008) and a percolation test (TS14405, 2005), as this combination allows many conclusions on release behaviour to be drawn (including the long term behaviour and after full disintegration). It also provides a reference base for comparison with any type of other leaching test. Present status of standardisation development, short descriptions and advantages of the main characterization leaching tests are provided in Annex VII.

In figure 2.4 the leaching data for Pb from a monolithic product are given with 4 graphs – Pb concentration as a function of pH at L/S=10 (size reduced material); concentration of Pb as a function of time (mg/l); Pb release as a function of time (mg/m^2); and pH as a function of time - that provide crucial leaching information from both characterization tests for monolithic materials. The first two graphs show the relationship between pH dependence and concentration from tank tests. The concentrations in the tank test correspond generally well with the appropriate pH conditions in the pH dependence test. This implies that solubility controls the release from monolithic waste. This also allows conclusions on other exposure conditions in long term exposure. The box in the pH dependence graph is the same as that discussed for granular material.

From the cumulative release curve no direct conclusion can be drawn based on criteria derived for release by diffusion, as the release is solubility controlled. In that case the pH change with time is more important than transport by diffusion. If it is clear that with ageing the pH will decrease further and the pH dependence test shows a decrease in release with decrease in pH, then the conclusion can be taken that release will in the long term not exceed a limit, if it is not exceeded in the short term.

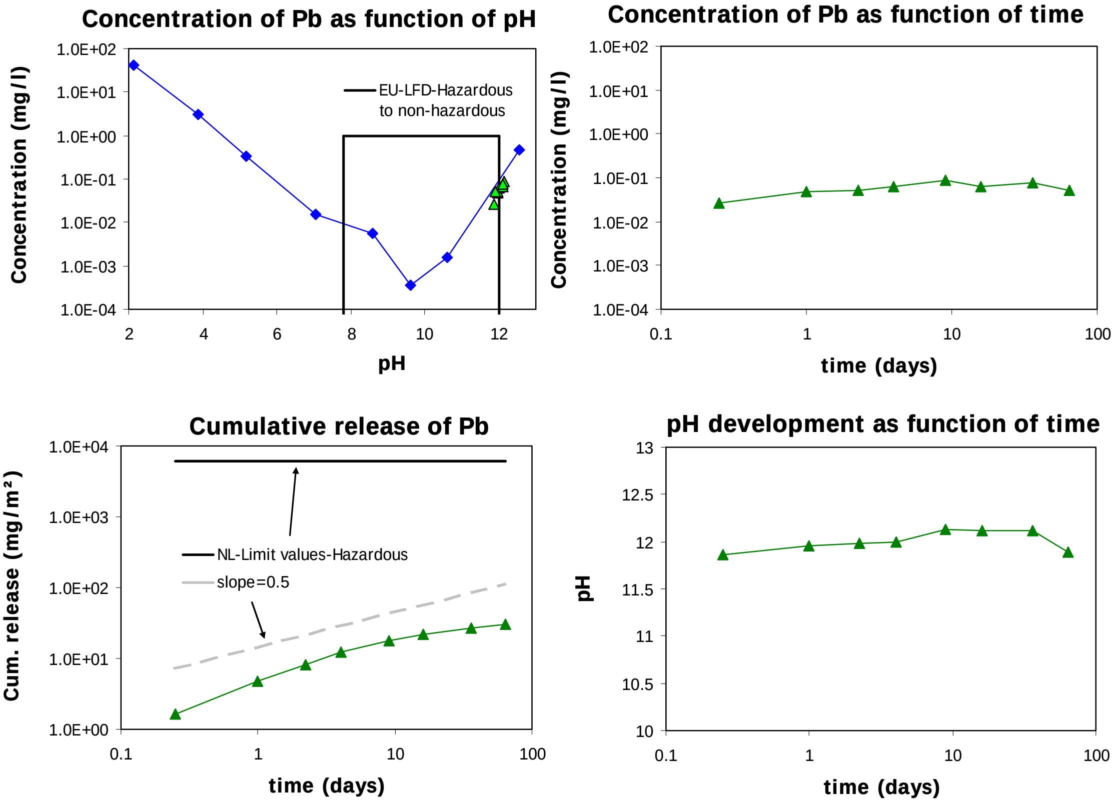


Figure 2.4 *Leaching behaviour of monolithic stabilised waste with release as a function of pH (size reduced), concentration as a function of time, release (mg/m^2) as a function of time, and pH as a function of time*

In figure 2.5 the leaching data for Pb from a size reduced monolith are given with the 4 graphs – Pb release as a function of pH at L/S=10; cumulative Pb release as a function of L/S (mg/kg); concentration of Pb as a function of L/S (mg/l) and pH as a function of L/S - that provide crucial leaching information from both characterization tests for size-reduced materials. The test provides insight in the release behaviour of size-reduced construction debris. The first two graphs show the relationship between pH dependence and release from column experiments. The L/S = 10 data points correspond generally well with the appropriate pH conditions in the pH dependence test. This implies that under the assumption of local equilibrium the release can be predicted based on the average pH in the percolation test provided there are not too big pH changes during the percolation experiment. As can be seen for Pb here the cumulative release at L/S=10 from the percolation test matches well with the release at L/S=10 in the pH dependence leaching test at the corresponding pH condition. A relative large range in released amounts can be found for the size-reduced stabilised waste, when the pH varies. Carbonation can lead to pH decrease in cement stabilised waste. The rate of which is dependent on the degree of exposure to CO_2 (e.g. atmosphere, soil, other)

The graph of cumulative release versus L/S allows conclusions on the main release mechanism. If a slope of 1 is observed, release is controlled by solubility limitations. In case the release curve goes horizontal (= no further release with increasing L/S), this points at depletion of a fully dissolved species (e.g. Cl).

The graph of concentration versus L/S gives for low L/S an indication of the pore water concentration that may be expected as the concentration being leached from the application.

The box in the pH dependence graph can be used to reflect the relevant pH domain for a give application. In the case of cement stabilised waste, this range for size-reduced material runs from the own pH of the fresh material (pH around 12.8) to pH 7.8 (equilibrium condition for fully carbonated waste). For the upper horizontal line a regulatory criterion can be inserted (here conversion from hazardous to non-hazardous waste in the EU LFD, 2003). The lower horizontal line denotes the lowest analytical detection limit. In the plot of cumulative release against L/S the same criterion is inserted.

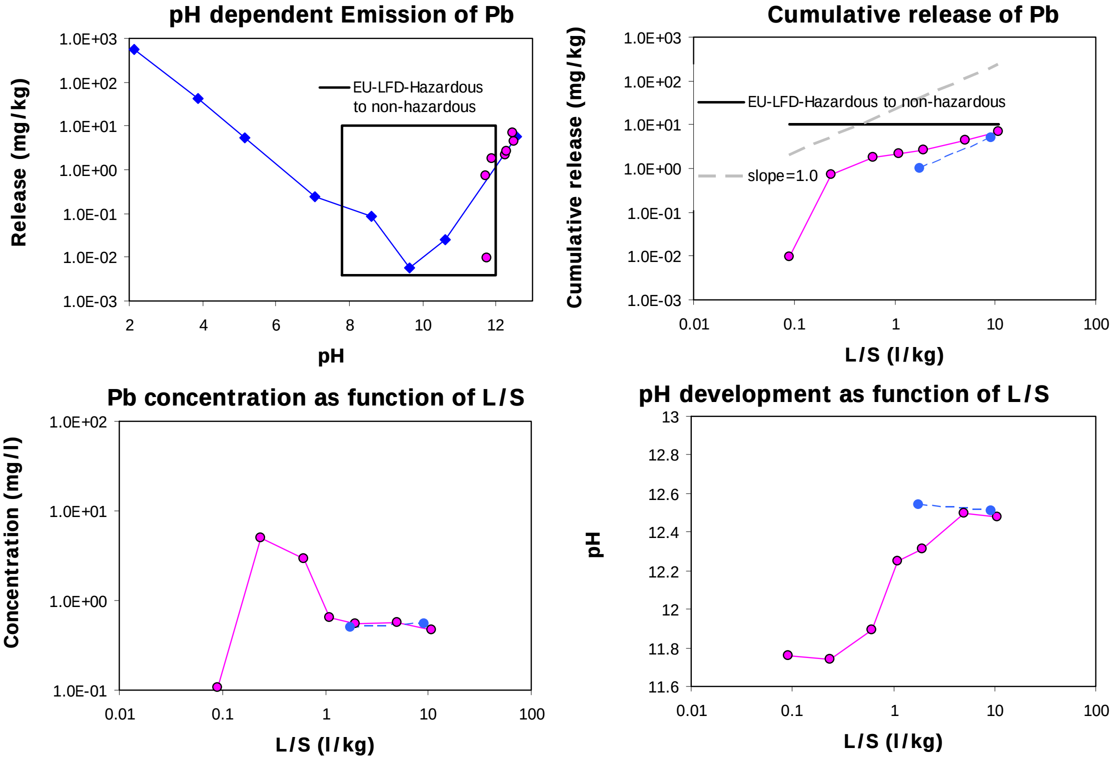


Figure 2.5 *Leaching behaviour of size-reduced stabilised waste with release as a function of pH, release as a function of L/S, concentration as a function of L/S and pH as a function of L/S*

Sometimes the concentrations as observed in leaching test are directly compared with drinking water quality criteria or groundwater quality objectives. This is incorrect, as many factors cause changes in the percolate concentrations in their transport through the soil; certainly when large transport distances are considered. A few aspects to be considered are: preferential flow (only a portion of the application is directly affected by percolation). Lysimeter and field data point at about 20 % of the total volume. Another factor is the change in pH, when leachate enters soil. This change brings about precipitation / dissolution reactions leading to substantial alterations in the percolate in the soil. The most frequently applied Kd concept does not take mutual reactions between substances released into account. This is a serious limitation as some substances react with others to form precipitates (contaminants may not reach subsoil or groundwater ever; example Pb). The main issue will be the substances that are mobile in the cement stabilised waste and which remain mobile in the subsoil and groundwater system in spite of pH change, etc.

The tank test data reflect that release as observed in cement mortars generally appears to be diffusion controlled, although not all elements will show this type of release in all cases. Figure 2.6 gives graphic examples of such different release behaviour. Time dependent release curves may reflect a number of different situations:

- Diffusion behaviour (slope 0.5 in cumulative release - time plot) - e.g. K.
- Depletion of soluble species, when the dimension of the tested specimen is rather small such that a very mobile species can be leached completely - e.g Al at neutral pH and Cd at own pH.
- Delayed release may occur, when a solubility controlling phase is limiting the release of a given constituent in the initial phase of leaching - e.g Al.
- Wash-off occurs, when in the first or first two eluates of the test an increased release is noted - e.g sulfate.
- Chemical changes may occur during the testing period, such as a change in redox state in the surface of the matrix or a change in pH such that the leachability of specific components is affected significantly - e.g Mn.

Several changes in behaviour as shown here can be related to interface reactions. The high initial pH of a cement product results in different solubility controlled conditions than at later stages of leaching, when the surface layer of the product is slightly modified.

Changes in release behaviour can be anticipated from the pH dependence test. As will be shown later from modelling work, the changes in a very thin interface layer form the key for a proper description of release. Previously carbonated materials show a different release than product not exposed to CO_2 during curing.

In the last few years new insights have emerged that lead to a different evaluation of monolith leach test data than at the start of the project. The key aspects will be highlighted here. The role of solubility limitations in tank leach tests have been underestimated. Carbonation during the test is rather prominent as CO_2 levels in a laboratory are higher than outside. This effect can be even more critical, when carbonation experiments are carried out in the laboratory or adjacent locations. In such cases noticeable effects on recorded pH in the tank can occur. Originally time steps were selected to match a square root of time relation as much as possible. A modified protocol with time steps with distinct deviations from this principle are recommended now as it allows to distinguish between release mechanisms. The latter is of relevance to use test data for long term release prediction.

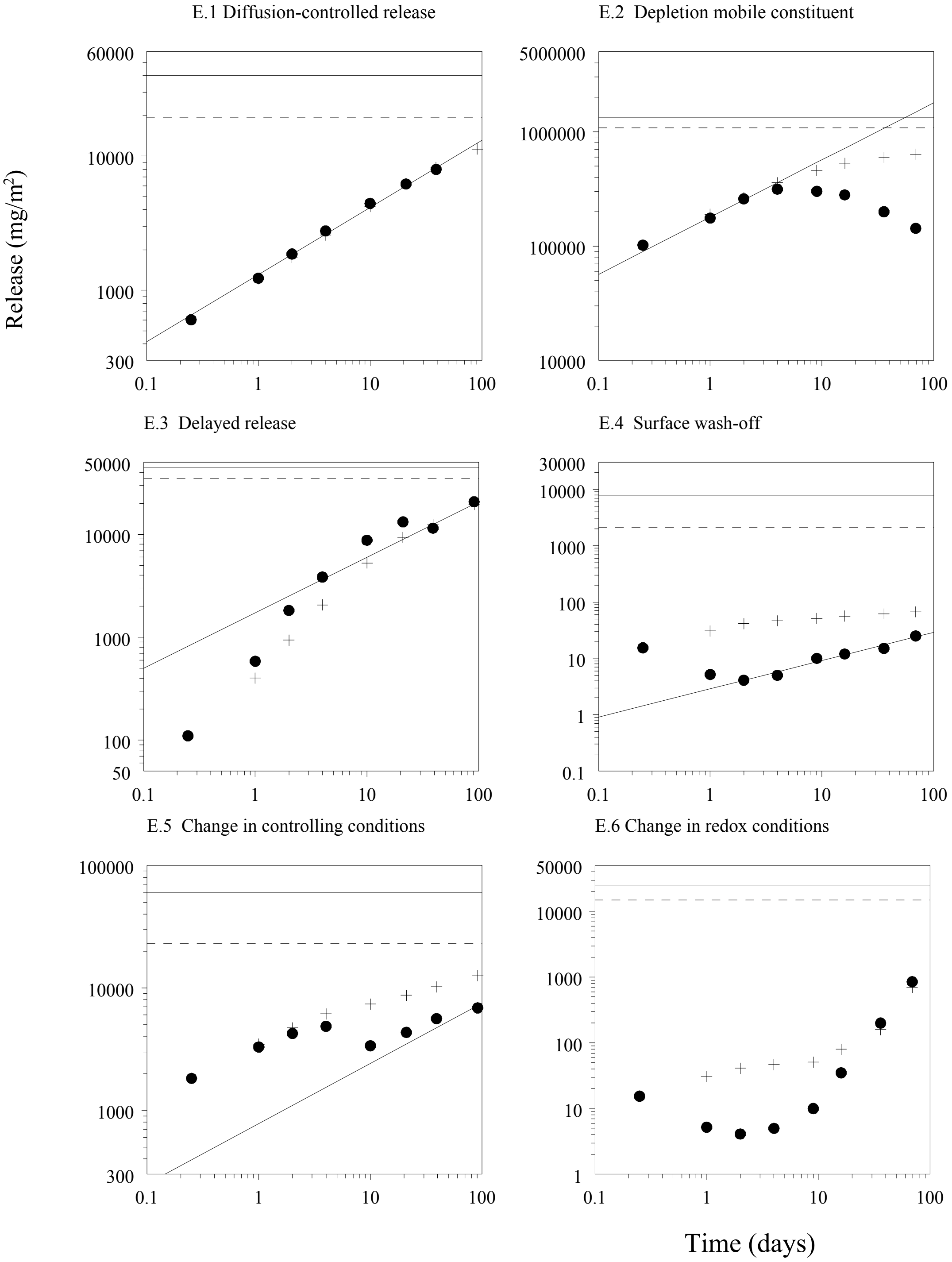


Figure 2.6 *Different types of release behaviour from monolithic specimen in the tank leach test. The horizontal drawn and dotted line represent the total and the availability for leaching expressed as mg/m^2 (this unit implies the data is specific to the specimen dimensions tested). The sloped line (0.5 slope) reflects theoretical diffusion. The plus symbols reflect the cumulative release using all previous fractions for calculation. The dots reflect the theoretical release, if the release rate for the interval is used for the entire period up to that of the measurement interval*

2.6 Geochemical Modelling

Understanding the controlling factors for release is crucial for long-term prediction of release. Chemical speciation modelling is a key element in obtaining such understanding. Saturation indices of potentially solubility controlling minerals in soil, sediments, wastes and construction materials are very useful in long term prediction. These saturation indices, can be calculated with geochemical models such as PHREEQC (2010), ECOSAT (2010) or the modelling environment ORCHESTRA (2003). The recent recognition of the concentration enhancing effect of DOC with respect to heavy metals and organic micro-pollutants, makes it desirable that these calculations include adsorption of metals by DOC, for example by using the NICA-Donnan model approach (Kinniburg et al, 1999). However, this type of geochemical modelling, especially when applied to many different leachates/materials with different properties, is time-consuming and requires specialist's skills. The development of a database/expert system, in which material data are grouped in a systematic way, opens the possibility of an instantaneously coupled geochemical model, saving substantial time and effort. Modelling the chemical speciation under realistic exposure conditions will provide information on which judgements can be made on the direction and magnitude of changes in release due to external factors. Such factors can be pH change due to carbonation, redox change due to oxidation or mobilisation due to interaction with external DOC sources. Primarily, the factors relating to the own material properties will be relevant.

Orchestra embedded in LeachXS has been used for the geochemical speciation modelling (van der Sloot et al, 2008). Data taken from the pH-dependence experiments as well as from the tank leaching test were used as input for the models. Davies equation was applied to correct for ionic strength effects. The saturation indices for the different chemical phases were calculated under the same conditions as measured in the leachates. Based on these saturation indices the relevant minerals are selected for a prediction calculation taking all element and all relevant phases into account.

2.6.1 Ettringite Solid Solution Description.

For the description of ettringite – element substitutions, which is particularly relevant for so-called 'oxyanionic' species, i.e. SO_4, Mo, Sb, Se, B, PO_4, V, or As but also Sr and Ba a new sold-solution model has been implemented in Orchestra. This option has been applied in the prediction of pH dependence leaching test data as well as in further modelling of release in different exposure scenarios. Details on how the parameters were obtained are given in section 3.7.3.

2.6.2 Modelling of Release from Cementitious Products

Based on previous experience made in modelling release of constituents from monolithic specimen (van der Sloot et al, 1997; van der Sloot, 2000; van der Sloot et al, 2007; Tiruta-Barna et al, 2001) the chemical reaction transport capabilities of Orchestra were exploited to provide estimates of the long term release in different exposure scenarios in the application of cementitious products on land, in water, in contact with drinking water and as construction debris (as unbound aggregate).

The modelling framework ORCHESTRA (**O**bjects **R**epresenting **CHE**mical **S**peciation and **TRA**nsport models) has been implemented in LeachXS which acts as the communication shell to query the database, create the input files for modelling and to generate the graphical and tabular output. It has been expanded to take into account chemical speciation and to allow a comparison between a traditional tank test and field exposed samples. Samples used for comparison include a concrete mortar and field exposed samples.

The following aspects of testing are covered:

- Presentation of tank test data in standardised data format
- Chemical speciation modelling based on pH dependence leaching test data
- Prediction of release in laboratory tests (percolation and tank) based on chemical phases from speciation modelling

In the model the following conditions can in principle be varied:

- Exposure of the leachant to CO_2 from the atmosphere, increased CO_2 levels (free choice of concentration) and no atmospheric exposure (sealed tank). This option is not practised now.
- Use of a fixed pH in the external solution (free choice of pH), which may be used to simulate a neutral pH environment or a CO_2 controlled pH in the external solution. Not applied now.
- The volume of the external solution can be varied (i.e L/A variation) for the entire test or part of the test. This allows concentration gradient relaxation to be verified
- The nature of the leachant can be varied
- The porosity of the specimen can be varied. At very low porosities, the non-porous surface (e.g concrete with about 5 % porosity) plays a major role in the release to the solution.
- The spatial configuration of the specimen is such that effects of depletion in specimen of limited thickness can be assessed.
- The role of gradient relaxation due to intermittent wetting on release by diffusion can be assessed.
- The release parameters for selected elements can be varied (available quantities, minerals).
- The time steps for leachant renewal can be varied from the standard set, shortening or lengthening exposure per liquid renewal cycle.

As output the model provides concentration profiles in pore water as a function of depth into the product for specified time intervals (here 0.5 hour) over the entire duration of the test. This allows visualization of the concentration development in the pore water as a function of depth and, simultaneously, precipitation reactions at the interface. In addition, the concentration build-up in the external solution is monitored at the same time steps, which allows visualising the slowing of concentration increase due to a decreasing concentration gradient between pore water and external solution.

This flexibility provides a basis for designing the optimal leaching conditions for monolithic specimen and to address the controlling release mechanisms. The key issue is not to force a certain release mechanism in the test (e.g. diffusion), but rather to identify for a given monolithic matrix, which mechanisms are relevant in that particular matrix for the constituents of interest.

2.7 Field Data Collection

Verification of release in field exposed samples of concrete provides a means to determine if the modelling of release is capable of describing properly, the observed effects. Samples have been taken from a few long-term exposed cementitious materials.

2.7.1 Field Exposed Concrete Cubes for 40 Years

In a long term outdoors exposure experiment, concrete cubes prepared from German Portland cements were exposed to partial immersion in flowing fresh water and natural rain for about 40 years (Schießl et al, 2003). Samples from this test site in Stuttgart were obtained for testing (samples coded F). Slices were sampled at 0.5, 3.5, 5.5 and 8 cm depth in the section that was exposed to air and at 9 cm in the middle of the cube in the section of the specimen that has been submersed permanently. Each slice was size reduced to 95 % of the mass was less than 1mm and subsequently extracted at L/S=10 with demineralized water. From the profile analysis with dye (phenolphthalein) it was clear that the carbonation front had progressed several mm’s inward. In the part exposed to the atmosphere this was at least 5 mm.

2.7.2 Sample Coded HFR

A sample was cored from the cooling water channel of the High Flux Reactor at Petten (The Netherlands) at a regular maintenance stop. At this time the duct is drained and the wall exposed continuously to fresh water from the North Holland Canal could be accessed and sampled. The channel is fully immersed during operation. The channel was built in 1956 and has been in operation since then. Annual cycles of reducing conditions in the sediments of the adjacent fresh water system has led to periodically increased Mn levels in the fresh water body, which are reflected by the increased Mn levels in the surface of the channel wall. Earlier SEM pictures reveal increased Mn levels at surface (van der Sloot et al, 1987). The carbonation after some 40 years of permanent exposure under water is only 2 mm inward based on the carbonation front as observed in a dye test (phenolphtalein). In figure 2.7 the dye profile is given.

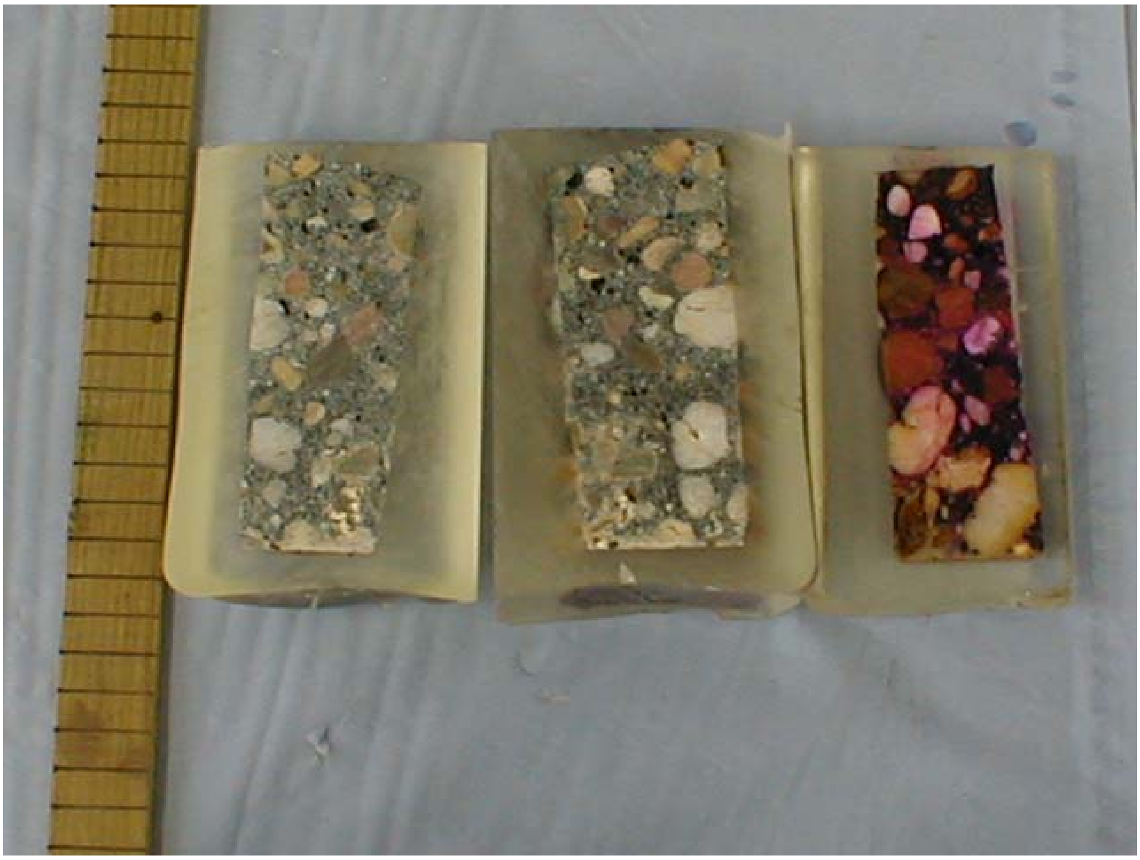


Figure 2.7 *Phenolphthalein dye colouring of the core from the cooling channel of the HFR*

2.7.3 Cement Mortar from 120 Year Old Fort Pampus.

From an old fort samples of cement mortar (type of cement not known) used in building an old fort at the entrance to Amsterdam from Lake IJssel were cored (Figure 2.8). Fort Pampus dates back to 1880. So at the time of sampling it was about 120 years old. The carbonation front has progressed several cm's (3 - 4 cm) inward. The profiles are variable as can be seen from the phenolphthalein dye colouring (Figure 2.9) This is probably related to the cement mix used, which was not up to specs as todays mortars.

Figure 2.8 *Fort Pampus (Amsterdam, The Netherlands) with 120 year old concrete walls*

Figure 2.9 *Phenolphthalein colouring of the specimen to assess the carbonation penetration depth of Fort Pampus cores*

2.7.4 Roman Mortar from an Aqueduct

A sample of very old mortar originating from a Roman aqueduct aged about 2000 years was obtained for analysis (Spanka, 2001). The sample was cored through the middle and the pH measured in an extract obtained after crushing the material and performing a leaching test at L/S=10 for 24 hours. In all samples the pH turned out to be neutral around 8. The entire specimen of about 20 cm across was fully carbonated. It has held together, so apparently the replacement of cement minerals by carbonate phases like calcite can hold the structure together. A full pH dependence test has been carried out on material sampled from the core of the specimen.

2.8 Description of the Database/Expert System LeachXS™

The expert system serves as a tool for research, environmental assessment, regulatory decision-making, material treatment evaluation and quality control based on understanding of the leaching behaviour of materials in the environment. The global set-up of the expert system is given in Figure 2.10.

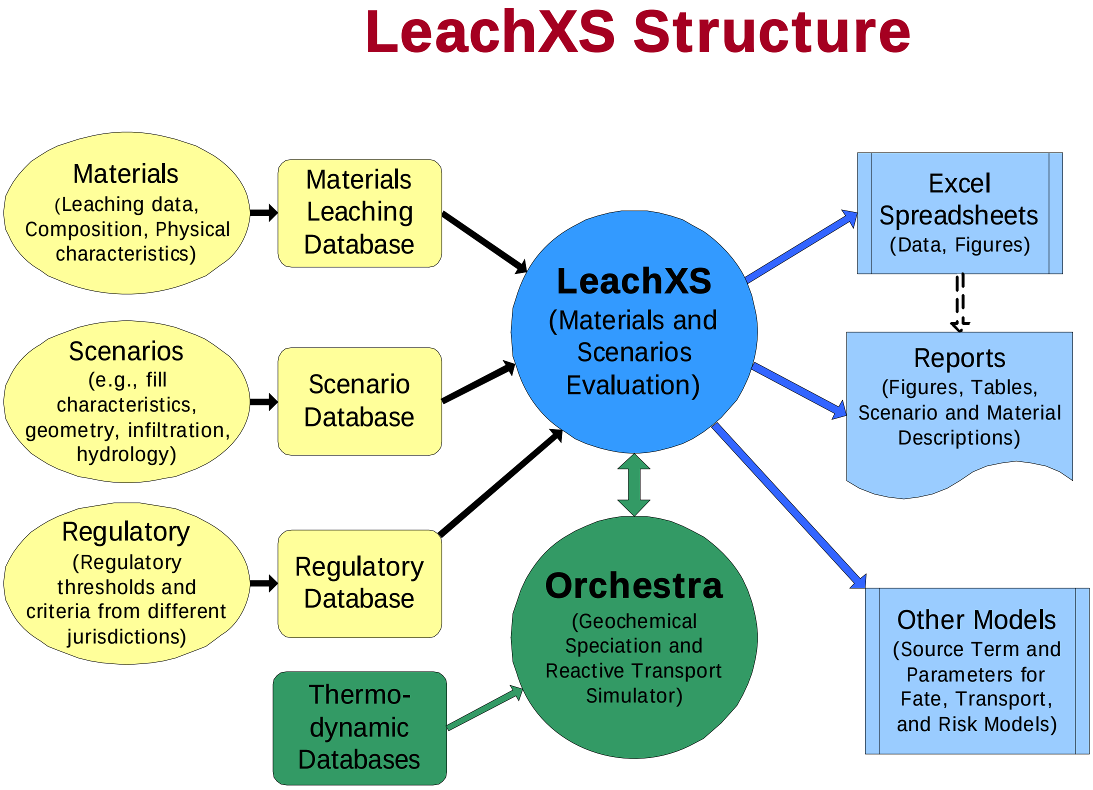


Figure 2.10 *Schematic representation of Database/Expert system*

Materials considered as part of the system include but are not limited to wastes, secondary materials, construction materials, contaminated soils, water treatment sludges, and sediments. The expert system can be used to evaluate waste management options, site-specific contaminant release scenarios, environmental impact of construction materials, land-application of sludges, waste treatment processes, and to define quality control criteria. The expert system includes selection and definition of testing protocols, integrated data management, quality control procedures, geochemical speciation evaluation, source term models to estimate potential future constituent release under various environmental conditions and management scenarios, environmental risk characterization, uncertainty analysis, and a reference database of leaching characteristics for previously evaluated materials. The expert system will be able to integrate laboratory and field data of various types and origins. The expert system is intended to make best-practices decision-making widely accessible (van der Sloot et al, 2003; van der Sloot et al, 2008). Recently, a free software version (LeachXS Lite) has been made available, which contains a data viewer and tools to upload test data in the attached database (http://vanderbilt.edu/leaching/downloads/leachxs-lite/).

3. Results of experimental work

3.1 Physical Properties

The results of the physical tests on cements and mortar samples according to the European cement standard EN 196 (2005) are given in Annex I.

All Portland cement samples are in compliance with the specifications given in the cement standard EN 197 (2000). Differences in compressive strength between the test cements are due to differences in granulometric and chemical characteristics and due to differences in the physical structure of the hydrated mortars (porosity, air voids etc.).

Except for one, all blended cement samples are in compliance with the specifications given in the cement standard EN 197. The 28-d compressive strength of test cement HOL-1 is below the required 32.5 MPa. Large differences in compressive strength between the test cements are due to differences in granulometric and especially chemical characteristics (composite cements with varying constituents such as slag or fly ash), and due to differences in the physical structure of the hydrated mortars (porosity, air voids etc.).

3.2 Particle Size Distribution

The particle size distribution of the test cements from ECRICEM phase I and phase II as determined by laser granolumetry is compiled in Annex II.

3.3 Chemical Composition

The chemical composition of all test cements is given in Annex III and IV for respectively major and minor oxides and trace elements. Four test cements (HOL-3, HOL-5, HOL-13, VDZ-4) exceed the limits for SO3 (3.5 – 4.5 %) given in the EU cement standard EN 197-1. Cement HOL-13 was not used in the leaching test program. Minimum, maximum and median trace element contents of the test cements are given in table 3.1.

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

	Slag cements			Composite cements			Composite cements (more than one additive)			Portland cements		
	min	max	median	min	max	median	min	max	median	min	max	median
As	1.3	6.1	4.5	2.7	12.6	5.6	4.2	46.6	8.3	5.4	12.6	5.9
Be	1.1	6.2	2.4	0.4	1.9	0.8	1.1	4.4	2.7	0.6	1.3	0.9
Cd	0.1	1.4	0.5	0.1	0.9	0.3	0.1	1.9	0.5	0.2	0.4	0.3
Co	2.3	9.5	7.1	3.8	23.1	8.5	6.3	15.8	12.9	13.3	16.3	14.1
Cr tot.	32.0	94.1	44.1	25.9	122	45.3	49.5	155	102.5	79.7	151	147
Cr VI	1.4	11.7	4.4	0.4	7.8	4.2	3.5	15.1	10.0	0.5	2.9	1.7
Cu	5.5	49.6	16.0	11.8	144.0	25.2	8.1	80.4	37.2	17.8	82.1	37.2
Hg	0.0	0.1	0.1	0.0	0.1	0.1	0.0	0.1	0.1	0.0	0.1	0.0
Mn	645	3305	1341	234	559	375	334	1558	1362	445	2780	1245
Ni	11.5	40.1	17.1	9.9	53.5	24.7	26.6	67.6	42.7	31.6	117.0	44.5
Pb	2.7	40.3	17.8	8.7	43.3	13.3	4.6	169.0	13.1	12.6	23.0	14.1
Sb	1.1	19.4	6.1	2.6	23.1	3.2	1.6	3.7	3.2	2.3	5.7	5.4

Sn	1.0	3.2	2.0	1.6	6.0	4.3	1.2	7.0	4.2	4.2	5.6	4.9
Tl	0.0	0.0	<0.1	0.0	0.0	< 0.1	1.8	1.8	1.8	0.0	0.0	< 0.1
V	38.7	212.0	57.5	24.5	139.0	65.0	69.4	138.0	92.1	31.7	774.0	53.6
Zn	15.9	318.0	77.7	26.0	170.0	60.3	26.8	372.0	169.2	53.5	115.0	102.0
Ba	120.0	1402.0	245.0	95.5	460.0	208.0	156.0	510.0	432.5	345.0	460.0	380.0
Mo	1.5	3.2	2.1	1.5	4.0	2.5	2.9	14.2	6.8	2.3	10.2	4.3

3.3.1 Commercial Cements

The individual data in Annex III and IV show elevated contents of some metals such as zinc (H1, H9), chromium (H6, N1), lead (D1), and vanadium (H1, H5). The high chromium content in test cement H6 originates mainly from the natural raw materials, and not from the waste fuels used in the production of the clinker.

Compared to the Portland cements investigated in ECRICEM phase 1, the concentration ranges (min – max) are increased for most metals mainly due to the existence of constituents substituting clinker in the composite cements such as blast furnace slag, coal fly ash, or natural puzzolans.

The individual data in Annex III and IV show elevated contents of metals such as arsenic (HOL-5), beryllium (HOL-1, HOL-2, HOL-6), nickel (HOL-7, NOR-2), lead (HOL-12), antimony (HOL-3, VDZ-1), vanadium (NOR-2) and molybdenum (VDZ-2, NOR-2). In many cases, these elevated contents reflect the presence of clinker substitutes such as blast furnace slag (ex.: beryllium) or coal fly ash (ex.: nickel) in the cement. In one case, the use of a steel slag in the raw mix for clinker production obviously leads to higher metal contents in the cement (NOR-2). In Table 3.2, the range of the trace element contents of the commercial cements are compared to the special ('spiked') cements W1 and W2.

Table 3.2 *Trace element contents of the test cements (in mg/kg)*

	Commercial 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 6+	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*

In Annex V a comparison of total contents in cement between ECRICEM data and VDZ data (VDZ 2000, 2001, 2002, ECRICEM I (2001) and ECRICEM II) is given in the form of histograms. The descriptive statistics for the major elements are summarized in Table 3.3.

Table 3.3 *Summary statistics of major constituents in ECRICEM worldwide cements*

	SiO_2	Al_2O_3	Fe_2O_3	CaO	Na_2O	K_2O	MgO	S as SO_3	Mn_2O_3	TiO_2	P_2O_5	Cl
	%	%	%	%	%	%	%	%	%	%	%	%
Average	23.2	6.1	3.0	57.4	0.30	0.79	2.7	3.0	0.20	0.37	0.17	0.024
Median	21.8	5.2	3.0	60.7	0.24	0.79	2.5	2.9	0.13	0.29	0.13	0.011
min	15.3	2.8	1.3	40.5	0.04	0.00	0.6	1.9	0.05	0.15	0.04	0
max	36.2	10.9	5.9	64.9	1.40	1.8	7.4	4.7	1.48	1.11	0.74	0.200
n	56	56	56	56	56	56	56	56	56	56	56	56

The ECRICEM cements classified as Slag cements and Portland cements show different calcium to aluminium ratios. The calcium to aluminium ratios have been calculated as oxides and are shown in table 3.4.

Table 3.4 *Calcium (CaO) to aluminium (Al_2O_3) ratios in ECRICEM slag- and Portland cements*

Ca/Al ratio slag cements	**Ca/Al ratio Portland cements**
4.5	18.3
5.2	19.5
8.4	12.9
10.4	
10.1	
5.1	
9.6	
7.7	

A summary of descriptive statistics of the datasets for trace elements is given in table 3.5. The statistics of selenium (Se) and tellurium (Te) are not incorporated. The analytical data of Se and Te in VDZ standard cements were below detection limits of respectively 2 mg/kg dm for Se and 0.5 mg/kg dm for Te, and in ECRICEM the Se and Te concentrations are not reported (Table 3.5).

Table 3.5 *Summary statistics of trace constituents in ECRICEM worldwide cements in comparison to VDZ data*

	Arsenic (As)		**Beryllium (Be)**		**Cadmium (Cd)**		**Cobalt (Co)**		**Chromium (Cr)**	
	VDZ	**Ecricem**	**VDZ**	**Ecricem**	**VDZ**	**Ecricem**	**VDZ**	**Ecricem**	**VDZ**	**Ecricem**
N	415	25	415	25	415	25	415	25	415	25
n < d.l.	4	0	1	0	49	0	0	0	0	0
Mean	7.0	11.25	1.30	2.08	0.34	0.55	8.69	9.99	40.71	78.10
Median	4.3	5.87	0.9	1.3	0.29	0.47	8.04	9.48	35.5	55.3
X_{min}	0.5	1.28	0.05	0.37	0.05	0.1	2.01	2.29	9.88	25.9
X_{max}	96.7	71.9	5.11	6.18	1.52	1.91	27.3	23.1	193	218
Standard deviation	9.30	15.60	1.12	1.66	0.25	0.43	4.22	4.80	22.66	50.55

	Copper (Cu)		**Mercury (Hg)**		**Manganese (Mn)**		**Nickel (Ni)**		**Lead (Pb)**	
	VDZ	**Ecricem**	**VDZ**	**Ecricem**	**VDZ**	**Ecricem**	**VDZ**	**Ecricem**	**VDZ**	**Ecricem**
N	415	25	415	25	415	25	415	25	415	25
n < d.l.	0	0	34	0	0	0	0	0	0	0
Mean	31.17	42.13	0.05	0.06	759.2	1057.6	23.25	37.20	16.86	25.16
Median	21.8	33.4	0.03	0.05	520.0	688	22.4	26.6	13.3	14.1
X_{min}	4.24	5.5	0.01	0.02	90.9	234	4.44	9.89	1.67	2.67
X_{max}	234	144	1.08	0.12	4670	3305	55.9	117	105	169
Standard deviation	26.81	35.10	0.074	0.028	698.0	810.9	9.78	26.69	14.28	32.30

	Antimony (Sb)		**Tin (Sn)**		**Thallium (Tl)**		**Vanadium (V)**		**Zinc (Zn)**	
	VDZ	**Ecricem**	**VDZ**	**Ecricem**	**VDZ**	**Ecricem**	**VDZ**	**Ecricem**	**VDZ**	**Ecricem**
N	415	25	415	25	415	25	415	25	415	25
n < d.l.	138	8	9	0	374	24	0	0	0	0
Mean	2.94	3.98	3.56	3.97	0.37	1.81	49.93	105.5	191.6	116.5
Median	1.5	2.56	3.02	3.79	0.25	-	43.4	69.4	150	82.1
X_{min}	0.5	0.5	0.5	1.03	0.25	-	17	24.5	9	15.9
X_{max}	53.3	23.1	27.3	9.78	4.84	-	186	774	1023	372
Standard deviation	5.07	5.57	2.31	2.22	0.55	-	25.9	145.8	155.7	95.2

The data match quite well with the data supplied in the report by Achternbosch et al (2003). The relevance of total composition for judging environmental aspects of cementitious materials has been questioned (van der Sloot, 2000), as the true environmental impact relates to a minor fraction of the total composition and the assumption that there is a proportionality between composition and leaching is a myth. The observed and projected increase in total concentration of specific elements due to the use of alternative fuels or alternative raw materials in cement production (Achternbosch et al, 2003) cannot be related to environmental impact in any application. Therefore evaluation of release by leaching is crucial. Setting of criteria on composition with the aim to limit environmental impact must be discouraged.

3.3.2 Special Cements

As, Cd, Cr, Mo, Pb, Sb and Zn were artificially 'spiked' to the raw meal of the clinker produced at the pilot test facility.

The analytical results (Table 3.2) demonstrate that As and Cr were nearly totally incorporated in the clinker, whereas only about 50 to 80 % of added Mo, Sb and Zn was retained in the clinker structure. Most of the Cd and Pb spiked to the raw meal was lost under the specific process conditions prevailing in the small test facility.

The behaviour of these elements in the test kiln is in contrast to their behaviour in a full scale commercial kiln. In a commercial kiln, these trace elements are almost completely (close to 100 %) bound to the solids produced – either clinker or kiln dust – due to the excellent retention capacity of a modern pre-heater kiln system (Rotary cement kiln, 1986).

Under the specific process conditions of the small test kiln – with limited contact of solids and gas due to the pelletised raw feed, the short residence time, and the lack of a preheater a larger portion of the spiked elements – especially the ones with higher volatility (Cd and Pb) - left the kiln with the exhaust gases and were finally deposited on the filter system (textile filter and activated carbon filter).

3.4 Structural Properties of Mortar Samples

The results of the microscopical investigations on the mortar samples are compiled in Annex VI together with the experimental details.

Thin section analysis demonstrates structural similarities, but also some differences in the test mortars, for example in homogeneity and porosity of the hardened cement paste, air void content and size, and development of microcracks.

The mortars produced from the different cements can be characterised as follows:
- H1 results in the densest, and H5 in the most porous hardened cement paste (capillary porosity).
- N1 and H6 result in the lowest contents of total air voids.
- H1 results in the highest content of total air voids and of small air voids < 0.25 mm.
- N2 results in the lowest content of small air voids < 0.25 mm.
- W1 results in the highest content of air voids > 0.25 mm.
- H6 results in a higher content of microcracks compared to the other samples.

The differences in air void structure and contents may influence the behaviour in the leaching tests. However, the air voids are in most samples evenly distributed – an indication of proper mortar compaction. The total content of air voids in the mortar samples ranges between 3.4 and 7.5 %. The content of small air voids < 0.25 mm is between 0.3 and 3.2 %.

The results of the microscopic investigations on the blended cement mortar samples are compiled in Annex VI together with the experimental details.

The results of the investigation of the first casting of the 25 different mortars showed that some of the samples had not been properly compacted. The 20 (of the 25) cements which were selected for further testing were cast once more. Of these mortar samples the 10 which were subjected to tank leaching tests were studied with optical microscopy.

All these 10 mortars are relatively homogeneous and show normal air content, indicating proper compaction and casting. The differences recorded in these mortar bars are caused by the differences in the cement types and not the casting. The variation in the recorded characteristics of these mortar samples do not show any obvious trend caused by high or low content of limestone, fly ash, slag or puzzolan.

The content of air voids varied from 1 to 4 %. Sample HOL 3 and HOL 7 had only 1 % air voids in the mortar. HOL 5 and VDZ 1 had the highest porosity with 4 % air voids.

Normal air content is usually reckoned up to 4 %.

The porosity of the mortar samples varied. The measured capillary porosity indicated that sample HOL 1 and VDZ 1 had highest porosity. HOL 2, HOL-7 and NOR 4 had the densest paste.

In general all the mortar bars with blended cements, which had a satisfactory casting, demonstrate homogeneous non-porous mortar, although differences are observed, as in Ecricem phase I (cements without substitutes). The substitutes, limestone, fly ash, slag and pozzolan are clearly observed in the matrix and are evenly distributed in the mortar.

3.5 Leaching Characteristics of Cementitious Materials in Different Life Cycle Stages

In this section the different aspects of leaching of cementitious products in different life cycle stages (service life, recycling and end of life) are addressed. In view of the large amount of data, the leaching test data have been provided in a dedicated LeachXS database (ECRICEM I and II) and on a CD-ROM for the Excel files.

Characterisation
In figure 3.1 the characterisation methods are highlighted covering chemical speciation aspects as obtained from the pH dependence test on size reduced materials (providing information on release conditions other than those observed during testing, e.g. resulting from carbonation) and time dependent release from a monolithic material. The first fractions of a percolation test on size reduced monolithic material provide insight in pore water concentrations, which are relevant for a proper description of long term release predictions. In Annex VII a short description with the capabilities and use of the tests is provided.

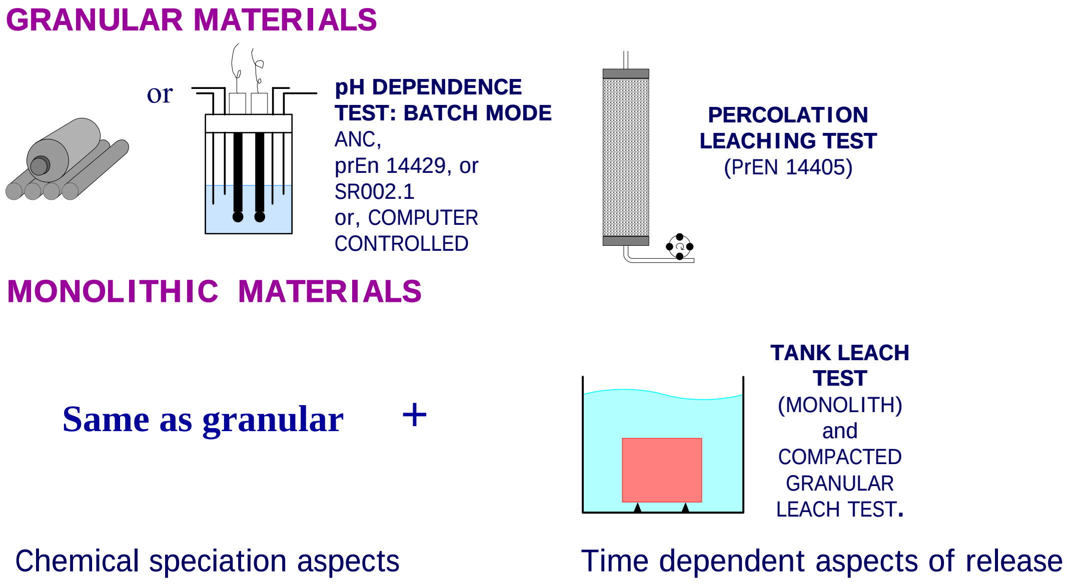


Figure 3.1 *Characterisation leaching test methods for granular and monolithic materials.*

3.5.1 pH Dependence Test

The pH dependence test provides means of evaluating the chemical speciation of cement mortars, which cannot be obtained from a tank leach test. The combination of pH dependence and tank test provides the necessary information for a full release description from cementitious materials and other related construction materials (van der Sloot, 2000; van der Sloot et al, 1997, Kosson et al, 2002). This information is crucial as it dictates the release behaviour from intact specimen. The pH dependence test data cover a much wider range of potential exposure conditions – service life (own pH and externally imposed pH), recycling stage as aggregate and end of life conditions after full carbonation. A recent addition to the basic test set is comprised of the first fraction(s) of the percolation test (CEN/TS14405, 2004) on size reduced mortar, as this provides a rather good estimate of pore water composition.

The pH dependence leaching test (**A**cid **N**eutralisation **C**apacity ANC mode) was used to compare the leaching characteristics of various cement mortars (van der Sloot and Hoede, 1997; van der Sloot, 1999; van der Sloot, 2000). The results derived from the pH dependence test for the cements studied are given as a generic behaviour in Figures 3.2 and 3.3. They show the same general leaching characteristics as found in the previous project using pH dependence leach test (in ANC mode).

Many other studies of cements and mortars have focussed on the behaviour of the highly alkaline matrix (Glasser at al, 1988; Cougar et al, 1996; Kindness et al, 1994; Kindness et al, 1994b; Serclerat, 1996; Klemm, 1998; Park and Bachelor, 2002), whereas from a point of view of release to the environment the surface chemistry may prove to be more determining. This has in part be addressed by models such as the shrinking core model (Hinsenveld, 1991), which takes changes in surface chemistry and a moving pH boundary into account.

As carbonation is the main factor controlling pH change in cementitious materials, the extent to which pH control in the eluate by CO_2 instead of NaOH and HNO_3 will produce the same or slightly different results in a pH dependence test and in the tank leach test for most substances. Obviously, there is a difference for the concentrations of Ca, Sr and Ba in solution, which are directly affected by carbonate.

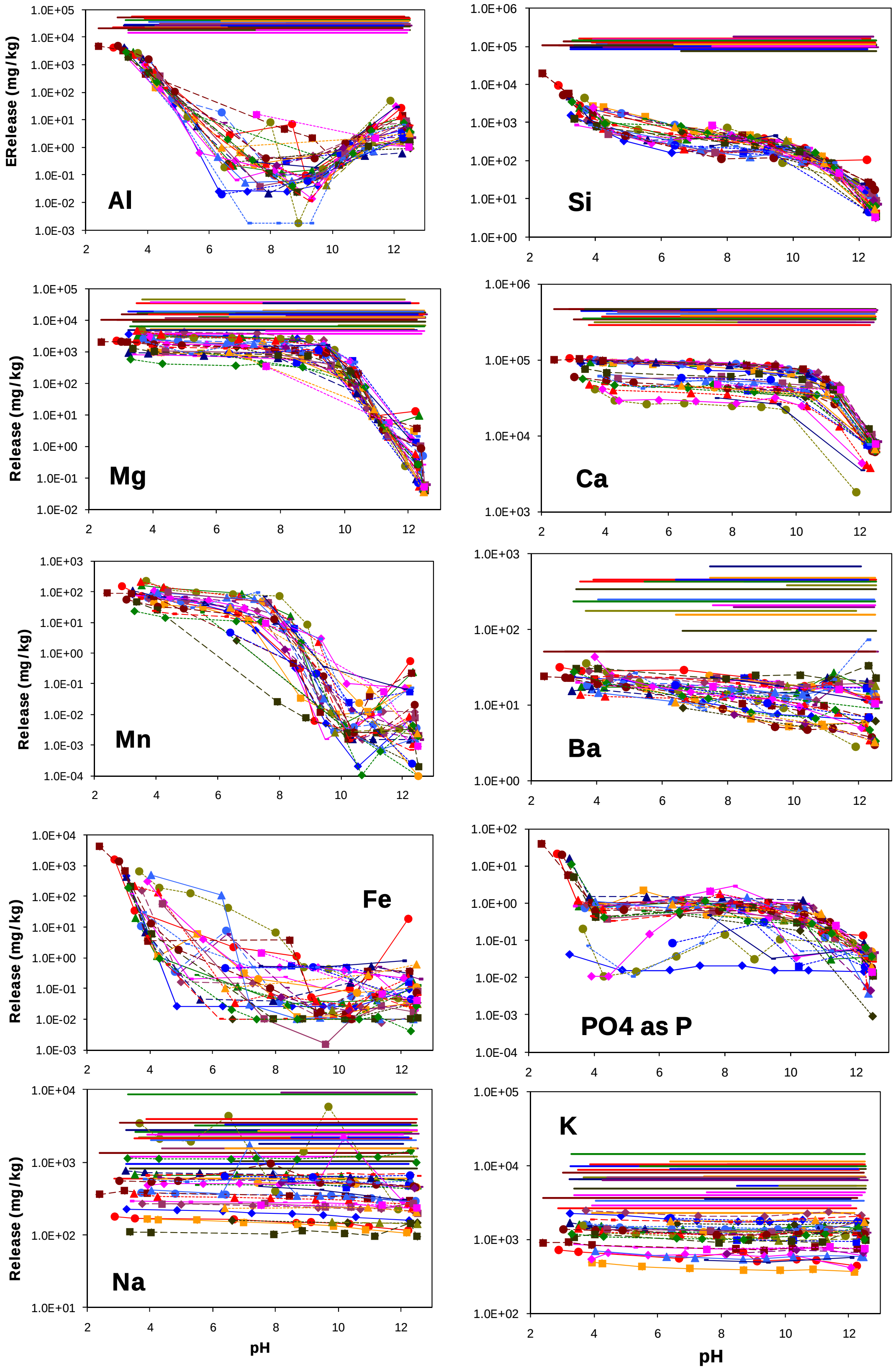


Figure 3.2 *Generic pH dependent leaching behaviour of major and minor elements from cement mortars (data from pH dependence leaching test on crushed mortar and total content measurement)*

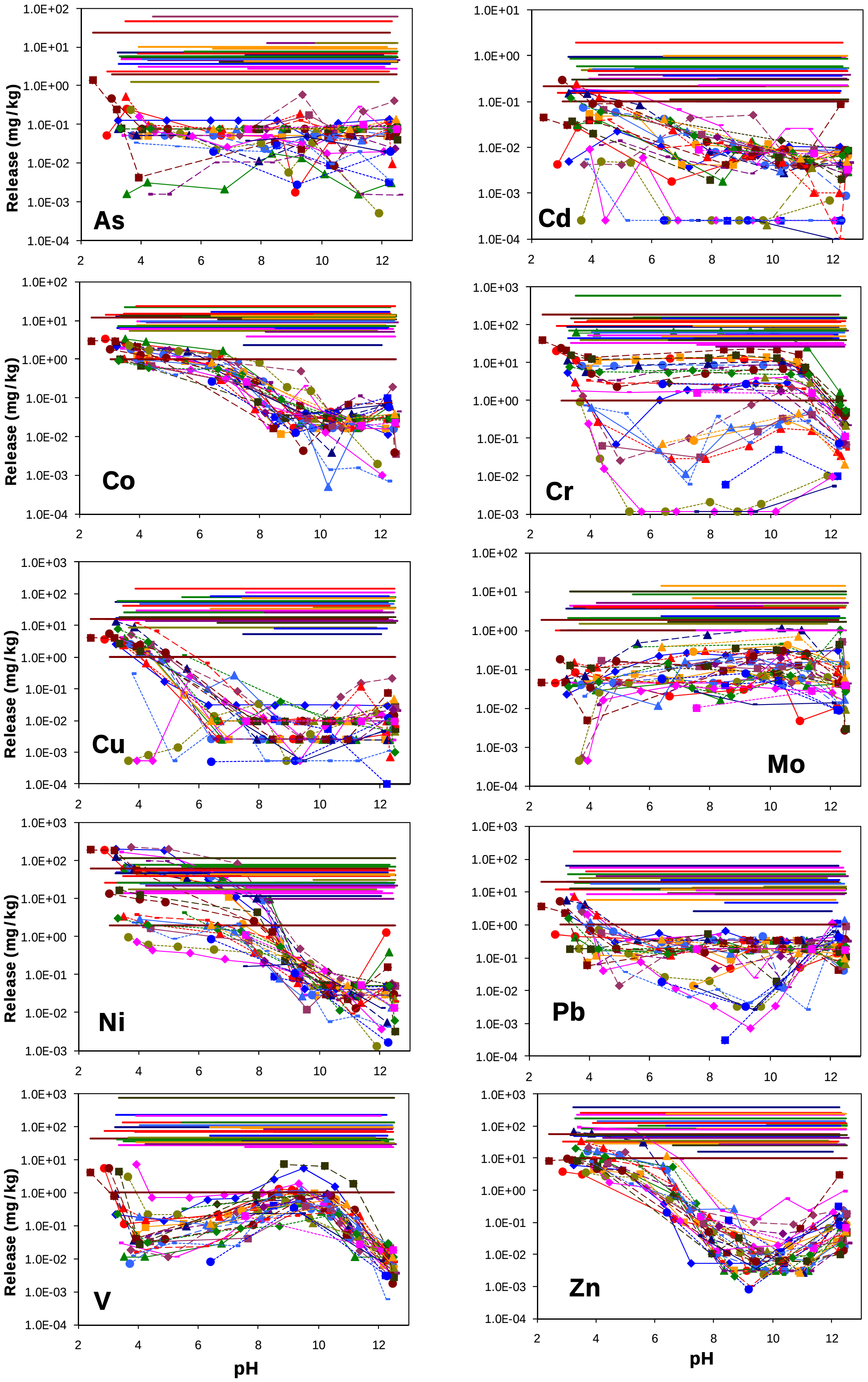


Figure 3.3 *Generic pH dependent leaching behaviour of trace elements from cement mortars (data from pH dependence leaching test on crushed mortar and total content measurement)*

3.5.2 Acid Neutralisation Capacity

The test provides also information on the acid neutralisation capacity. This property in combination with field exposure properties acidification, carbonation and other sources of neutralisation dictate how long it takes for the surface of the specimen to be neutralised. This will then lead to another leaching characteristic.

The acid neutralisation capacity (ANC) of cementitious products is high (Figure 3.4). The blended cements generally have a lower ANC than the Portland cements. This is also reflected in the own pH in the pH dependence test and in the tank leach test. Therefore only the surface of cementitious products can be neutralised and thus shows leaching characteristics corresponding to the neutral pH. In Figure 3.5 it is schematically illustrated, that element solubility is controlled by different conditions within the mortar and on the surface of a carbonated specimen. Since the surface is in direct contact with the surrounding environment, this condition is more determining for the release than the highly alkaline interior of the material.

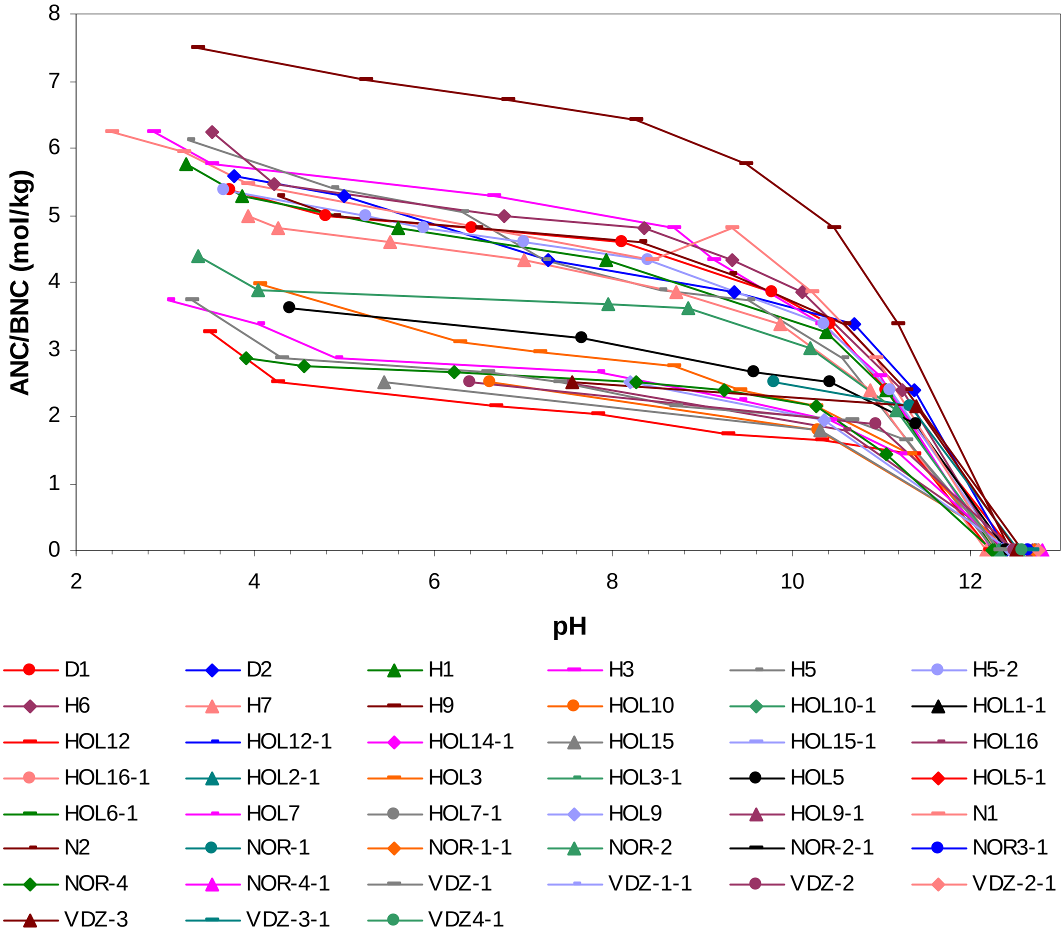


Figure 3.4 *Acid Neutralisation Capacity (ANC) for cement mortars (pH dependence leaching test)*

Beside Fe(II)SO_4, also Sn(II)SO_4 has been applied for reduction. From an environmental point of view the use of Fe would be preferred.

The leaching characteristics of the hardened cement mortars of slag cement, fly ash cement and Portland cement mortars have been determined by examining the leaching behaviour as a function of pH in the pH range 3 -13, which has revealed very consistent and systematic leaching patterns, which are largely consistent with the information generated in phase I.

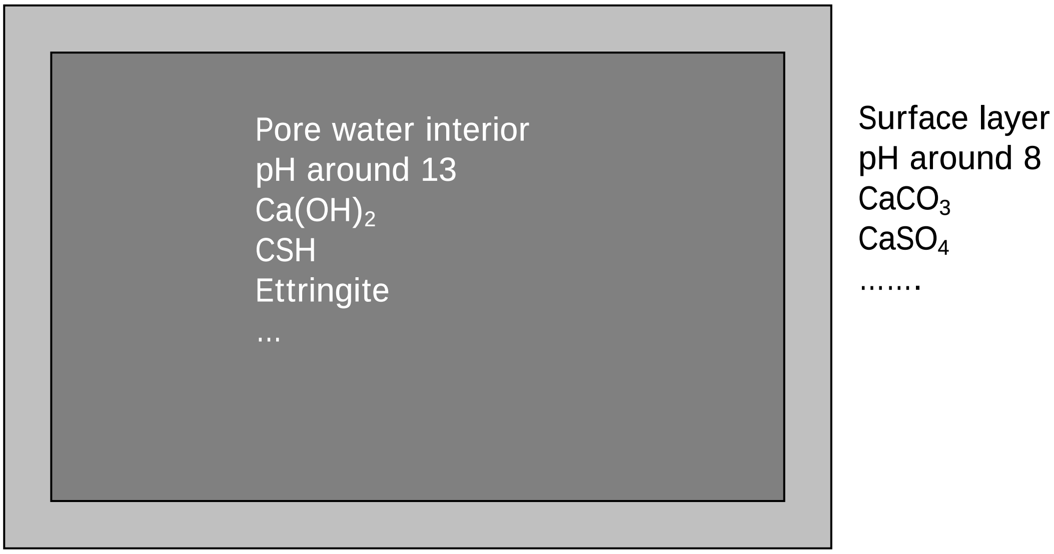


Figure 3.5 *Bulk versus surface chemistry in concrete. Thin surface coating of minerals dictates environmental properties*

3.5.3 Availability Test

In the Netherlands, the availability of the elements for leaching is assessed as a convention by NEN 7341 (1994) (particle size < 125 micrometer; two test conditions: pH = 4 and pH = 7). The test results serve as ‘driving force’ in release models. In table 3.6 this availability for the cements tested in ECRICEM is given as minimum, maximum and median values. Sand used in preparing mortars is generally not contributing to the leachable fraction significantly. The availability varies significantly from one cement to another. Only Sr availability is very consistent throughout all cement samples. The elements Cr, Co, Mn, Cu and Zn show a rather high availability for leaching. Almost all Sr is available for leaching. There is no systematic trend by element. Values exceeding 100 % can occur as a result of comparing two numbers with each their own analytical uncertainty.

Table 3.6 *Availability according to NEN 7341 (n = 33)*

	min	max	median
Al	55	2097	1155
As	0.21	0.63	0.21
Ba	21	188	57
Be	0.02	0.50	0.13
Ca	39826	94862	81001
Cd	0.01	0.13	0.04
Cl	10	298	148
Co	11	127	18
Cr	0.1	11	3
Cu	0.1	15	1
Fe	7	590	48
Hg	1.0	1.0	1.0
K	640	3369	1950
Mg	891	5585	3054
Mn	16	435	38
Mo	0	41	0
Na	353	2478	831

Ni	1.1	70	4
P	1.0	10	3
Pb	0.1	1.4	0.8
S	1127	3331	2451
Sb	0.1	1.6	0.3
Si	4762	9712	6330
Sn	0	0	0
Sr	48	344	132
Ti	0.1	3.4	0.5
Tl	0.2	1.1	0.4
V	0.4	2.8	1.0
Zn	2.2	43	14

Recent experience has shown that with the maximum in the pH dependence test good modelling results can be obtained, which implies that the availability test as separate test is not needed any more. When a short method is needed a single step extraction at low pH would suffice.

3.5.4 Comparison of Content, Availability and Release

There is generally no systematic correlation between the total content of trace elements in cement mortar and the leaching from intact mortar even under worst case conditions. This is largely due to the fact that in most cases solubility (very pH dependent) appears to control release.

Table 3.7 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 3.7 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 3.7 *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.

Table 3.8 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 blended cements. The ratio between the leached amounts 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 3.8 *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)

3.5.5 Comparison of Release in Service Life with Regulatory Criteria

In table 3.9 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, 1995) category I limit values for unrestricted use. The more recent Soil Quality Degree (2007) specifies slightly different limit values following new impact calculation (Verschoor et al, 2006; Verschoor et al, 2009). 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 3.9 *Comparison of release in mg/m^2 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)	SQD (2007) category 1 (mg/m^2 at 64 days)
As	0.75	41	260
Ba	129	600	1500
Cd	0.044	1.1	3.8
Co	0.54	29	60
Cr	7.4	140	120
Cu	2.8	51	98
Hg	< 0.3	0.43	1.4
Mo	0.45	14	144
Ni	2.6	50	81
Pb	1.8	120	400
S (as SO4)	1500	27000	165000
Sb	0.45	3.7	8.7
Se	n d	1.4	4.8
Sn	0.93	29	50
V	7.2	230	320
Zn	3.1	200	800

The comparison of the end of life conditions reflected by full carbonation and size reduction indicates that under these worst case conditions significantly lower leached quantities (Table 3.9) are observed than in comparison with the availability data (Table 3.6). These conditions can be seen as different worst case estimates, which are both better alternatives for judgement than total composition. Experiments were not carried out on fully carbonated material. The pH control is used to reflect the major pH effect resulting from carbonation.

3.5.6 Tank Leach Test

The tank leach test according to NEN 7345 has been applied to assess the release from monolithic specimen both under own pH (generally pH > 11 in eluate) and under imposed neutral pH. The latter situation is more relevant for cementitious products in contact with natural surface water, where the external neutralisation surmounts the supply of alkalinity from within the matrix. The difference between own pH and imposed pH has been evaluated further in the framework of a NEN project (Van der Sloot, 2008). In this work pH was controlled in the leaching in a tank test with CO_2 aiming at constant pH 11, 10, 9 and 8. In addition, pre-carbonation was studied using 5 bar CO_2 for 7 days, as well as leaching under imposed reducing conditions. The results are shown in figure 3.6 and 3.7 for Ca, Al, K, V and Zn. Further information is given in Annex VIII.

In relation to the pH control using CO_2 a significant effect is noted for Al, where the leachability decreases after this treatment. For several oxyanions (e.g. SO_4, Mo, As, V, Sb) a significant increase is noted, since leachability of oxyanions is maximal at pH 9 - 10. The band width of leaching data worldwide is limited. Where relevant a horizontal line indicating an acceptance limit for construction products is given (Building Materials Decree, 1995). Since this is one of the first notified regulations, this regulation has been applied. It indicates that for service life there are generally few problems to be expected. Only Se appears to exceed the limit in a few cases, but here a more sensitive hydride measurement should be applied, as generally Se by ICP may be overestimated. From the graphs it is clear that diffusion is a relevant transport mechanism. However, the chemistry shall not be ignored, as mobilisation and precipitation processes at the cement mortar - water interface occur as a result of the very large pH gradient across the interface. Leaching of Cr shows the largest variation as a function of pH. Since this relates to Cr VI, this warrants a separate discussion. The lower Pb leachability for some cement mortars is worth investigating. Apparently, there is a different chemistry involved, which may be related to the reducing slag or increased reactive Fe phases.

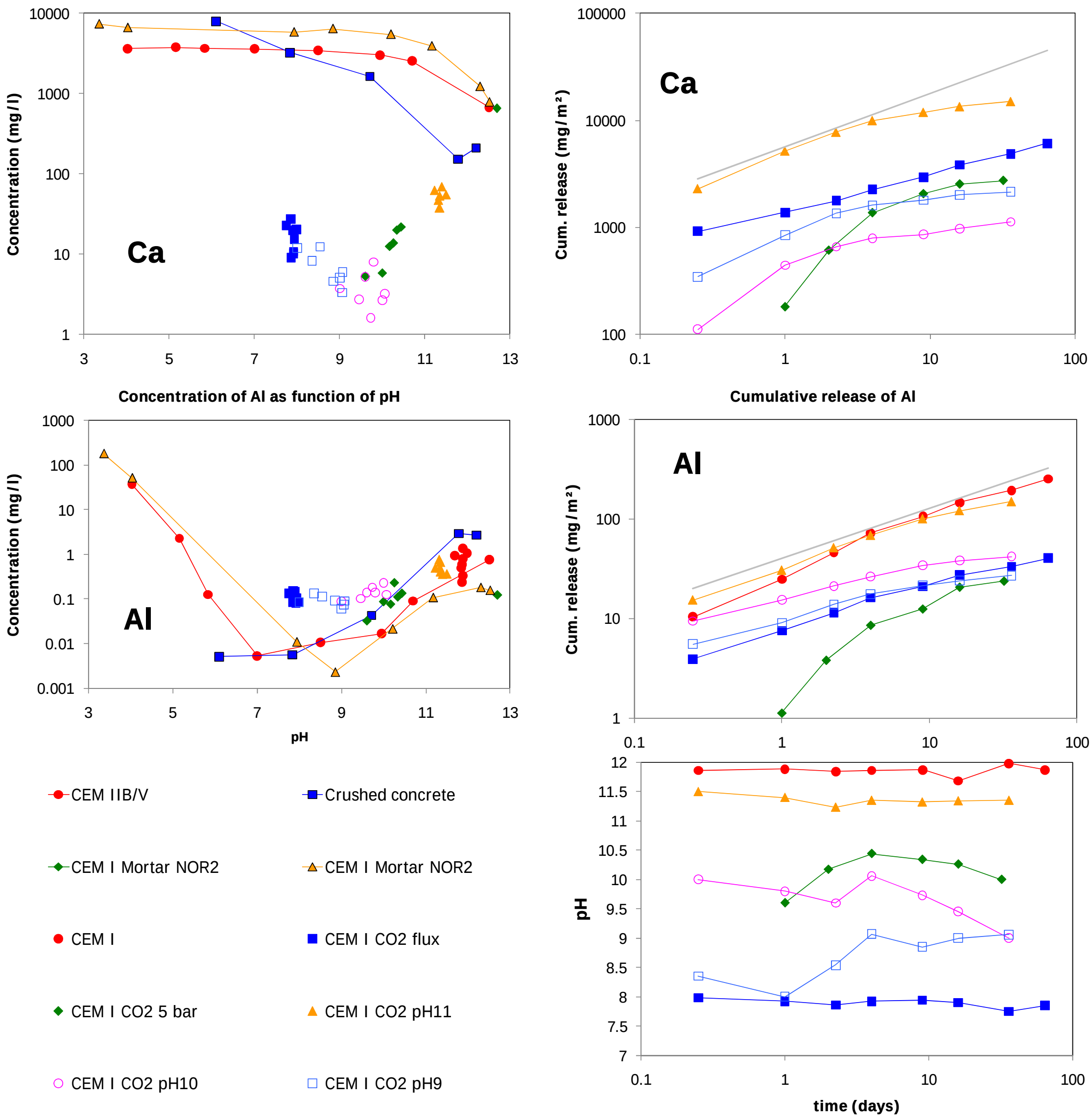


Figure 3.6 *Release of Ca and Al at ‘own pH’ and imposed pH (CO_2 bubbling in solution) in the tank leach test*

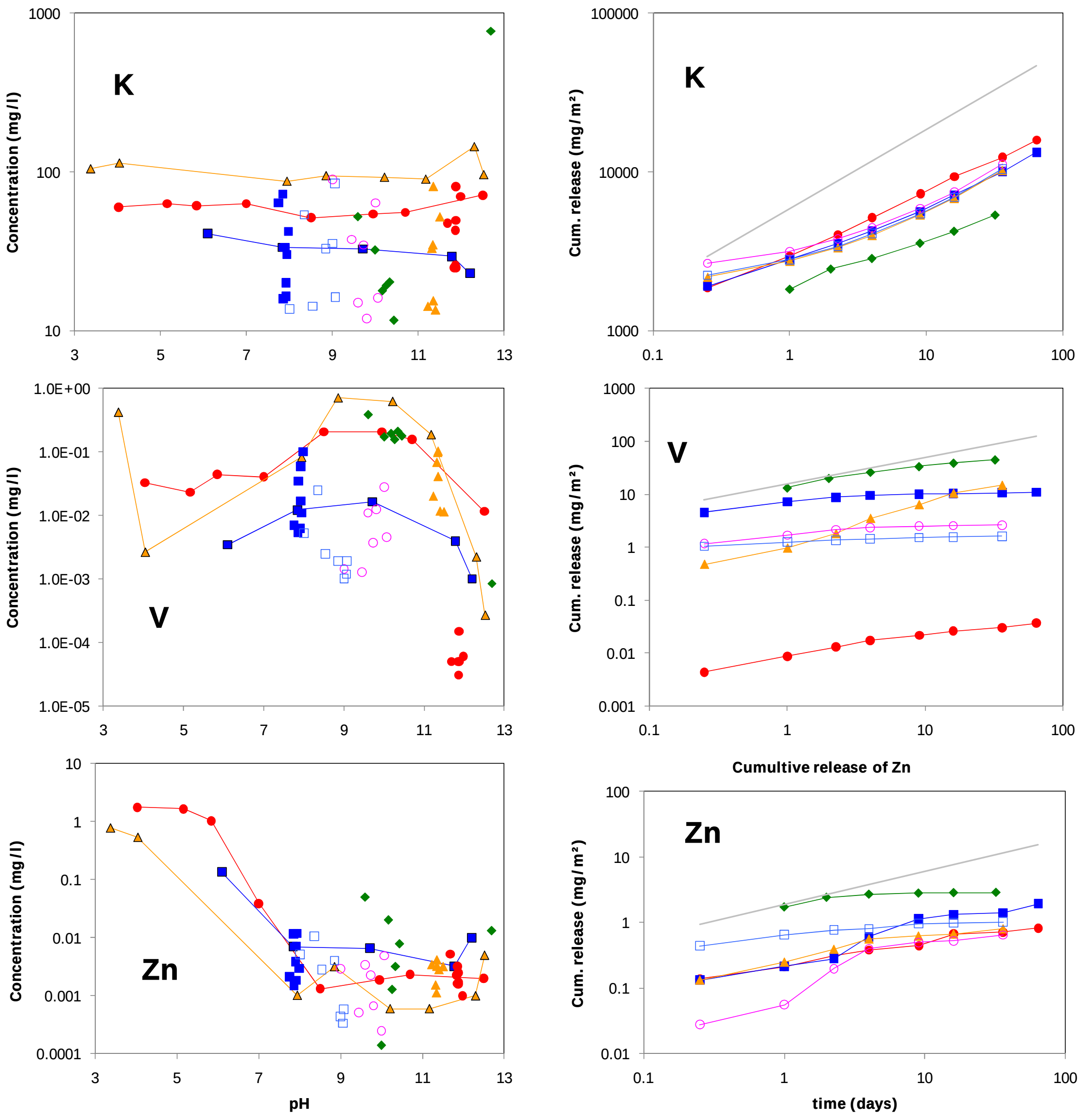


Figure 3.7 *Release of K, V and Zn at 'own pH' and imposed pH (CO_2 bubbling in solution) in the tank leach test*

From the tank leach test effective diffusion coefficients for the mortar have been derived, which within certain assumptions and as a simplification allows prediction of release at longer time-scale than measured in the lab. The effective diffusion coefficients (expressed as $pD_e = -\log D_e$; De in m^2/s) can only be used together with the corresponding availability data (in mg/kg mortar) to avoid over-predicting long term release. However, due to interactions at the interface (carbonation) the release based on an effective diffusion coefficients are over-predicting release. Using these data as starting point predictions can be made of release in long term (see section 3.9). Either the 'own pH' test data or the 'neutral pH' test data are used, depending on the exposure condition of the construction product (see discussion in section 3.6.4).

Tortuosity

From the tank test data, tortuosities for the different cement mortars can be derived. This the most crucial parameter to be derived from the test as it is a unique product specific property, that depends on a range of parameters (constituents in the mix, w/c ratio, curing conditions, ..). The tortuosity τ^2 describes the relation between the free mobility of a substance in water compared to the free mobility in the pore system of the mortar. Therefore the tortuosity is a measure for the porosity of the mortar, as it represents the tortuous path a diffusing ion (Na) has to travel through the matrix to reach the surface of the specimen. In table 3.10 the tortuosities calculated from K free mobility (assuming no retention in the matrix) for the mortars prepared from the different test cements are given. In comparison with the microstructural analysis very similar data on the cement mortars are obtained. N1, H6 and H1 are indicated as being least porous. H5 is the most porous from a microscopic observation, which is confirmed by the tortuosity measurement.

Table 3.10 *Tortuosities calculated from K mobility*

Code	τ^2	Code	τ^2
H5	250	H7	370
D2	270	N2	400
W2	310	N1	500
W1	370	H6	500
D1	370	H1	530
H3	800	H9	710
HOL-1	820	HOL-12	650
HOL-2	3836	NOR-2	1370
HOL-3	970	NOR-4	210
HOL-5	440	VDZ-1	Nd
HOL-7	Nd	VDZ-2	Nd
HOL-9	Nd		

3.5.7 Concise Test

The concise test is carried out on crushed material and is relevant for an evaluation in conjunction with the long-term behaviour of size reduced materials (construction debris) with neutralisation by carbonation and percolation dominated release regimes (van der Sloot et al, 1994). The 4 steps of the concise test address each of these issues:

- Two extractions at own pH using low (L/S=2) and high L/S (L/S=10). These results give an indication of solubility controlled species versus species being washed out easily. The low L/S reflects a relatively short time scale and L/S=10 reflects a long-time scale. The results of this part of the test are discussed in connection with the pore water data.
- Two further steps comprising leaching tests at L/S = 10 and pH 7 (in this study pH 8) and pH 4. The results from these tests are linked to the pH dependence test data. The pH = 7 measurement is relevant to identify the direction and magnitude of change in leachability as a result of neutralisation by carbonation. The pH 4 measurement provides a measure for the availability for leaching. In comparison with the total composition, this value, which is generally a fraction of the total, can be considered as a worst case environmental exposure condition.

The concept of this test, namely to assess key properties with a limited set of targeted test conditions, is very useful. Based on the present knowledge the conditions would have to be adjusted to provide efficient testing results. In the discussion on testing recommendations this aspect will be addressed. In figure 3.8 a comparison of the concise test data and the extended data is given.

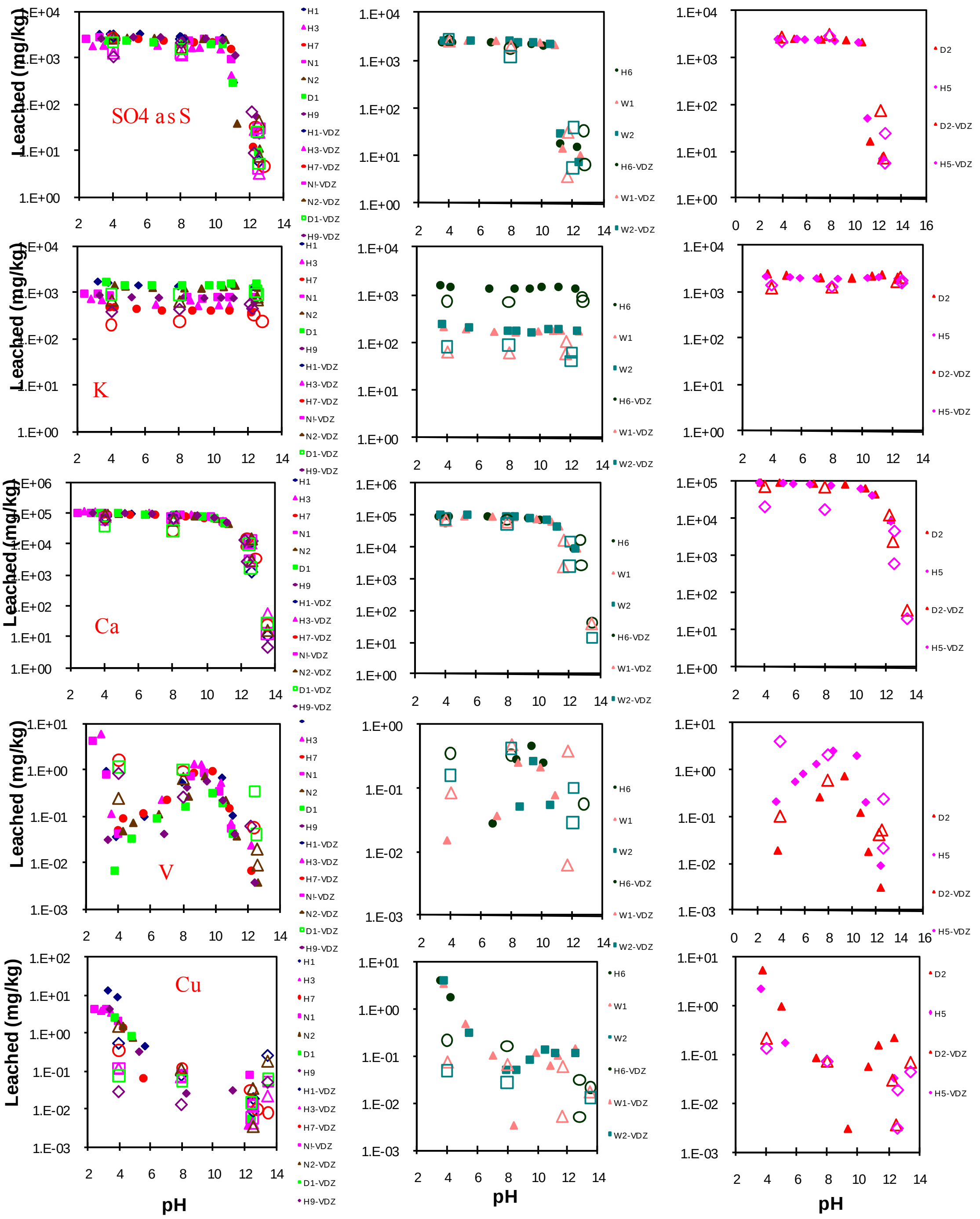


Figure 3.8 *Comparison of concise test and full characterisation tests for SO_4, K, Ca, V and Cu*

3.5.8 Pore Water Tests

In ECRICEM phase I pore water data were obtained by pressing water out of hardened mortar bars with a powerful press. This results in very small volumes, which limits the number of constituents that can be measured. In spite of this limitation, very useful data have been obtained. The data from the concise test and the pore water form a series of L/S values, which provide insight into the chemistry changes at low L/S (high salt load, larger pH differences).

The concentrations as measured in pore water are given in comparison with L/S 2 and L/S=10 data from the concise test (Figure 3.9). For K it is clear that almost straight dilution provides a rather good prediction of the concentration. However for other elements the relationship is not as clear cut. For Ca it is clear that at very low L/S solubility limitations are quite strong. For Cr, Cu, Zn and Ni, it seems a fairly straight relation is observed from L/S 2 down to pore water conditions for several specimen.

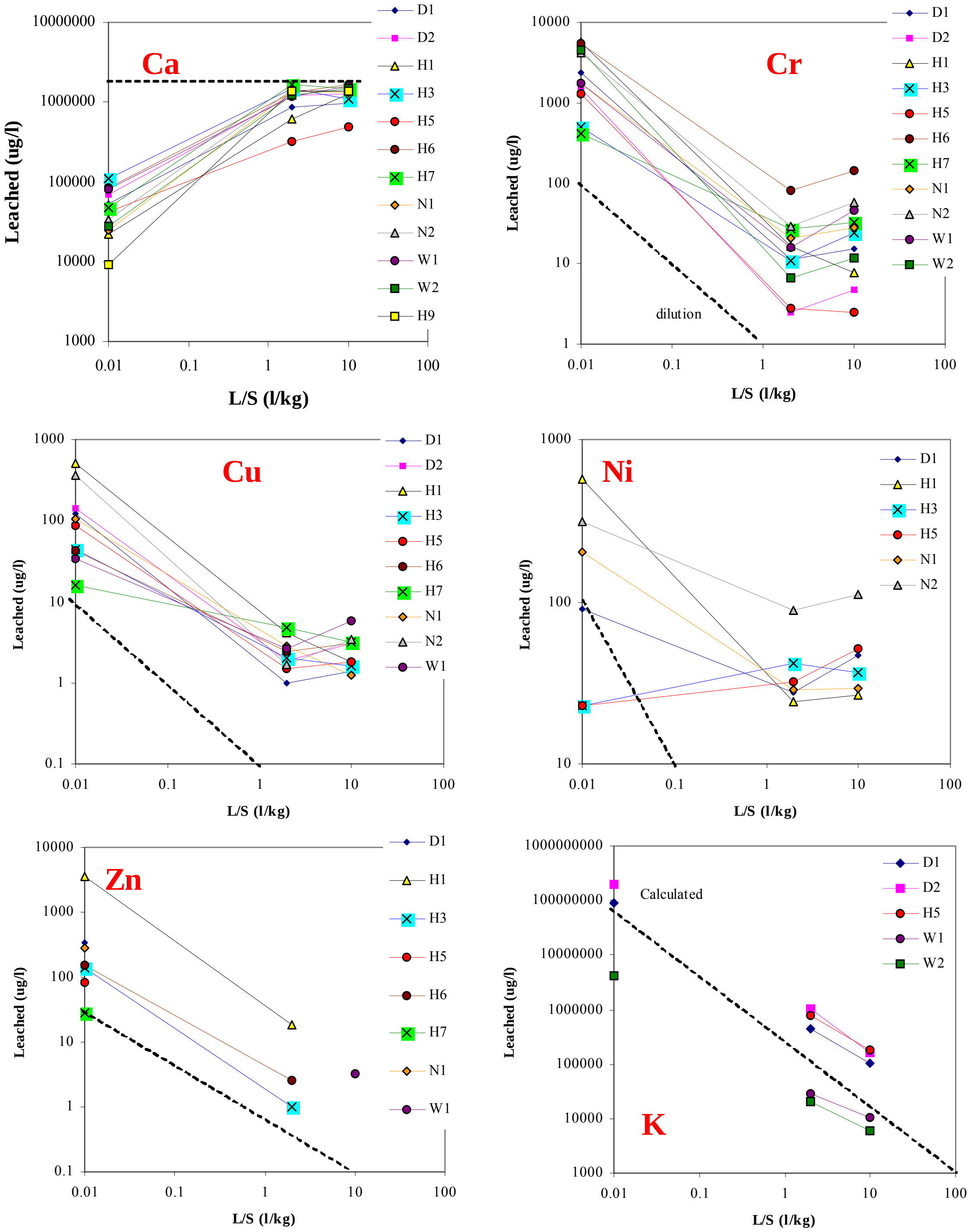


Figure 3.9 *Comparison of measured pore water concentrations with test data at L/S 2 and 10*

In table 3.11 the projected pore water concentrations as modelled using Orchestra starting from the solubility controlling minerals as obtained in the pH dependence test are given. The L/S used is 0.1.

Table 3.11 *Comparison of modelled and measured pore water composition*

	model	pore water		model	pore water		model	pore water
pH	13		pH	13		pH	13	
[Al+3]	26	3.5	[F-]	470		[PO4-3]	0.057	
[Ca+2]	119	43	[Na+]	2300	870	[H2CO3]	2.2	
[Fe+3]	0.14		[K+]	23000	15500	[SeO4-2]	0.052	
[H4SiO4]	18		[Cd+2]	0.062		[CrO4-2]	0.23	1.3
[SO4-2]	0.96	3	[Cu+2]	2.4	0.09	[H3AsO4]	0.62	
[Ba+2]	1.1		[Mn+2]	0.00002	0.07	[H3BO3]	2.1E-05	
[Mg+2]	0.00038		[Pb+2]	1.6		[MoO4-2]	0.12	0.063
[Sr+2]	1.07		[Zn+2]	59	0.08	[VO2+]	0.22	
[Li+]	49		[Ni+2]	0.05	0.02			

The prediction of pore water composition based on the chemical speciation information is quite good for several elements. The main deviation is observed for Cu and Zn, where a significant over-prediction of the concentration is observed. This is caused by the fact that incorporation of metals in hydrogarnets and similar solid solutions is not yet implemented in the model (thermodynamic data not yet incorporated in the Orchestra thermodynamic database).

3.5.9 Performance of Leaching Tests, Analysis and Uses of Test Data

Information on repeatability of the main test methods is available from in house comparison of the same sample for quality control purposes at ECN.

In ANNEX IX results of in house repeatability studies are presented for pH dependence test, percolation test and for the monolith leach test. (van der Sloot et al report, 2010)

For the elements of interest the repeatability in testing is quite satisfactory, provided the concentrations are not too close to the limit of detection.

The methods specified here have shown to have good repeatability, but information on the reproducibility (between lab variability) is not fully covered as yet. This information needs to be generated through an intercomparison validation study (ongoing work in CEN/TC351).

In a summary of performance of characterisation leaching tests related to the validation of the leaching tests applied in this work, the various parameters possibly affecting release have been addressed (van der Sloot et al, 2010).

3.5.10 Leaching of Chromate

A EU regulation on Cr reduction in cements (EU Directive 2003/53/EC) has been implemented. The objective is to reduce the formation of chromate upon wetting cement and the occupational exposure of the skin due to this chemical. The method to be applied involves an extraction with water and the solution is analysed spectrophotometrically at 540 nm. From figure 3.10 it is clear that there is no direct relationship between Cr VI in cement and total Cr in cement. The Cr VI measurements may have been carried out at a time beyond the time scale considered safe for having an active ingredient. This implies that some data should have been lower than observed here. This aspect can become a serious limitation.

The relationship between leachable Cr VI (All Cr leached at pH > 7 is chromate) and total Cr is lacking for blast furnace slag (BFS) cement, blended cement, fly ash cement, lime cement and Cr reduced cements. The shelf life of additions to ensure Cr reducing are limited in most cases, which could pose a problem in the market. For CEM I there appears to be a rather good correlation between leachable Cr VI and total Cr. This relationship shows that a more or less fixed fraction of the total Cr entering the kiln is converted to Cr VI.

Leachable Cr (L/S=10, pH 9 - 10, 24 hrs) in mg/kg = 0.11 (± 0.02) * Total Cr (mg/kg)

BFS cement and blended cements containing slag all show a low Cr VI leachability. When the Cr VI in cement is compared with Cr VI leachable, the correlation is very poor (figure 3.11). This probably relates to the fact that in case of the Cr VI measurement in cement only a very short contact time is allowed. This factor would be expected to be the most sensitive parameter in this analysis. A time series measurement is expected to reveal that Cr VI continuously drops with time.

In figure 3.12 the Cr and Zn leaching from cement mortar as function of pH is given. The shape of the leaching curve for Cr is typical for Portland cement in that the leachability is highest at low pH (Cr III leaching). Then from pH 5 to 11 leachability is not affected by pH (Cr VI leaching) and subsequently at pH > 11 Cr substitution for sulphate in ettringite is kicking in. In BFS cement, a markedly different behaviour is noted. Here Cr leaches at low pH (Cr III) and then leachability is very low at pH 6 -11. Then a slight increase is noted. All situations in between are related to varying degrees of Cr VI reduction and interaction with the matrix (PbCrO4?). From the comparison between total and leachability it is clear that total has no relation to leaching. For cements with the same content the leachability can be a factor 1000 to 10000 different. In case of Zn, the leachability is unaffected by the slag addition. The same conclusion as for Cr applies that there is no relationship between leachability and content.

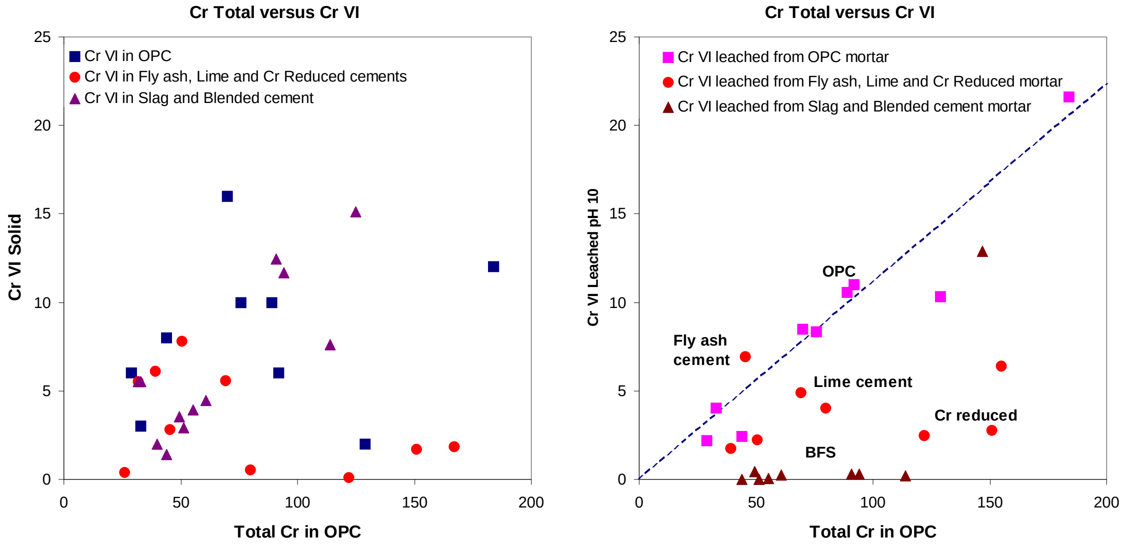


Figure 3.10 *Cr VI in solid cement (TRGS 613, similar to EN 196-10, 2004) versus total Cr and Leachable Cr VI (L/S=10, t=24 hr, pH 9 - 10) versus total Cr*

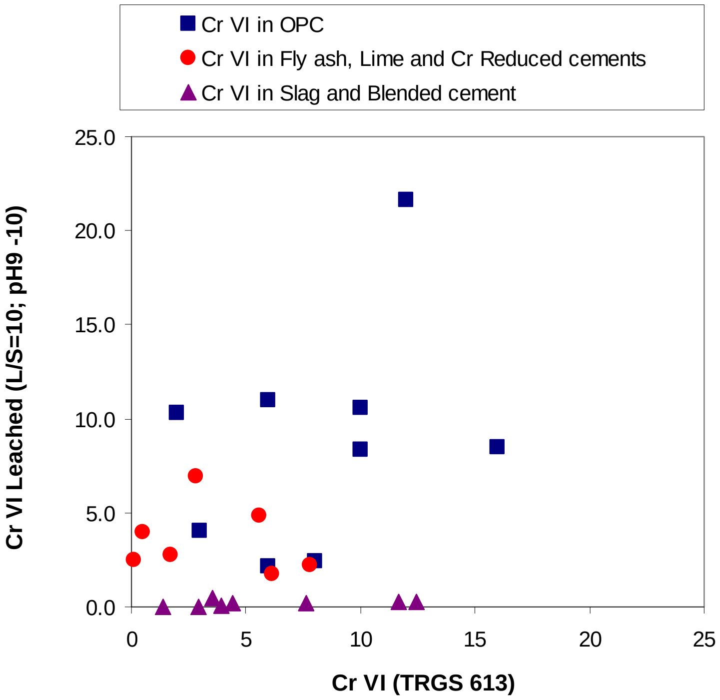
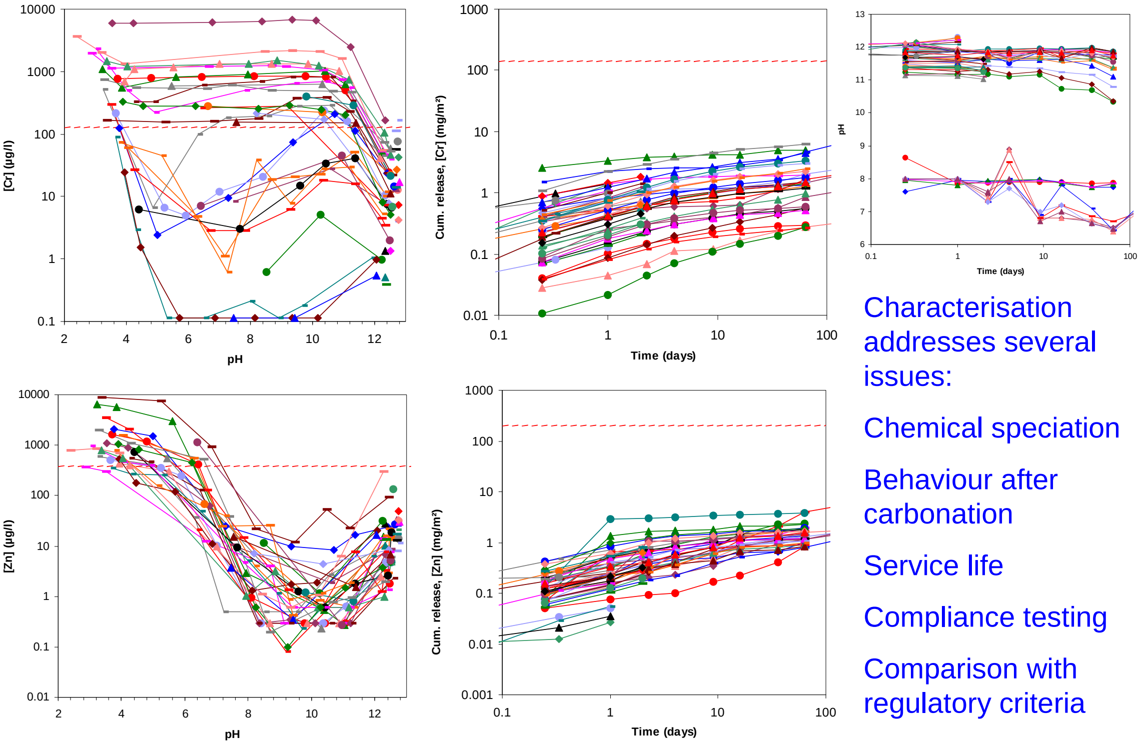


Figure 3.11 *Cr in solid cement (TRGS 613, similar to prEN 196-10: 2004) versus leachable Cr VI ((L/S=10, t=24 hr, pH 9 - 10)*



Characterisation addresses several issues:

Chemical speciation

Behaviour after carbonation

Service life

Compliance testing

Comparison with regulatory criteria

Figure 3.12 *Characterisation test results (TS 14429 and DMLT renewal) for > 50 worldwide OPC and blended cement mortars with and without carbonation for Cr and Zn*

3.5.11 Chemical Speciation and Binding Aspects of Cr

Based on the pH dependence leaching test data chemical speciation modelling (here LeachXS-Orchestra, 2006; Meeussen, 2003) can be applied to identify the solubility controlling phases and the binding mechanisms for elements in the cement matrix. In figure 3.13 and 3.14 this type of modelling is shown for Cr illustrating the partitioning in solution as well as the partitioning in the solid phase. In the solid phase, the role of $Cr(OH)_3$, $BaSO_4$-$BaCrO_4$ solid solution and incorporation of Cr in ettringite is of relevance. It is also clear that different phases control solubility in different pH domains, which is important to assess the consequences of carbonation after long term exposure to field exposure conditions. The potential for this type of modelling for new development in cement application may prove an interesting spin-off of this environmental evaluation work.

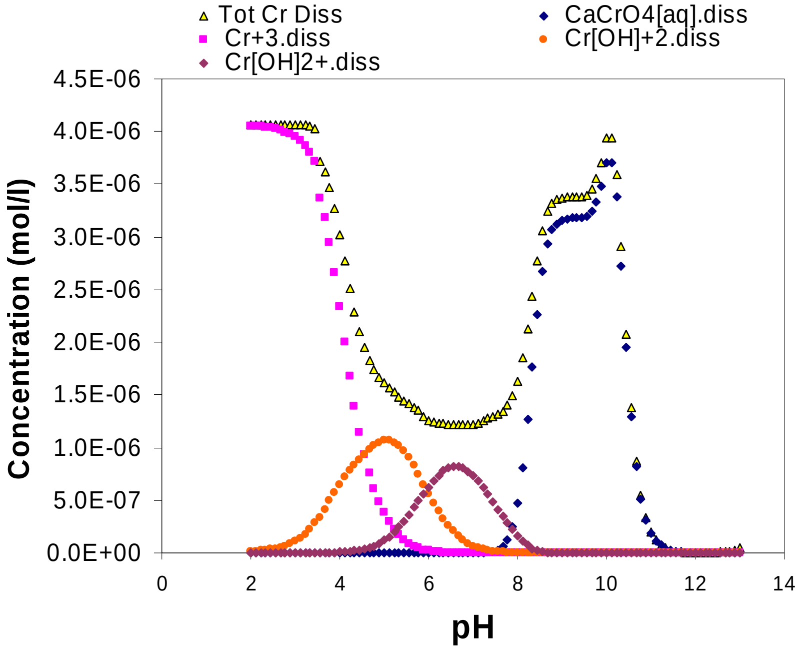


Figure 3.13 *Chemical speciation also provides information on specific dissolved chemical forms present as illustrated here for pH dependent leaching test results for Cr in cement mortar*

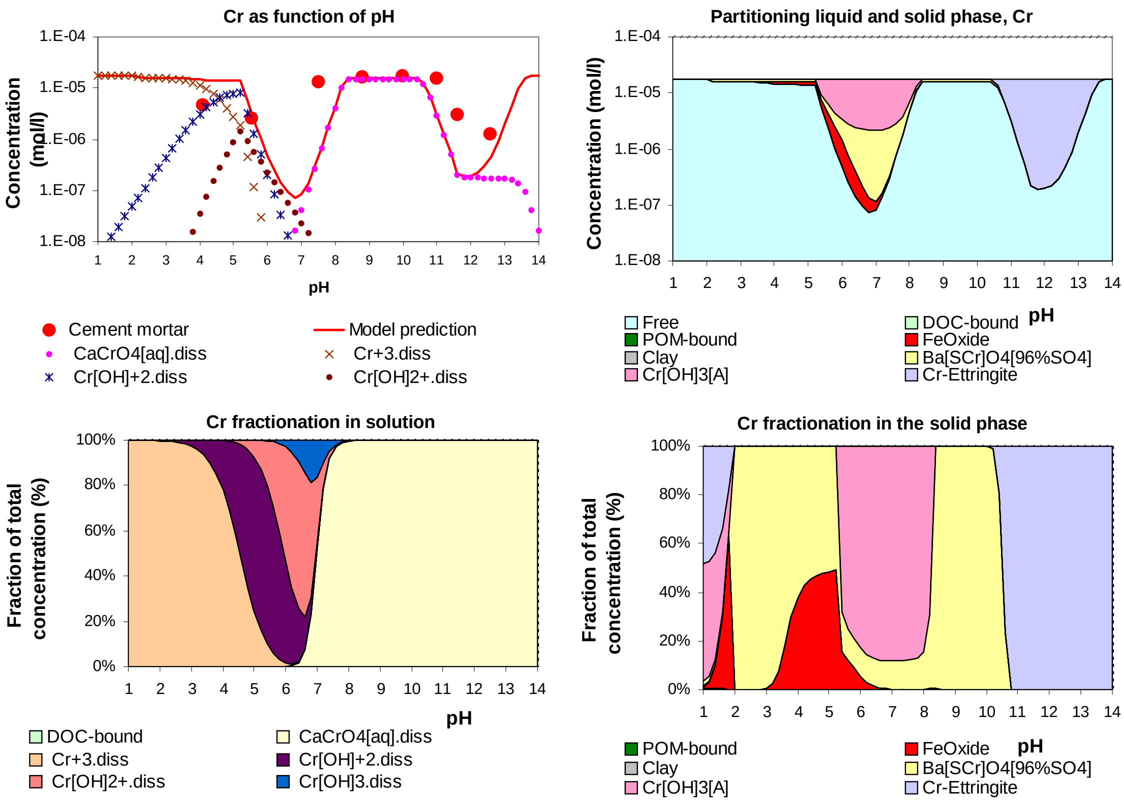


Figure 3.14 *Chemical speciation of Cr in cement mortar leaching in both solid and liquid using the LeachXS-Orchestra model environment*

A major misunderstanding in relation to environmental impact of materials, is that mineralogy of the solid matrix is a determining step in the release. This is often not the case. The mineral phases at the interface of the product, which are formed in the interaction with the surroundings, are crucial in the release process. An element may be mobile in the alkaline matrix, but as soon as the pH has reached a given pH precipitation occurs and the release process stops. The surface may be oxidised and carbonated and may as such be changed. For oxyanions an important binding mechanisms is the substitution for sulphate in ettringite or related phases. This ettringite formation and interaction with ettringite can be observed for sulphate, Mo, As, Se, Cr and V from the decrease in leachability at pH >11. For the metals minerals would be relevant, but in addition sorption may very well be relevant for the release characteristics.

3.5.12 Conversion of Chromate to Cr III During Service Life

The question arises what happens to chromate in concrete during service life. Will it be leached or is it slowly converted to Cr III and thus rendered non-leachable?

Concrete has been studied that has been exposed to leaching in halfway submersed condition for about 40 years (Test facility in Stuttgart, Germany).

Samples of mortar were isolated from coarse gravel to obtain a true comparison with mortar samples tested in the ECRICEM program.

The concentration profile has been analysed from a depth profile above water, while a core sample form the underwater section was recovered. In the core samples from above and below water pH controlled leaching was carried out at mild alkaline and neutral pH conditions.

Characterisation leaching data for fresh German cements (D1, D2, VDZ 1 and VDZ 4) are available. This information has shown that leachability of Cr is maximal at mild alkaline conditions (pH 9 -10). Besides Cr as chromate, leaching data for oxyanions like Mo, V and B are available.

Hypothesis: Chromate Cr from Portland cement is slowly converted to Cr III in the cement matrix during service life. This process goes faster under submersed conditions than above water. Chromate is leaching from the carbonated surface layer and depleted in that section, but also limited to that section.

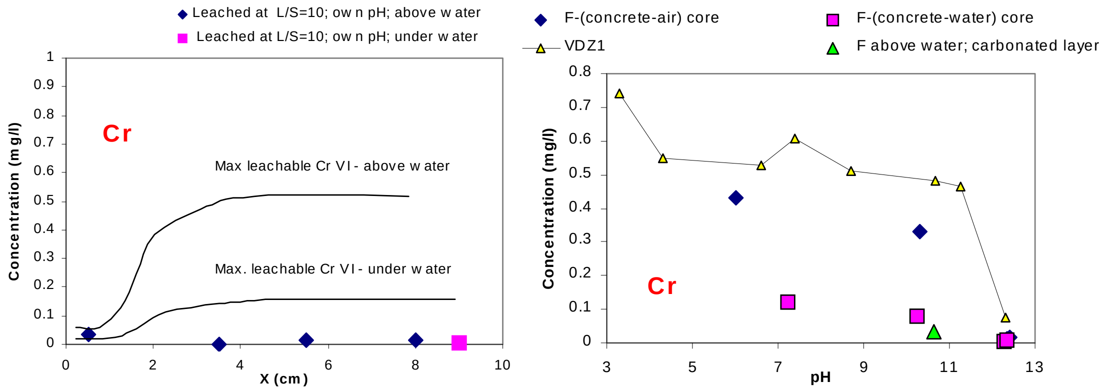


Figure 3.15 *Left: Profile of Cr in the F Stuttgart sample in section above water (blue diamand) and in core sample from the section below water (purple square). Based on pH dependent data the total Cr VI profiles above and below water are derived. Right: pH dependence data for core sample above water (blue diamond) and for core sample below water. For comparison, pH dependence data for Germans cement mortar are given*

Cr in core above water is reduced, Cr below water is more reduced and in the carbonated layer even more reduced (figure 3.15). In the profile, Cr is very low compared to the available Cr. It corresponds to Cr leaching at the high pH in the profile, except for the surface carbonated sample. Since the pH in the carbonated sample is 10.6, this is the point where Cr leaching is highest. Consequently, the Cr measured in the carbonated layer reflects the total leachable Cr. The drawn lines in the left figure reflect this. These observations imply that Cr has not been leached from the part of the concrete with high pH (pH >12). The difference in Cr between the under water and above water section can thus only be attributed to conversion of Cr VI to Cr III during service life. It would seem that also the Cr in the above water part of the concrete has been reduced. This is further supported by the observation that oxyanions like B, Mo and V, which show similar leaching behaviour as Cr (Mo more mobile that Cr) do not show any change between above and under water core (figure 3.16). The lower Cr leachability in C&D waste as compared to fresh mortar further supports this observation.

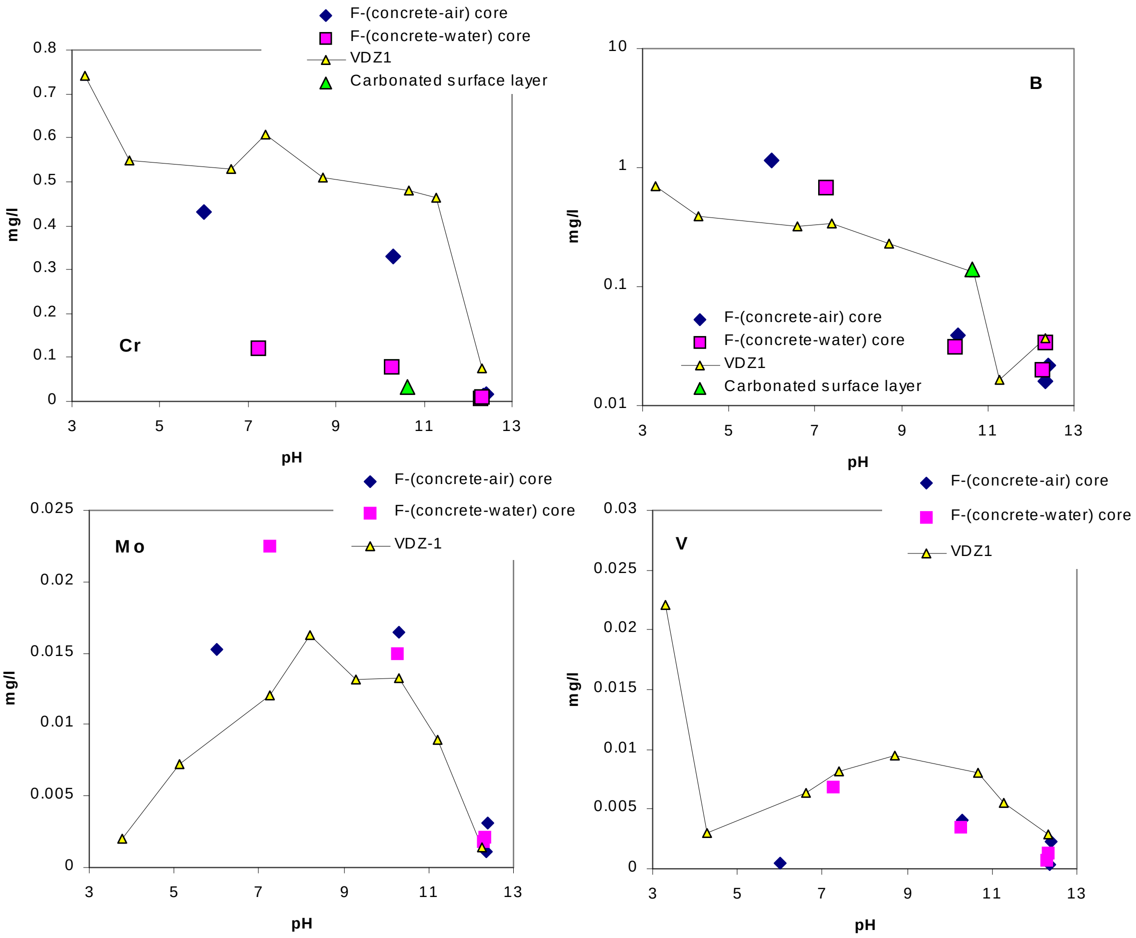


Figure 3.16 *pH dependence test data on Mo, Cr, B and V for the F Stuttgart sample in comparison with pH dependence test data for German cement mortar*

3.5.13 Effect of Very High Metal Loadings from Aggregates or Additives

Pb and Zn Additions

Leaching experiments with Pb/Zn-slag as aggregate in concrete, as fine ground material and as straight addition of PbO and ZnO to cement paste have been carried out as a side study in relation to a study on alternative materials in pavement applications (UNH, 2000). This work has resulted in levels of Pb and Zn in the concrete cubes far exceeding any of the compositions in this work. The Pb concentrations in the concrete containing Pb/Zn-slag as aggregate and concrete containing PbO/ZnO as addition to the cement paste are respectively 8750 and 9190 mg/kg. The Zn concentrations in these two materials are respectively 29800 and 22800 mg/kg.

In Figure 3.17 the pH dependence test data on size reduced cubes are shown in comparison with cements studied in this work. In the relevant pH domain pH 7 - 11 no significant change in leachability was observed with PbZn slag for Pb due to the solubility control dictated by the cement matrix. For Zn added as ZnO an increased leachability is noted. At pH > 12 both Pb and Zn increase significantly. No change is observed for Zn in the Pb/Zn-slag as aggregate

In the tank test on specimen with Pb/Zn-slag and with PbO and ZnO addition to cement, the almost 400 fold increase of the Zn and more than 500 fold increase in Pb concentration in ZnO and PbO doped mortar results in a 20-fold increase in the leachability from the tank test at own pH. For Zn in Pb/Zn slag aggregate mortar, no increase is observed (Figure 3.18). It appears that, Zn incorporated during the clinker production (special 'spiked' cements) does not lead to a different leaching behaviour than direct addition of ZnO to the cement paste. If over the testing period only a limited change in pH occurs, the pH dependence test data can be used to obtain an estimate of the magnitude of change in release from the tank leach test.

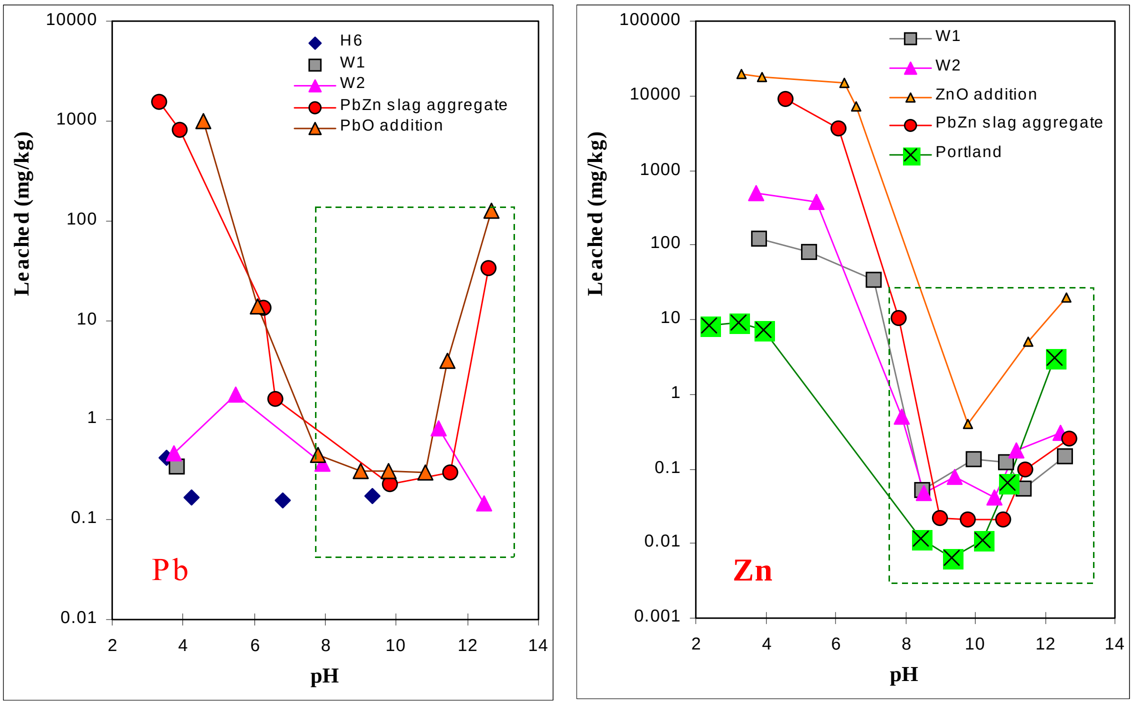


Figure 3.17 *Leaching behaviour of crushed concrete with different levels of Pb and Zn*

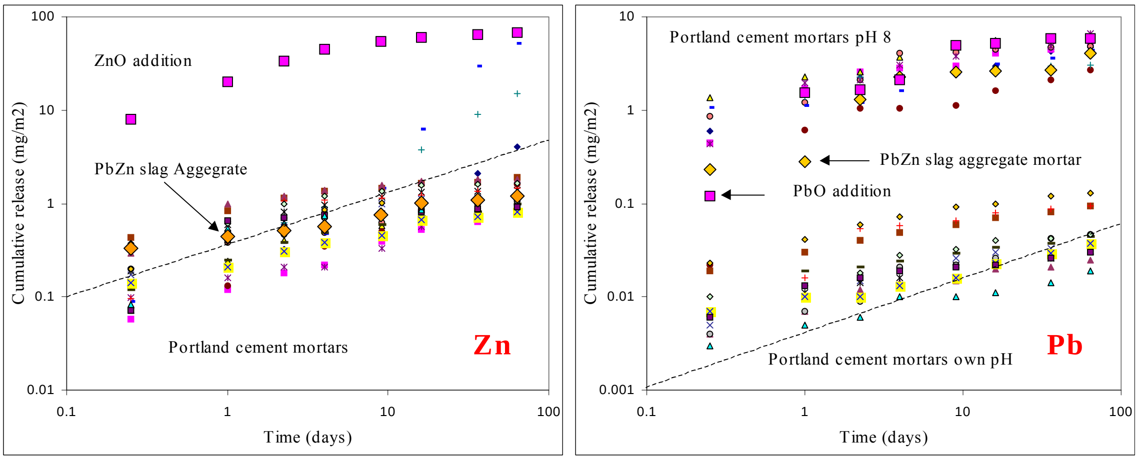


Figure 3.18 *Tank test results for Pb and Zn from Pb/Zn-slag as aggregate and PbO and ZnO additions to the paste in comparison with regular Portland cement*

The leaching characteristics of the hardened cement mortars have been determined by examining the leaching behaviour as a function of pH in the pH range 3 -13, which has revealed very consistent and systematic leaching patterns, which are not as obvious from tank leach tests (dynamic leach test providing time dependent release information). The leachability in the pH range 5 to 13 is most relevant from an environmental point of view, as field exposure conditions may well cover this range.

The special “spiked” cements have leaching characteristics very similar to the other regular OPC‘s. The leached amount for elements occurring mainly as oxyanions (Cr, Mo, As, Sb) is increased.

Significant differences in generic leaching behaviour as a function of pH as determined in previous work for metals, oxyanions and salts have been reconfirmed. Metals generally show a minimum leachability at neutral pH. Oxyanions feature a maximum leachability at neutral pH, and salts show no relation with pH.

Similar to the situation on other fields, the pH dependence test forms a solid basis of reference for mutual comparison of hardened cement mortars in various exposure scenarios.

A distinction must be made between the cement phases controlling the leachability of the bulk of the element present in the cement matrix and the solubility controlling phases dictating leachability of elements at the surface of the test specimen, which are exposed to external conditions (air, water, etc). The leachability amounts generally to a small fraction of the total composition.

3.5.14 Relationships between Test Methods

All leaching tests are conventions, by which leaching is examined under the specific conditions of the individual test. For example compliance tests provide short-term testing of monolithic or granular samples. Full characterisation tests provide longer-term information on granular materials under various pH conditions. The different tests can individually and complementarily contribute to the overall understanding of the leaching behaviour. At the end only through modelling it will be possible to describe this leaching behaviour under certain environmental exposure conditions. A single test, however, can give useful information if the general leaching behaviour of a trace element is known and single test data are shown together with full characterisation data. Therefore, it is important to know, how the different test results are related to each other.

The magnitude of change in leachability in the pH dependence test is to a large extent reflected in the change in leachability from a monolith in a tank test exposed to different chemical environments. However, while the pH dependence test is aimed at steady state conditions, the tank leach test reflects the dynamic aspects of leaching due to the 8 times changing of leachant during the test.

In table 3.12 a comparison is given of differences in release in the tank leach test between pH 8 and the own pH (generally in the eluate 11-11.5; for the cement matrix pH >12) and pH dependence test data between pH 8 and pH >12 and pH 8 and pH ~11, respectively. A number smaller than 1 points at a higher release at high pH (Al, Zn). Although a direct conversion is not possible the trends as observed in the pH dependence test can definitely be recognised and even to a large extent quantified in the tank leach test. This type of consistency would be expected, but given the variability within leaching tests it is good that it has been confirmed.

Table 3.12 *Comparison of pH effects between tank test (own pH and pH control at pH=8) and pH dependence test*

	Tank test	pH dependence test	
	Ratio pH8/pHown	pH8/pH>12	pH8/pH11
Al	0,07	0,04	
Co	5,12	4,90	
Cr	0,88	21,29	1,13
Fe	1,34	2,29	
Mo	4,30	10,61	0,74
Na	1,02	1,20	1,11
P	23,21	22,92	6,69
S	1,17	218,15	22,39
Si	13,59	41,91	4,65
V	117,54	146,73	
Zn	0,27	0,45	

The difference between tank leach test results at own pH and controlled pH is significant for several elements (Al, Pb, Cd, Sb, Cr, Mo). In the judgment of the exposure conditions in a given application this aspect has to be factored in.

3.5.15 Leaching of Construction Debris

To assess the release from cementitious materials in recycled and end of life scenarios, size reduced material is tested. A preliminary evaluation can be obtained from the pH dependence test, as it indicates release behaviour in size reduced form and release at a lower pH as imposed by carbonation (figure 3.19 and 3.20). An aspect not covered in that evaluation is the particle size effect, which will generally lead to a lower release for larger particles, except in cases where solubility controls release.

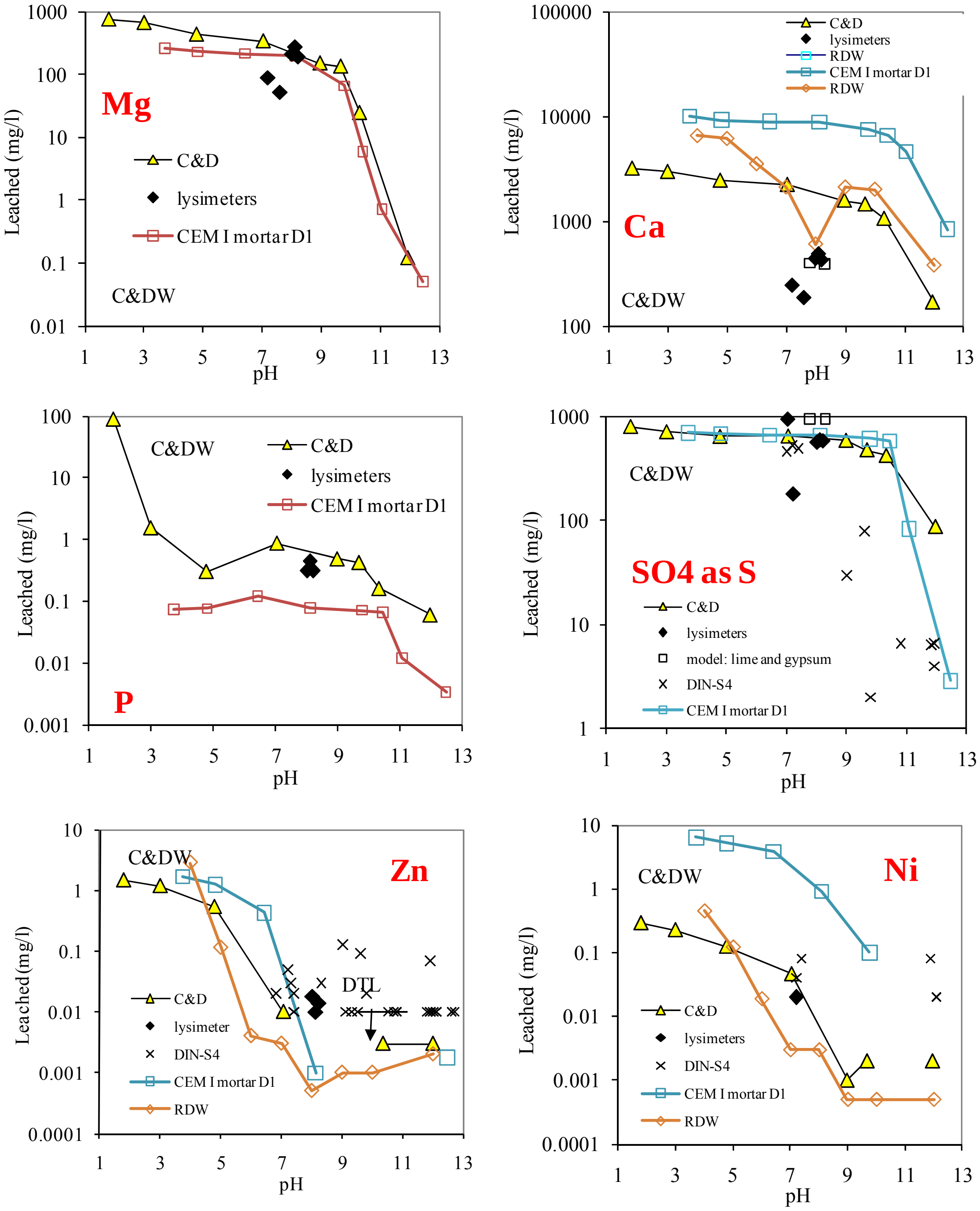


Figure 3.19 *C&D waste leaching in comparison with field data. For comparison, a cement mortar is included.*

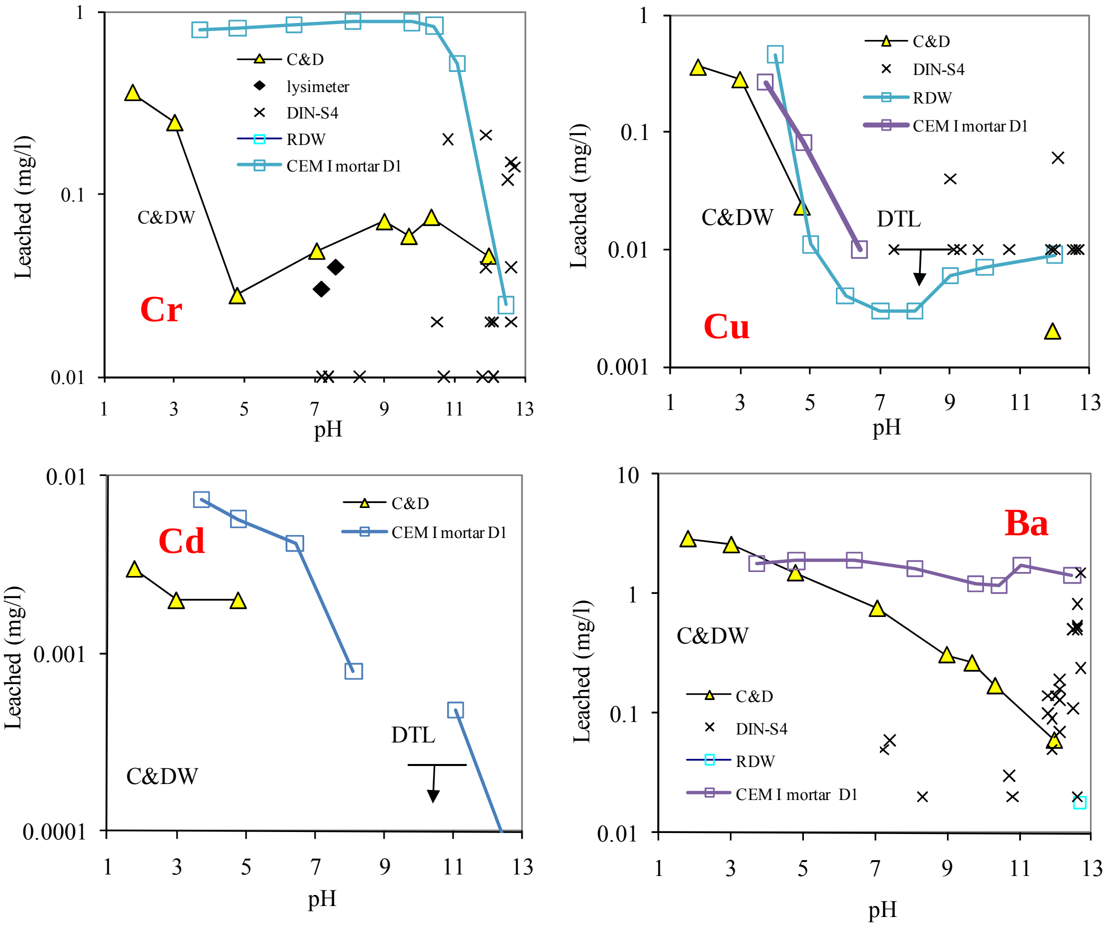


Figure 3.20 *C&D waste leaching in comparison with field data*

For several parameters the results between C&D and cement mortar are not very different (Mg, Zn, P, SO_4, Cu). For Cr, the leachability is substantially less (see discussion in section 3.5.12). For Ca, the release is affected by the degree of carbonation. The lysimeter data on C&D waste fall fairly well in range with the pH dependence test data for Ni, Mg, Zn, P, Cr and sulphate. The batch test data (marked DIN-S4) show a wider scatter, but generally fall within the range between mortar and C&D.

Using leaching data for granular C&D waste the release of constituents can be projected by assuming either high pH (uncarbonated material) or fully carbonated material. In table 3.13 the comparison with criteria for unbound, free application (SQD, 2007) are given.

Table 3.13 *Comparison of size reduced material at high (uncarbonated) pH and after full carbonation with regulatory criteria for unbound use*

Parameter	High pH condition C&D	Size reduced to < 4 mm Fully carbonated	Criteria unbound, free use
L/S	10	mg/kg	mg/kg
As	0.03		0.9
Ba	0.1	20	22
Cd	0.002	0.016	0.04
Cl	190		616
Co		0.24	0.54
Cr	0.23	13.2	0.63

Cu	0.033	0.03	0.9
Mo	0.044	0.33	1
Ni	0.0158	9.7	0.44
DOC	33.4		107
Pb	0.2	0.32	2.3
SO_4 as S	93	2300	5200
Sb		0.08	0.16
Se		0.10	0.15
V	0.01	0.8	1.8
Zn	0.1	0.14	4.5

More detailed modelling is needed, as the particle size does not correspond with actual use of construction debris. A larger particle size will most likely lead to a lower release.

3.6 Field Observations as Reference Base for Model Prediction

Samples taken from a core from a 120 year old fort (Pampus, island 10 km east of Amsterdam) of a concrete wall exposed to moist conditions were subjected to leaching at L/S=10. The mortar is more porous than current Portland cement mortars. In the 120 year exposure, the carbonation front has progressed 2 – 3 cm into the product, as shown by the dye test (see section 2.7.2). Samples taken from a test concrete exposed to partial immersion for 40 years (Schiessl et al, 2003) were also subjected to a leach test at L/S=10 at own pH conditions. The cores were taken from the section above and below water. Samples taken from the interior of a piece from a Roman aqueduct (2000 years old and fully carbonated) were also tested at L/S=10. All test data obtained from cores taken from the field samples by batch leaching tests at own pH or controlled pH (according to individual steps of the pH dependence test) have been compared with two regular Portland cement mortars (D1 and NOR 2) as shown in figure 3.21 and 3.22.

Under wet / dry cycles of exposure the carbonation progresses faster as CO_2 from the atmosphere diffuses faster in air filled pores than carbonate can diffuse in water saturated pores. Since the leaching of substances is influenced strongly by pH, changes in pH in the surface of exposed specimen will affect release of substances.

On the other hand, the alkaline concrete surface forms a sink for dissolved metals. This was observed for Mn, in particular, when Mn levels in surface water increase in autumn as a result of reducing conditions developing in the sediments due to decay of organic matter (van der Sloot et al, 1987).

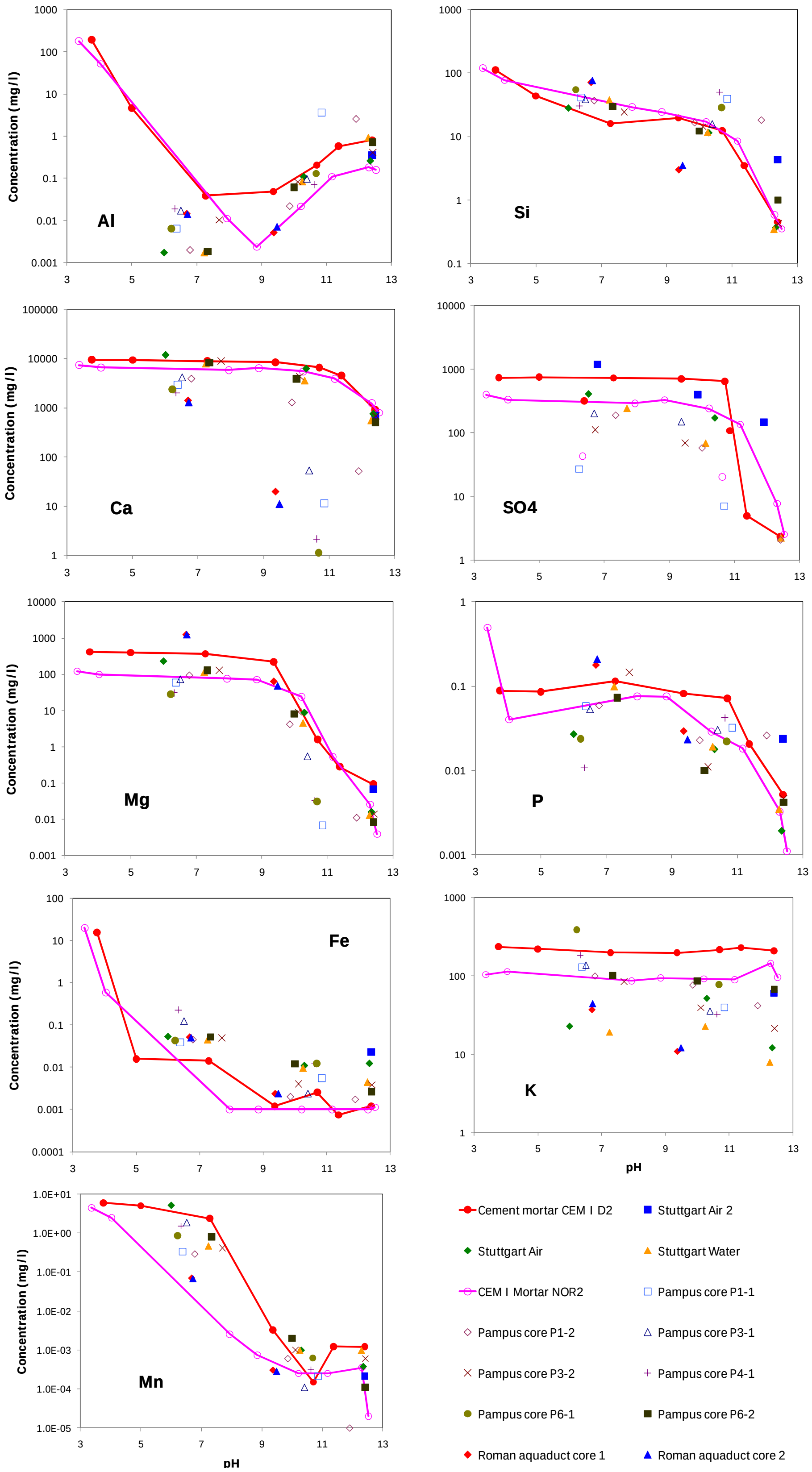


Figure 3.21 *Comparison between extracted samples from cores taken from the field and pH dependence test results for cement mortars*

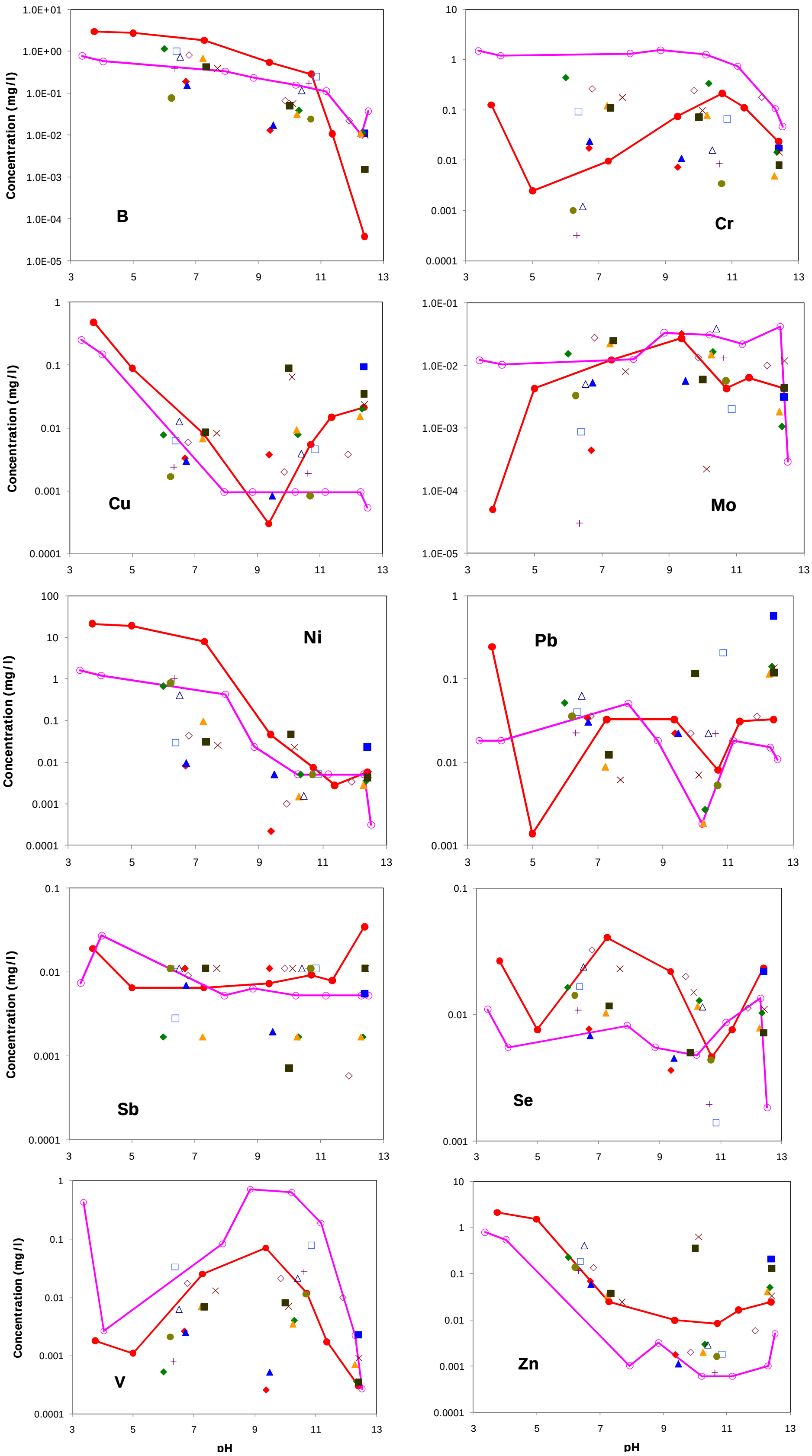


Figure 3.22 *Comparison between extracted samples from cores taken from the field and pH dependence test results for cement mortars*

The leaching trends between the field samples and the pH dependence test data are generally consistent, in particular for the major elements. The exception is Ca, which reflects the carbonation that leads to formation of calcite and subsequent lower Ca leachability. With the exception of Cr, which shows a much wider scatter in release (see also 3.5.12), the trends in leaching as a function of pH are largely followed in the field samples as compared to the characterisation testing of the mortar samples. In some cases, lower concentrations can be attributed to already leached substances from surface exposed materials (e.g. K, Mo, SO_4).

3.7 Geochemical Modelling

The modelling of geochemical reactions in cementitious materials forms the basis for the prediction of a long-term release of constituents. The understanding of the solubility controlling factors will provide a basis for predicting long term behaviour and as such can be used as a means to set limits for the input of specific constituents in clinker.

The output of the LeachXS program (see www.leachxs.net) is a list of saturation indices (SI value) for element-mineral combinations. This allows a comparison of the extent to which a given mineral phase may be controlling solubility of a particular element. An SI close to 0 is indicative of possible solubility control. Generally, a range of measured pH values should show SI values approaching 0. A single data point is insufficient. Over the entire pH range from pH 4 to 12 a few mineral phases may be relevant. SI values between +0.5 and – 0.5 (factor 2 in concentration) are considered a good match.

The geochemical modelling focuses at the phases in hardened cement paste that are relevant from a leaching point of view. It should be realised that the external conditions of cement products exposed to the environment largely determine the release. The material may have a very high buffer capacity, but, if that buffer capacity is supplied in a very slow rate, the surface may become neutralised and as such reflect leaching behaviour under neutral conditions rather than behaviour in a high pH environment.

By geochemical modeling relevant solubility controlling phases have been identified, that play a role for a wide range of cement mortars. Ettringite substitution has been implemented to describe leaching behaviour at high pH. Chemical reaction/transport modelling is the only means of making long term predictions of release from cementitious products.

3.7.1 Geochemical Modelling of the Cementitious System from pH Dependence Leaching Test

Using Orchestra embedded in LeachXS (van der Sloot et al, 2008) the geochemical fingerprint of cement mortars is obtained by taking all relevant mineral phases (minerals marked with AA are from Lothenbach et al, 2007 and 2008) , solid solutions and sorption reactions into account.

In figure 3.23 the full mechanistic model prediction is provided in relation with the actual measurements.

In figure 3.24 the partitioning of elements between dissolved and particulate phases is given for a few elements. More details are provided in Annex X for a typical cement mortar (NOR2). In Annex XI, the results of using the same chemical speciation fingerprint to describe release from different cement mortars is given.

Table 3.14 Input data for geochemical modelling

Prediction case	CEM NOR 2		
Sum of pH and pe	15.00		
L/S	10.0000		
Clay	0.000E+00	**kg/kg**	
HFO	2.000E-04	**kg/kg**	
Reactant concentrations		**Selected Minerals**	
Reactant	**mg/kg**	AA_2CaO_Al2O3_SiO2_8H2O[s]	
Ag+	not measured	AA_2CaO_Fe2O3_8H2O[s]	
Al+3	1.855E+03	AA_2CaO_Fe2O3_SiO2_8H2O[s]	
H3AsO4	7.626E-02	AA_3CaO_Al2O3[Ca[OH]2]0_5_[CaCO3]0_5_11_5H2O[s]	
H3BO3	8.026E+00	AA_3CaO_Al2O3_6H2O[s]	
Ba+2	3.299E+01	AA_3CaO_Al2O3_CaCO3_11H2O[s]	
Br-	not measured	AA_3CaO_Al2O3_CaSO4_12H2O[s]	
Ca+2	7.572E+04	AA_3CaO_Fe2O3[Ca[OH]2]0_5[CaCO3]0_5_11_5H2O[s]	
Cd+2	3.638E-02	AA_3CaO_Fe2O3_6H2O[s]	
Cl-	5.000E+01	AA_3CaO_Fe2O3_CaCO3_11H2O[s]	
CrO4-2	1.577E+01	AA_3CaO_Fe2O3_CaSO4_12H2O[s]	
Cu+2	2.599E+00	AA_4CaO_Al2O3_13H2O[s]	
F-	5.000E+01	AA_4CaO_Fe2O3_13H2O[s]	
Fe+3	2.045E+02	AA_Al[OH]3[am]	
H2CO3	5.000E+03	AA_Anhydrite	
Hg+2	not measured	AA_Brucite	
I-	not measured	AA_Calcite	
K+	1.251E+03	AA_CaO_Al2O3_10H2O[s]	
Li+	1.568E+00	AA_CO3-hydrotalcite	
Mg+2	1.249E+03	AA_Fe[OH]3[microcr]	
Mn+2	4.562E+01	AA_Gibbsite	
MoO4-2	4.197E-01	AA_Gypsum	
Na+	1.250E+02	AA_Jennite	
NH4+	not measured	AA_Magnesite	
Ni+2	1.665E+01	AA_Portlandite	
NO3-	5.000E+01	AA_Silica[am]	
PO4-3	5.108E+00	AA_Syngenite	
Pb+2	5.194E+00	AA_Tobermorite-I	
SO4-2	1.363E+03	AA_Tobermorite-II	
Sb[OH]6-	9.102E-02	AA_Tricarboaluminate	
SeO4-2	1.347E-01	Cd[OH]2[A]	Pb3[VO4]2
H4SiO4	1.231E+03	Cr[OH]3[C]	PbCrO4
Sr+2	5.570E+01	Fe_Vanadate	PbMoO4[c]
Th+4	not measured	Manganite	Rhodochrosite
UO2+	not measured	Ni[OH]2[s]	Strontianite
VO2+	7.312E+00	Pb[OH]2[C]	Tenorite
Zn+2	8.093E+00	Pb2V2O7	Willemite

It is important to realise that modelling the behaviour of a single element in isolation is bound to fail as the constituent behaviour cannot be separated from its chemical environment, which dictates key factors such as pH, redox and EC. Element leaching is also affected by interaction with other constituents (e.g. through precipitation). Mutual competition of elements for sorption sites also implies that failure to take along crucial competing elements will lead to a poor prediction. The challenge has therefore been to input all major, minor and trace elements and all relevant sorption processes into the geochemical model description of a material. Ignoring minerals or the description of sorption processes leads to an insufficient description of the system. The latest developments in modelling (Dijkstra et al, 2003; Dijkstra et al, 2004; Dijkstra et al, 2008; Dijkstra et al, 2009; van der Sloot et al, 2007; van der Sloot et al, 2008) attempt to integrate all relevant solubility controlling aspects. This type of approach is highly relevant for a proper understanding of release controlling processes from cementitious products.

The pH dependent leach test data for a specific cement mortar has been modelled using LeachXS (with ORCHESTRA embedded). The input parameters and the selected mineral phases are given in ANNEX X. The mineral phases were selected by means of calculated saturation indices obtained from preliminary speciation calculations of the leachates.

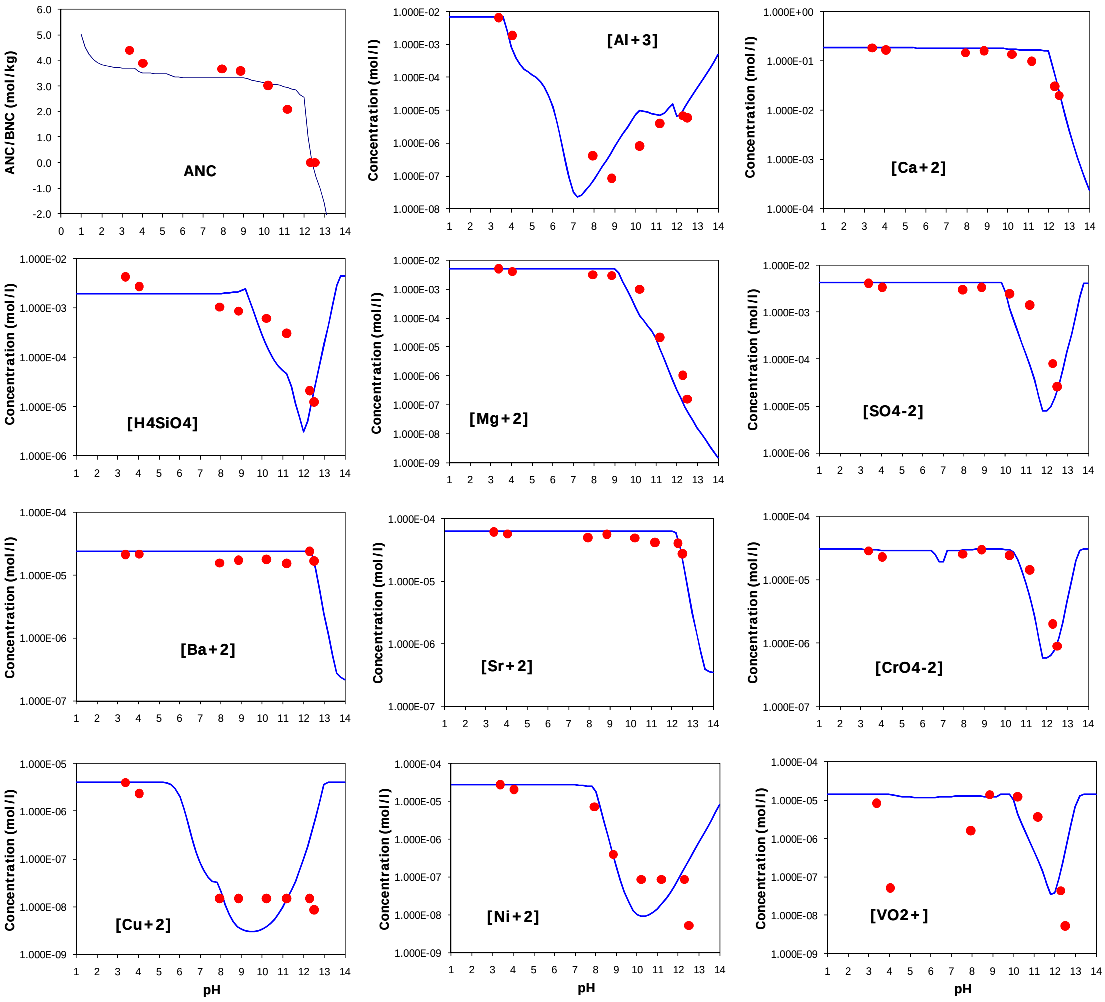


Figure 3.23 *Description of pH dependence test data of mortar NOR-2 with a chemical speciation fingerprint*

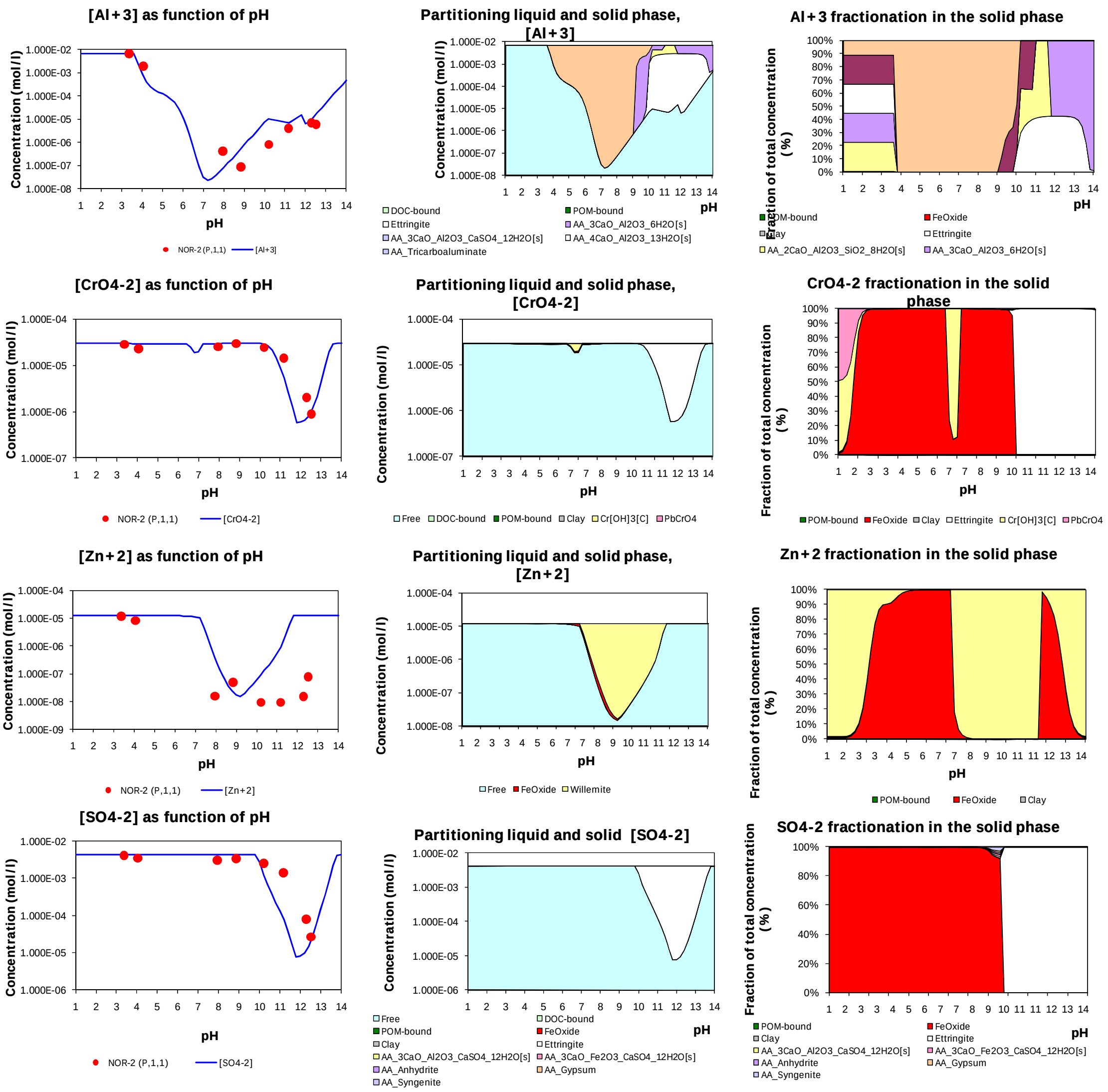


Figure 3.24 *Partitioning of phases in NOR-2 as obtained from chemical speciation modelling*

pH prediction shows that the model description works quite well, as the complexity to predict pH from a mineral composition and availability is quite a challenge.

The prediction of "non" interacting species like Na and K works very well indicating that the physical release parameters used in terms of diffusion and tortuosity and porosity is describing the actual behaviour of release from the monolith well.

The behaviour of many major and trace components following a full thermodynamic description is rather good. Particularly, when it is realised at what concentration levels these predictions are made (often well below any regulatory limit).

3.7.2 ANC Prediction Based on Mineral Composition

The pH in the eluate is modelled based on the minerals identified in the speciation run in Annex II. The match between measurement and prediction for the NEN method is quite promising. For the two other test conditions the modelled pH response is given as well.

3.7.3 Ettringite Solid Solution Parameters

In literature only a limited set of parameters for substitution of oxyanions (Cr, Mo, Se, Fe) for sulphate in ettringite are available (Kindness et al, 1994; Kindness et al, 1994b; Cougar et al, 1996; Bauer and Johnson, 2003). Besides oxyanions earth alkali elements like Ba and Sr can be substituted for Ca (Klemm, 1998). Furthermore Fe may be substituted for Al (Klemm, 1998). In view of the importance of ettringite or ettringite type phases in cement mortars a description of solid solutions for all of these possible solid solutions have been implemented in Orchestra. Using the literature data as starting point constants have been derived for the missing parameters by assuming that ettringite substitution dominates the release behaviour in the pH domain from 10.5 to 13. The parameters for CrO_4^{-2}, AsO_3^{-3}, MoO_4^{-}, VO_4^{-3}, PO_4^{-3}, SeO_3^{-2}, SO_4^{-2}, BO_3^{-3}, Ba and Sr have been derived from modeling the dissolved concentration as obtained from two cement mortars (prepared according to EN 197-1) and tested in a pH dependence leaching test (CEN/TS 14429). One of the two cements is a regular Portland cement and the other a cement with increased trace element levels prepared in a special test facility. (W1). The solubility of ettringite, and a number substituting of oxyanions and cations was calculated as an ideal solid solution model #.

The following stability constants have been derived:

Ca6(Al(OH)4)2(SO4)3(OH)4.12H2O	1.0e+45
Ca6(Al(OH)4)2(CrO4)3.(OH)4.12H2O	2.5e+47
Ca6(Al(OH)4)2(AsO4)3.(OH).9H2O	6.2e+40
Ca6(Al(OH)4)2(H3BO3)3(OH)10.18H2O	2.4e+66
Ca6(Al(OH)4)2(SeO4)3.(OH)4.12H2O	2.5e+44
Ca6(Al(OH)4)2(VO4)3(OH).9H2O	2.5e+45
Ca6(Al(OH)4)2(Sb(OH)6)3.(OH)7.24H2O	1.5e+58
Ca6(Al(OH)4)2(MoO4)3(OH)4.12H2O	2.5e+46
Ca6(Al(OH)4)2(PO4)3(OH). 9H2O	1.3e-12
Ba6(Al(OH)4)2(SO4)3(OH)4.12H2O	1.0e+60
Sr6(Al(OH)4)2(SO4)3(OH)4.12H2O	1.0e+60

Other cement mortars with varying concentrations of oxyanions and cement stabilized wastes modelled with these parameter settings show a generally good match between measurement and predicted concentrations. Obviously, independent experimental verification of the constants is desirable, but at present the descriptions provide an adequate quantification, which holds up even at low L/S conditions, which is very helpful in subsequent transport modelling runs.

Solid solutions in Orchestra, in the standard LeachXS input files, are modelled as ideal solid solutions. (see Phreeqc manual) This means that the activity of each member phase is equal to its mole fraction. By choosing the solubility products of the end members equal to the equivalent pure phases, the solid solution will always be less soluble than the pure phases of any of the member solids. So the pure phases will not form in the calculations. The solid solution will dissolve completely if the product of saturation indices of all member phases is less than 1.

Literature values: Cr 2.56e-61 (Kindness et al, 1994) ; Se (Bauer and Johnson, 2003) ; Fe 2.57e 50 (Lothenbach et al, (2005).

When applying these parameters in modeling of cement mortars a very satisfactory match between measurement and model is obtained for several oxyanions and other substitution parameters. Verification of these estimates by actual stability constant measurement is still needed, however, for the time being these parameters provide a good estimate of release behaviour.

3.7.4 Prediction of Release from Dynamic Laboratory Tests

The modelling framework ORCHESTRA (Objects Representing CHEmical Speciation and TRAnsport models) has been expanded to take into account chemical speciation and to allow a comparison between a traditional tank test, a modified DMLT with liquid renewal used for both aspects of modelling. Samples used for comparison include a concrete mortar, the cement stabilized waste prepared by INSA, a cement mortar containing MSWI fly ash and a cement stabilized waste sample with a high waste loading.

The steps of the modelling comprise the following steps:

- Measurement of release from specimen according to different tank leaching test modifications.
- pH dependence leaching test on size reduced mortar for chemical speciation purposes.
- Speciation modelling using a database-coupled version of the modelling environment ORCHESTRA.
- Refined prediction of leaching behaviour based on selected minerals using ORCHESTRA.
- The resulting speciation is used as input for the transport modelling to describe the release from a monolithic specimen under the different test conditions.

The following aspects of testing will be addressed:

- Presentation of DMLT data in standardised data format.
- Comparison of cementitious materials with different waste loading.
- Chemical speciation from pH dependence leaching test data and tank test data.
- Prediction of release based on chemical phases from speciation modelling and a model description of the DMLT:
  - Comparison of eluate concentrations at different liquid renewal times with model output for selected elements (NEN 7345).
  - Comparison of outcome of model predictions for traditional NEN 7345 test results with the proposed modified test conditions (wash-off step, low L/A step for solubility check and stabilization, subsequent dynamic leaching steps with one short renewal cycle as intermediate check on release behaviour).
  - Comparison of the proposed new DMLT with the dynamic leaching part in stepwise liquid renewal mode and continuous flow mode (5, 50 and 200 ml/hr).

In the model the following conditions can be varied:

- Exposure of the leachant to CO_2 from the atmosphere, increased CO_2 levels (free choice of concentration) and no atmospheric exposure (sealed tank) This option is not practised now.
- Use of a fixed pH in the external solution (free choice of pH), which may be used to simulate a neutral pH environment or a CO_2 controlled pH in the external solution. Not applied now.
- The volume of the external solution can be varied (i.e. L/A variation) for the entire test or part of the test. This allows concentration gradient relaxation to be verified (proposed DMLT method has one low L/A step).
- The porosity of the specimen can be varied. At very low porosities, the non-porous surface (e.g. concrete with about 2 % porosity) plays a major role in the release to the solution.
- The spatial configuration of the specimen is such that effects of depletion in specimen of limited thickness can be assessed.
- The role of gradient reduction on release by diffusion can be assessed.
- The release parameters for selected elements can be varied (available quantities, minerals).
- The time steps for leachant renewal can be varied from the standard set, shortening or lengthening exposure per liquid renewal cycle.

As output the model provides concentration profiles in pore water as a function of depth into the product for specified time intervals (here 0.5 hour) over the entire duration of the test. This allows visualization of the concentration development in the pore water as a function of depth and, simultaneously, precipitation reactions at the interface. In addition, the concentration build-up in the external solution is monitored at the same time steps, which allows visualising the slowing of concentration increase due to a decreasing concentration gradient between pore water and external solution.

This flexibility provides a basis for designing the optimal leaching conditions for monolithic specimen and to address the issues of concern voiced by the discussion about objectives for the test to be developed. The key issue is not to force a certain release mechanism in the test (e.g. diffusion), but rather to identify for a given monolithic matrix, which mechanisms are relevant in that particular matrix for the constituents of interest.

The results of modelling release from a cement mortar in comparison with leaching data obtained by NEN 7375 are given in Annex XII.

Based on the speciation data as described in Annex X the release from the concrete cube was modelled. The calculated concentrations in the pore water as a function of depth have been recalculated using the same mineral phases for the condition that a higher dilution is applied in a leaching test of cored subsamples in the depth profile of the 40 year exposed concrete specimen. In figure 3.26 and 3.27 the results are presented.

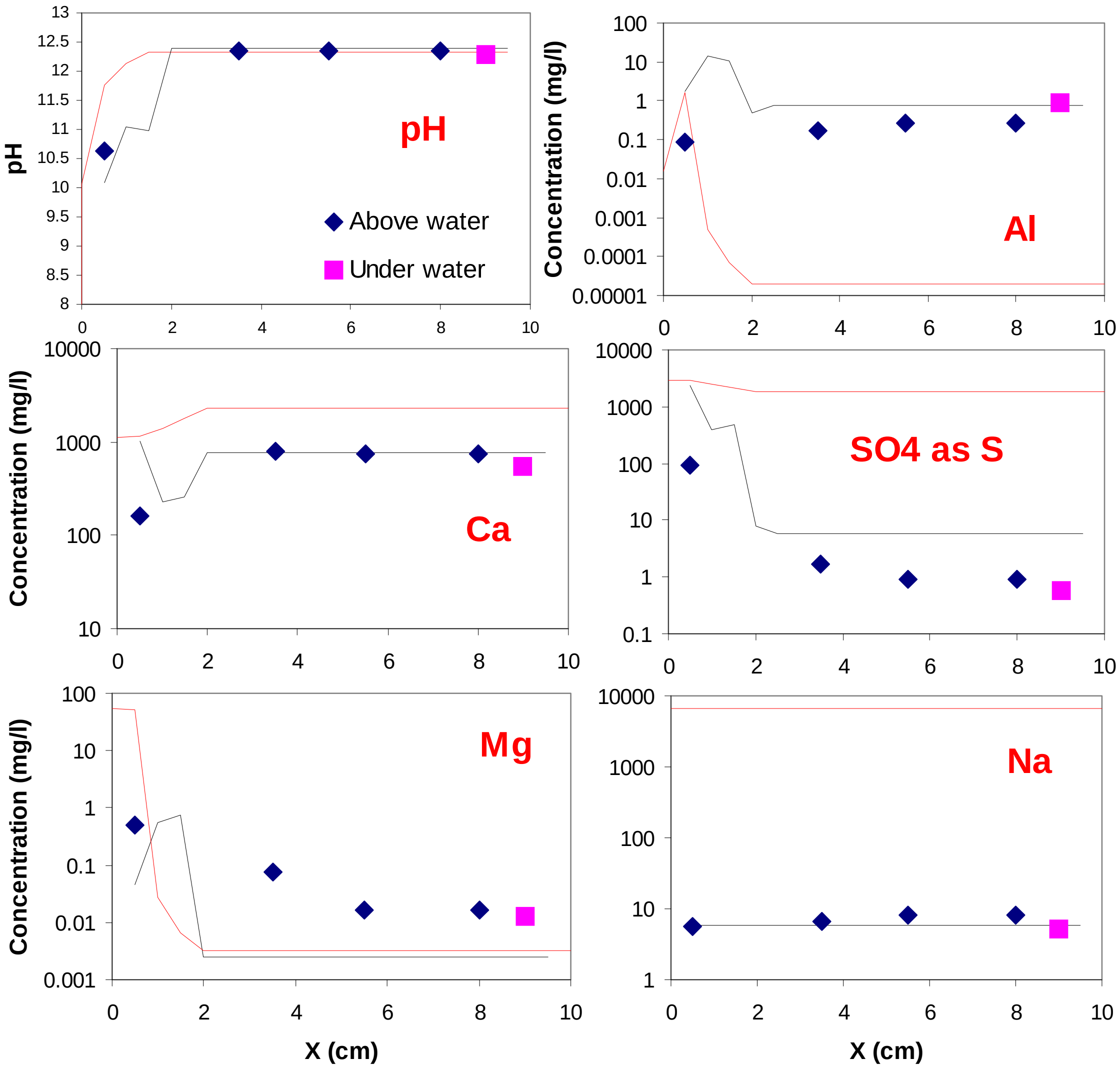


Figure 3.25 *Measured concentration profiles in a 40 year exposed concrete specimen in comparison with ORCHESTRA modelled data of release*

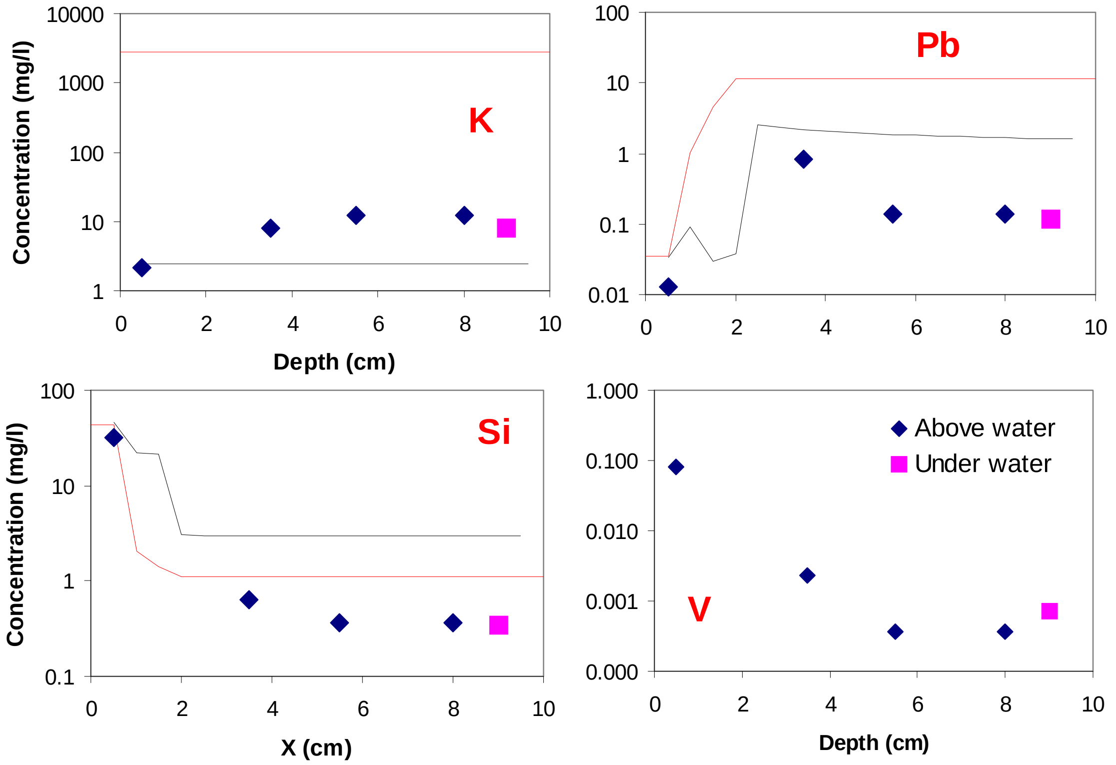


Figure 3.26 *Measured concentration profiles in a 40 year exposed concrete specimen in comparison with ORCHESTRA modelled data of release*

In general, the forward model predictions of the tank test results in different configurations is quite promising, which implies that the complex system is reasonably well described with the minerals identified in the chemical speciation. When this prediction can even be improved, the potential for developing actual scenarios of exposure is a logical next step. The description of the actual behaviour of a concrete wall exposed to rainwater and or permanent contact with water taking into account atmospheric CO_2 influences and possibly pore sealing is a challenge. The challenge to describe damage to concrete based on sulphate attack taking into account full mechanistic chemistry has already been successful (Sarkar et al, 2010).

4. Methodology Development of Criteria for Impact Assessment of Concrete and Cement mortars

There are several judgement aspects of cement mortars and concrete, which require a different level of information. Examples of such needs are: the development of criteria to assess impact from cement mortar and concrete use in different construction scenarios and the quality control to verify compliance with the specified limit values. Such questions have been raised as a result of the requirements in the Construction Products Directive Essential Requirement number 3 on Health and Environment (1989). In view of the unknown consequences of the more extended use of alternative fuels and raw materials in cement production and the recycling of aggregates, these aspects have become of relevance for products like cement mortars and concrete.

For assessment of impact in different scenarios of application a range of exposure conditions may occur. In addition, the material will undergo changes with time (e.g. carbonation), which requires an assessment of other conditions than the one obtained from a fresh sample. This may involve pH and, possibly, redox changes resulting from carbonation, weathering and remineralisation.

In all scenarios the degree of contact with water will be the key aspect determining the release. This calls for insight in changes of leaching behaviour as a function of time. The difficult part is that a pH change resulting from carbonation in a laboratory test does not necessarily keep pace with the exposure in the field (too short relative to field). Therefore a tank test in the lab will never reflect precisely what will happen in practice. Only through modelling, a prediction can be made based on understanding the relevant processes.

A hierarchy in testing can provide the necessary detail required to answer some specific questions as well as the simple straightforward testing needed to verify compliance with previous characterisation data and subsequently with derived criteria based on characterisation test results. A well-defined link between characterisation test and compliance procedures is essential to be able to make the inferred relation.

A full characterisation of monolithic materials will generally consist of:
- *Composition*. In case of construction materials this is not a preferred means of judgement, but may be required for other regulations and other purposes
- *pH static test data* These test results provide insight in the chemical speciation of elements and form the basis for full mechanistic chemical reaction/transport modelling
- *percolation test* The first fractions from this test provides insight in the pore water concentrations within the cement mortar matrix, which is necessary for proper modelling release by multi-element speciation modelling
- *tank test A*and compliance options (preferred first fraction of elaborate method) The tank test reflects many aspects that are relevant for the translation from lab to field. This relates in particular to the tortuosity of the product (measure for the pore structure).
- *physical characteristics* (Not covered here) e.g. strength, porosity, permeability, density. Several physical parameters are relevant for modelling transport in field scenarios.

Questions arise with respect to:
- Variability in production (between facilities and in time within one facility) and variability between different countries.
- Behaviour of material in reuse/recycling options in a size reduced form.

Approach to address multiple questions related to a material (in line with EN 12920 Methodology, 1996)

- Evaluation of the question to be answered.
- Perform the proper testing to assess the relevant properties.
- Evaluate possible critical components.
- Model the release in the scenario under consideration.
- Verify the outcome against field observations.
- Adjust model when needed.
- Develop criteria by comparison of impact against target objectives or identify compliance with regulatory targets.
- Identify key controlling factors and based on the understanding select a suitable test condition for compliance purposes.
- Draw conclusion on acceptance or rejection.

Verification against regulatory criteria will allow
- Determination of crucial elements (limitation of the number of parameters to be tested in compliance testing, if needed).
- Frequency of testing (less frequent testing when values sufficiently far from the critical limit).

Method of evaluation of a scenario
- Define exposure window in terms of pH and time (identify relevance of redox, atmospheric exposure and dissolved organic carbon - DOC).
- Define exposure conditions (wet / dry cycles, temperature, etc).
  Check elements based on this against limit values, if more than X times lower (to be decided by the regulators) - non critical.
- Check for variability in production

Earlier very consistent leaching behaviour for cement mortars and concrete was demonstrated based on characterisation leaching tests on cements produced at different locations worldwide (figure 4.1). This implies that a generic judgment on release behaviour will be relevant for a large portion of all cements produced worldwide. This will be helpful to focus on key parameters for compliance/conformity with reference data (preliminary characterisation or initial type testing).

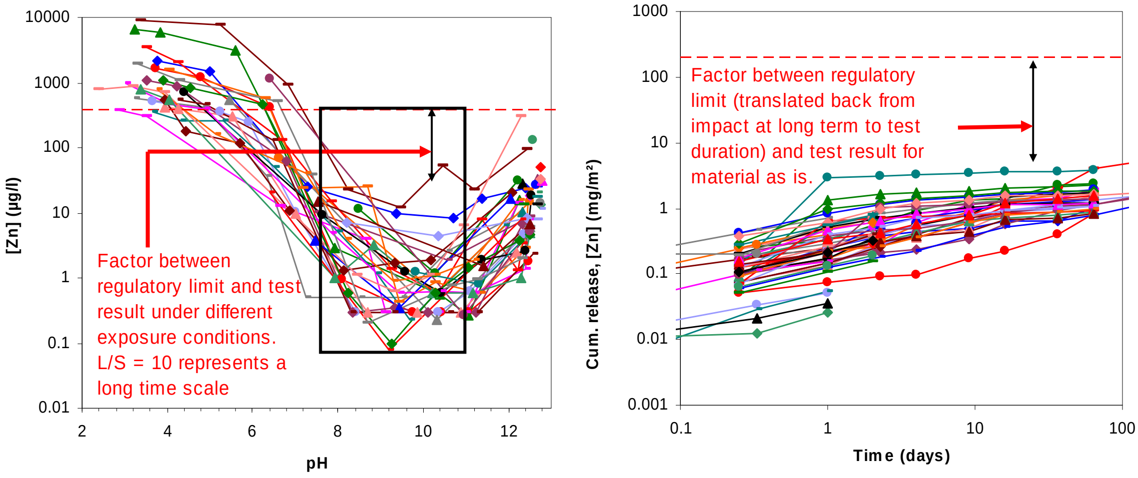


Figure 4.1 *Judgement of cementitious products and recycled concrete aggregate based on characterisation test data*

Status of standard development as methods for source term characterisation

During the past decades, many release test methods have been developed that attempt to simulate individual field conditions for a specific product. Most of these test methods are 'conditional' as their results only apply to a specified scenario (e.g. test simulating initial carbonation and subsequent release from a drinking water pipe, (EN 14944-1, 2006; EN 14944-3, 2007; EUR 19602, 2000). The consequence of such 'conditional' testing is that test results can neither be compared to results from other test methods, nor to results of different materials, and/or to conditions met in practice that are beyond the testing conditions.

For monolithic materials like concrete, tank test of different configuration have been developed in The Netherlands, Germany, France, and Austria to assess the time dependent release (NEN 7345, 1995 ; Hohberg et al, 1996; De Groot and van der Sloot, 1991, 1997; AFNOR XP X 31-211, 1994; Önorm S 2116-4, 2001). For wood preservatives a similar type of test for intact wood specimen has been developed (EN1250-2, 1994). The data interpretation is rather limited, but the basic approach is very similar to tests developed for monolithic construction materials, which have been used in regulatory context. This provides a basis for harmonisation of methods as experimental conditions (contact times, leachant, temperature, specimen size, liquid to area ratio, etc) are aspects that can be discussed and agreement reached.

In a recent report, the selected conditions in the different characterisation leaching tests and their influence on the outcome of a test have been evaluated (van der Sloot et al, 2010).

The absence of a common basis for judgement of a variety of products under a variety of conditions greatly complicates the development of common regulation criteria that any product has to fulfil. Therefore, the development of as many different test methods as there are materials and application scenarios, is an unnecessary costly and inefficient route.

In CEN/TC 292 (Characterisation of waste) test methods have been and are still being developed for characterisation of the leaching behaviour of granular and monolithic materials with a more general applicability than just waste (Van der Sloot et al, 1997). For granular materials the main characterisation methods have been finalised. For monolithic materials the standardisation process is still ongoing. In recent studies, the combination of a pH dependent leaching test and a percolation test was identified for granular materials. The combination of a pH dependent leaching test, a percolation test and a dynamic monolith leach test (type of tank test for monolithic materials) has been identified as a suitable combination to derive the needed parameters for impact modelling for monolithic materials. The pH dependent leaching test provides the necessary insight in the chemical speciation aspects, whereas the percolation test provides time-dependent release information as well as an indication of pore water composition. The dynamic monolith leach test provides time dependent release characteristics for monolithic materials. The suitability of these tests for a much wider range of materials has been shown by the standardisation of very similar methods for leaching of soil and soil like materials in ISO/TC190 (Soil). More recently, the test methods have been proposed for the evaluation of construction products under the Construction Products Directive (CPD, 1989), as experiences have shown the wide applicability of the methods to a wide range of granular and monolithic materials. This standardisation work falls under CEN TC 351 "Construction Products: Assessment of Release of Dangerous Substances". The advantage of a horizontal (defined as covering different fields which in CEN until now have seen independent development of tools) approach in testing to assess a time dependent source term is that no double testing is needed when a material switches categories (i.e. changes from a waste into a product and vice versa). Through geochemical modelling a description of the source material can be provided, which can be used as input in a chemical reaction transport model that allows prediction of release in a give utilisation or disposal scenario.

The test methods proposed are adequate as they properly represent key release parameters or they provide a basis to derive such properties. In addition, repeatability has been shown to be quite satisfactory. In 1995 already a first intercomparison was launched using a tank test (NEN 7345, 1995) on stabilised waste (Van der Sloot et al, 1995). Although the material produced at the time contained a waste, the limited waste loading (only 15 % w/w) led to a test sample with a strength similar to low strength concrete (32 N/mm2). This test sample was tested several times since 1995 and in addition tested in 10 fold for repeatability assessment. In Annex XI the results are given. In figure 4.2 typical test results are given for Cr leaching from cement mortars. In Annex VII, a short description and the functionality of the test methods in judging release are given. The pH dependence test (CEN TS 14429, 2006) mentioned before has been applied to over 60 worldwide cement mortars with very consistent results. This test allows other field exposure conditions to be assessed than the laboratory conditions using fresh material.

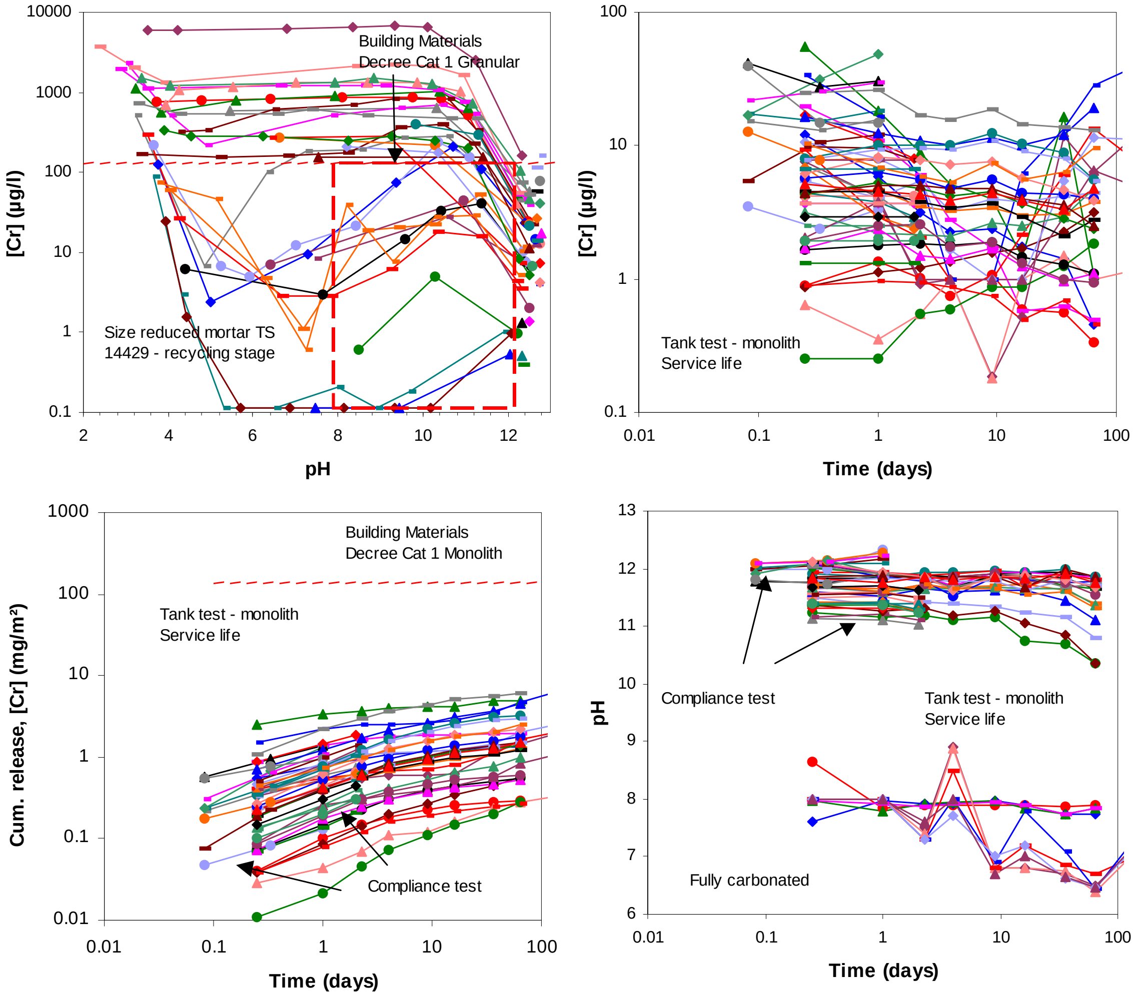


Figure 4.2 *Characterisation test data for Cr from worldwideworldwide cement mortars according to EN 197-1 Left top: pH dependence test data (TS 14429) on size reduced mortar; top right: concentrations as measured in a tank test on intact monolithic mortar bar; bottom left: cumulative release as a function of time; bottom right: pH in tank test reflecting response of fresh and fully carbonated test specimen. In the latter 3 graphs also compliance test data are given for comparison. As an example the judgment against regulatory criteria is given as an example, in the pH dependence test it implies judgment of recycled aggregate, while in the bottom left graph judgment of service life is made.*

In a recent report, the selected conditions in the different characterisation leaching tests and their influence on the outcome of a test has been evaluated (van der Sloot et al, 2010). This report also contains information on repeatability and reproducibility of related materials studied in national intercomparison studies.

5. Modelling Approach

Test methods alone are not sufficient as test results need to be linked to an assessment of impact, which implies that results obtained from leaching tests should provide the necessary information to describe a source term for impact modelling, as coupled chemical reaction-transport modelling is the only option available to provide insight in the long term behaviour of materials under changing exposure conditions in the field (van der Sloot and Dijkstra, 2004; Dijkstra et al, 2005). The use of more complex, detailed modelling can be balanced with the use of simplified, semi-empirical and semi-analytical models, which when knowingly over-predict release (i.e., are conservative), can be used for initial screening purposes. The results of such modelling can then be verified against field observations. Below examples of relatively simple models for long term prediction, as well as more sophisticated approaches will be highlighted.

In EN 12920 (1996) the sequence of steps from problem definition to verification between model prediction and field observation are indicated. Although initially developed for waste the approach is very generic and more widely applicable It would be useful to develop a similar generic description as laid down in EN 12920 to cover environmental aspects of construction products as the basic methodology is not fundamentally different. A further worked out framework for judgment of materials is given in Kosson et al (2002). In CEN TC 351 a tiered approach is now in development for construction materials.

Defining a source term

In many environmental impact-modelling approaches a constant source term is applied, which in many cases is not a proper representation of the long term leaching behaviour from construction materials. A limited number of impact model descriptions have been published for monolithic construction materials (Aalbers et al, 1999; Hendriks and Raad, 1997; DIBT -Part I and II, 2005; Tiruta-Barna et al, 2005; Tiruta-Barna et al, 2001; Eighmy et al, 1997 and 2002; Meeussen and van der Sloot, 2006; Volpracht et al, 2006; Schiessl et al, 2003). In several cases, a limited set of constituents is taken along in the modelling. More complete and mechanistically-based modelling is often necessary to achieve improved understanding of controlling processes and make more realistic (less overly conservative) estimates of long-term release and performance. Based on the current full element modelling, it is clear that there are more inter-element interactions that cannot be ignored. For instance, when Pb is modelled it cannot be done without taking into account Fe-oxide sorption, interaction with DOC (dissolved organic carbon) and POM (particulate organic matter), as well as Mo and V, which form leadmolybdates and -vanadates in many matrices. Several of the aspects such as organic matter interaction, redox changes, gas reactions (volatility, carbonation and oxidation), pH changes are not considered. Such simplifications are often applied to reduce the complexity of the required calculations. In many source term descriptions for impact modelling independent release functions are applied for individual constituents, thus negating the effect of interactions between elements and changes in mobility due to significant changes in solubility controlling factors. In virtually all soil and groundwater impact models a Kd type of interaction is applied to describe coupled reaction and transport, when for many cases several processes (including non-linear sorption, precipitation/dissolution, aqueous phase complexation/chelation, orthogonal diffusion) are responsible for actual behaviour and cannot be reasonable represented by linear equilibrium sorption.

A challenging new approach is to take along as much complexity as present models can handle, which presently implies taking into account mineral solubility, sorption to Fe and Al oxides, interaction with dissolved organic matter, incorporation in solid solutions, changes in pH and redox as a result of atmospheric exposure, biological degradation or biologically mediated conversion, physical aspects such as particle size, permeability, preferential flow aspects, organic matter degradation, gas intrusion under varying degrees of saturation. Current computational advances, both in hardware and software, now start to make this approach practical for many applications.

Developments and approach in source term and chemical reaction transport modelling
For geochemical speciation/ transport the modelling framework ORCHESTRA (Objects Representing CHEmical Speciation and TRAnsport models) is used (Meeussen, 2003), which is embedded in the database/expert system LeachXS. The latter forms the integrated approach that allows linking various aspects of materials together. Proper thermodynamic stability data and other solubility controlling parameters (Fe-oxide, Al-oxide, dissolved organic carbon and particulate organic matter) are crucial for the above indicated complexity in modelling to be successful.

Within this system the following subsequent steps are applied:
- Measurement of constituents with pH dependent leaching test on granular material or size reduced monolithic specimen (chemical speciation aspect).
- Measurement of release of constituents by percolation as a function of L/S (liquid/solid ratio) or as a function of time from monolithic materials (dynamic release). For monolithic materials the first fractions of a percolation test provide a suitable estimate for the pore water composition of monolithic materials.
- Prediction of the pH dependent release from size-reduced construction debris based on a set of selected minerals, sorption on Fe and Al - oxides, interaction with dissolved and particulate organic matter and incorporation in solid solutions (chemical speciation fingerprint).
- This chemical speciation fingerprint is used in combination with transport in a percolation scenario with dual porosity to describe the outcome of the laboratory test.
- This chemical speciation fingerprint is also used in combination with transport from a monolithic material by taking into account leachant renewal cycles, continuous renewal, product tortuosity (measure for porosity and pore structure).
- When a satisfactory prediction is obtained for the chemical speciation fingerprint and for the time (or L/S) dependent release, the material can be assumed to be well characterised over a wide range of pH and time or L/S conditions relevant for long term behaviour. The chemical speciation fingerprint of the material can then be used as the basis for reactive transport modelling to predict release under well-defined field scenarios with external influencing factors, such as carbonation (CO_2 uptake), redox change, degree and variation in water contact, including varying degrees of preferential flow.

An integrated system for leaching testing and evaluation is under development as LeachXS (www.LeachXS.com). The integration of data storage in an unified data format to facilitate easy comparison of the wide range of laboratory data, lysimeter data and field data, a scenario database to facilitate environmental impact evaluation under different exposure conditions for different materials, a regulatory database with judgement criteria for different utilisation and disposal options, a thermodynamic database for speciation modelling and a chemical reaction transport code (Orchestra) in a model that facilitates data retrieval, model input and post modelling data processing creates new possibilities for the use of speciation information in the decision making process.

Although in this work the main focus has been on inorganic constituents (metals and oxyanions), the principles largely apply to organic substances and radionuclides as well, as far as their release to the water phase is concerned.

Typical intended use scenarios for cementitious materials are:
Monolithic material applications:
A 1. Utilisation of concrete in direct contact with drinking water (concrete pipes and basins)

A 2. Utilisation of concrete in structures exposed to fresh surface water (e.g. pillars for bridges, quays, breakwaters, locks)
A 3. Utilisation of concrete in the marine environment (breakwaters, oil rigs, embankments, etc)
A 4. Utilisation of concrete in contact with ground water (pilings, shafts, etc)
A 5. Utilisation of concrete in surface structures (all forms of building on land)

Recycling aspects(secondary application):
Granular material applications
R 1. Recycling of concrete construction debris in new concrete as aggregate
R 2. Recycling of construction debris as unbound aggregate

End of life aspects:

L 1. Landfilling of fines from construction debris and multiple recycled material not meeting criteria for reuse.

6. Methodology for Criteria Development for Monolithic Products

Three main scenarios can be distinguished:
- Release by diffusion under stationary conditions (i.e. no flowing water).
- Release in direct contact with drinking water, surface water, groundwater or seawater.
- Release from structures intermittently wetted by rain or spray water.

The models to describe these three scenarios have distinct features setting them apart. The modelling approach will be discussed per group. After that examples of modelling experiences are provide per group.

6.1 Release by Diffusion

This situation exists in all cases where cementitious materials are in direct contact with an unsaturated soil. There is no water flow, just diffusion through porewater in the concrete and the soil. In figure 6.1 the conceptual model is shown. The degree of water saturation in concrete and soil is of relevance, as the release decreases with decreasing water saturation (Schaeffer, 1995).

Conceptual model:

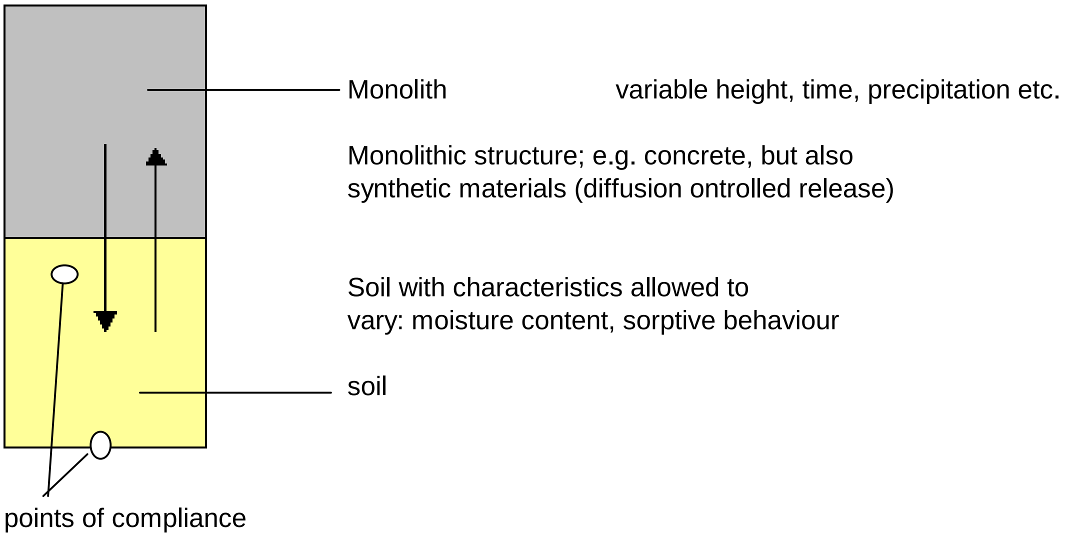


Figure 6.1 *Scenario schematic for diffusion controlled release model*

Here the option exists to use a simple one dimensional diffusion model or a more sophisticated approach taking the interaction between soil and mortar into account. The soil buffer capacity will neutralise the alkalinity released from the cementitious matrix. However the buffer capacity of the mortar exceeds that of the soil, which implies movement of a pH front. Soil organic matter is mobilised at high pH and may affect release of substances from concrete. Using the sophisticated model approach the progression of the pH front and the concentrations of constituents released or mobilised by the cementitious matrix can be quantified in their interaction with soil. In figure 6.2 an example of such modelling is given. In particular the interactions at the interface between cement matrix and soil are of interest due to the large gradient in pH between the two matrices.

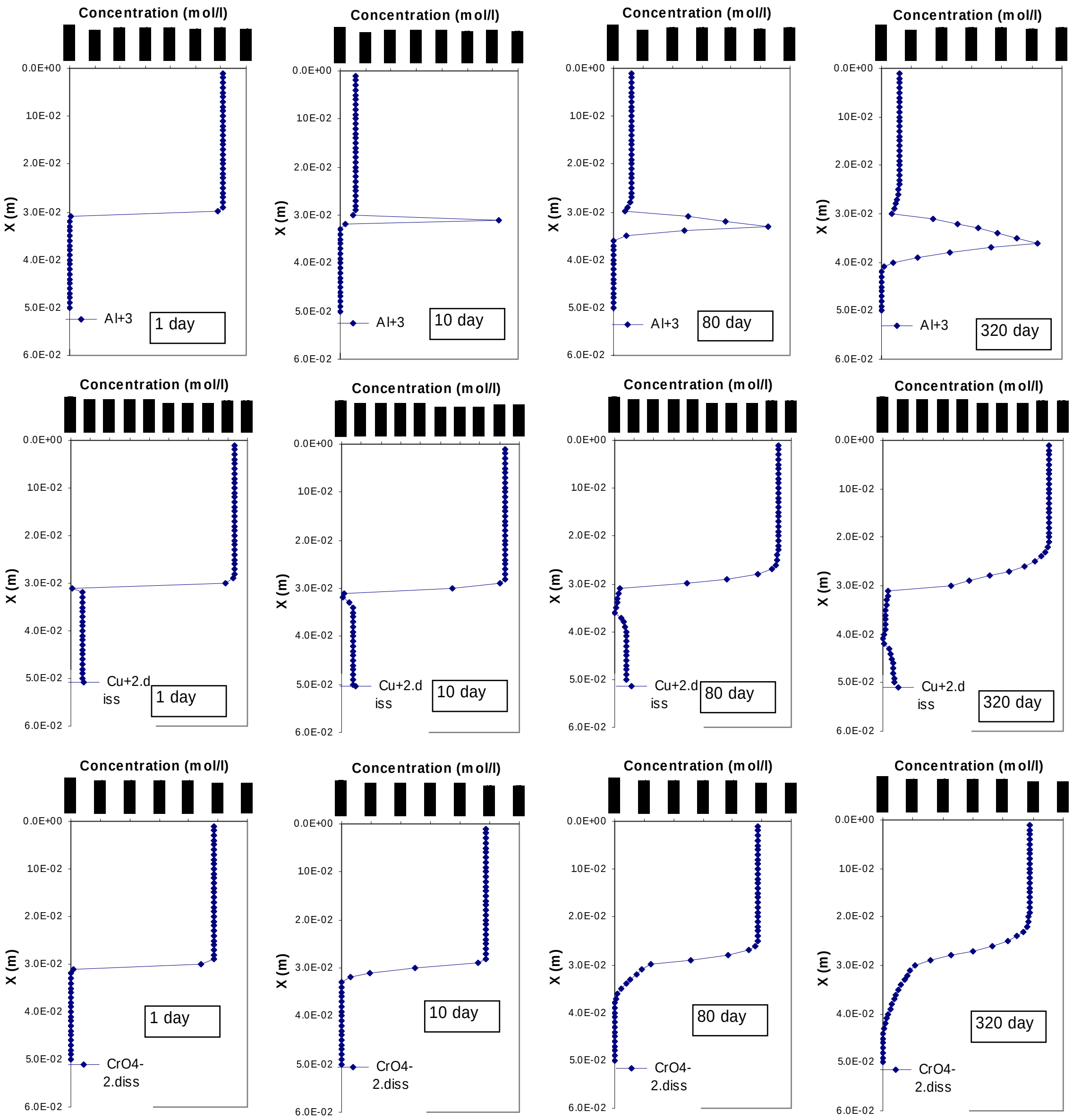


Figure 6.2 *Element transport by diffusion from a cement mortar in contact with soil by full mechanistic modelling shown as concentration in pore water as a function of depth along the profile. Note the difference in rate of migration in the mortar with low porosity (0.05) and soil with a much higher porosity (0.35)*

6.2 Release by Direct and Permanent Contact with Water

The tank leach test itself is the first example, which can be used to model the release as measured by exposing a test specimen to leachant renewal cycles. This can either be done by empirical methods by using a simple diffusion model or more sophisticated by taking the full chemistry and physics into account. The former option has limitations in extrapolating the information to long term. The latter is still in development, although very promising results are obtained now. The advantage of the latter method is that changes in exposure conditions can be factored in thus leading to a more accurate estimate of long term behaviour. The trade-off between the simple approach and the more sophisticated approach lies in the level of uncertainty that is allowed in the judgement.

6.2.1 Utilisation of Concrete in Direct Contact with Drinking Water (Concrete Pipes and Basins).

In this application a direct exposure exists as constituents released are affecting the quality of water used for human consumption. The high initial pH of cement mortar leads to the need to carbonate the inner surface of concrete drinking water pipes to the extent that the pH in drinking water falls within an acceptable range for human consumption. Pre-carbonation of pipes prior to taking pipes in service is of importance. The testing developed in TC 164 is focussed on that aspect. For an assessment of release at the long term a good description of the interface processes is needed to be able to properly describe release under varying flow conditions and water hardness levels. The present modelling capabilities are close to reaching a full description of the release in a pipe with flowing water. The release as obtained in a tank test at own pH does not reflect proper release behaviour as the pH remains too high and forward projection would lead to overestimation of release. Testing after carbonation does not reflect the actual release either as release is too low initially. In figure 6.3 the projected release is indicated in the pH dependence and different presentations of tank test results. The pH development with time is a major controlling factor for release of Al. The concentration initially can exceed the regulatory limit for Al in drinking water until the pH has dropped below the drinking water limit of 9.5.

Since carbonation of a wetted alkaline surface proceeds faster than carbonation under saturated conditions, one may envisage that carbonating a drinking water pipe can be achieved more quickly under unsaturated moist conditions than by applying carbonated water. This observation may provide a technical spin-off potentially leading to a faster commissioning of drinking water pipes than currently experienced.

For a proper description of release from a specific length of a drinking water pipe under specified flow conditions, which includes possible periods of stagnant water conditions, a more sophisticated scenario description is needed. In Annex XII the results of full speciation reactive transport modelling for cement mortar exposed to flowing water is given. This provides the basis for a scenario with a given length of pipe, an exposed surface area and a flow rate (constant or varying with time). A conceptual model for the release from drinking water pipes is given in figure 6.3. The chemical speciation fingerprint for concrete can be used as basis for such a model. Carbonation resulting from dissolved carbonate in equilibrium with atmospheric CO_2 can be described by defining the solution composition.

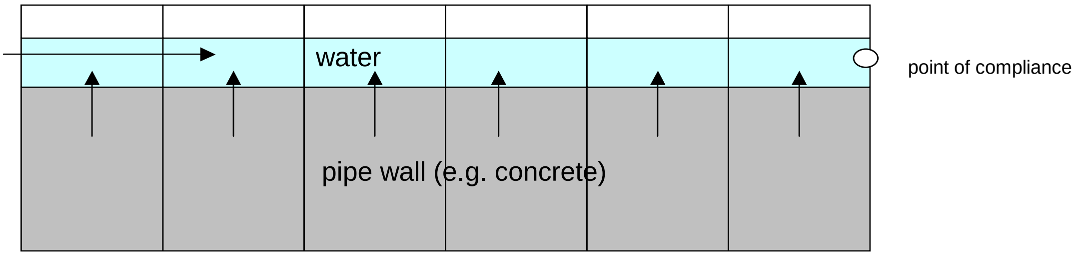


Figure 6.3 *Conceptual model to describe release from a concrete drinking water pipe*

6.2.2 Utilisation of Concrete in Structures Exposed to Fresh Surface Water (e.g. Pillars for Bridges, Quays, Breakwaters, Locks, Ponds)

In this application constituents released are rapidly diluted in a relatively large volume of water. In addition, elements may be taken up from the surface water into the concrete surface layer rather than being released. An example is the uptake of Mn from surface water with elevated Mn levels due to reducing conditions in sediments and enhanced release during autumn of Mn^{2+} (van der Sloot et al , 1989). This phenomenon was observed in the cooling water channel of the research reactor in Petten taking surface water from the North Sea canal.

Under water the carbonation is limited due to the rather slow supply of materials by diffusion in water. The release is almost never a problem as the volume of water in contact with the cementitious construction material is generally large. Only in cases where the volume becomes relatively low and water renewal is low or absent release may become critical. Using data that are taken from tank leaching test results on cement mortars (van der Sloot et al, 2001), it is possible to estimate release by means of an effective diffusion coefficient. An example is given in Figure 6.4.

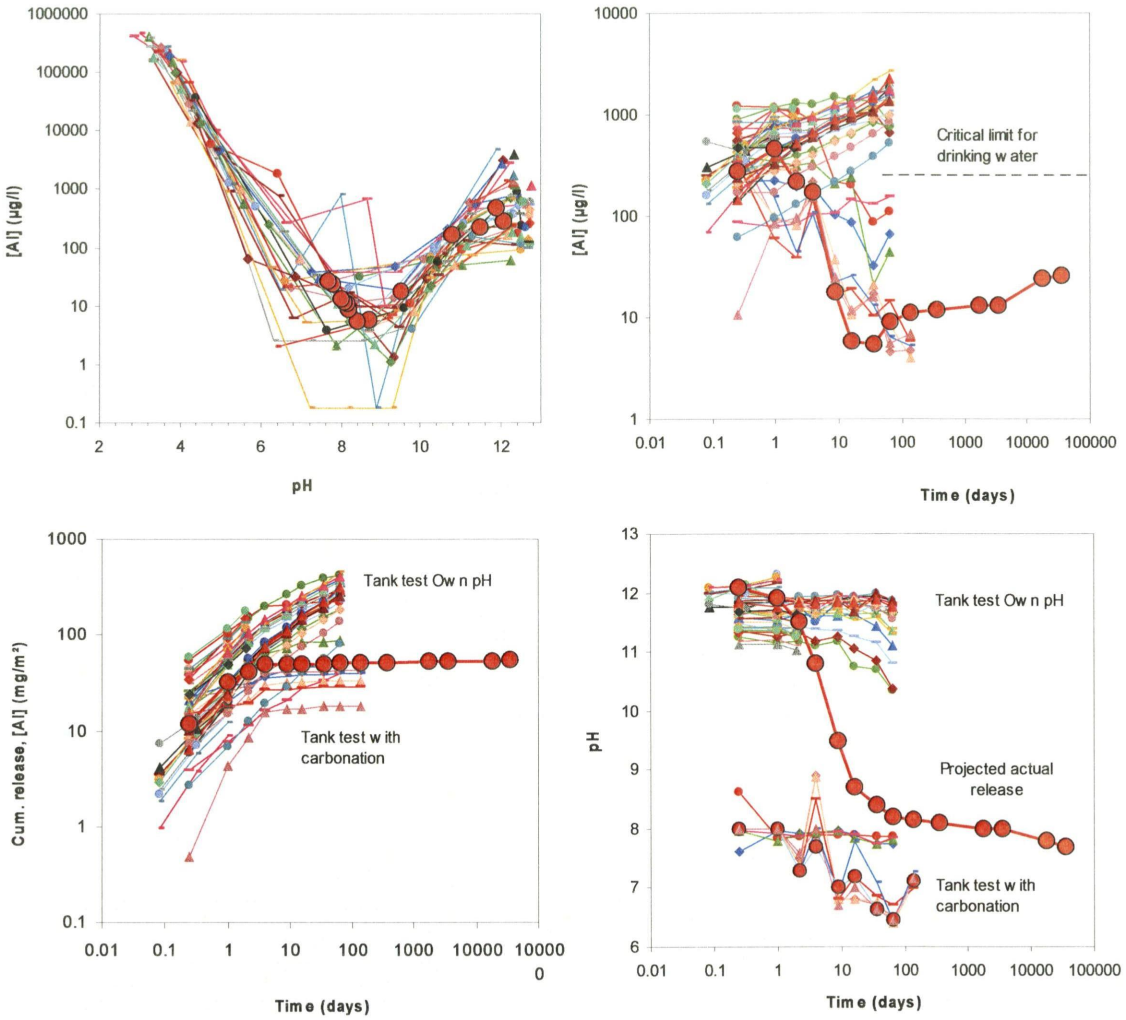


Figure 6.4 *Characterisation of Al leachability from cement mortars and concrete. Top left: pH dependence test data showing release as a function of pH (data inserted are concentration - pH data for the projected long term release from a drinking water pipe); top right: concentration as a function of time in a tank test at own pH and after carbonation - inserted data is the long term projection of concentrations as a function of time taking pH change into account ; left bottom: cumulative release as a function of time for tank test at own pH and after carbonation; right bottom: pH in tank test at own pH and tank test after carbonation - inserted data is the long term projected pH change with time for a drinking water pipe exposed to carbonated water.*

The cumulative release (E at time t) can be described by:

$$E_t = 2.\rho.U_{bes}.(\sqrt{t}).\sqrt{\frac{D_e}{\pi}}$$

with ρ as the density (kg/m^3), U_{bes} the availability for leaching (mg/kg), t is the time of consideration (s) and D_e as the effective diffusion coefficient (m^2/s). For a given period t, the average concentration increase due to release from a cementitious material can be estimated from:

$C_t = E_t * A / V$

with A as the exposed surface area of a cementitious material and V the volume of water in contact with this area over the contact period t (Table 6.1). Complete mixing is assumed.

Table 6.1 *Release from a tank test (highest value from > 50 worldwide cements) as basis for estimating concentration in water in contact with the cement mortar*

Element	Release at t=64 days mg/m^2	Concentration mg/l (A=1 m2; V= 1000 l)	Element	Release at t=64 days mg/m^2	Concentration mg/l (A=1 m2; V= 1000 l)
Al	450	0.45	Mn	5.4	0.0054
As	3.5	0.0035	Mo	2.5	0.0025
B	16	0.016	Na	5800	5.8
Ba	168	0.168	Ni	2.6	0.0026
Ca	48000	48	P	8	0.008
Cd	0.3	0.0003	Pb	7	0.007
Cl	880	0.88	Sb	1.9	0.0019
Co	0.63	0.00063	Se	2.8	0.0028
Cr	6.2	0.0062	Si	3800	3.8
Cu	2.2	0.0022	Sn	2.5	0.0025
Fe	5.2	0.0052	SO4 as S	1900	1.9
K	30300	30.3	Sr	350	0.35
Li	27	0.027	V	10	0.01
Mg	1730	1.73	Zn	3.8	0.0038

Volumes less than 1 m^3 per m^2 of cementitious surface area may lead to concentrations exceeding critical levels. Volumes well beyond that level do not lead to any problem.

An interesting example is the use of concrete for garden ponds. In this case, practical guidance is given to the user to prevent fish and plants from dying because pH of the water is still too high due to release of alkalinity into the relatively small volume of water relative to the concrete surface. It is recommended to replace the water a number of times over a period of a few weeks to reach a status, where the pH buffering by the water, the CO_2 from the air and the buffer capacity of the sediment can keep the pH within acceptable limits. This water renewal is also helpful to reduce the aluminium, vanadium and chromate level.

In table 6.2 the pH as predicted in pond water after 4 water renewal cycles from leaching test data is given. The pH in the pond water at the end of a contact cycle is based on the alkalinity released in laboratory experiments. The calculated pH is corrected first for CO_2 uptake from the air (16 meq/m^2 water surface/day). Subsequently, the pH is corrected for the buffer capacity of the fresh water used for renewal assuming half of the capacity is consumed in a week (0.5 meq/l; Mol, 1983). Finally, the pH buffering by sediment (as obtained from the acid neutralisation capacity information obtained in the pH dependence leaching test) can be factored in. Clearly, the water in the pond can be expected to be neutral after 3 to 4 renewal cycles.

Table 6.2 *Calculation of the pH in a pond with concrete lining taking different sources of neutralisation into account*

	Calculated pH	After correction for		
Days	in pond after weekly water renewal	Atmospheric CO_2 neutralisation	pH buffering by surface water	pH buffering by sediment
7	11.1	11.1	10.9	10.9
14	10.7	10.6	10.1	9.9
21	10.6	10.4	8.4	7.0
28	10.5	10.3	7.0	7.0

6.2.3 Utilisation of Concrete in the Marine Environment (Breakwaters, Oil Rigs, Embankments, etc)

For these applications, release to water is irrelevant as the quantities released to a large volume of seawater are non-detectable. However, uptake of constituents from seawater in a cement mortar can be quite significant, as major ions in seawater have a tendency to react with the alkaline cement matrix (Locher, 1968). Similar processes were observed for cement stabilised waste placed in the ocean as an artificial reef (Hockley and van der Sloot, 1991). Na, K and Cl are taken up as the concentration in seawater is much higher than the concentration in the pore water. Mg is taken up and forms brucite, carbonate is taken up and forms calcite. The latter can given the right circumstances lead to pore sealing, thus reducing the further uptake of salts in the matrix. This type of process may help prevent damage to concrete in the marine environment, when this process can be engineered even better. The present modelling capabilities of transport and chemical reaction may provide a spin-off for engineering (durability aspects) rather than environmental concerns. In Annex XII concentration profiles as a function of depth from the surface obtained from modelling a cementitious monolith exposed to seawater is shown for a few relevant elements. It is clear that Mg substantially increased in the surface layer due to uptake from seawater. A substantial amount of calcite is formed as a result of the relatively high carbonate levels in seawater, which diffuses into the pores and precipitates as calcite. As a result of the pH change calcium alumino-silicate phases dissolve in the surface layer and transform into other mineral phases.

6.2.4 Utilisation of Concrete in Contact with Ground Water (Pilings, Shafts, etc)

For application in groundwater under relatively low flow conditions a limited initial effect of pH on local groundwater may be expected. Shortly after placement, this effect is compensated by neutralisation through carbonate from the surroundings. The release of oxyanions, which will release more prominently under carbonated conditions, is limited by the thickness of the layer between surface and the neutralisation front. The speed of the neutralisation front can be estimated, when no further processes (sealing) are assumed. The release of oxyanions can then be estimated relatively straight forward. Metal leaching is marginal to non-existent at the pH conditions in concrete even after some initial carbonation. In a relatively simple approach the release as observed in the tank leach test can then be extrapolated to long term. A more sophisticated approach can be provided from a full mechanistic modelling according to Annex XI.

6.3 Release from Structures Intermittently Wetted by Rain or Spray Water

Utilisation of concrete in surface structures (all forms of building on land) is characterised by intermittent wetting and drying, which greatly facilitates uptake of carbonate as uptake of CO_2 from the air by gas diffusion is 5 orders of magnitude faster then under saturated conditions. Here also the release can be estimated based on the progression of the neutralisation front.

Modern concretes have a rather low connected porosity, which delays ingress of substances as well as release of substances. In Roman cements, which at the time of placement were considerably more porous, full carbonation is observed after 2000 years (ECN, 2006). This process may even have been enhanced by the higher porosity and the uptake of moisture in the structure, which would thus effectively act as a CO_2 pump.
Based on such observations one may envisage that carbonating a drinking water pipe can be achieved more quickly under unsaturated moist conditions than by applying carbonated water. This observation may provide a technical spin-off potentially leading to a faster commissioning of drinking water pipes than currently experienced. The practical aspects of such an approach and the economic consequences would have to be considered. A schematic representation of this type of exposure is given in figure 6.4.

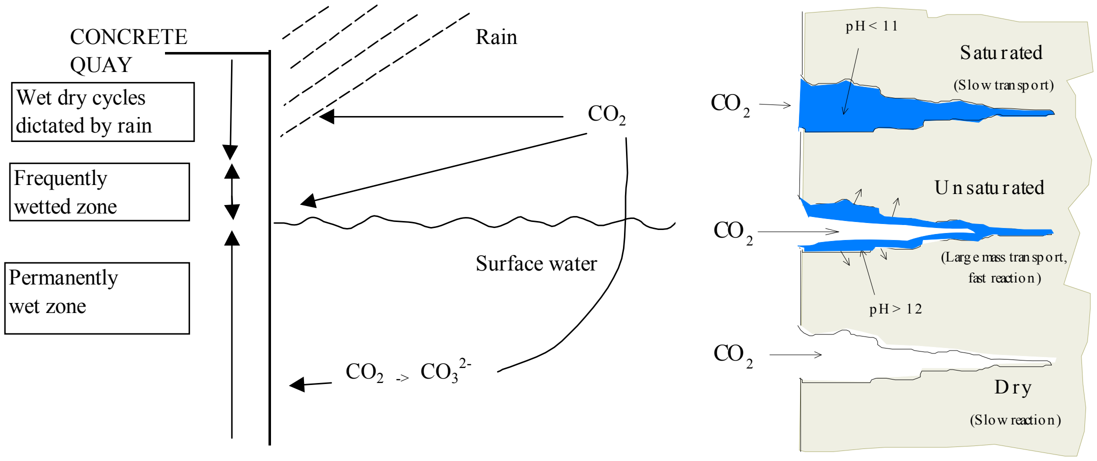


Figure 6.5 *Schematic representation of exposure of a concrete quay to weathering and a clarification of the mechanism and rate of CO_2 uptake in the paste through pores*

In the schematic graph given in Figure 6.4 the frequently wetted zone is the zone where the most significant uptake of CO_2 will take place. The wetting of the internal pores will ensure maximum transfer of CO_2 from the atmosphere (CO_2 pump).

The boundary conditions will define when the monolith and granular leach test data need to be used. The potential for pH change will determine whether pH dependence test data are needed to translate results to other exposure conditions.

The release of substances due to capillary suction of water above the water level leads to a situation where release of soluble substances from a zone above the water level can occur, which is schematically visualized in figure 6.5. (see also experimental results described in section 3.6).

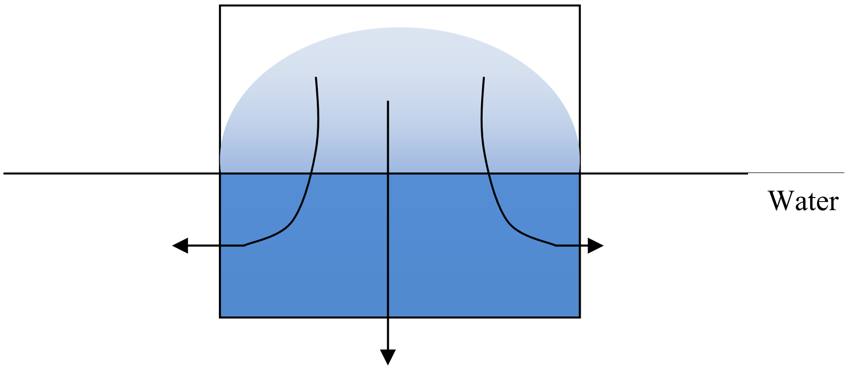


Figure 6.6 *Possible flux of mobile elements derived from field exposed materials from partially saturated zones above the water level*

6.4 Temperature

There is a noticeable difference in release at different temperatures of exposure. Generally laboratory testing is carried out at an average lab temperature of around 20 ˚C. Average outdoor temperature may vary depending on the latitude. For the Netherlands, an average annual temperature of 10 ˚C is used (KNMI, 1990). This means about a factor 2 in effective diffusion coefficient.

6.5 Examples of Modelling Results

Here results are presented that have a wider applicability as the release processes are similar in many different scenarios. However, the degree of contact with water, the temperature or the exposure to carbonation may differ.

6.5.1 Release for Monolithic Specimen Permanently in Contact with Water.

The results from characterisation test can be used to assess long term release (Workshop Source term, BRGM, 2006). Relatively simple models can be applied as well as more sophisticated models. A very commonly used modelling approach is to assume diffusion controlled release with a one-dimensional release model based on Fickian diffusion. Based on the characterisation using pH dependence test data and tank test data for the time dependent release, a distinction in the behaviour of metals, oxyanions and major elements can be made.

6.5.1.1 Oxyanion Leaching Behaviour

Oxyanions show a pH dependent release behaviour that implies an increase in leachability as pH decreases due to carbonation (see figure 6.6 and 6.7 as examples for V and Cr). Using the range of data observed from worldwide cement mortars, effective diffusion coefficients can be estimated covering the upper and lower bounds as observed in tank test measurements. In table 6.3 these data are gathered for Cr, Mo, sulphate and V. In the case of Mo, the range of availabilities for leaching can be covered with one effective diffusion coefficient. From the release curves as a function of time with the inserted one dimensional diffusion model data inserted it is obvious that the model does not describe the data well, as the pH influence has not been factored in (figure 6.8). The release decreases faster with time than predicted by the simple model. This implies a gross overestimation of release can be made, when the extrapolation is made well beyond the testing time in the lab experiment.

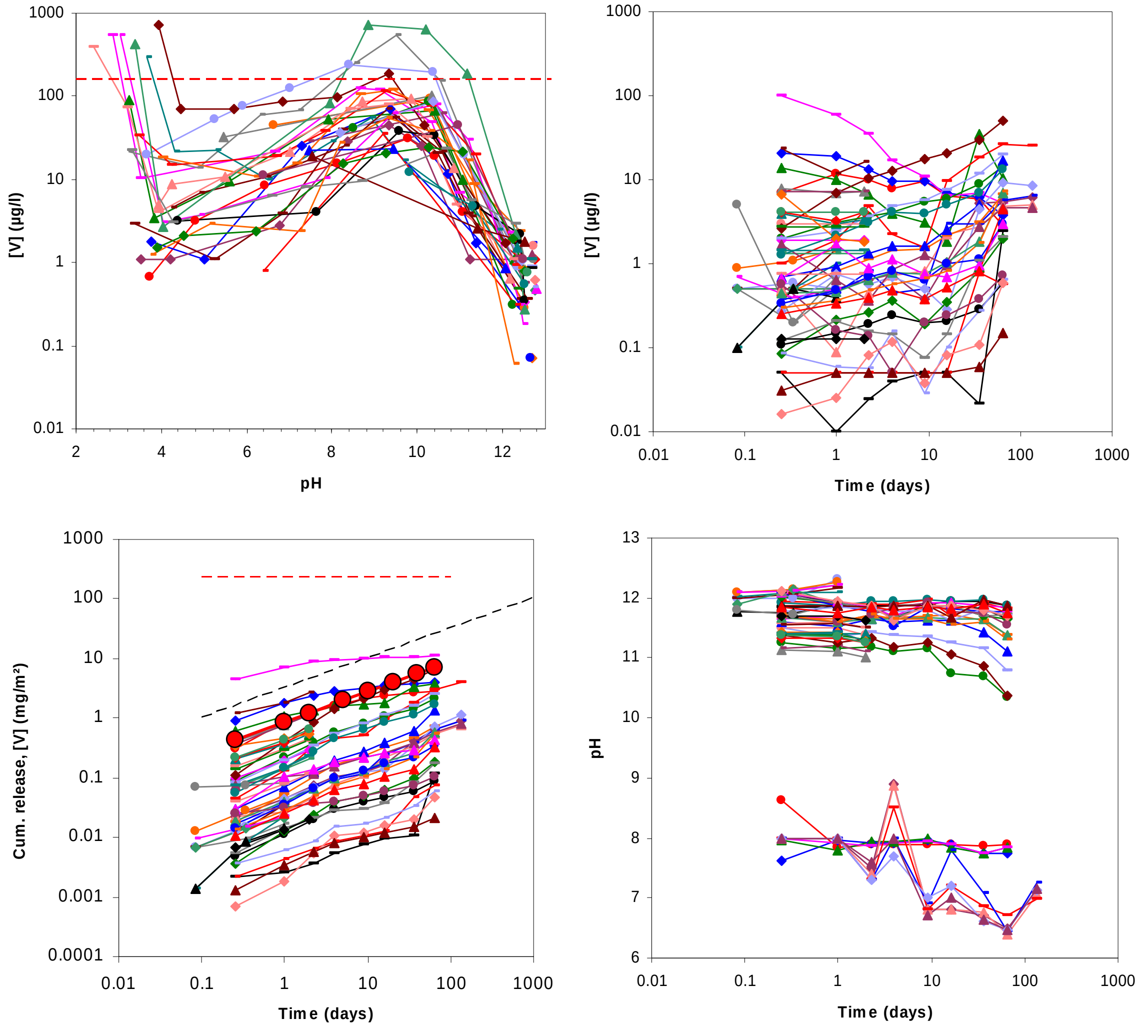


Figure 6.7 *Characterisation of leaching behaviour of V from cement mortars and concrete. Top left: pH dependence test data showing release as a function of pH; top right: concentration as a function of time in a tank test at own pH and after carbonation ; left bottom: cumulative release as a function of time for tank test at own pH and after carbonation- inserted data projected release based on a one dimensional diffusion model with an effective diffusion coefficient D_e of 1.10^{-12} m^2/s, availability of 1.2 mg/kg and density of 2200 kg/m^3(no pH change assumed); right bottom: pH in tank test at own pH and tank test after carbonation*

Table 6.3 *Release parameters based on a simple one dimensional diffusion model giving upper and lower bounds for the range of data observed from worldwide cements*

	V	V	Cr	Cr	Mo	Mo	SO_4 as S	SO_4 as S
Time(days)	mg/m^2	mg/m^2	mg/m^2	mg/m^2	mg/m^2	mg/m^2	mg/m^2	mg/m^2
0.1	0.28	0.001	0.30	0.008	0.07	0.003	310	7.3
0.25	0.44	0.001	0.48	0.013	0.11	0.005	490	12
1	0.88	0.003	0.96	0.025	0.23	0.010	979	23
2	1.2	0.004	1.4	0.036	0.3	0.014	1385	33
5	2.0	0.006	2.2	0.057	0.5	0.022	2190	52
10	2.8	0.008	3.0	0.080	0.7	0.03	3097	73
20	3.9	0.011	4.3	0.11	1.0	0.04	4379	103
40	5.5	0.016	6.1	0.16	1.4	0.06	6193	146
64	7.0	0.020	7.7	0.20	1.8	0.08	7834	185
182.5	12	0.034	13	0.34	3.1	0.13	13229	312
365	17	0.048	18	0.49	4	0.19	18708	441
1825	37	0.11	41	1.1	10	0.4	41832	986
3650	53	0.15	58	1.5	14	0.6	59160	1394
7300	75	0.22	82	2.2	20	0.8	83665	1972
18250	118	0.34	130	3.4	31	1.3	132286	3118
27375	145	0.42	159	4.2	38	1.6	162016	3819
36500	167	0.48	184	4.9	44	1.9	187080	4410
Range De	1E-12	3E-16	1E-14	1E-15	2E-13	2E-13	2E-13	1E-15
Release range	167	0.48	184	5.8	138	5.9	187080	4410
Avail range	1.2	0.2	13.2	1.1	0.7	0.03	3000	1000

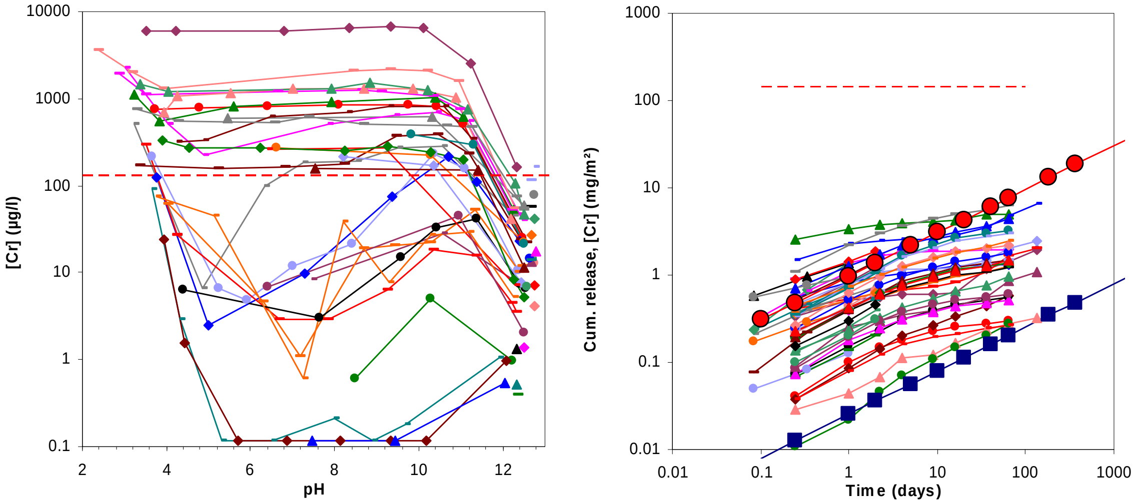


Figure 6.8 *Characterisation of the leaching behaviour of Cr from cement mortars and concrete. Left: pH dependence test data showing release as a function of pH; right: cumulative release as a function of time for a tank test at own pH and after carbonation- inserted data of projected long term release based on a one dimensional diffusion model with an effective diffusion coefficient D_e of 1.10^{-14} m^2/s, availability of 13.2 mg/kg and density of 2200 kg/m^3 and an effective diffusion coefficient D_e of 1.10^{-15} m^2/s, availability of 5.8 mg/kg and the same density as upper and lower bounds of the worldwide cement mortar data*

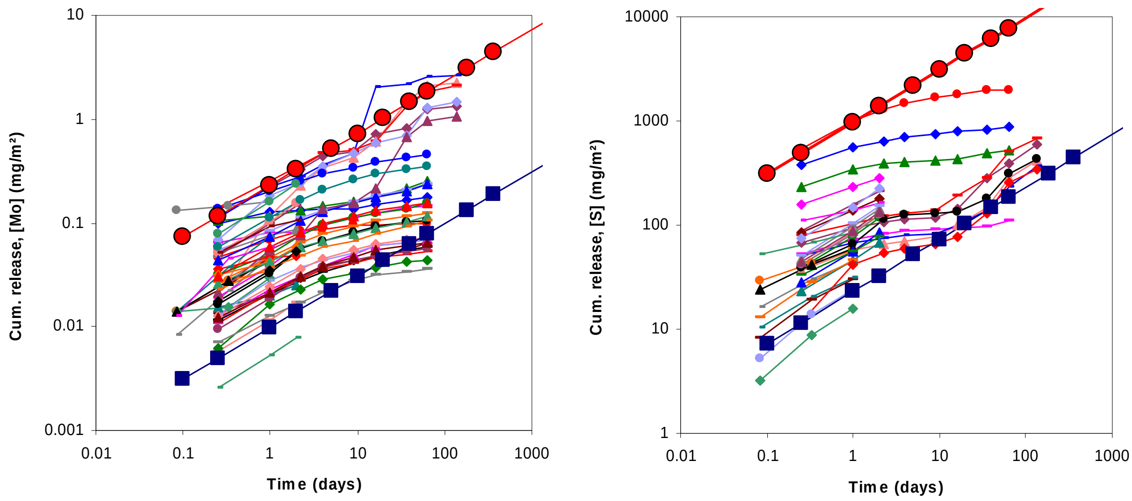


Figure 6.9 *Release behaviour of Mo and SO_4 from cement mortars and concrete. Left: cumulative release of Mo as a function of time for tank test at own pH and after carbonation- inserted data of projected long term release based on a one dimensional diffusion model with an effective diffusion coefficient D_e of $2.0.\ 10^{-13}$ m^2/s, availability of 0.7mg/kg and density of 2200 kg/m^3 and an effective diffusion coefficient D_e of 2.10^{-13} m^2/s, availability of 0.03mg/kg and the same density as upper and lower bounds of the worldwide cement mortar data; right: cumulative release of sulphate(as S) as a function of time for tank test at own pH and after carbonation- inserted data of projected long term release based on a one dimensional diffusion model with an effective diffusion coefficient D_e of $2.\ 10^{-13}$ m^2/s, availability of 3000 mg/kg and density of 2200 kg/m^3 and an effective diffusion coefficient D_e of 1.10^{-15} m^2/s, availability of 1000 mg/kg and the same density as upper and lower bounds of the worldwide cement mortar data*

From the pH dependence test it is clear that oxyanions (e.g. SO_4, Mo, V, Sb, Se, As) show an increase in leachability as pH decreases (see figure 6.6 and 6.7). In cement mortar in contact with surface water a pH front develops, that migrates inward. Based on an observed migration of 2 mm in 10 years and the assumption of front movement proportional with a square root of time, the layer of cement mortar that is neutralised can be calculated. Under the assumption of complete depletion of oxyanions from the neutralised zone, the mass of neutralised zone (kg) and the availability of the oxyanion of consideration (mg/kg), the released amount as a function of time can be calculated. Given the dimensions of the concrete tube, the tube segment volume and the water renewal, the concentrations in solution can then be calculated. In figure 6.9 these concentrations as a function of time are given for sulphate, Cr, Mo and V. In table 6.4 the corresponding cumulative release data are given for sulphate, Cr, Mo and V. These are probably still overestimated as a concentration increase in the outer carbonated layer will also lead to diffusion into the product as also a substantial concentration gradient exists between the surface layer and the concentration well within the product.

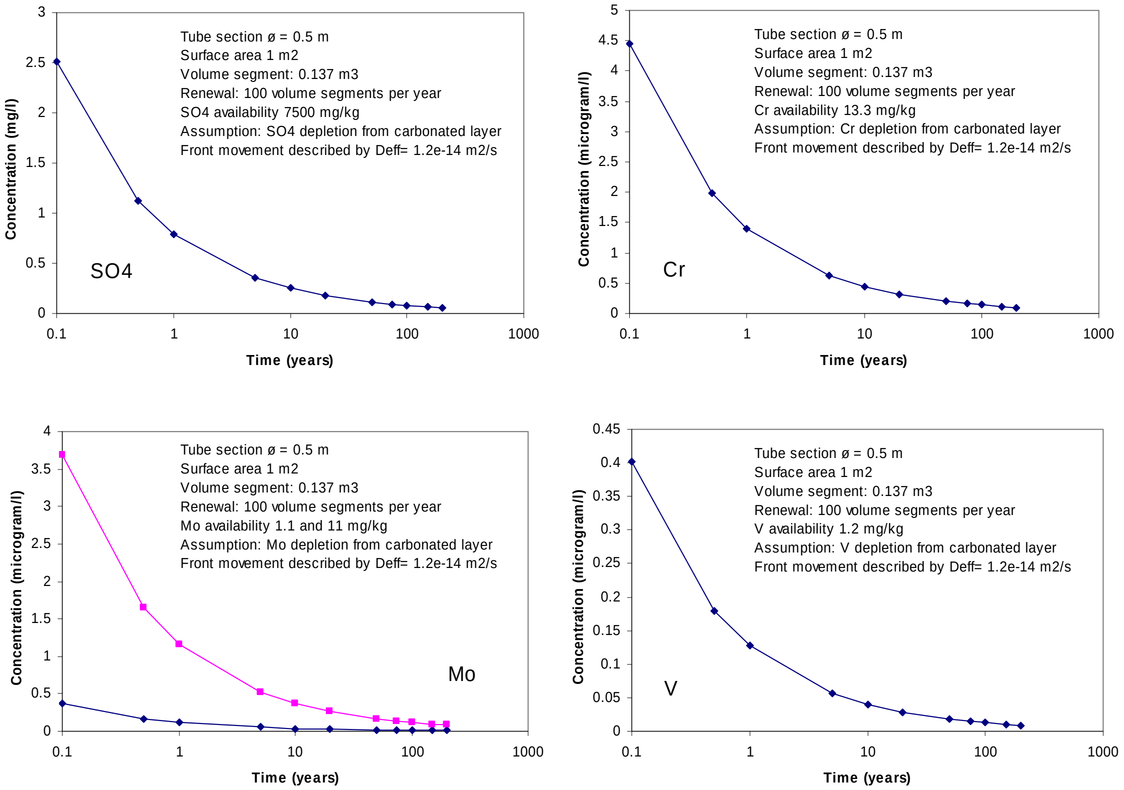


Figure 6.10 *Predicted concentrations of oxyanions sulphate, Cr, Mo and V as a function of time in water flowing through a concrete tube or along a flat concrete surface assuming complete depletion from the neutralised surface layer*

Table 6.4 *Prediction of the long term release of oxyanions assuming depletion of the carbonated surface layer of a cement mortar*

Time	Mo	SO_4 as S	V	Cr
Yr	mg/m^2	mg/m^2	mg/m^2	mg/m^2
0.1	1	1150	0.55	6.1
0.5	1	2571	1.2	14
1	2	3637	1.7	19
5	4	8132	3.9	43
10	5	11500	5.5	61
20	7	16263	7.8	86
50	11	25715	12	137
75	14	31494	15	167
100	16	36366	17	193
Availability	1.1	2500	1.2	13.2

From this it is clear that a substantially lower release is predicted for V following the assumed depletion of the carbonated layer. For Mo and sulphate the difference is limited to a factor 3 to 4 as the rate of carbonation is not too different from the release rate estimated from the test. In case of Cr there is almost no difference as the projected pH front movement and the release front of Cr are very similar in magnitude.

6.5.1.2 Metal Leaching Behaviour

The leaching behaviour of metals is also affected by pH. In this case, the leaching decreases as pH decreases after carbonation. However, at a pH level around 8 the leachability tends to increase again. In figure 6.10 the characterisation of the leaching behaviour of worldwide cement mortars by pH dependence leach test and the tank test is shown for Zn. After an initially higher release level, the release decreases as reflected in the cumulative release behaviour. In figure 6.11 the projected long term release behaviour of Zn from cement mortar is shown, when slow carbonation is taken into account. In the case of Zn, the simple one dimensional diffusion model would seem not to be too far off. However, if the pH change is taking place earlier a much higher release could be envisaged than projected here.

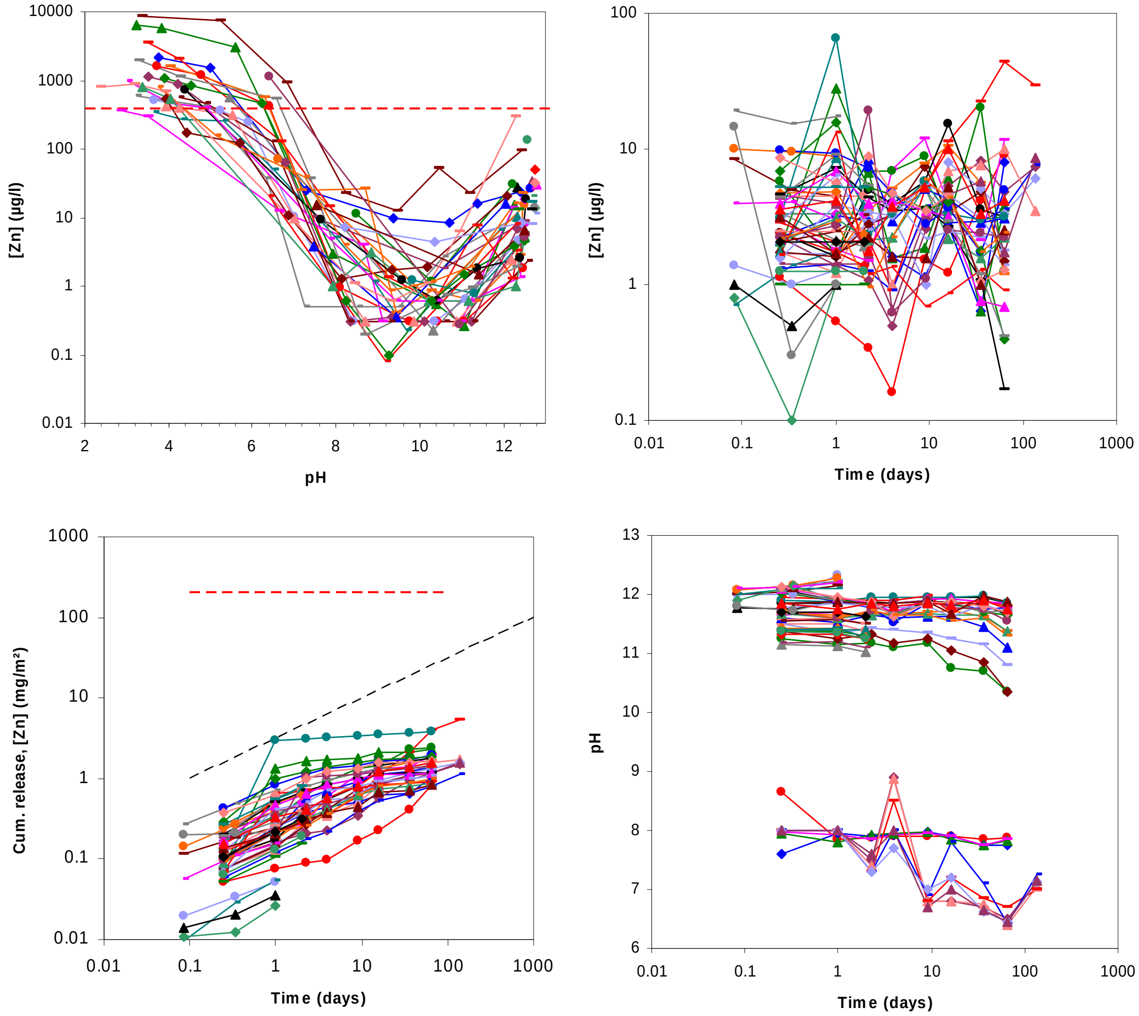


Figure 6.11 *Characterisation of the leaching behaviour of Zn from cement mortars and concrete. Top left: pH dependence test data showing release as a function of pH; top right: concentration as a function of time in a tank test at own pH and after carbonation ; left bottom: cumulative release as a function of time for tank test at own pH and after carbonation- inserted data projected release based on a one dimensional diffusion model with an effective diffusion coefficient* D_e *of* 1.10^{-12} *m*^{2}*/s, availability of 1.2 mg/kg and density of 2200 kg/m*^{3}*(no pH change assumed); right bottom: pH in tank test at own pH and tank test after carbonation*

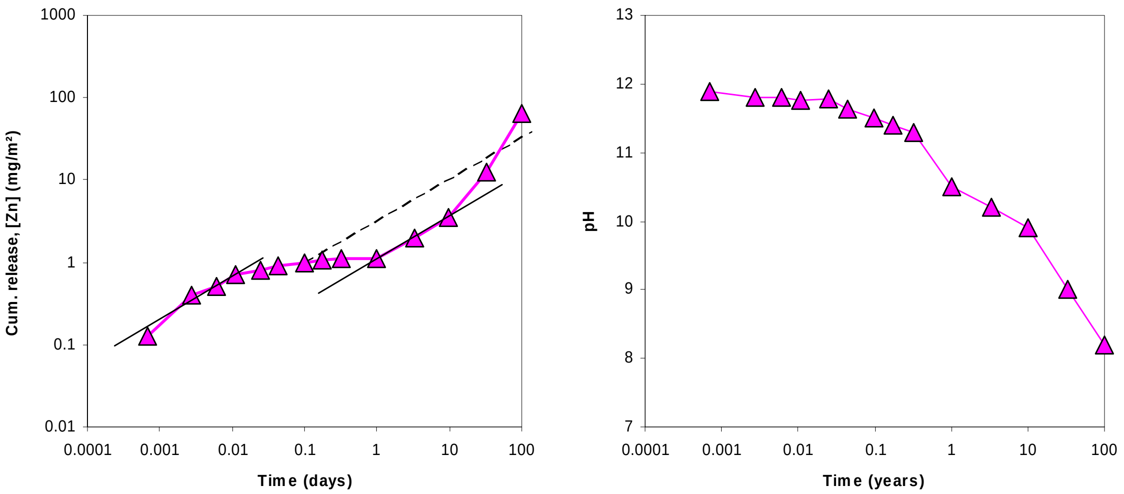


Figure 6.12 *Projected leaching behaviour of Zn from cement mortar exposed to slow carbonation. Left: cumulative release as a function of time illustrating decrease and later increase in release; right: pH change in contact solution showing effect of slow carbonation*

6.6 Full Chemical Reaction Transport Modelling for Monolithic Materials

The modelling framework ORCHESTRA (Objects Representing CHEmical Speciation and TRAnsport models) embeddded in LeachXS is used to identify solubility controlling phases relevant for cementitious applications (Meeussen and van der Sloot, 2006). Subsequently, this information has been applied to model the tank test results by taking chemical speciation and transport into account to predict release. Following this verification, release is modelled under a few field scenarios. Proper thermodynamic stability data and other solubility controlling parameters (Fe-oxide, Al-oxide, dissolved organic carbon and particulate organic matter) are crucial for the above indicated complexity in modelling to be successful.

The modelling comprises the following steps:

- Measurement of release from specimen according to different tank test modifications.
- pH dependence leaching test on size reduced samples for chemical speciation purposes and the first fractions of a percolation test on size reduced material to estimate the pore water concentration in the mortar.
- Speciation modelling using LeachXS a database-coupled version of the modelling environment ORCHESTRA to identify relevant mineral phases
- Refined prediction of leaching behaviour in a pH dependence test based on the selected minerals obtained by using ORCHESTRA in step 3 and using relevant sorption phases at L/S 10 used in the pH dependence test and at a low L/S representative of pore water conditions.
- This resulting chemical speciation fingerprint is used as input for the chemical reaction/transport modelling to describe the release from a granular or a monolithic specimen under the different test conditions (liquid renewal mode as well as flow mode) as well as the starting point for the modelling of field scenarios with specific exposure conditions.

As output the model provides concentration profiles in pore water as a function of depth into the product for specified time intervals over the entire duration of the test or the field scenario. This allows visualization of the concentration development in the pore water as a function of depth and, simultaneously it shows precipitation/dissolution reactions at the interface.

In addition, the concentration build-up in the external solution is monitored at the same time steps, which allows visualising the slowing of concentration increase due to a decreasing concentration gradient between pore water and external solution.

The modelling approach is illustrated in Annex X for cement mortar, where the pH dependence test predictions as well as the tank test predictions are given. In Annex XII the concentration profiles in the pore water within the solid phase as a function of depth at a given time or as a function of time at a given depth are given after exposure to carbonation by external sources (atmosphere or carbonate rich water)

6.7 Impact Modelling to Soil and Groundwater

When it comes to impact modelling affecting surface water, the process is straighter forward than in case of interaction with soil and soil solution, although in some cases the effect of the water to which the material is exposed is important as it may both enhance and decrease release. An example of the first case is an acidic environment, which occurs in natural systems with sulphide present, where due to sulphide oxidation acid is produced, which may lead to serious degradation of the cement matrix (sewer pipes, certain natural rock formations). An example of the latter is a situation where substantially increased carbonate levels occur in groundwater, which may lead to significant calcite precipitation in the surface and interface region of the material leading to a sealing process resulting in a reduction to possibly a complete stop of release from the solid matrix.

In the impact modelling the interaction of released constituents with soil can be addressed in different ways. One option is to assign the released amount to a certain soil layer thickness or in case of groundwater a certain thickness of the saturated zone to assess, if release does not increase levels in soil or groundwater beyond the levels considered safe based on ecotoxicological criteria derived from exposure of organisms and plants to certain concentration levels of contaminants. This approach was originally adopted when the Dutch Building Materials Decree was developed (1995). Another approach is to describe the source term and assess impact based on interaction of released components using a Kd type of approach to evaluate the retardation resulting from released components with soil. This approach has been followed in setting criteria for the EU Landfill Directive (Hjelmar et al, 2001). The limitation of this approach is that constituents are judged independent from one another, while in reality constituents may be released simultaneously readily precipitate once released to soil. This aspect is missed in a Kd type of approach. Full mechanistic modelling by taking all interactions and physical aspects of release into account will prevent such problems. It is, however, a more ambitious approach as the complexity of the model increases substantially.

The building blocks for a full mechanistic modelling of release from a monolith with carbonation of the surface, intermittent wetting and penetration of rain water loaded with released elements into soil is near completion and the scenario can be expected to be available in 2007. First steps of such modelling have been developed in the context of stabilised waste evaluation (van der Sloot et al, 2006). An illustration of the scenario for this exposure route is given in figure 6.12. The release is split in two release modes: intermittent wetting and infiltration and diffusion release under the structure (discussed in section). In the scenario intermittent wetting (e.g. 14 % of the time during a year rain will fall), carbonation of the surface, correction for field temperature, need to be considered.

Conceptual model:

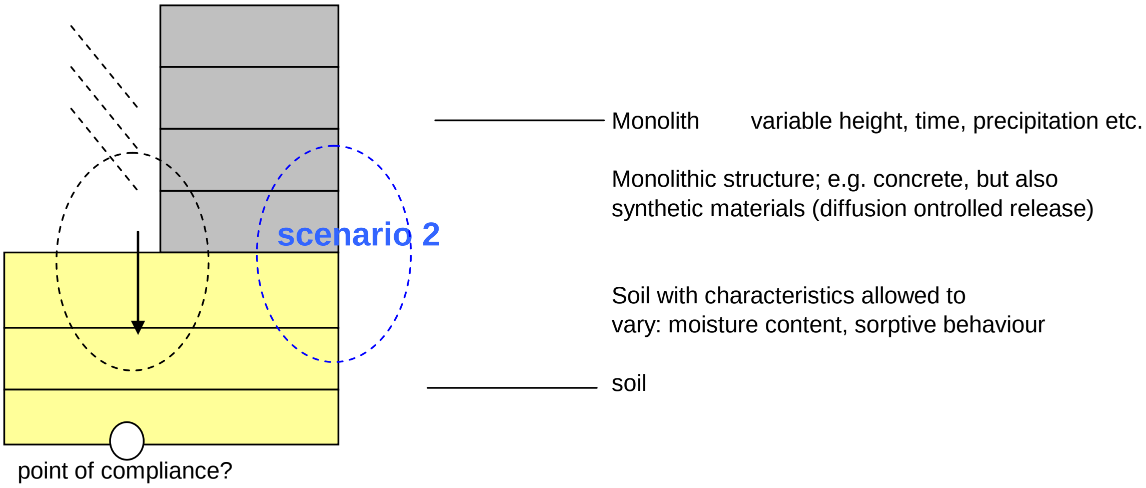


Figure 6.13 *Scenario for structures exposed to intermittent wetting*

7. Methodology for Criteria Development for Unbound Granular Material

In the recycling stage of construction debris, two main options of use exist. These are application of recycled aggregate in bound form, so basically as an alternative aggregate in concrete, and application of an unbound aggregate, for instance as a road base material. The latter can be subdivided in covered and uncovered unbound applications. For bound applications the methodology as presented in section 2 applies.

The basic methodology for the scenario approach to evaluate impact from granular material in unbound application is addressed below. There may not be just one scenario. There are a number of conditions that need to be addressed before to assess their relevance for the impact evaluation. Then a choice can be made as to what scenario(s) best suit the needs to derive criteria for road base application. A number of the issues are:

- Height of application.
- Effective infiltration (covered/uncovered).
- Combination of release mechanisms in one application.
- Role of carbonation, oxidation.
- Interaction of alternative materials in subsequent layers.
- Role of cracking, aging, re-mineralisation.

These aspects need to be addressed through modelling and then their relative importance evaluated. Given the number of possible variables there would seem almost no solution. The main goal will be to synthesize one or a limited set of scenarios that covers the most relevant applications. Since no choice has been made by the regulators at which point in the route from the application to groundwater they want to define points of compliance, this aspect must be left open. In relation to the judgement criteria, the question becomes if relatively stringent water quality criteria are a sufficient protection against undesirable impacts or that ecotoxicity testing will be needed. Ecotoxicity testing directly on the alternative or traditional materials is not very useful, as the quality of the leachate will never meet eco-toxicologically acceptable conditions. This implies that a dilution must be factored in. Since impact at any point of compliance implies element or compound specific attenuation, the ratio of elements or compounds at a point of compliance does not match with their proportion as obtained in a leaching test. The best option for ecotoxicity testing on applications of alternative materials is to assess the sensitivity of organisms at a point of compliance. This implies that ecotoxicity testing should be limited to receiving water systems. Simulation through leach testing is not a suitable means of deriving ecotoxicity derived criteria. Here the emphasis will be on criteria for leaching tests based on meeting water or soil quality objectives at a given point of compliance. Since the modelling covers the entire path from the source to the furthest point of compliance, information on any intermediate point of compliance is automatically obtained.

7.1 Development of a Methodology for Unbound Materials

The basis for judging impact will be a number of relatively simple and more complex scenario descriptions covering the type of applications identified above. The time-dependent source term is derived from the characterisation leaching tests (i.e. a column test in case of granular material). This source term is used as a starting point for the impact to soil, surface and groundwater.

7.1.1 Source Term for an Unbound Application without Top Cover

This situation applies to a non-covered application of (granular) aggregate derived from construction debris in a road or an embankment. In this case direct infiltration applies. The principle for this scenario is shown in figure 7.1. This scenario is also relevant for the unprotected shoulder of a road. The source term is derived from the release as a function as L/S as obtained from a percolation test, in which case L/S is related to the time scale by the relationship: t = (L/S * h * d)/N with h as height, d as density and N the infiltration rate. A refinement of the source term is obtained when changes in material characteristics are factored in, as they may occur for alkaline materials, which with time will become carbonated and feature a lower pH with time. This can be done either empirically through a known pH change with time and assuming local equilibrium (this requires the use of pH dependence test data) or through more rigorous modelling using external CO_2 as neutralising factor and real time modelling using a scenario described in Orchestra. Within this scenario height can be varied to cover a road base and an embankment scenario. Another modification in the scenario is a variation in the particle size, which leads to a greater role of preferential in case of coarse granular material and a lower pH in leachate due to carbonation.

Conceptual model:

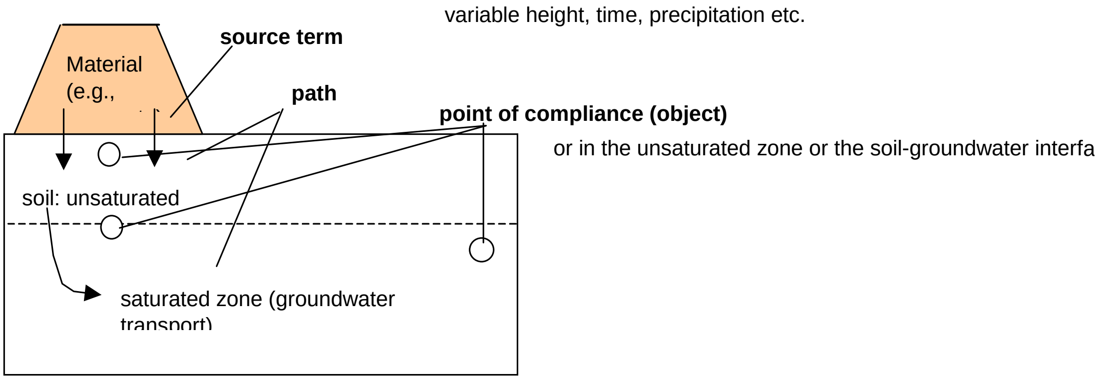


Figure 7.1 *Infiltration scenario for non-covered road base application of granular material*

A source term may consist of multiple layers of granular material, such as material use in the wearing course, as well as in the base and subbase. In the framework of another EU project (SAMARIS, 2006) a detailed description of road construction in relation to environmental aspects of different layers was addressed. An understanding of the mutual interaction of subsequent layers is relevant to be able to make a proper judgement. Some interactions can be envisaged in advance. For instance an alkaline layer will mobilise organic matter from a layer that contains organic matter and as a consequence metals and organic micropollutants may be mobilised. Such interactions can only be assessed with rather sophisticated models, as any empirical model will fail to deal with this level of complexity.

7.1.2 Source Term for an Aapplication of Unbound Material under a Water-Tight Cover

When a concrete or asphalt wearing course is applied and this layer can be considered to be virtually impermeable, then the release from the layer directly beneath this layer is diffusion controlled. This calls for another release evaluation. In this case tank test data are applied as basis for the release prediction. There are two options to deal with this scenario. A simple model using a one - D description provides for a release per m^2 of surface. This impact of the soil can be assigned to a certain soil layer thickness and calculated as an impact (approach of BMD for first meter of soil underneath an application). This approach does not provide insight in the partitioning between solid and liquid phase. In that case another approach is needed. This required a description using Orchestra, where prior to release modelling, the source material is described in terms of the solubility and readily leachable constituents. Then this information derived from geochemical speciation modelling is applied in chemical reaction - transport modelling. For the soil layer an earlier described European reference soil is used. The model output is a pore concentration profile across the alternative material layer and the soil layer, which shows interface interaction (precipitation and mobilisation).

7.1.3 Source Term for Unbound Coarse Granular Material

In this scenario a more significant contribution of preferential flow must be taken into account and associated with that a more intense carbonation leading to neutral exposure conditions in the source term. This implies that the change resulting from carbonation reflected by a pH change in the pH dependence leaching test must be factored in.

7.2 Identification of Relevant Points of Compliance

The regulators have not indicated yet where they consider the point of compliance should be. This implies that choice must be left open. In the Annex II of the landfill Directive the point of compliance (POC) has been chosen at point in groundwater at 20 m beside the landfill (Hjelmar et al, 2001). At this point drinking water criteria were applied as target. In Germany, the boundary between the unsaturated zone and groundwater has been used as point of compliance (DIBT, 2005; BBodSchV, 1999; DafStb-Guideline, 2005). At this moment also a point located in the soil relatively close to the application is under consideration. So for the present evaluation each of these points has to be addressed in subsequent modelling. In the full modelling from source to target al intermediate locations are modelled as well, so the choice of the POC is not critical.

7.3 Identification of Relevant Modelling Parameters for Impact Assessment

The relevant parameters are transport parameters, which are taken as fixed values such as:
Transversal dispersion
Longitudinal dispersion
Porosity of soil
Infiltration rate
Soil interaction parameters
    For simple model: Kd values for relevant constituents
    For more sophisticated model: parameters for sorption sites and organic matter interaction parameters as obtained for a European reference soil.
Parameters used as variables are:
Height of the application
Percolation or diffusion domination or combination of both
Material characteristics
On outside contact with atmospheric CO_2 is assumed

7.4 Modelling of Impact

As indicated relatively simple models can be used, which then have their limitations. Previously, modelling a scenario in more detail was a rather complicated matter. Now, using the chemical reaction-transport capabilities of Orchestra creates the possibility to run rather detailed scenario descriptions in a relatively quick and meaningful manner.

7.4.1 CSTR Approach for Granular Material

In this case, a relatively simple approach is to describe release by a simple decay function (Aalbers et al, 1999). This was the approach applied in the development of the Building Materials Decree (1995). RIVM developed a description of the immission based on the above relationship between L/S and time.

The same approach was used in combination with attenuation factors as derived from impact modelling for the criteria in the EU Landfill directive (1999; 2003). In the case of an utilisation scenario of for instance construction debris the inert waste conditions (i.e. no isolation measures) were applied. From actual leaching data the relevant release parameter of the source term (kappa) was derived. In the modelling for the BMD as well as for the EU Landfill Directive fixed release parameters per element were applied. This is a limitation of this modelling approach as release parameters vary per material. This may not be so critical for known mobile elements like K, Na, Cl and SO_4, but it may prove critical for materials with very different release behaviour of trace elements. A net infiltration of 100 mm/year was assumed. Calculations are made for a road subbase of 1 m and for an embankment of 10 m height. Annex VII.

7.4.2 Full Mechanistic Modelling

The full mechanistic approach follows the steps as outlined in section 2:

- Measurement of constituents with pH dependent leaching test on granular material (chemical speciation aspect).
- Measurement of release of constituents by percolation as a function of L/S (liquid/solid ratio)
- Prediction of the pH dependent release based on a set of selected minerals, sorption on Fe and Al - oxides, interaction with dissolved and particulate organic matter and incorporation in solid solutions (chemical speciation fingerprint).
- This chemical speciation fingerprint is used in combination with transport in a percolation scenario with dual porosity to describe the outcome of the laboratory test.
- When a satisfactory prediction is obtained for the chemical speciation fingerprint and for the time (or L/S) dependent release, the material can be assumed to be well characterised over a wide range of pH and time or L/S conditions relevant for long term behaviour. The chemical speciation fingerprint of the material can then be used as the basis for reactive transport modelling to predict release under well-defined field scenarios with external influencing factors, such as carbonation (CO_2 uptake), redox change, degree and variation in water contact.

In figure 7.2 and 7.3 pH and the concentration profiles as a function of depth are given for C&D waste in contact with soil using a full mechanistic modelling approach. An infiltration flow of 300 mm has been applied. The chemical speciation fingerprint as obtained by LeachXS - Orchestra was used as input for resp. the C&D waste and the soil (Eurosoil 4).

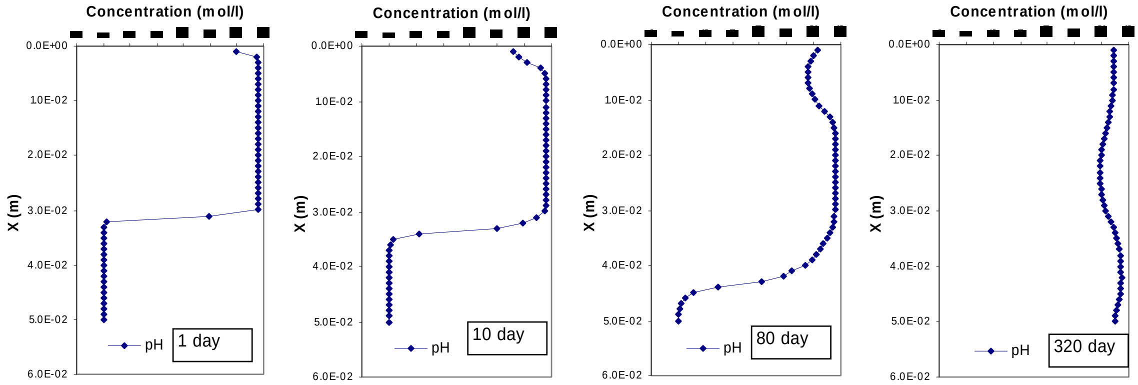


Figure 7.2 *pH profiles as a function of depth in a two layer system consisting of C&D waste and Eurosoil 4 at different times of infiltration equivalent to 300 mm/yr*

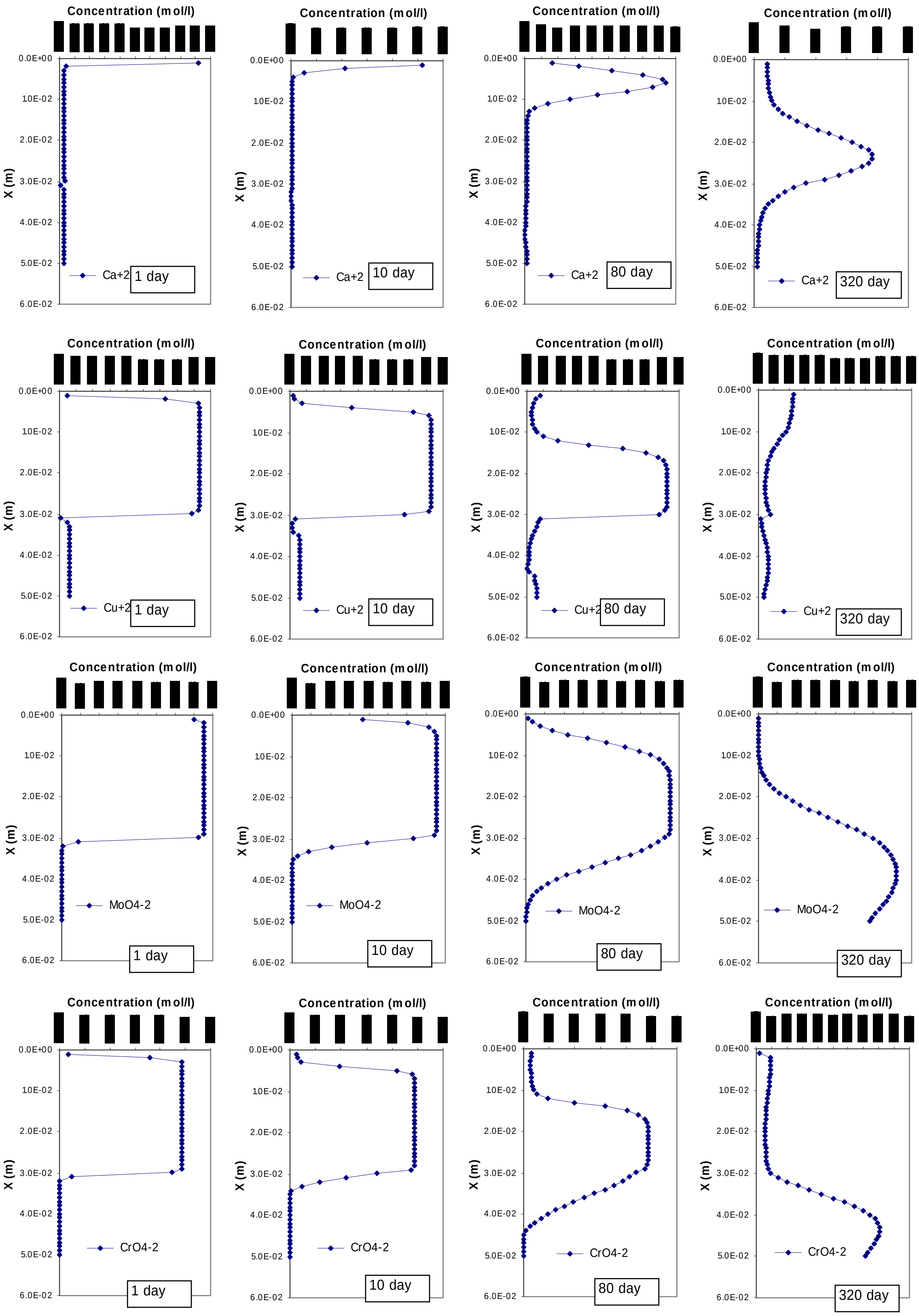


Figure 7.3 *Concentration profiles for Ca, Cu, Mo and Cr as a function of depth in a two layer system consisting of C&D waste and Eurosoil 4 at different times of infiltration equivalent to 300 mm/yr*

8. Prediction of the Leaching Behaviour of Composite Cement and Blended Cement

Based on the chemical speciation fingerprint for different materials, the leaching behaviour of material mixes can be assessed with quite reasonable accuracy, when the availabilities as well as reactive phases such as Fe and Al surfaces, dissolved and particulate organic matter are assigned proportionally to the mix. This type of prediction is useful for Portland-coal fly ash, Portland-slag mixes and other mix compositions. For the blended cement mortars the model prediction needs to take into account the reducing properties of the mortar.

In figure 8.1 the prediction of a blend of OPC with coal fly ash (CFA) is given for two mixing ratios. The basis for this prediction is that the individual end members for the mixture are both well characterised by pH stat measurements. The element availabilities are averaged, all minerals identified in both matrices (several already present in both) are taken along. As shown in the example below the Cr leaching is not affected by the addition of coal fly ash, but the V leachability is increased substantially in CFA OPC mixtures relative to the pure OPC. Once the characterisation of individual constituting substances are available, the behaviour of the mixture can be predicted. As no matching samples are available verification of this type of mixture design is still to be carried out. As it takes only minutes to make these complex calculations, it is potentially a powerful tool to develop optimal cement blends from an environmental perspective.

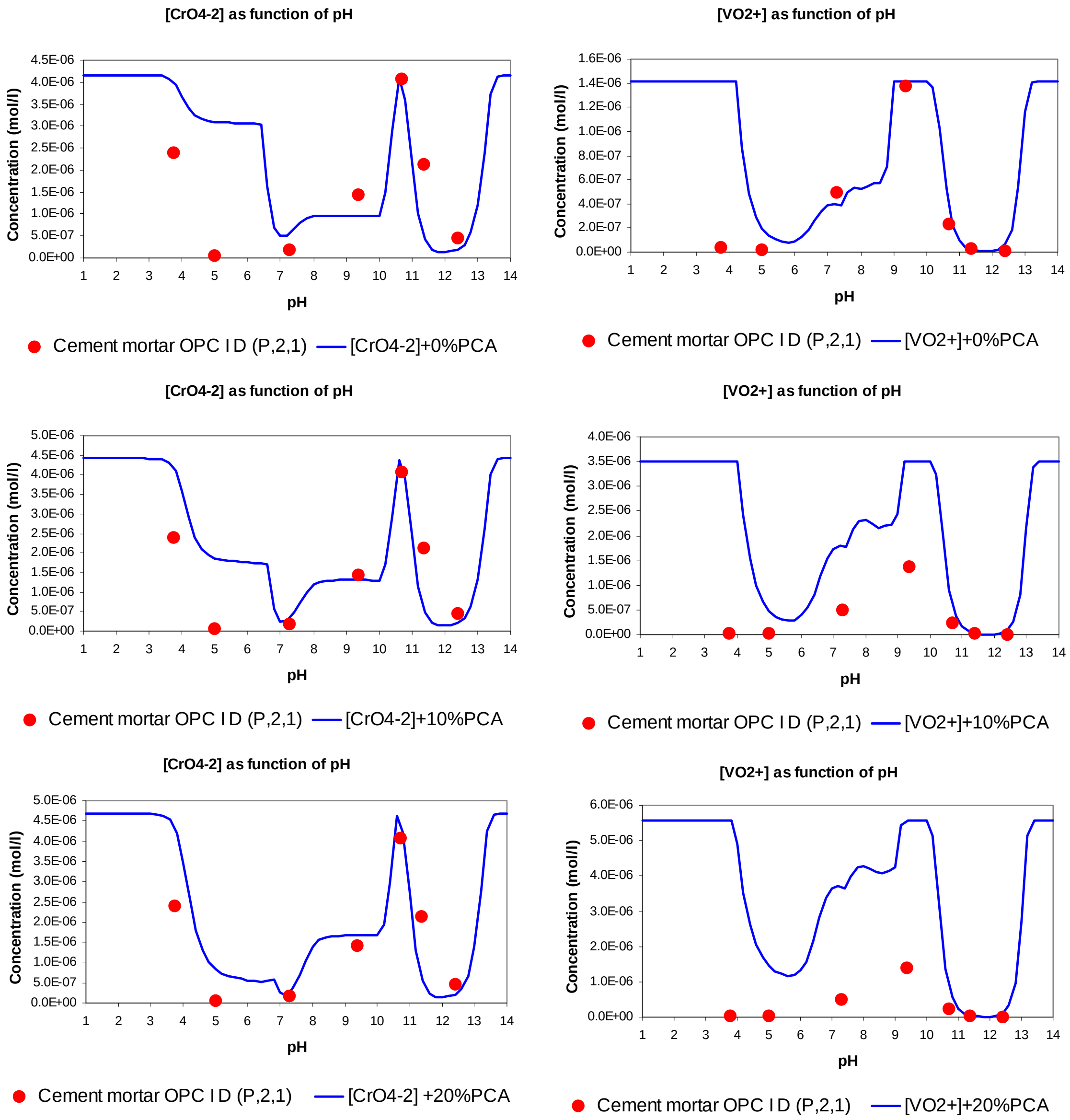


Figure 8.1 *Speciation modelling of material mixtures based on constituting parts. Top: Cr and V model prediction of cement mortar; middle: predicted release behaviour of Cr and V with 10 % coal fly ash addition; bottom: predicted release behaviour of Cr and V with 20 % coal fly ash addition. Note: y-axis scales are different for the three cases*

8.1 Summary: Exposure Scenarios and Corresponding Test Procedures

As a starting point for evaluation of different stages of the life cycle of cementitious products table 8.1 summarises the possible scenarios, the stage in the life cycle, the relevant characterisation test and the relevant compliance test. This evaluation needs to be worked out further in the next phase of the project. Figure 8.2 gives the same information in a more schematic fashion.

Table 8.1 *Exposure scenarios and recommended tests*

SCENARIO	STAGE	CHARACTERISATION	COMPLIANCE
Concrete in contact with groundwater	Service life	pH dependence test on crushed material for speciation and Tank leach test (own pH)	Monolith compliance test (own pH)
Concrete in contact with surface water and constructions on land (pilars, quays, breakwaters, locks)	Service life	pH dependence test on crushed material for speciation and Tank leach test (own pH)	Monolith compliance test (own pH)
Concrete in contact with sea water (oil rigs, quays, breakwaters)*	Service life	No effect expected on water quality, only effect on product (sealing, etc)	
Concrete in contact with drinking water	Service life	Tank leach test (imposed neutral pH after preconditioning)	Monolith compliance test (imposed neutral pH after preconditioning)
Concrete debris recycled as aggregate	Recycling	pH dependence test on crushed material for speciation and Tank leach test (own pH)	Monolith compliance test
Concrete debris reused in roadbase (unbound) , embankment and structural fill	Reuse	pH dependence test on crushed material and percolation test	Granular compliance test
Concrete debris in landfill	Disposal	pH dependence test on crushed material and percolation test	Granular compliance test

* Only relevant from a product durability point of view

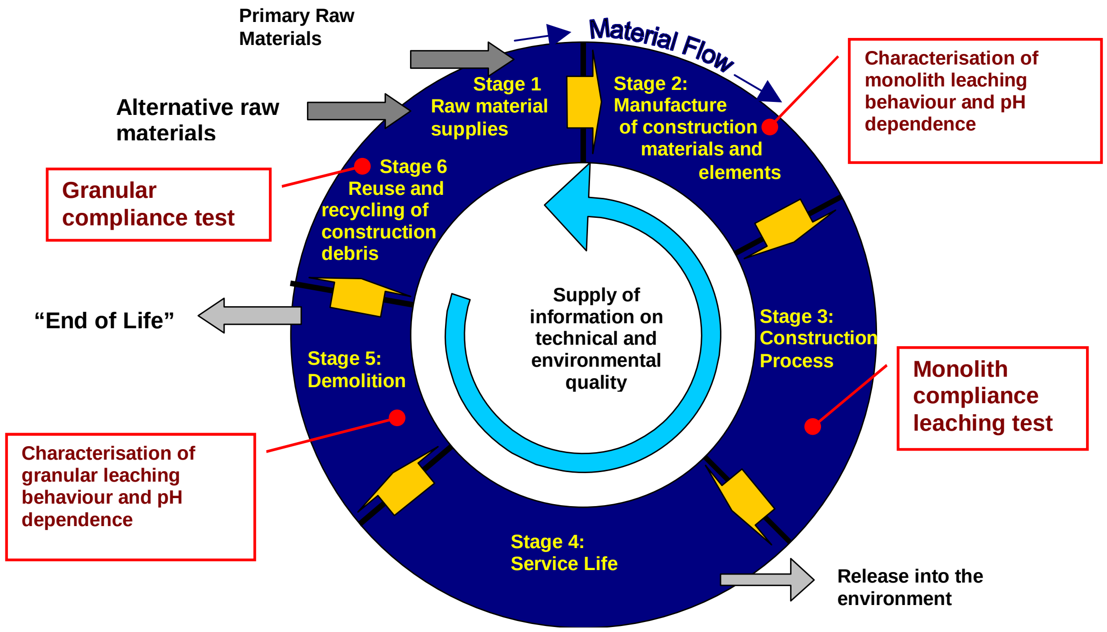


Figure 8.2 *The building cycle with associated test methods at the different levels (characterisation and compliance) for the various stages in the life cycle of cementitious building materials.*

9. Ecotoxicological Testing of Leachates

The use of leachate samples of cement mortars for environmental risk assessment and testing with ecotoxicological test methods are new disciplines in relation to assessment of the impact from use of cementitious products.

In this project, preliminary experiments with ecotoxicological testing of leachate samples were conducted and the experimental difficulties of obtaining well defined exposure concentrations with samples diluted in (growth) media for aquatic testing identified. The test methods were internationally standardised short term tests with algae, daphnia. The samples used for the testing were selected among those of the leachate tests to cover a range of pH conditions, which originated from the pH stat test. The ecotoxicological tests and evaluations are reported separately (Samsøe-Petersen 2005) and summarised here. In the full report, testing and assessment strategies for ecotoxicological evaluation of complexly contaminated samples are discussed.

The environmental toxicity of the samples was expressed as dilution factors necessary to obtain no effect levels. For this, three combinations of parameters were applied:

- Measured toxicity of the complexly contaminated samples.
- Information regarding concentrations of single substances (elements) in the samples and Water Quality Standards.
- Predicted environmental concentrations calculated by the ORCHESTRA modelling tool and Water Quality Standards.

The results of the project demonstrate that the use and interpretation of aquatic ecotoxicological tests with leachate samples from pH-stat tests is impeded for several reasons:

- Samples extracted at low pH with HNO_3 have high salinity and water hardness.
- Samples extracted at low pH with CO_2 are unstable and precipitates are formed.
- The presence of buffers in the test media influence the exposure concentrations in tests solutions, resulting in requirements for measured exposure conditions.
- The presence of EDTA in the algae test medium may interfere with elements in the samples, resulting in requirements for measured exposure conditions.

That part of the toxicity, which was caused by the concentrations of Mg++ and Ca++, could be accounted for. For samples, which had been extracted with HNO_3, EC50-values corrected for the toxicity contribution of the two ions could be used. Dilution factors based on concentrations of single substances in leachate samples, which were not environmentally realistic, were a factor of 3-8 higher than those based on toxicity of the complex samples. This emphasises that testing of intact samples will reflect the toxicity of such complex samples better than the single substances approach. Leachate samples from pH-stat tests are not suitable for ecotoxicological risk assessment due to unrealistically high concentrations of elements. Testing of environmental samples of waters (surface or groundwater) exposed to concrete structures would be more relevant.

Risk assessments based on information about concentrations of single substances in pH stat eluates and Water Quality Standards (Predicted No Effect Concentrations, PNEC) lead to overly conservative estimates of environmental risk, because the conditions of the pH stat test are not comparable to environmental conditions. The risk assessment could be refined by application of predicted environmental concentrations of elements obtained from speciation modelling with environmentally realistic conditions. Refinement of the PNEC values would require evaluation and possibly extension of the data base regarding the toxicity of individual elements to aquatic organisms.

10. Evaluation of Acceptability and Limitations

The evaluation of acceptability of release from specific materials will be based on scenarios of intended use to ensure a proper evaluation of impact. To decide on without testing (WT), without further testing (WFT) or further testing (FT), the distance between observed behaviour and possible critical levels can be used. For OPC and blended cement mortars ANNEX XIII provides guidance.

10.1 Service Life

In the initial stages of commissioning drinking water pipes of concrete lead to elevated levels of pH and possibly of Al. During service life this situation of elevated pH and increased Al levels can only occur after a certain time of stagnant water conditions. Management measures can prevent unacceptable pH and Al levels after such an event. For almost any other application with permanent contact with water or on land with intermittent wetting no exceeding of regulatory criteria as judged against the Dutch Building Materials Decree (BMD, 1995) or Soil Quality Decree (2007) is observed.

10.2 Recycling

For bound applications, the same observation applies as mentioned under 10.1. For unbound applications, potentially critical constituents are Ba, Cr, Mo, Ni, SO_4, Sb and V, when judged against the BMD for granular materials. However, this judgement is made for material size reduced to < 4 mm. Aggregate applications are often in a coarser size range, which implies that release may be expected to be smaller. A proper evaluation of these conditions is still needed, as the particle porosity plays a major role in the judgement of the long term behaviour in this type of material. In the framework of CEN/TC351 activities, this aspect will be covered in robustness work about to be started with support of the European Commission.

10.3 Applicability of Methodology for Other Construction Products

In evaluating the above highlighted integrated approach for environmental impact assessment, it is clear that the applicability is much wider than construction materials. The approach covers wastes, stabilised waste, mining wastes, soils, soil amendments, contaminated soils, sediments and sludges. The main issue being a proper description of the source term for release to soil and groundwater. Points of compliance depend on choices made by regulators, but may be set at the material - soil interface for some very hazardous components, at the soil-groundwater interface or a varying distances from the application in groundwater. In figure 10.1 the various impacts to soil and groundwater that can be addressed by a common approach are indicated. The key aspect in all of these applications is a proper description of the source term. The impact to soil and groundwater will at the European level have to follow a fairly generic approach, as it will be impossible to deal with all the different soil qualities and types in the context of a generic regulatory framework.

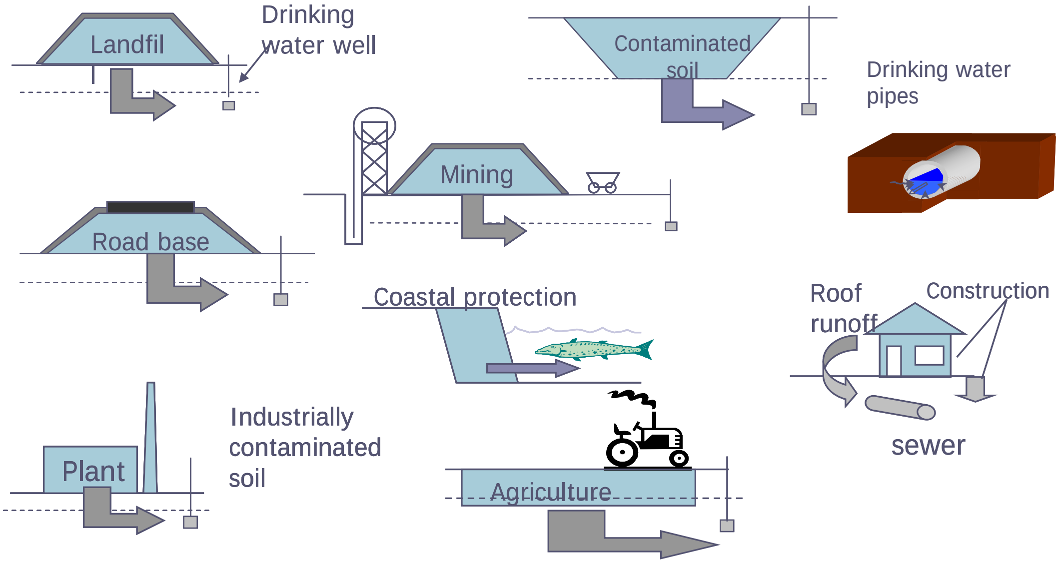


Figure 10.1 *Different impact scenarios on soil and groundwater*

11. Regulatory Developments

On March 16th 2005 the European Commission published the mandate M /366 “Development of horizontal standardised assessment methods for harmonised approaches relating to regulated dangerous substances under the Construction Products Directive (CPD)”. The mandate deals with the subject of emissions of regulated dangerous substances from construction products as defined in the CPD that may have harmful impacts on human health and the environment in relation to Essential Requirement No. 3 of the CPD. The mandate is intended to provide harmonised European measurement/test standards that are needed in order to bring about the “approximation” of laws, regulations and administrative provisions of the Member States. The measurement/test standards will have to provide results that can be expressed in performance terms and be suitable for addressing the emission of regulated dangerous substances in harmonised European Technical Specifications (ETS). These product ETS will need to be reviewed/revised to take into account the intended uses of the product, the release of regulated dangerous substances and the content (where necessary), the assessment of conformity and the information needed to accompany the CE marking. In 2013 the Construction Product Regulation (CPR) will replace the CPD, which implies that recycling and end of life (EoL) need to be considered in addition to service life. The testing tools described here largely cover the additional needs, as size reduction and carbonation effects are largely covered by the pH dependence test in the pH range 7-13.

11.1 Overview of Regulations for Dangerous Substances in View of the Release to Soil, Groundwater and Surface Water

Quantitative requirements related to the release of dangerous substances from construction products in contact with soil, groundwater and surface water exist in the Netherlands “Dutch Building Materials Decree” (1995) and in Germany “Principles for assessment of the effects of construction products on soil and groundwater” (2005) of the German Institute of Structural Engineering (DIBt), in the following called DIBt-Principles. Whereas the DIBt-Principles only apply to new non-standardized products which need a technical approval, and not to those which are already standardized at European or national DIN level, the Dutch Building Materials Decree applies to all products independent on the relevant type of technical specification.

Both regulations contain lists with inorganic and organic parameters. According to the DIBt-Principles inorganic and organic substances are assessed by release with an associated limit value in µg/l. In the Dutch regulation only inorganic substances are assessed by release with an associated limit value in mg/m^2 per 100 years. Moreover, the Dutch regulation does not assess any organic substance by release but only by content and sets limit values on that basis in mg/kg. Furthermore, the mandate M /366 contains a list of inorganic and organic substances that shall be considered in view of the emission released from the tested construction product into soil, groundwater, surface water and indoor air. In this list there are no limit values, because the requirements have to be defined by the Member States. The list from the mandate M/366 was taken over into the draft business plan of the new CEN/TC 351 “Construction products: Assessment of release of dangerous substances”. Guidance on compliance with regulatory criteria and statistical evaluation of test data is given in Annex XIII.

Table 11.1 and 11.2 summarise the inorganic and organic parameters listed in the Dutch Building Materials Decree, in the DIBt-Principles and in the mandate M /366 for construction products (building materials).

11.2 Dutch Building Materials Decree

Buildings materials which fall under the Building Materials Decree (1995) are stone-like materials that are applied and used outdoors. Stone like materials are defined as materials containing at least a total concentration of 10 % silicon, calcium or aluminium (in ionic form). Examples are bricks, paving stones, demolition waste aggregate, sieve sand, earth, clay, concrete etc. Wood, synthetic materials, sheet glass and metals do not fall under the Building Materials Decree, nor does a wall of bricks indoors.

The Building Materials Decree is limited to new construction works such as road construction works, civil engineering or hydraulic engineering works or building works. In the decree, no distinction is made between primary and secondary materials.

Primary and secondary building materials contain inorganic und organic substances which may be released by leaching when the building materials are exposed to rain or groundwater. The environmental burdening of the soil and surface water by leaching of substance is called immission. The Building Materials Decree sets standards for inorganic substances in building materials with regard to the immission of such substances into soil and surface water. These standards are called maximum immission values. The basis for the standards is the maximum quantity of inorganic substances which may disperse into soil and surface water without causing unacceptable burdening. The standards are identical for soil and surface water. The maximum immission values per 100 years of contact between the building material and the environment for inorganic substances are summarised in table 11.1.

For organic substances in building materials suitable leaching tests have been developed, but sufficient information for judgment of materials is lacking. Therefore, composition values (see table 11.2) for organic substances are determined instead of immission values.

To determine the immission values for inorganic substances potentially released from a building material, it is necessary to carry out leaching tests in the laboratory first. In the leaching tests a distinction is made between moulded and unmoulded building materials, because e. g. a brick leaches in a different way to gravel. The leaching tests for building materials are described in the Dutch standard NEN 7340. The leaching values are converted into immission values by means of a formula. This formula takes into account the way the building materials are applied. Also, a correction is made for the temperature, the size of the layer in which the materials is used, the type of work and the type of building material. The formula for the conversion of leaching values into immission values is described in the Ministerial Decision related to the Building Materials Decree (1995). A summary of the formula is given in literature (Aalbers, Th.G. et al., 1999). The formulae also provide a means to calculate back the maximum permitted release in the specific leaching test for particular ways of using the material, e. g. in relation to the thickness of a layer of unmoulded building materials.

Table 11.1 *Inorganic parameters regulated in the Netherlands and Germany as well as substances provided in the mandate M/366*

Parameter	Dutch Building Materials Decree Limit value in mg/m^2 per 100 years	Soil Quality Decree Limit value in mg/m^2 at 64 days in tank test	DIBt-Principles1) Limit value (insignificance thresholdl) in µg/l	Mandate M/366 draft business plan CEN/TC 351
Antimony (Sb)	39	8.4	5	-
Arsenic (As)	435	260	10	+
Barium (Ba)	6300	1500	340	-
Boron (B)	-		740	-
Cadmium (Cd)	12	3.8	0,5	+
Chromium (Cr)	1500	120	7 (Cr III)	+
Cobalt (Co)	300	60	8	+

Copper (Cu)	540	98	14	+
Lead (Pb)	1275	400	7	+
Molybdenum (Mo)	150	144	35	-
Nickel (Ni)	525	81	14	+
Mercury (Hg)	4,5	1.4	0,2	+
Selenium (Se)	15	4.8	7	-
Thallium (Tl)	-		0,8	+
Tin (Sn)	300	50	-	-
Vanadium (V)	2400	320	4[2)]	+
Zinc (Zn)	2100	800	58	+
Bromine (Br^-)	300	670	-	-
Chloride (Cl^-)	30000 mg/m^2 (1 year)	110,000	250000	+
Cyanide (CN^-), total,	75		50	+
volatile	15		5	
Fluoride (F^-)	14000	2500	750	+
Sulphate (SO_4^{2-})	45000 mg/m^2 (1 year)	165,000	240000	+
Asbestos	-	100	-	+

[1)] DIBt-Principles, Draft April 2005: Germany has given this draft to the notification procedure. The Standstill Date is 11-May-2006

[2)] Not valid up to 31-December-2007

Table 11.2 *Organic parameters regulated in the Netherlands and Germany as well as substances provided in the mandate M /366*

Parameter	Dutch Building Materials Decree Limit value (content) in mg/kg	Soil Quality Decree Limit value (content) in mg/kg	DIBt-Principles[1)] Limit value (insignificance threshold) in µg/l	Mandate M /366 draft business plan CEN/TC 351
∑ PAH	75	50	0,2	+
Antracene	10	10	0,01	-
Benzo[a]pyrene	10	10	0,01	-
Benzo[a]antracene	50	40	-	-
Dibenzo[a,h]anthracene	-		0,01	-
Benzo[b]fluoranthene	-		0,025	-
Benzo[k]fluoranthene	50	40	0,025	-
Benzo[ghi]perylenen	50	40	0,025	-
Chrysene	10	10	-	-
Fluoranthene	35	35	0,025	-
Indeno(123-cd)pyrene	50	40	0,025	-
Naphthalene	5	5	-	-
Phenanthrene	20	20	-	-
∑ Naphthalene, Methylnaphthalenes	-		1	-
Volatile halogenated hydrocarbons	-		20	-
1,2 Dichloroethane	-		2	-
Chloroethene	-		0,5	-
Remaining halogenated hydrocarbons	3 mg Cl/kg		-	-
∑ PCB	0,5	0.5	0,01	+
Hydrocarbons	500	500	100	+
Benzene	1,25	1	1	+
Ethylbenzene	1,25	1.25	-	-
Toluene	1,25	1.25	-	-
∑ Xylenes	1,25	1.25	-	-
∑ Alkylated benzenes	-		20	-

Phenol	1,25	1.25	8	+
Nonylphenol	-		0,3	-
Pentachlorophenol	-		-	+
∑ Chlorophenols	-		1	-
Hexachlorobenzene	-		0,01	-
∑ Chlorobenzenes	-		1	-
∑ PCT	-		-	+
Polychlorinated dibenzodioxin	-		-	+
Polychlorinated dibenzofuran	-		-	+
MTBE	-		15	-
Epichlorhydrine	-		0,1	-
Creosote	-		-	+
∑ Pesticide (chloric)	0,5		-	-
∑ Pesticide (non-chloric)	0,5		-	-
Organic carbon TOC/DOC	-		-	+

1) DIBt-Principles, Draft, April 2005. Germany has given this draft to the notification procedure. The Standstill Date is 11-May-2006

11.3 Dutch Soil Quality Decree

The Building Materials Decree has been revised following the experience of about 10 years. In the development of limit values for the new decree, a source term was defined for release from monolithic waste based on test results from NEN 7345 taking into account the temperature difference and wet/dry cycles in the exposure. Existing data from typical Dutch soil profiles were used to define the properties of the underlying soil profile (i.e., in terms of water saturation, and sorbent surfaces present in the soil such as clays and organic matter). The calculations were performed with ORCHESTRA (Verschoor et al, 2009) using 1D-flow of water along a streamline. Next, on a given “point of compliance”, breakthrough curves were established and concentrations were compared to limit values for groundwater (e.g., ecotoxicological values). Using an iterative process, limit values were then derived for building materials for each contaminant (expressed in mg/m^2 at 64 days) in such a way that predicted concentrations at the point of compliance just fulfils the criteria at the point of compliance.

The advantage of this semi-mechanistic approach over the often used Kd-approach is obviously that important interactions between contaminants (and major elements such as Fe, Al and Ca in the soil and groundwater) are captured by the model. In addition, this way of modeling is fully transparent as all thermodynamic constants used in the modelling are justified in scientific literature. The latest developments in modelling also describe the source term of the construction product in a full mechanistic manner (van der Sloot et al, 2006).

As of 2008 the Soil Quality Decree (2007) replaces the criteria set by the Building Material Decree (1995).

11.4 German DIBt-Principles

The DIBt-Principles for assessing the effects of construction products on soil and groundwater are intended to be applied in the approval procedure of the DIBt. The “Principles” are divided into two Parts. Part I comprised the general assessment concept for construction products with regard to protection against harmful changes to soil and/or harmful changes to the quality of the groundwater. Part II puts the assessment concept into more precise terms for specific construction products. At the moment part II is only available for concrete’s constituent materials and concrete itself (2005).

Part II of the DIBt-Principles considers the constituents of concrete – including the constituents of structural mortar – cement, concrete additives, concrete admixtures, and aggregates (including concrete aggregates) as well as concrete itself which may be the subject of approval as a construction product. An assessment of these constituents of concrete may be necessary on account of their components as well as their manufacture. To evaluate the constituents under real conditions it may be necessary to batch, mould and cure a standard/reference concrete within which the constituent under test is incorporated.

An assessment of concrete that is to be approved is only necessary if the concrete contains non-standard or non-approved constituents the effects of which on soil and groundwater are unknown. As a rule, the hardened concrete phase shall be tested and assessed. The relevant constituents to be tested are established on the basis of the details that are to be submitted by the applicant (type, origin, manufacturing process, and chemical details of the material).

Hardened concrete in contact with the unsaturated soil zone is generally unproblematic from the point of view of both groundwater and soil protection. In this case tests shall be carried out only if the relevant components and the area of application make a relevant mobilization of components likely.

For the assessment of the constituents of concrete or concretes themselves, hardened concretes are usually tested at an age of 56 days. For details of production and storage of test specimens see (DiBT, 2005). The test specimens (cubes 100 mm x 100 mm x 100 mm) are eluted using a long-term laboratory immersion test (DafStb-Guideline, 2005). The results of the long-term test can not be compared directly with the insignificance thresholds (table 11.1 and table 11.2), because the boundary conditions under which the laboratory tests are carried out do not reflect actual conditions in the field. Therefore, modeling is necessary to translate the laboratory results into results expected under real situations.

For concrete placed in the groundwater, the site for compliance with the insignificance thresholds is a layer of groundwater in contact with the surface of the building component (contact groundwater). Due to the diffusion-controlled release of substances from concrete, substance concentrations decrease markedly with time and with increasing distance from the material surface. As short-term elevated concentrations in thin interface zones are not relevant in legal terms, it is therefore permissible to compare the mean of both small-scale and short-term concentrations with the insignificance thresholds.

To calculate the substance concentration in the contact groundwater in relation to time the substance input must be determined and the boundary conditions under which the calculations are made must be defined. The substance input can be calculated by means of a diffusion model on the basis of the results of the long-term immersion test. The combination of this diffusion model with a geological flow and transport model for the dispersion of the substance in the groundwater makes it possible to calculate substance concentrations in the contact groundwater in relation to time. The assessment concept for "the constituents of concrete and concrete itself" [5] stipulates the stringent boundary conditions listed in table 11.3 in order to create a scope of use as wide as possible.

Table 11.3 *Boundary conditions for the calculation of substance concentrations in the contact groundwater for "the constituents of concrete and concrete itself" according to [5]*

Parameter	**Symbol**	**Unit**	**Size**
Surface area of building component	-	m^2	40 x 20
Permeability coefficient, effective porosity	k_f; n_e	m/s; -	10^{-4}; 0,1
Groundwater gradient	i	-	10^{-3}
Small-scale average determination in the contact groundwater	-	m	0 to 2,0

Period of time over which times are averaged	-	Months	6
Temperature	T	°C	10
Retardation, chemical or biological degradation	-	-	No retardation, no degradation

By modeling various different concretes with these boundary conditions a functional relationship could be identified between the averaged concentration of trace elements in the contact groundwater and released quantities during the long-term immersion test. Using the linear equation a permissible release of the respective trace elements in the long-term immersion test can be derived corresponding to the respective insignificance threshold by the following equation:

Insignificance threshold [µg/l] / 0,97 [µg m^2/l mg] = Permissible release$_{(56\ \text{days})}$ [mg/m^2]

Assuming that the release of organic substances from concretes is diffusion controlled too, the same equation should be valid for these substances.

12. Conclusions – ECRICEM II

12.1 General

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 3 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 and Soil Quality Decree), 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 cementitious 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 cementitious 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. For cementitious materials, the experimental and modelling results obtained in ECRICEM Phase I and Phase II have contributed already significantly to the work of CEN/TC 351 ‘Construction products: Assessment of release of dangerous substances' in the development of test methods for soil and groundwater impact as part of the Essential Requirement No. 3 (ER 3) of the CPD.

The cement mortar leaching data are embedded in a dedicated LeachXS database. The model runs are assessable through LeachXS, as they are available as case files in the system. This set of data provides a sound starting set for modelling release from any cementitious product.

12.2 Specific

The composition of extended measurements of German cements match quite well with the data on cements from worldwide origin obtained in ECRICEM I and II. For a number of elements the spread towards the higher range is larger for the cements from world-wide origin. This may very well relate to the source materials (more mineral rich environments).

The relevance of total composition for judging environmental aspects from cementitious materials to soil and groundwater is limited as judgement on composition does not take into account the variability in leaching independent of composition. It may well lead to a false sense of security, as a low concentration does not automatically imply low leachability nor that a high concentration does necessarily mean high leachability.

The release from monolithic materials like cementitious products is very complex as the release is very much determined by changes in a very thin surface layer of the product. This aspect of release is largely related to pH changes and associated mineral transformations. Assuming diffusion only leads to overestimation of release. A more accurate description of release under a variety of exposure conditions (e.g. carbonation, oxidation, salt intrusion) requires chemical reaction transport modelling.

The combination of the pH dependence test and the tank test provide basic information that allows a chemical fingerprint for the mortar or concrete to be established, that with additional information such as tortuosity (from Na and K from the tank test), dimensions, water exposure, etc allow the prediction of many different exposure scenarios for that material.

Composite cement mortars containing slag all show reduced Cr leachability, which is attributed to the reducing properties of slag. This phenomenon is already quite marked at 10 % slag addition. The Cr reduced cement mortars using Fe II and Sn II salts show significantly reduced Cr leachability. The chemical speciation modelling also allows the form of dissolved species to be identified, which in case of Cr is particularly relevant, as Cr III forms are less toxic than Cr VI species.

When the chemical speciation fingerprint for materials that are blended in cement is available, the leaching at different mixing ratios and material combinations in a blend can be modelled. This allows design of blends based on environmental properties rather than technical specifications alone.

The particle size distribution of aggregates derived from construction debris is important for release. Currently, no proper information on particle size distribution is available. Size ranges in practice are 0-6 mm, 0 - 32 mm or 0 - 40 mm. The effect of particle size distribution on release is clearly insufficient.

There is no significant difference for most elements between leaching from cement mortar bars or from concrete cubes as solubility in the porewater of the cement matrix dictates release for most elements and the main solubility controlling phases are the same in both types of materials. There may be a difference for some of the more mobile elements like Na and K, which vary in proportion to the cement content of the concrete.

The repeatability of the tank test as well as the pH dependence leaching test is such that the variation within one cement plant (variation in operation and feed) as well as variation between different cement plants can be separated.

Geochemical modelling capabilities of cement mortar leaching using the ORCHESTRA software for chemical reaction and transport modelling embedded in LeachXS, it is not only possible to predict the release from cement mortar to the water phase under a wide range of conditions (continuous wet or intermittent wetting, flowing or stagnant water, atmospheric exposure, seawater exposure), but also to assess the evolution damage due to chemical attack (e.g. sulfate ingress)

The present model adequately predicts pH dependence test and tank test results for more than 30 major, minor and trace elements and their partitioning over dissolved and solid phases simultaneously. Input parameters are maximum concentration of major, minor and trace elements in the pH dependence test, sorption parameters, a set of selected minerals, system dimensions, and surrounding water volume and composition.
It turns out that a basic set of typical cement minerals will adequately describe the leaching behaviour of all major and minor elements. For some trace constituents additional mineral phases may be needed. This means that a very limited testing can provide a wealth of relevant information through the combination with modelling.

The concentration profiles as obtained by leaching (mortar only; L/S=10 at own pH) from a 40 year exposed concrete slab half-submersed in water have indications have been obtained that Cr VI slowly converts to Cr III during service life.

A main conclusion from the field verification studies is that after 40 year carbonation fronts progress only a few mm's in concrete that meets current specifications. In less specific mortars (old fort), carbonation has progressed much further (up to 30 - 40 mm's). In Roman "cement" aged 2000 years, carbonation has progressed throughout the matrix. The carbonation has been linked with leaching data showing changes in surface chemistry.

The different stages of the life cycle of cement mortar can be tested adequately with available standardised methods. For recycling of bound aggregate from demolished concrete, this implies following the same approach as for the primary materials. For recycling of demolished concrete aggregate in unbound applications the combination of pH dependence test and percolation test is of relevance.

The methodology developed for cementitious materials in terms of test use, modelling and prediction is, possibly with some adaptations due to materials specific properties, equally applicable to other construction materials (sintered bricks, other cementitious materials than the ones studied here, asphalt concrete, etc, ...)

Based on the current understanding of process, QC testing can be targeted to the relevant parameters, thus avoiding unnecessary testing of irrelevant parameters. This can be addressed by using a decision scheme to classify materials as WT (without testing), WFT (without further testing) and FT (further testing) currently in development.

Ecotoxicity testing on eluates from laboratory leaching tests is not straightforward. The conditions in the eluates differ too much from actual exposure conditions to give a realistic insight in the risk.

13. Recommendations

Expand the current database for the cement and concrete industry with quality control data and field data to the extent available. Thus avoiding unnecessary duplication of testing, facilitating quality control and design of blended cements optimized for theirlong term environmental properties.

Development of dedicated scenario models for specific applications of cementitious materials in different exposure conditions using easy user defined parameter modifications.

Application of the methodology for inorganic constituents on organic admixtures. The role of chemical changes due to high pH and restrictions of mobility in the cement matrix. Tortuosity is a relevant factor in this context, as well as possible mobilisation of otherwise much less mobile constituents (metals).

The description of ettringite solid solutions for several oxyanions, Sr and Ba are based on estimates from one standard cement. The values need to be verified independently by experimental solubility measurements. Other solid solution descriptions need to be implemented for hydrogarnets and LDH.

In future work, the potential release of substances from construction debris with a given particle size should be modelled rather than tested to evaluate the contribution of the different size fractions in the leaching process.

References

Aalbers, Th.G. et al. Environmental quality of primary and secondary construction materials in relation to reuse and protection of soil and surface water. RIVM/RIZA, Bilthoven. No. 771402997, 1999.

Achternbosch, M., K.-R. Brautigam, N. Hartlieb, C. Kupsch, U. Richers and P. Stemmermann and M. Gleis. Heavy metals in cement and concrete resulting from the co-incineration of wastes in cement kilns with regard to legitimacy of waste utilisation. FKZA 6923. October 2003.

Andersson, Ase. Leaching of hazardous substances from concrete constituents. PhD Thesis Chalmers University. Göteborg, Sweden 2000.

AFNOR XP X 31- 211 1994 Waste – Leaching test for a solid initially massive or produced by a solidification process

Baur, I. and Annette Johnson,C. The solubility of selenate-Aft (3CaO.Al2O3.3CaSeO4.37.5H2O) and selenate AFm (3CaO.Al2O3.3CaSeO4.xH2O). Cement and concrete Research, 33, 2003, 1741 – 1748.

Bestimmung der Freisetzung anorganischer Stoffe durch Auslaugung aus zementgebundenen Baustoffen, Teil 1: Grundlagenversuch zur Charakterisierung des Langzeitauslaugverhaltens (Determination of the release of inorganic substances by leaching from cementitious building materials, part 1: fundamental principles for the characterisation of the long-term leaching behaviour). Deutscher Ausschuss für Stahlbeton - DAfStb, Germany, DAfStb-Guideline (Draft April 2005). Beuth Verlag GmbH, Berlin und Köln, Purchase order number: 650xx

Building Materials Decree (Soil and Surface Water Protection). Bulletin of Acts, Orders and Decrees of the Kingdom of The Netherlands (Staatsblad), No. 567, 30. November 1995 (in Dutch; English: http://international.vrom.nl/docs/internationaal/BMDtexts.pdf)

Building Materials Decree soil and surface water protection'. (BMD) (*). Bulletin of acts, orders and decrees, No 567, 1995. (http://www.vrom.nl/international). Ministerial Decision belonging to the Building Materials Decree. The Netherlands Government Gazette (Staatscourant), No. 247, 22. December 1995 (in Dutch). An English translation is available under: http://international.vrom.nl/docs/internationaal/BMDtexts.pdf, see also: http://international.vrom.nl/docs/internationaal/BMDexplan.pdf).

Bundes-Bodenschutz- und Altlastenverordnung (BBodSchV) vom 12. Juli 1999. Bundesgesetzblatt Jahrgang 1999 Teil I Nr. 36, Bonn 16. Juli 1999.

CEN report TC51 TC 104 (1999): *A study of the characteristic leaching behaviour of hardened concrete for use in the natural environment* N614 (in preparation).

CEN/TC 164 Water supply, EN 14944-1:2006 "Influence of cementitious products on water intended for human consumption – Test methods – Part 1: Influence of factory made products on organoleptic parameters"

CEN/TC 164 Water supply, prEN 14944-3: "Influence of cementitious products on water intended for human consumption – Test methods – Part 3: Migration of substances from factory made cementitious products".

CEN, (1996) Methodology guideline for the determination of the leaching behaviour of waste under specified conditions. PrENV 12920, CEN/TC 292 WG6 Characterisation of waste, 1996..

CEN/TC292 (2004): Characterization of waste - Leaching behaviour tests - Up-flow percolation test (under specified conditions), CEN/TS 14405

CEN/TC292 (2005). Characterization of waste - Leaching behaviour tests - Influence of pH on leaching with initial acid/base addition. CEN/TS 14429

Chandelle, J.M. Alternative fuels: the valorisation of waste in the cement industry. Cement international. Vol 1, 4/2003, 50 - 60.

Co-normative research on test methods for materials in contact with drinking water. MAT1-CT94-0058. CEN/TC 164/WG3/AHG6/99-06, 1999.

Cougar, M.L.D., B. E. Scheetz and D.M. Roy (1996): *Ettringite and C-S-H Portland cement phases for waste ion immobilisation: a review.* Waste Management, 16 (4), 295-303, 1996.

Council Decision 2003/33/EC of 19 December 2002 establishing criteria and procedures for the acceptance of waste at landfills pursuant to Article 16 and Annex II to Directive 1999/31/EC.

Council Directive 1999/31/EC of 26 April 1999 on the landfill of waste.

Council Directive 89/106/EEC of 21 December 1988 on the approximation of laws, regulations and administrative provisions of the Member States relating to construction products.

Council Directive 89/106/EEC of December 21, 1988 concerning construction products. Construction Products Directive: Interpretative document No. 3: Hygiene, health and the environment.

Construction Products Directive (CPD).89/106/EEC, 1988 and 93/68/EEC, 1993.

Council Directive 98/83/EC of 3 November 1998 on the quality of water intended for human consumption.

Degre, J.P. (1996): *Waste Co-processing in Industry. Criterias for an optimal waste management in the Cement Industry*. Ditec, Obourg, November 1996 (unpublished).

Dijkstra, J.J., Meeussen, J.C.L., van der Sloot, H.A. and Comans, 2003. Modelling speciation and transport in MSWI bottom ash. In: Ortiz de Urbina, G. and Goumans, J.J.J.M., WASCON 2003, conference proceedings, San Sebastian, Spain.

Dijkstra, J.J., Meeussen, J.C.L., Comans, R.N.J., 2004. Leaching of heavy metals from contaminated soils: an experimental and modeling study. *Environ. Sci. Technol*., **38**, 4390-4395.

Dijkstra, J. J., van der Sloot, H. A., Spanka, G., Thielen, G. 2005. How to judge release of dangerous substances from construction products to soil and groundwater - CPD Topic 1 - Soil and groundwater impact - CPD Topic 2 - Hierarchy in testing: Characterisation, initial type testing, further testing and selection of tests in specific stages of material judgement - CPD Topic 3 – Proposal for reference to ER 3 aspects in product standards and in CE marking. ECN-C--05-045.

Dzombak, D.A. and Morel, F.M.M. (1990). *Surface complexation modeling: hydrous ferric oxide*, John Wiley & Sons, Inc., New York.

Eighmy, T.T., Cook, R.A., Gress, D.L., Coviello, A., Spear, J.C.M., Hover, K., C., Pinto, R., Hobbs, S., Kosson, D., Sanchez, F., van der Sloot, H., Korhonen, C.,Simon, M., 2002. Use of accelerated aging to predict behavior of recycled materials in concrete pavements - Physical and environmental comparison of laboratory-aged samples with field pavements. Transportation Research Record (TRR) Series 1792(Sustainability and Environmental Concerns in Transportation 2002), 118-128.

Eighmy, T.T., Grimi, D., Whitehead, I.E., Zhang,X., Gress, D.L., The influence of monolithic physical properties on diffusional leaching behaviour of asphaltic pavements constructed with MSW combustion bottom ash. In: Waste materials in Construction, putting theory in pratice, Ed. J.J.J.M. Goumans, G.J. Senden, H.A. van der Sloot, Elsevier, 1997, 125-148.

EN 1250-2:1994 Wood preservatives - Methods for measuring losses of active ingredients and other preservative ingredients from treated timber - Part 2: Laboratory method for obtaining samples for analysis to measure losses by leaching into water or synthetic sea water

EN12920, CEN TC 292 WG6, 1996.

Environment Canada, 1990. Compendium of waste leaching tests. Environmental Protection series. Report EPS 3/HA/7.

Environmental Benefits of Using Alternative Fuels in Cement Production: A LIFE-CYCLE APPROACH. Cembureau. D/1999/5457/February.

European Commission, Directorate General XII – Science, Research and Development: Co-normative research on test methods for materials in contact with drinking water. Report EUR 19602 EN, Luxembourg (2000).

EN 197 , 2000 Cement. Composition, specifications and conformity criteria for common cements.

EN196-1: *Test methods for Cement*. Part 1: Determination of strength

EU project SMT4-CT96-2066 (2000): *Technical support to the Network Harmonisation of Leaching/Extraction tests* (2000).

European patents: *Chromate neutralisation by Aalborg* Portland, 0054314, 84 115 414.9, 84 115 413.1

Felmy, A.R., D.C Girvin,. E.A Jenne(1984):. *MINTEQA2 computer program for calculating aqueous geochemical equilibria*, EPA-600/3-84-032, U.S. Environmental Protection Agency, Athens.

Fregert, S. et al (1997): *Reduction of chromate in cement by iron sulfate*. Contact Dermatitis 1979: 5: 39-42

Glasser, F.P., D.E. Mcphee and E.E. Lachowski(1988): *Modelling approach to the prediction of equilibrium phase distribution in slag-cement blends and their solubility properties*. Mat. Res. Soc. Symp. Vol 112, 1988, 3- 12.

Groot de, G. J. und Sloot van der, H. A.: Determination of leaching characteristics of waste materials leading to environmental product certification. 2nd International Symposium on Stabilization/Solidification of Hazardous, Radioactive and Mixed Wastes, Williamsburg, USA (1991).

Groot G.J. de, H.A van der Sloot (1990): *Determination of leaching characteristics of waste materials in relation to environmental product certification. Proc. Sec. Int. Symp. Stabilisation/solidification of Hazardous, Radioactive and Mixed wastes*. Williamsburg, Virginia, May, 29 to June 1, 1990.

Groot, G.J. de, I. Hohberg, F.J.M. Lamers, A.M.H. van der Veen, W. Wassing, Ph. Quevauviller, Development of a Leaching Method for the Determination of the Environmental Quality of Concrete, bcr information EUR17869, 1997.

Hendriks, Ir.Ch.F. and Raad,J.S.: Principles and background of the Building Materials Decree in The Netherlands. Materials and Structures/Matériaux et Constructions, 30 (1997) pp. 3/10.

Hinsenveld, M (1991): *Towards a new approach in modelling leaching behaviour*. In: Waste materials in Construction Eds. J.J.J.M. Goumans, H.A. van der Sloot, Th.G. Aalbers, Elsevier Science Publishers, Amsterdam, 1991, 331-340.

Hjelmar, O., H.A. van der Sloot, D. Guyonnet, R.P.J.J. Rietra, A. Brun & D. Hall: Development of acceptance criteria for landfilling of waste: An approach based on impact modelling and scenario calculations. In T.H. Christensen, R. Cossu and R. Stegmann (eds.): Sardinia 2001, Proceedings of the Eigth International Waste Management and Landfill Symposium, S. Margharita di Pula, Cagliari, CISA , Vol. III, CISA, 2001, 712-721.

Hockley, D. en H.A. van der Sloot, Long-term processes in a stabilized waste block exposed to seawater. 1991. Environ. Sci. & Technol., 25, 1408 - 1414.

Hohberg, I., Chr. Müller, P. Schießl, G. Volland, Umweltverträglichkeit zementgebundener Baustoffe, Deutscher Ausschuss für Stahlbeton, Heft 458, Beuth Verlag, Berlin 1996.

Hohberg, I.; Groot de, G. J.; Veen, A. M. H. und Wassing, W.: Development of a leaching protocol for concrete. The International Conference for the Environmental and Technical Implications of Construction with Alternative Materials, Proceedings, Houthem St. Gerlach, The Netherlands (1996)

IAWG (International Ash Working Group; A.J.Chandler, T.T.Eighmy, J.Hartlen, O.Hjelmar, D.S.Kosson, S.E.Sawell, H.A.van der Sloot, J.Vehlow). (1997): *Municipal Solid Waste Incinerator Residues.* Studies in Environmental Science 67, Elsevier Science, Amsterdam, 974.

Irene Smith. Co-utilisation of coal and other fuels in cement kilns. IEA Clean Coal Center. PF 03-02. August 2003.

Johnson, C. A.: Metal binding in the cement matrix – An overview of our current knowledge. Dept. Water Resources and Drinking Water, Water-rock Interaction Group, EAWAG, PO box 611, 8600 Duebendorf, Switzerland (2002).

Johnson, A. and Kersten, M. Solubility of Zn(II) in Calcium Silicate Hydrates in alkaline solutions. Environ.Sci. Technol., 33, No13, 1999, 2296-2298.

Johnson, C.A. and Glasser, F.P. Hydrotalcite-like minerals (M2Al(OH)6(CO3)0.5.XH2O, where M=Mg,Zn,Co, Ni) in the environment: synthesis, characterisation and thermodynamic stability. Clays and clay minerals, 51, No1, 1-8, 2003.

Karstensen, K.H.(1994): *Burning of hazardous waste as co-fuel in a cement kiln- does it affect the environmental quality of cement?* In: Environmental Aspects of Construction with Waste Materials. Studies in Environmental Science 60. Eds. J.J.J.M. Goumans, H.A. van der Sloot, Th.G. Aalbers. Elsevier Science Publishers, Amsterdam, 1994

Keizer, M. G. and W.H. van Riemsdijk (1998): *ECOSAT. Department of Environmental Sciences, Subdepartment Soil Science and Plant Nutrition*, Wageningen Agricultural Univ., Netherlands.

Kindness A., A. Macias and F.P. Glasser (1994): *Immobilisation of Cr in cement matrices.* Waste Management, 14 (1), 3-11, 1994.

Kindness, A., E.E. Lachowski, A.K. Minocha and F.P. Glasser (1994): *Immobilisation and fixation of molybdenum VI by Portland cement.* Waste Management 14, 2, 1994, 97-102.

Kinniburgh, D.G., van Riemsdijk, W.H., Koopal, L.K., Borkovec, M., Benedetti, M.F., and Avena, M.J. (1999). Ion binding to natural organic matter: competition, heterogeneity, stoichiometry and thermodynamic consistency, *J. Colloids Surf., A,* Vol. 151, pp. 147-166.

Klemm, W.A.: *Ettringite andoxyanion substitutes ettringites – their characterisation and applications in the fixation of heavy metals: A synthesis of the literature*. Portland Cement Association, 1998.

KNMI Information on average annual temperature (9.2 ± 0.5) over 1961 to 1990 at 1.5 m above ground KNMI De Bilt The Netherlands.

Kosson, D.S. and H.A. van der Sloot (1997): *Integration of Testing Protocols for Evaluation of Contaminant Release from Monolithic and Granular Wastes. In: Waste Materials In Construction - Putting Theory into Practice. Studies in Environmental Science 71.* Eds. J.J.J.M. Goumans, Senden G.J., H.A. van der Sloot: Elsevier Science Publishers, Amsterdam, 1997, 201-216.

Kosson, D.S., Sanchez, F., van der Sloot, H.A. (2001): *USA Paving project. Aggregate leaching behaviour*, 2001 (in preparation)

Kostka, J.E. and Luther III, G.W. (1994). Partitioning and speciation of solid phase iron in saltmarsh sediments, *Geochim. Cosmochim. Acta*, Vol. 58, 1701-1710.

P. Kumarathasan, G.J. McCarthy, D.J. Hassett, D.F. Pflughoeft-Hasset, Oxyanion substituted ettringites: synthesis and characterization; and their potential role in immobilization of As, B, Cr, Se and V, Mater. Res. Soc. Symp. Proc. 178 (1990) 83-104.

Lang. Th.A. Use of alternative materials at HOLCIM plants in Europe. Cement international. Vol 1, 4/2003, 62 - 70.

Leroy, P., Rigal, S., Baron, J., van den Hoven, Th., Slaats, N., Morlt, M., Autugelle, C., Wagner, I., Werner, W., Oliphant, P., Conroy, R., Miller, R., Quevauviller, Ph. (2000): *Co-normative research on test methods for materials in contact with drinking water.* Final report Mat 1-CT94-0058, EUR 19602, 2000.

LeachXS (2005): A Database-expert system for leaching and environmental impact assessment. http://www.leachxs.com.

Locher, F.W. Untersuchung des Betons von Uferschutzbauten auf Helgoland. Beton Nr. 18, H. 2, S. 47-50 and H. 3, 82-84, 1968.

Lothenbach, B., Matschei, T., Moschner, G. and Glasser, F. P. 2008. Thermodynamic modelling of the effect of temperature on the hydration and porosity of Portland cement. Cement and Concrete Research, 2008(38) 1-18.

Lothenbach, B., Winnefeld, F., Alder, C., Wieland, E. and Lunk, P. 2007. Effect of temperature on the pore solution, microstructure and hydration products of Portland cement pastes. Cement and Concrete Research, 37, 483-491.

Mantus, E.K., K. Kelly, G.A. Pascoe(1992): *All Fired Up – Burning hazardous waste in cement kilns* Environmental Toxicology International.

G.J. McCarthy, D.J. Hassett, J.A. Bender, Synthesis, crystal chemistry and stability of ettringite, a material with potential applications in hazardous waste immobilization, Mater. Res. Soc. Symp. Proc. 245 (1992) 129-140.

Meeussen, J C. L. (2003). ORCHESTRA, Environmental Science and Technology 37, 1175-1182.

Mohammed, T.U. and Hamada, H. Relationship between free chloride and total chloride contents in concrete. Cement and concrete Research, 33, 2003, 1487 – 1490.

Mol, RIZA Restricted Publication, 1983

Mostbauer, P. Lechner, P. Extended summary of the study “facgrundlagen zur Beurteilung der Deponiefahigkeit von Bauschutt, 1991” ABF BOKU, Oostenrijk, september 2000.

H. Motzet, H. Pöllmann, Synthesis and characterisation of sulfite-containing AFm phases in the system CaO-Al_2O_3-SO_2-H_2O, Cem. Concr. Res. 29 , 1999, 1005-1011.

S.C.B. Myneni, S.J. Traina, T.J. Logan, G.A. Waychunas, Oxyanion behavior in alkaline environments: sorption and desorption of arsenate in ettringite. Environ. Sci. Technol. 31, 1997, 1761-1768.

Nischer.(1992): *Leaching behaviour of concrete and cement-bonded materials. Concrete* *precasting plant and technology*, 12, 1992, 76 – 80

NEN 7341 (1994): *Determination of the availability for leaching from granular and monolithic contruction materials and waste materials.*1994.

NEN 7345 (1994): *Determination of leaching from monolithic construction materials and waste materials by means of a diffusion test*. October 1994.

ÖNORM S 2116-4: 2001 Examinations of solidified wastes - Elution tests during 24 hours, 64 days, 2 days.

Park, J-Y. and Batchelor, B., 2002 A multi-component numerical leach model coupled with a general chemical speciation code. Water Research, 36, 156-166.

R.B. Perkins, C.D. Palmer, Solubility of chromate hydrocalumite ($3CaO. Al_2O_3.CaCrO_4 .nH_2O$) 5-75 °C, Cem. Concr. Res. 31 (2001) 983-992.

R.B. Perkins, C.D. Palmer, Solubility of $Ca_6[Al(OH)_6]_2(CrO_4)_3.26H_2O$, the chromate analog of ettringite; 5-75 °C, Appl. Geochem. 15(2000)1203-1218.

Pisters H.(1966): *Chrom im Zement und Chromatekzem*. Zement-Kalk-Gips, 19, 1966, H10, 467 – 472.

H. Pöllmann, S. Auer, H.-J. Kuzel, Solid solution of ettringites: Part II. Incorporation of $B(OH)_4^-$ and CrO_4^{2-} in $3CaO.A1_2O_3.3CaSO_4.32H_2O$, Cem. Concr. Res. 23, 1993, 422-430.

Principles for the assessment of the effects of construction products on soil and groundwater, Part I. German Institute of Structural Engineering – DIBt – Berlin, Germany (Draft April 2005; English: http://europa.eu.int/comm/enterprise/tris/index_en.htm - Search in the 98/34 Database, search by number, country, date…..etc., number: 90)

Principles for the assessment of the effects of construction products on soil and groundwater, Part II: Assessment concepts for particular construction products “Concrete starting materials and concrete”. German Institute of Structural Engineering – DIBt – Berlin, Germany (Draft April 2005). The English version is available under: http://europa.eu.int/comm/enterprise/tris/index_en.htm).

Rilem Workshop(1992): *Auslaugverhalten von Beton und zementgebundenem Material* 1992,Vienna

Sloot, H.A. van der, Susset, B., Hjelmar, O., Kalbe, U., Mehu, J., Galen, J., Chateau, L., Schnuriger, B., Kosson, D.S., Garrabrants, A., Steketee, J., Sakanakura, H., Nielsen, P., Lewin, K., Hyks, J., Guyonnet, D., Keren, R., Bendz, D., Suer, P. & van Gerven, T. (2010) Evaluation of ruggedness testing needs for the percolation test, pH dependence leaching test and monolith leaching test based on existing information. 10th Draft of an internal report of the European Standardisation Organisation CEN/TC 292/WG 2 and 6.

The Rotary Cement Kiln. 1986. 2nd ed. Chemical Publishing Co., Inc., New York.

SAMARIS, Sustainable and advanced material for Road infrastructure. Methodology for assessing alternative materials in road construction. .Final report D14, 2006.

Sarkar, S, Mahadevan, S, Meeussen, JCL, van der Sloot, HA & Kosson, DS 2010, Numerical simulation of cementitious materials degradation under external sulfate attack, Cement & Concrete Composites, vol. 32, no. 3, pp. 241–252.

Schaeffer, C.E., Arands, R.R., van der Sloot, H.A., Kosson, D.S. 1995. Prediction and experimental validation of liquid phase diffusion resistance in unsaturated soils. J. Cont. Hydr. 20,1995,145-166.

Schießl, P.; Hanehara, S.-S.; Hohberg, I.; Jacobs, F.; Meyer, L.; Sommer, P. und Volland, G.: Environmental effects of concrete. International Federation for Structural Concrete (fib), Sprint-Digital-Druck, Stuttgart (2003)

Spanka, 2001 Roman sample

Sprung S. and W. Rechenberg: *Einbindung von Schwermetallen in Sekundärstoffen durch Verfestigen mit Zement. Beton*, 38, 1988 H 5, 193 – 198.

Sprung, S.; Rechenberg, W. und Bachmann, G.: Environmental compatibility of cement and concrete. Environmental Aspects of Construction with Waste Materials, J.J.J.M. Goumans et al., Elsevier Science B.V., 1994, S. 369/386.

Swiss Agency for the Environment, Forests and Landscape (BUWAL) (1998): *Guidelines for the Disposal of Wastes in Cement Plants* - 1998.

Tiruta-Barna, L., Rethy, Z. & Barna, R. 2005. Release dynamic process identification for a cementitious material in various leaching conditions. Part II: Modelling the release dynamics for different leaching conditions, Journal of Environmental Management, 2005, 4, 171-180.

Tiruta-Barna, L., Barna, R. & Moszkowicz, P. 2001. Modeling of solid/liquid/gas transfer for environmental evaluation of cement-based solidified waste, Environmental Science & Technology, 2001, 35, 149-156.

Thesis Ivan Serclerat (1996): *Les métaux traces dans le clinker de ciment Portland: Rétention dans les mortiers et intégration dans les hydrates de ciment*. December 1996.

Thielen, G.; Spanka, G. und Rechenberg, W.: Leaching characteristics of cement bound materials containing organic substances and inorganic trace elements. Emerging Technologies Symposium on Cement and Concrete in the Global Environment, Portland Cement Association (PCA), Skokie, USA (1993).

UNH, 2000. *Development Of A Predictive Approach for Long Term Environmental Performance of Waste Utilisation in Pavements Using Accelerated Aging*: PCC Pavements Containing CFA. UNH, USA (In preparation). 2000.

Versluijs, C.W., Anthonissen, I.H. and Valentijn, E.A. (1990):. Mammoet ‘85. Report 738504008. RIVM, June 1990.

Van der Sloot, H.A, de Groot, G. J., J. Wijkstra. Leaching Characteristics of construction materials and stabilization products containing waste materials, in: Environmental Aspects of stabilization and solidification of hazardous and radioactive wastes, ASTM STP 1033, P. L. Côté and T. M. Gilliam, Eds., American Society for Testing and Materials, Philadelphia, 1989, 125-149.

Van der Sloot, H.A, van der Wegen, G.J.L., Hoede, D., de Groot, G.J, and Quevauviller, Ph. Intercomparison of leaching tests for stabilized waste. Commission of the European Communities, EUR 16133 EN, 1995.

Van der Sloot, H.A. (1996): *Developments in evaluating environmental impact from utilisation of bulk inert wastes using laboratory leaching tests and field verification. Waste Management 16* (1-3), 1996, 65-81.

Van der Sloot, H.A., L. Heasman and Ph. Quevauviller (1997): Eds.: *Harmonisation of leaching/extraction tests,* 1997b. Studies in Environmental Science, Volume 70., Elsevier Science, Amsterdam, 292 pp.

Van der Sloot, H.A., D.S. Kosson, T.T. Eighmy, R.N.J. Comans and O. Hjelmar (1994): *An approach towards international standardisation: a concise scheme for testing of granular waste leachability. In: Environmental aspects of Construction with waste materials*. Eds. J.J.J.M. Goumans, H.A. van der Sloot, Th.G. Aalbers, Elsevier Science Publishers, Amsterdam, 1994, 453-466.

Van der Sloot, H.A. (1995): *Environmental efficiency of immobilisation techniques for wastes in relation to utilisation and disposal*. Stabilisation Conference. Nancy, France, November

1995

Van der Sloot, H.A. and Hoede, D. (1997): *Long term leaching behaviour of cement mortars*. ECN –97-042.

Van der Sloot, H.A. (1999): *Characterisation of the leaching behaviour of concrete mortars and of cement - stabilized wastes with different waste loading for long term environmental assessment.* Waste Stabilisation & Environment, Eds J. Mehu, G. Keck, A. Navarro, Lyon, 13-16 April 1999. Proceedings 131 – 139.

Van der Sloot H.A. (2000): *Comparison of the characteristic leaching behaviour of cements using standard (en 196-1) cement-mortar and an assessment of their long-term environmental behaviour in construction products during service life and recycling.* Cement & Concrete Research 30, 1 – 18.

Van der Sloot, H.A. , Hoede, D., Rietra, R.P.J.J. , Stenger, R., Lang, Th., Schneider, M. , Spanka, G., Stoltenberg-Hansson, E. , Lerat, A. 2001. Environmental criteria for cement based products, ECRICEM I, ECN C--01-069.

Van der Sloot, H.A., Hjemar, O., Bjerre-Hansen, J. ,Woitke, P., Lepom, P., Leschber, R., Bartet, B., Debrucker, N. (2001): *Validation of CEN/TC 292 Leaching Tests and Eluate* Analysis Methods PrEN 12457 part 1- 4, ENV 13370 and ENV 12506 in Co-operation with CEN/TC 308. 2001 ECN-C-01-117.

Van der Sloot, H.A., Hoede, D.and Rietra, R.P.J.J. (2001): *Leaching behaviour of synthetic aggregates.* EU project BRST-CT98-5234, 2001, ECN-C-01-014.

Van der Sloot, H.A. , A. van Zomeren, J.C.L. Meeussen, J.J. Dijkstra, R.N.J. Comans, P. Seignette, D.S. Kosson, F. Sanchez, A. Garrabrants, O. Hjelmar, J.Holm, J. Bjerre Hansen, D. Lærke Baun. Evaluation of environmental impacts from wastes, mining waste, secondary raw materials, construction materials, sediments, sludge and (contaminated) soil using horizontal harmonised standards by a database/expert system. 2004 International Workshop on Water Movement and Reactive Transport Modeling in Roads. February 21-24, Portsmouth, NH, 2004.

(http://www.rmrc.unh.edu/Research/workshops/2004workshop/2004workshop.asp)

Van der Sloot, H.A., Meeussen, J.C.L., Dijkstra, J.J., Comans, R.N.J., Seignette, P., Hjelmar, O., Kosson, D.S. 2006. Recent developments in characterisation leaching tests and geochemical modeling to define a source term for assessment of environmental impact. and J.C.L. Meeussen and H.A. van der Sloot. Predicting Leaching of Reactive Substances from Porous Monolithic Materials with Orchestra-LeachXS. Workshop Source term October 19, 2006, Paris - France.

Van der Sloot, H.A. & Dijkstra, J.J. (2004): Development of horizontally standardized leaching tests for construction materials: a material based or released based approach? ECN-C--04-060, Energy Research Centre of the Netherlands (ECN): Petten, The Netherlands.

Van der Sloot, H.A., van Zomeren, A., Meeussen, J.C.L., Seignette, P., Bleijerveld, R. Interpretation of test method selection, validation against field data, and predictive modelling for impact evaluation of stabilised waste disposal Journal of Hazardous Materials (2007) J. Haz mat. 41, 2007, 354-369.

Van der Sloot, 2008 NEN project carbonation cement mortar

Workshop Source term: from characterisation to prediction, BRGM, October 19 - 20, 2006.

Verschoor, A.J., Lijzen, J.P.A., van den Broek, H.H., Cleven, R.F.M.J., Comans, R.N.J., Dijkstra, J.J., en Vermij, P., Kritische emissiewaarden voor bouwstoffen; Milieuhygiënische onderbouwing en consequenties voor bouwmaterialen. RIVM rapport 711701043 /2006.

Verschoor, A.J., Lijzen, J.P.A., van den Broek, H.H., Cleven, R.F.M.J., Comans, R.N.J., Dijkstra, J.J., 2010. Revision of the dutch building materials decree: alternative emission limit values for inorganic components in granular building materials. 9th International Symposium on Environmental Geotechnology and Global Sustainable Development – 1-4 June 2008 – Hong Kong.

VDZ "Umwelt daten der deutschen Zement Industrie" 2000, 2001, 2002. Verein der deutschen Zementwerke e.V. Dusseldorf.

Ziegler, F., Giere, R. and Annette Johnson, C. Sorption mechanisms of Zn to Calcium Silicate Hydrate: soption and microscopic investigations. Environ. Sci. Technol, 2001, 35, 4556-4561.

Ziegler, F. and Annette Johnson, C. The solubility of calcium zincate CaZn2(OH)6.2H2O). Cement and concrete Research, 31, 2001, 1327 – 1332.

M. Zhang, Incorporation of oxyanionic B, Cr, Mo, and Se into hydro-calumitc and ettringite: application to eementitious systems, PhD thesis, University of Waterloo, Canada, 2000.

Glossary

Leaching: is the extraction, by a leachant (demineralised water or others) of inorganic and/or organic components of a solid material, into a leachate by one or more physico-chemical transport mechanisms.

Leachant: is the solvent used in a leaching test (demineralised water or others).

Eluate: is the solution obtained after leaching a solid material with a leachant.

L/S: is the abbreviation for liquid (volume) to solid (mass) ratio; L/S is expressed in [l/kg].

Availability test: is a standard test method in which a crushed or finely ground solid sample is immersed in acidified water, with or without agitation; availability tests are intended to simulate "worst-case" conditions.

Available amount: is the quantity of a component which can potentially leach from a crushed or finely ground material as indicated in a standard test using a specified leachant under specified conditions (ie. availability test).

Tank (diffusion) test: is a standard test method in which an intact solid material is immersed in a leachant (usually demineralised water), typically under static conditions (ie. without agitation).

Monolith: is a solid material sample in the form of an intact single specimen to which specified criteria for dimensions and/or physico-mechanical properties apply.

Characterization test: is a standard leaching procedure, or group of related leaching procedures, used to determine the controlling transport mechanisms, the short and long term behaviour and the basic properties of a solid material, subject to specified sequential or periodic leaching.

Compliance test: is a standard leaching method used to determine if a material is either acceptable, or inacceptable, for a given application, by comparing its performance, under specified leaching conditions (usually single extraction, without agitation, under temperature control), against specified criteria for specified components.

Coefficient of diffusion: is a measure of the mobility of a component in a saturated porous material, as a function of total porosity, pore size distribution, tortuosity, concentration gradient, and chemical interactions within the pores.

Oxyanions: is a synonym for a group of metals which in aqueous solutions, do not form cationic species, but anionic complexes with oxygen, for example $[MoO_4]^{2-}$.
Chromium, molybdenum, vanadium, selenium, and arsenic belong to the group of oxyanions.

Primary application: application of intact concrete or mortar structures ("service life") under various exposure scenarios (i.e. exposure to groundwater, seawater, drinking water, or soil).

Secondary application: crushed concrete debris reused either as recycled aggregates in new concrete structures ("bound") or as ("unbound") aggregates in road constructions, dam fillings etc ("second life").

End-of-life application: concrete debris which is not reused but disposed of in a landfill (“end of life”).

Composite (or blended) cements: cements which contains one or more mineral components (i.e. blast furnace slag, coal fly ash, limestone, microsilica etc.) besides clinker and set regulator (gypsum, anhydrite).

W/C ratio: describes, as part of the mix design, the ratio between mixing water and cement in concrete or mortar (typically between 0.4 and 0.6 in concrete).

Curing: the treatment of freshly prepared concrete or mortar samples under well defined conditions (time, temperature, humidity etc.) specified in cement or concrete standards.

APPENDIX A. PHYSICAL PROPERTIES OF THE CEMENTS

ECRICEM II : Physical Characterisation of Test Cements **SLAG CEMENTS**

Type		Slag Cements					
Identification		CEM III/B (80% GBFS)	CEM III/B 32.5 N (66% GBFS)	CEM II/B-S 32.5 R (29% GBFS)	CEM II/B-S 32.5 R (29% GBFS)	CEM II/A-S 32.5 R (20% GBFS)	CEM III/A 32.5 (69% GBFS + 5% LS)
Production period		02/05/2002	29/04/2002	29/04/2002	18-19/04/2002	15/07/2002	14/05/2002
Reception date		29/05/2002	22/05/2002	22/05/2002	08/05/2002	18/07/2002	21/05/2002
Ecricem Code		HOL-1	HOL-2	HOL-3	HOL-4	HOL-5	HOL-6
DTA Code		021001	020949	020948	020865	021377	020934
Mortar Preparation		09/07/02	04/07/02	08/07/02	03/07/02	23/07/02	02/07/02
Cement	g	450	450	450	450	450	450
Water	g	225	225	225	225	225	225
Sand	g	1350	1350	1350	1350	1350	1350
W/C		0.50	0.50	0.50	0.50	0.50	0.50
Curing		95%HR	95%HR	95%HR	95%HR	95%HR	95%HR
Setting time [t1]	min	320	180	125	140	165	195
Setting time [t2]	min	550	280	190	235	240	325
Water demand	%	29.0	29.0	25.0	27.0	26.2	28.4
Soundness	mm	1.0	2.0	0.0	0.5	0.0	0.0
Mean CS [1 day]	N/mm^2	**0.9**	**3.3**	**8.2**	**7.7**	**10.0**	**2.7**
Standard deviation	N/mm^2	**0.00**	**0.12**	**0.10**	**0.23**	**0.14**	**0.05**
Mean CS [2 days]	N/mm^2	**3.5**	**6.9**	**15.9**	**14.9**	**18.4**	**6.7**
Standard deviation	N/mm^2	**0.14**	**0.09**	**0.45**	**0.66**	**0.36**	**0.65**
Mean CS [7 days]	N/mm^2	**18.7**	**20.0**	**29.9**	**27.1**	**31.9**	**24.3**
Standard deviation	N/mm^2	**0.29**	**0.16**	**0.19**	**0.97**	**0.42**	**0.43**
Mean CS [28 days]	N/mm^2	**30.8**	**46.9**	**49.3**	**41.4**	**46.0**	**40.6**
Standard deviation	N/mm^2	**0.24**	**0.13**	**0.47**	**0.32**	**0.33**	**1.20**
Specific density	g/cm3	2.94	2.97	3.03	3.02	3.08	2.93
Blaine	cm^2/g	3117	4588	3798	3118	3255	4049

ECRICEM II : Physical Characterisation of Test Cements COCKTAIL CEMENTS

Type		Cocktail Cements				
Identification		CEM V/A 32.5 N (32% GBFS+20% FA)	CEM V/A 32.5 N (23% GBFS+22% FA)	CEM II/B-M 32.5 R (33% GBFS+9% LS)	CEM IV/A 32.5 R (15% FA+17% P)	CEM II/B-M 32.5 R (14% GBFS+12% LS+5% FA)
Production period		03/05/2002		01/05/2002	06/05/2002	06/05/2002
Reception date		28/06/2002	02/07/2002	21/05/2002	16/05/2002	16/05/2002
Ecricem Code		HOL-12	HOL-13	HOL-14	HOL-15	HOL-16
DTA Code		021233	021262	020933	020914	020913
Mortar Preparation		04/07/02	10/07/02	04/07/02	09/07/02	08/07/02
Cement	g	450	450	450	450	450
Water	g	225	225	225	225	225
Sand	g	1350	1350	1350	1350	1350
W/C		0.50	0.50	0.50	0.50	0.50
Curing		95%HR	95%HR	95%HR	95%HR	95%HR
Setting time [t1]	min	335	200	170	150	120
Setting time [t2]	min	515	325	250	215	180
Water demand	%	30.2	27.0	25.2	29.6	26.2
Soundness	mm	0.0	0.0	1.0	2.0	0.0
Mean CS [1 day]	N/mm²	3.3	5.7	9.4	11.3	11.5
Standard deviation	N/mm²	0.04	0.16	0.29	0.13	0.33
Mean CS [2 days]	N/mm²	7.3	11.2	16.7	18.3	17.9
Standard deviation	N/mm²	0.28	0.27	0.16	0.25	0.61
Mean CS [7 days]	N/mm²	17.1	24.0	30.0	28.3	30.3
Standard deviation	N/mm²	0.37	0.52	0.19	0.09	0.45
Mean CS [28 days]	N/mm²	34.0	43.8	42.4	41.2	43.7
Standard deviation	N/mm²	0.35	0.51	0.27	0.44	0.19
Specific density	g/cm3	2.80	2.86	2.97	2.84	2.93
Blaine	cm²/g	3805	3915	3944	5110	4032

ECRICEM II : Physical Characterisation of Test Cements

FLY ASH CEMENTS

Type		Fly Ash Cements		Pozzolan	Limestone Cements	
Identification		CEM II/B-V 32.5 N (33% FA)	CEM II/A-V 42.5 N (10% FA)	CEM II/B-Q (32% P)	CEM II/B-L (28% LS)	CEM II/A-L 32.5 R (13% LS)
Production period		17/07/2002	26/04/2002	01/05/2002	09/05/2002	ND
Reception date		26/07/2002	14/05/2002	16/05/2002	24/05/2002	03/06/2002
Ecricem Code		HOL-7	HOL-8	HOL-9	HOL-10	HOL-11
DTA Code		021428	020887	020895	020959	021015

Mortar Preparation		31/07/02	02/07/02	04/07/02	08/07/02	10/07/02
Cement	g	450	450	450	450	450
Water	g	225	225	225	225	225
Sand	g	1350	1350	1350	1350	1350
W/C		0.50	0.50	0.50	0.50	0.50
Curing		95%HR	95%HR	95%HR	95%HR	95%HR
Setting time [t1]	min	190	125	195	135	155
Setting time [t2]	min	310	205	310	205	220
Water demand	%	28.8	27.4	29.6	24.6	25.2
Soundness	mm	1.0	0.0	0.0	1.0	0.0
Mean CS [1 day]	N/mm²	**5.6**	**11.1**	**6.0**	**10.1**	**12.0**
Standard deviation	N/mm²	**0.11**	**0.41**	**0.14**	**0.07**	**0.09**
Mean CS [2 days]	N/mm²	**12.7**	**19.1**	**12.2**	**16.6**	**23.6**
Standard deviation	N/mm²	**1.55**	**0.14**	**0.19**	**0.03**	**0.36**
Mean CS [7 days]	N/mm²	**24.3**	**35.6**	**23.9**	**26.5**	**38.9**
Standard deviation	N/mm²	**0.22**	**0.69**	**0.64**	**0.24**	**0.62**
Mean CS [28 days]	N/mm²	**36.4**	**50.0**	**36.6**	**33.5**	**46.4**
Standard deviation	N/mm²	**0.65**	**0.76**	**0.37**	**0.45**	**0.42**
Specific density	g/cm3	2.93	3.02	2.86	2.97	3.07
Blaine	cm²/g	3580	3547	4303	4379	4147

ECRICEM II : Physical Characterisation of Test Cements

PORTLAND CEMENTS

Type		VDZ Cements					Norcem Cements			
Identification		Ecricem II A	Ecricem II B	Ecricem II C	Ecricem II D	Ecricem II E	CEM I without LD slag in raw mix	CEM I with LD slag in raw mix	CEM I 42.5 R with chromate reduction	CEM II/A-V R (FA) with chromate reduction
Production period		ND	ND	ND	ND	ND	ND	ND	07/06/02	07/06/02
Reception date		20/06/2002	20/06/2002	20/06/2002	20/06/2002	20/06/2002	12/06/2002	12/06/2002	12/06/2002	12/06/2002
Ecricem Code		VDZ-1	VDZ-2	VDZ-3	VDZ-4	VDZ-5	NOR-1	NOR-2	NOR-3	NOR-4
DTA Code		021170	021171	021172	021173	021174	021085	021084	021082	021083
Mortar Preparation		03/07/02	03/07/02	02/07/02	02/07/02	03/07/02	09/07/02	10/07/02	09/07/02	08/07/02
Cement	g	450	450	450	450	450	450	450	450	450
Water	g	225	225	225	225	225	225	225	225	225
Sand	g	1350	1350	1350	1350	1350	1350	1350	1350	1350
W/C		0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50
Curing		95%HR	95%HR	95%HR	95%HR	95%HR	95%HR	95%HR	95%HR	95%HR
Setting time [t1]	min	135	165	135	150	165	125	150	135	120
Setting time [t2]	min	215	235	220	225	250	210	225	185	200
Water demand	%	27.2	31.8	25.6	25.8	27.6	24.4	24.8	27.0	29.2
Soundness	mm	0.0	0.5	1.0	0.0	2.0	1.0	0.0	0.0	0.5
Mean CS [1 day]	**N/mm²**	**10.7**	**17.2**	**10.0**	**11.0**	**6.0**	**7.8**	**10.5**	**18.2**	**20.1**
Standard deviation	**N/mm²**	**0.17**	**0.30**	**0.11**	**0.35**	**0.35**	**0.19**	**0.21**	**0.52**	**0.66**
Mean CS [2 days]	**N/mm²**	**19.1**	**28.4**	**19.2**	**20.8**	**12.2**	**15.8**	**20.7**	**28.4**	**28.3**
Standard deviation	**N/mm²**	**0.19**	**0.64**	**0.48**	**0.42**	**0.31**	**0.47**	**0.56**	**0.47**	**0.27**
Mean CS [7 days]	**N/mm²**	**34.8**	**43.9**	**35.0**	**33.4**	**26.1**	**30.5**	**37.1**	**39**	**39.9**
Standard deviation	**N/mm²**	**0.63**	**0.47**	**0.91**	**0.59**	**0.53**	**0.89**	**0.06**	**0.51**	**0.37**
Mean CS [28 days]	**N/mm²**	**50.6**	**60.4**	**48.4**	**48.2**	**45.2**	**48.1**	**52.9**	**47.2**	**53.5**
Standard deviation	**N/mm²**	**0.50**	**0.58**	**1.01**	**0.95**	**0.16**	**0.44**	**0.49**	**0.62**	**0.16**
Specific density	g/cm3	2.91	3.02	3.06	3.09	3.01	3.19	3.16	3.13	2.97
Blaine	cm²/g	4390	4653	3315	3490	3044	3252	3425	3561	4485

APPENDIX B. GRANULOMETRY OF THE CEMENTS

ECRICEM II : Granulometry of Test Cements **SLAG CEMENTS**

Type			**Slag Cements**							
Identification			**CEM III/B (80% GBFS)**	**CEM III/B 32.5 N (66% GBFS)**	**CEM II/B-S 32.5 R (29% GBFS)**	**CEM II/B-S 32.5 R (29% GBFS)**	**CEM II/A-S 32.5 R (20% GBFS)**	**CEM III/A 32.5 (69% GBFS + 5% LS)**	**CEM II/A-S 32.5 R**	**CEM II/B-S 32.5 R**
Production period			**02/05/2002**	**29/04/2002**	**29/04/2002**	**18-19/04/2002**	**15/07/2002**	**14/05/2002**	**ND**	**ND**
Reception date			**29/05/2002**	**22/05/2002**	**22/05/2002**	**08/05/2002**	**18/07/2002**	**21/05/2002**	**20/06/2002**	**20/06/2002**
Ecricem Code			**HOL-1**	**HOL-2**	**HOL-3**	**HOL-4**	**HOL-5**	**HOL-6**	**VDZ-4**	**VDZ-5**
DTA Code			**021001**	**020949**	**020948**	**020865**	**021377**	**020934**	**021173**	**021174**
		Passing								
0.5	µm	%	0.21	0.13	0.35	0.37	0.20	0.06	0.51	0.09
1.0	µm	%	1.47	2.17	1.71	1.57	1.39	1.57	1.72	1.38
1.5	µm	%	2.88	5.22	3.18	2.69	2.88	3.92	2.81	3.15
2.0	µm	%	4.21	8.31	4.71	3.72	4.45	6.33	3.86	4.87
3.0	µm	%	7.13	14.51	8.35	6.13	8.06	11.23	6.57	8.36
4.0	µm	%	10.49	22.73	12.69	9.25	12.11	16.20	10.20	12.05
6.0	µm	%	17.68	32.46	21.98	16.73	20.35	25.59	18.80	19.50
8.0	µm	%	24.52	42.59	30.63	24.60	27.79	33.61	27.51	26.30
10.0	µm	%	30.63	51.10	38.11	32.11	34.17	40.23	35.42	32.20
12.0	µm	%	36.01	58.15	44.40	38.98	39.59	45.72	42.26	37.29
16.0	µm	%	45.54	69.56	54.79	51.05	48.97	55.11	53.56	46.23
20.0	µm	%	54.10	78.20	63.35	61.28	57.22	63.24	62.74	54.13
24.0	µm	%	61.54	84.18	70.21	69.71	64.31	69.86	70.23	60.72
32.0	µm	%	73.09	90.73	79.74	81.77	75.38	79.17	80.97	70.51
48.0	µm	%	86.84	96.21	89.94	93.51	88.94	89.60	92.27	82.89
64.0	µm	%	92.75	97.97	94.14	97.20	94.72	94.15	96.33	89.38
96.0	µm	%	97.53	99.50	97.85	99.58	99.06	98.33	99.33	96.03
128.0	µm	%	98.86	100.00	99.09	100.00	99.96	99.58	99.99	98.52
200.0	µm	%	99.18	100.00	99.84	100.00	100.00	99.98	100.00	99.83
250.0	µm	%	99.34	100.00	100.00	100.00	100.00	100.00	100.00	100.00
Mean diameter	µm		26.92	14.29	21.88	20.06	22.59	21.18	20.19	27.74
Median diameter	µm		18.03	9.73	14.06	15.63	16.48	13.76	14.65	17.84
d 10	µm		3.86	2.28	3.39	4.22	3.49	2.75	3.95	3.45
d 50	µm		18.03	9.73	14.06	15.63	16.48	13.76	14.65	17.84
d 90	µm		54.93	30.69	48.13	41.14	50.09	48.90	43.32	66.16

ECRICEM II : Granulometry of Test Cements

FLY ASH CEMENTS

Type			**Fly Ash Cements**			**Pozzolan Cements**		**Limestone Cements**		
Identification			**CEM II/B-V 32.5 N (33% FA)**	**CEM II/A-V 42.5 N (10% FA)**	**CEM II/A-V (with chromate reduction)**	**CEM II/B-Q (32% P)**	**CEM II/B-P 32.5 R (26 % Trass)**	**CEM II/B-L (28% LS)**	**CEM II/A-L 32.5 R (13% LS)**	**CEM II/A-LL 32.5 R (13 % LS)**
Production period			**17/07/2002**	**26/04/2002**	**07/06/02**	**01/05/2002**	**ND**	**09/05/2002**	**ND**	**ND**
Reception date			**26/07/2002**	**14/05/2002**	**12/06/2002**	**16/05/2002**	**20/06/2002**	**24/05/2002**	**03/06/2002**	**20/06/2002**
Ecricem Code			**HOL-7**	**HOL-8**	**NOR-4**	**HOL-9**	**VDZ-1**	**HOL-10**	**HOL-11**	**VDZ-3**
DTA Code			**021428**	**020887**	**021083**	**020895**	**021170**	**020959**	**021015**	**021172**
		Passing								
0.5	µm	%	0.14	0.14	0.33	0.00	0.00	0.00	0.06	0.09
1.0	µm	%	1.16	1.40	1.69	1.37	1.44	1.94	1.60	1.76
1.5	µm	%	2.49	3.09	3.17	4.35	4.62	6.00	4.11	4.21
2.0	µm	%	3.89	4.87	4.68	7.47	7.95	9.82	6.76	6.54
3.0	µm	%	7.13	8.90	8.35	13.48	14.14	16.14	12.16	10.84
4.0	µm	%	10.84	13.45	12.93	19.15	19.68	21.24	17.45	14.92
6.0	µm	%	18.52	22.93	23.42	29.36	29.05	29.15	26.91	22.49
8.0	µm	%	25.54	31.68	33.94	37.96	36.50	34.97	34.51	29.10
10.0	µm	%	31.57	39.30	43.62	45.13	42.49	39.37	40.50	34.84
12.0	µm	%	36.71	45.84	52.17	51.16	47.44	42.89	45.33	39.90
16.0	µm	%	45.62	57.09	66.51	61.50	56.05	49.39	53.63	49.21
20.0	µm	%	53.56	66.76	77.69	70.30	63.62	55.60	61.14	57.81
24.0	µm	%	60.41	74.65	85.68	77.24	69.75	60.89	67.49	65.16
32.0	µm	%	71.04	85.33	94.04	86.34	78.48	69.22	76.95	76.31
48.0	µm	%	84.78	94.78	98.51	94.70	88.91	81.50	88.64	89.46
64.0	µm	%	91.79	97.43	99.12	97.23	93.85	88.62	94.05	94.84
96.0	µm	%	98.06	99.55	99.85	99.40	98.30	95.78	98.81	98.96
128.0	µm	%	99.84	99.99	100.00	99.99	99.65	98.13	99.96	99.96
200.0	µm	%	100.00	100.00	100.00	100.00	100.00	98.96	100.00	100.00
250.0	µm	%	100.00	100.00	100.00	100.00	100.00	99.20	100.00	100.00
Mean diameter	µm		25.57	17.97	14.14	16.84	21.04	29.24	21.48	22.14
Median diameter	µm		18.15	13.41	11.47	11.60	13.14	16.38	14.20	16.35
d 10	µm		3.78	3.25	3.38	2.41	2.32	2.02	2.60	2.78
d 50	µm		18.15	13.41	11.47	11.60	13.14	16.38	14.20	16.35
d 90	µm		58.73	37.62	27.19	36.93	50.69	68.47	51.04	49.00

ECRICEM II : Granulometry of Test Cements

COCKTAIL CEMENTS

Type			**Cocktail Cements**					
Identification			**CEM V/A 32.5 N (32% GBFS+20% FA)**	**CEM V/A 32.5 N (23% GBFS+22% FA)**	**CEM II/B-M 32.5 R (33% GBFS+9% LS)**	**CEM IV/A 32.5 R (15% FA+17% P)**	**CEM II/B-M 32.5 R (14% GBFS+12% LS+5% FA)**	**CEM II/B-T 42.5 R (Burnt Oil Shale)**
Production period			**03/05/2002**		**01/05/2002**	**06/05/2002**	**06/05/2002**	**ND**
Reception date			**28/06/2002**	**02/07/2002**	**21/05/2002**	**16/05/2002**	**16/05/2002**	**20/06/2002**
Ecricem Code			**HOL-12**	**HOL-13**	**HOL-14**	**HOL-15**	**HOL-16**	**VDZ-2**
DTA Code			**021233**	**021262**	**020933**	**020914**	**020913**	**021171**
		Passing						
0.5	µm	%	0.32	0.56	0.09	0.00	0.14	0.00
1.0	µm	%	1.43	1.73	1.55	1.35	1.56	1.38
1.5	µm	%	2.53	2.57	3.80	4.49	3.49	4.25
2.0	µm	%	3.65	3.25	6.17	7.75	5.48	7.17
3.0	µm	%	6.51	5.04	11.14	13.85	9.88	12.61
4.0	µm	%	10.23	7.82	16.16	19.36	14.64	17.59
6.0	µm	%	18.85	15.54	25.32	28.79	23.98	26.35
8.0	µm	%	27.47	24.47	32.84	36.28	31.99	33.58
10.0	µm	%	35.32	33.42	38.84	42.22	38.50	39.53
12.0	µm	%	42.20	41.74	43.72	47.08	43.78	44.54
16.0	µm	%	53.87	55.70	52.03	55.57	52.59	53.46
20.0	µm	%	63.64	66.13	59.41	63.16	60.22	61.53
24.0	µm	%	71.71	73.84	65.65	69.41	66.61	68.23
32.0	µm	%	83.00	84.06	75.30	78.52	76.20	78.31
48.0	µm	%	93.42	94.04	87.80	89.36	88.05	90.15
64.0	µm	%	96.60	97.43	93.77	94.06	93.56	95.15
96.0	µm	%	98.96	99.76	98.94	98.33	98.26	99.20
128.0	µm	%	99.72	100.00	99.97	99.53	99.54	99.99
200.0	µm	%	99.98	100.00	100.00	99.93	99.95	100.00
250.0	µm	%	100.00	100.00	100.00	100.00	100.00	100.00
Mean diameter	µm		19.83	18.95	22.24	21.14	22.59	20.69
Median diameter	µm		14.59	14.24	14.98	13.33	14.77	14.41
d 10	µm		3.94	4.63	2.77	2.36	3.03	2.51
d 50	µm		14.59	14.24	14.98	13.33	14.77	14.41
d 90	µm		40.46	39.48	52.62	49.50	52.40	47.71

ECRICEM II : Granulometry of Test Cements

PORTLAND CEMENTS

			Portland Cements		
Type					
Identification			**CEM I (without LD slag in raw mix)**	**CEM I (with LD slag in raw mix)**	**CEM I 42.5 R (with chromate reduction)**
Production period			**ND**	**ND**	**07/06/02**
Reception date			**12/06/2002**	**12/06/2002**	**12/06/2002**
Ecricem Code			**NOR-1**	**NOR-2**	**NOR-3**
DTA Code			**021085**	**021084**	**021082**
		Passing			
0.5	µm	%	0.56	0.39	0.51
1.0	µm	%	1.66	1.50	1.56
1.5	µm	%	2.69	2.66	2.53
2.0	µm	%	3.81	3.91	3.53
3.0	µm	%	6.90	7.09	6.29
4.0	µm	%	11.00	11.08	10.03
6.0	µm	%	20.40	19.91	18.79
8.0	µm	%	29.52	28.30	27.46
10.0	µm	%	37.55	35.62	35.16
12.0	µm	%	44.36	41.86	41.66
16.0	µm	%	55.78	52.40	52.18
20.0	µm	%	65.49	61.47	60.70
24.0	µm	%	73.52	69.02	67.62
32.0	µm	%	84.84	80.03	77.53
48.0	µm	%	95.34	92.04	88.59
64.0	µm	%	97.92	96.39	93.56
96.0	µm	%	99.54	99.38	98.06
128.0	µm	%	99.99	99.99	99.63
200.0	µm	%	100.00	100.00	100.00
250.0	µm	%	100.00	100.00	100.00
Mean diameter	µm		18.23	20.42	22.70
Median diameter	µm		13.89	15.04	15.10
d 10	µm		3.77	3.74	3.99
d 50	µm		13.89	15.04	15.10
d 90	µm		37.60	43.97	51.48

APPENDIX C. CHEMICAL COMPOSITION OF THE CEMENTS, MAJOR ELEMENTS

ECRICEM II : Chemical Composition of Test Cements					**SLAG CEMENTS**				
Type		**Slag Cements**						**CEM II/A-S 32.5 R (20% GBFS)**	**CEM II/B-S 32.5 R (29% GBFS)**
Identification		**CEM III/B (80% GBFS)**	**CEM III/B 32.5 N (66% GBFS)**	**CEM II/B-S 32.5 R (29% GBFS)**	**CEM II/B-S 32.5 R (29% GBFS)**	**CEM II/A-S 32.5 R (20% GBFS)**	**CEM III/A 32.5 (69% GBFS + 5% LS)**	**Ecricem II D**	**Ecricem II E**
Production period		**02/05/2002**	**29/04/2002**	**29/04/2002**	**18-19/04/2002**	**15/07/2002**	**14/05/2002**	**ND**	**ND**
Reception date		**29/05/2002**	**22/05/2002**	**22/05/2002**	**08/05/2002**	**18/07/2002**	**21/05/2002**	**20/06/2002**	**20/06/2002**
Ecricem Code		**HOL-1**	**HOL-2**	**HOL-3**	**HOL-4**	**HOL-5**	**HOL-6**	**VDZ-4**	**VDZ-5**
DTA Code		**021001**	**020949**	**020948**	**020865**	**021377**	**020934**	**021173**	**021174**
1. Chemical Composition									
1.1 Major Oxides									
SiO_2	%/dry	30.91	31.00	24.50	25.96	22.69	28.03	21.95	24.26
Al_2O_3	%/dry	9.83	9.41	6.68	5.41	5.86	9.30	6.04	7.23
Fe_2O_3	%/dry	1.49	1.28	2.20	2.32	2.95	1.46	2.77	2.08
CaO	%/dry	43.96	48.53	56.29	56.46	59.45	47.39	58.01	55.63
Na_2O	%/dry	0.30	0.32	0.27	0.38	0.21	0.24	0.36	0.20
K_2O	%/dry	0.83	0.34	0.40	0.66	0.82	0.42	0.89	0.92
MgO	%/dry	7.39	5.85	3.01	4.14	1.83	5.41	4.08	3.03
SO_3 tot.	%/dry	4.49	2.70	3.67	3.28	3.92	3.96	3.73	3.00
Mn_2O_3	%/dry	0.33	0.22	0.13	0.39	0.21	0.53	0.23	0.13
TiO_2	%/dry	0.47	0.85	0.47	0.29	0.26	0.40	0.47	0.36
P_2O_5	%/dry	0.09	0.14	0.27	0.06	0.07	0.07	0.12	0.11
Cl	%/dry	0.18	0.01	0.03	0.02	0.00	0.07	0.03	0.02
LoI	%/dry	0.40	- 0.32	1.84	0.85	1.49	2.43	1.05	2.48
Total	%/dry	100.67	100.32	99.76	100.22	99.76	99.71	99.73	99.45
CaO free	%/dry	0.50	0.64	1.02	2.08	1.44	1.05	1.78	0.97
1.2 Cement Composition (calculated):									
Gypsum	%	4.1	1.4	4.8	4.0	4.1	3.9	5.2	3.9
Limestone	%	0.0	0.0	3.3	0.0	0.0	3.8	0.0	3.4
Slag	%	76.9	68.6	26.9	26.3	13.5	60.5	17.2	23.8
Pozzolan/Fly Ash	%	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Clinker	%	19.0	30.0	65.0	69.7	82.4	31.8	77.6	68.8
1.3 Cement Composition (theorical):									
Gypsum/Anhydrite	%	6	0	6	5	ND	4	ND	ND
Limestone/CKD	%	0	0	5	0	ND	4	ND	ND
Slag	%	82	69	32	30	ND	69	ND	ND
Pozzolan/Fly Ash	%	0	0	0	0	ND	0	ND	ND
Clinker	%	12	31	57	65	ND	23	ND	ND

ECRICEM II : Chemical Composition of Test Cements FLY ASH CEMENTS

Type			**Fly Ash Cements**		**Pozzolan**	**Limestone Cements**	
Identification			**CEM II/B-V 32.5 N (33% FA)**	**CEM II/A-V 42.5 N (10% FA)**	**CEM II/B-Q (32% P)**	**CEM II/B-L (28% LS)**	**CEM II/A-L 32.5 R (13% LS)**
Production period			**17/07/2002**	**26/04/2002**	**01/05/2002**	**09/05/2002**	**ND**
Reception date			**26/07/2002**	**14/05/2002**	**16/05/2002**	**24/05/2002**	**03/06/2002**
Ecricem Code			**HOL-7**	**HOL-8**	**HOL-9**	**HOL-10**	**HOL-11**
DTA Code			**021428**	**020887**	**020895**	**020959**	**021015**
1. Chemical Composition							
1.1 Major Oxides							
SiO_2	%/dry		27.44	22.84	35.88	15.34	18.32
Al_2O_3	%/dry		9.57	7.33	7.37	4.47	4.46
Fe_2O_3	%/dry		5.11	3.58	2.81	2.07	2.42
CaO	%/dry		47.91	57.71	43.77	59.45	61.57
Na_2O	%/dry		0.48	0.22	1.25	0.14	0.13
K_2O	%/dry		0.95	0.27	1.23	1.06	1.07
MgO	%/dry		2.40	1.42	2.06	2.81	1.76
SO_3 tot.	%/dry		3.16	2.72	2.24	2.93	3.20
Mn_2O_3	%/dry		0.06	0.12	0.10	0.06	0.05
TiO_2	%/dry		0.50	0.43	0.25	0.24	0.27
P_2O_5	%/dry		0.08	0.33	0.10	0.06	0.23
Cl	%/dry		0.011	0.014	0.009	0.02	0.02
LoI	%/dry		2.31	2.94	2.59	11.98	6.97
Total	%/dry		99.98	99.92	99.66	100.63	100.47
CaO free	%/dry		2.08	1.39	0.51	1.62	0.51
1.2 Cement Composition (calculated):							
Gypsum	%		4.7	4.2	3.3	4.3	4.8
Limestone	%		3.1	2.1	0.0	21.1	12.2
Slag	%		2.9	1.4	0.0	2.8	0.0
Pozzolan/Fly Ash	%		24.7	10.3	32.8	2.5	2.2
Clinker	%		64.6	81.9	63.9	69.4	80.8
1.3 Cement Composition (theorical):							
Gypsum/Anhydrite	%		4	5	4	5	ND
Limestone/CKD	%		5	3	0	27	14/3
Slag	%		0	0	0	0	0
Pozzolan/Fly Ash	%		31	9	32	0	0
Clinker	%		60	83	64	68	ND

ECRICEM II : Chemical Composition of Test Cements

COCKTAIL CEMENTS

Type		**Cocktail Cements**					**CEM II/B-M 32.5 R (14% GBFS+12% LS+5% FA)**
Identification		**CEM V/A 32.5 N (32% GBFS+20% FA)**	**CEM V/A 32.5 N (23% GBFS+22% FA)**	**CEM II/B-M 32.5 R (33% GBFS+9% LS)**	**CEM IV/A 32.5 R (15% FA+17% P)**	**CEM II/B-M 32.5 R (14% GBFS+12% LS+5% FA)**	**Ecricem II B**
Production period		**03/05/2002**		**01/05/2002**	**06/05/2002**	**06/05/2002**	**ND**
Reception date		**28/06/2002**	**02/07/2002**	**21/05/2002**	**16/05/2002**	**16/05/2002**	**20/06/2002**
Ecricem Code		**HOL-12**	**HOL-13**	**HOL-14**	**HOL-15**	**HOL-16**	**VDZ-2**
DTA Code		**021233**	**021262**	**020933**	**020914**	**020913**	**021171**

1. Chemical Composition

1.1 Major Oxides

		HOL-12	HOL-13	HOL-14	HOL-15	HOL-16	VDZ-2
SiO_2	%/dry	32.89	29.11	22.70	29.16	24.71	23.56
Al_2O_3	%/dry	10.89	9.88	6.73	8.07	7.62	7.19
Fe_2O_3	%/dry	2.90	3.38	2.22	3.33	2.48	3.79
CaO	%/dry	40.49	44.03	55.52	47.24	51.33	53.97
Na_2O	%/dry	0.29	0.30	0.30	0.43	0.36	0.21
K_2O	%/dry	1.03	1.49	0.64	1.16	0.86	1.34
MgO	%/dry	5.64	5.11	3.19	1.95	3.30	1.95
SO_3 tot.	%/dry	3.22	3.67	2.74	2.74	2.89	4.28
Mn_2O_3	%/dry	0.24	0.23	0.27	0.07	0.21	0.08
TiO_2	%/dry	0.74	0.44	0.32	0.35	0.35	0.35
P_2O_5	%/dry	0.17	0.28	0.13	0.14	0.11	0.26
Cl	%/dry	0.01	0.04	0.06	0.027	0.035	0.01
LoI	%/dry	1.24	1.94	4.64	5.69	5.88	2.99
Total	%/dry	99.75	99.90	99.46	100.36	100.14	99.98
CaO free	%/dry	0.51	0.82	1.86	1.13	1.45	2.18

1.2 Cement Composition (calculated):

		HOL-12	HOL-13	HOL-14	HOL-15	HOL-16	VDZ-2
Gypsum	%	4.3	4.9	3.2	3.9	3.7	6.6
Limestone	%	0.0	0.0	7.9	4.9	8.2	5.2
Slag	%	24.1	26.3	23.8	0.0	18.5	6.8
Pozzolan/Fly Ash	%	23.2	19.9	0.0	26.1	11.1	11.7
Clinker	%	48.4	48.8	65.1	65.1	58.5	69.7

1.3 Cement Composition (theorical):

		HOL-12	HOL-13	HOL-14	HOL-15	HOL-16	VDZ-2
Gypsum/Anhydrite	%	5	5	5	4	4	ND
Limestone/CKD	%	0	1	10	0	12	ND
Slag	%	32	22	33	0	13	ND
Pozzolan/Fly Ash	%	20	23	0	31	6	ND
Clinker	%	43	50	52	65	65	ND

ECRICEM II : Chemical Composition of Test Cements

PORTLAND CEMENTS

Type		**VDZ Cements**					**Norcem Cements**			
Identification		**Ecricem II A**	**CEM II/B-M 32.5 R (6% GBFS+5% LS+10% FA)**	**Ecricem II C**	**Ecricem II D**	**Ecricem II E**	**CEM I without LD slag in raw mix**	**CEM I with LD slag in raw mix**	**CEM I 42.5 R with chromate reduction**	**CEM II/A-V R (FA) with chromate reduction**
Production period		**ND**	**ND**	**ND**	**ND**	**ND**	**ND**	**ND**	**07/06/02**	**07/06/02**
Reception date		**20/06/2002**	**20/06/2002**	**20/06/2002**	**20/06/2002**	**20/06/2002**	**12/06/2002**	**12/06/2002**	**12/06/2002**	**12/06/2002**
Ecricem Code		**VDZ-1**	**VDZ-2**	**VDZ-3**	**VDZ-4**	**VDZ-5**	**NOR-1**	**NOR-2**	**NOR-3**	**NOR-4**
DTA Code		**021170**	**021171**	**021172**	**021173**	**021174**	**021085**	**021084**	**021082**	**021083**
1. Chemical Composition										
1.1 Major Oxides										
SiO_2	%/dry	29.14	23.56	20.63	21.95	24.26	22.09	22.27	19.99	25.87
Al_2O_3	%/dry	7.79	7.19	3.39	6.04	7.23	3.51	3.31	4.83	8.81
Fe_2O_3	%/dry	3.23	3.79	1.28	2.77	2.08	4.06	3.97	3.26	3.99
CaO	%/dry	48.64	53.97	63.27	58.01	55.63	64.08	64.41	62.31	52.19
Na_2O	%/dry	1.15	0.21	0.37	0.36	0.20	0.16	0.11	0.45	0.53
K_2O	%/dry	1.72	1.34	0.52	0.89	0.92	0.64	0.59	1.06	1.26
MgO	%/dry	1.00	1.95	0.72	4.08	3.03	1.10	1.40	2.41	2.50
SO_3 tot.	%/dry	2.11	4.28	2.91	3.73	3.00	2.78	2.61	3.16	2.90
Mn_2O_3	%/dry	0.11	0.08	0.05	0.23	0.13	0.22	0.48	0.08	0.08
TiO_2	%/dry	0.32	0.35	0.19	0.47	0.36	0.26	0.32	0.28	0.45
P_2O_5	%/dry	0.33	0.26	0.15	0.12	0.11	0.13	0.16	0.25	0.40
Cl	%/dry	0.05	0.01	0.04	0.03	0.02	0.01	0.01	0.04	0.04
LoI	%/dry	4.10	2.99	6.55	1.05	2.48	1.62	0.81	2.31	1.30
Total	%/dry	99.69	99.98	100.07	99.73	99.45	100.66	100.45	100.43	100.32
CaO free	%/dry	1.04	2.18	0.74	1.78	0.97	0.69	1.82	1.17	1.18
1.2 Cement Composition (calculated):										
Gypsum	%	3.5	6.6	4.7	5.2	3.9	3.6	3.6	4.5	4.1
Limestone	%	3.1	5.2	12.1	0.0	3.4	0.0	0.0	2.9	0.0
Slag	%	3.9	6.8	0.0	17.2	23.8	1.2	1.8	1.8	2.2
Pozzolan/Fly Ash	%	22.7	11.7	0.0	0.0	0.0	0.0	0.0	0.0	17.8
Clinker	%	66.7	69.7	83.2	77.6	68.8	95.2	94.6	90.9	75.9
1.3 Cement Composition (theorical):										
Gypsum/Anhydrite	%	ND	ND	ND	ND	ND	ND	ND	ND	ND
Limestone/CKD	%	ND	ND	ND	ND	ND	ND	ND	ND	ND
Slag	%	ND	ND	ND	ND	ND	ND	ND	ND	ND
Pozzolan/Fly Ash	%	ND	ND	ND	ND	ND	ND	ND	ND	ND
Clinker	%	ND	ND	ND	ND	ND	ND	ND	ND	ND

APPENDIX D. CHEMICAL COMPOSITION OF THE CEMENTS, TRACE ELEMENTS

ECRICEM II : Chemical Composition of Test Cements SLAG CEMENTS

Type		**Slag Cements**						**CEM II/A-S 32.5 R (20% GBFS)**	**CEM II/B-S 32.5 R (29% GBFS)**
Identification		**CEM III/B (80% GBFS)**	**CEM III/B 32.5 N (66% GBFS)**	**CEM II/B-S 32.5 R (29% GBFS)**	**CEM II/B-S 32.5 R (29% GBFS)**	**CEM II/A-S 32.5 R (20% GBFS)**	**CEM III/A 32.5 (69% GBFS + 5% LS)**	**Ecricem II D**	**Ecricem II E**
Production period		**02/05/2002**	**29/04/2002**	**29/04/2002**	**18-19/04/2002**	**15/07/2002**	**14/05/2002**	**ND**	**ND**
Reception date		**29/05/2002**	**22/05/2002**	**22/05/2002**	**08/05/2002**	**18/07/2002**	**21/05/2002**	**20/06/2002**	**20/06/2002**
Ecricem Code		**HOL-1**	**HOL-2**	**HOL-3**	**HOL-4**	**HOL-5**	**HOL-6**	**VDZ-4**	**VDZ-5**
DTA Code		**021001**	**020949**	**020948**	**020865**	**021377**	**020934**	**021173**	**021174**
1. Chemical Composition									
1.4 Trace elements									
Arsen	µg/g	1.28	3.0	4.9	4.5	60?	6.1	3.96	4.54
Beryllium	µg/g	6.18	5.4	2.4	1.1		4.9	1.27	1.27
Cadmium	µg/g	0.49	0.3	0.5	1.4		0.1	0.35	0.75
Kobalt	µg/g	5.52	9.3	9.5	7.1		2.3	8.73	3.45
Chrom	µg/g	40.10	51.3	60.9	32.9		44.1	94.10	32.00
Kupfer	µg/g	8.92	29.6	49.6	16.0		5.5	35.70	8.30
Quecksilber	µg/g	0.05	0.0	0.1	0.1		0.0	0.08	0.02
Mangan	µg/g	1830.00	1174.0	645.0	2113.0		3305.0	1341.00	688.00
Nickel	µg/g	17.10	15.6	25.0	18.7		11.5	40.10	16.20
Blei	µg/g	26.70	8.5	17.8	40.3		2.7	11.40	20.10
Antimon	µg/g	<1.00	7.2	19.4	1.1		<1.00	4.97	<1.00
Zinn	µg/g	1.31	2.0	2.6	2.8		1.0	3.23	1.37
Thallium	µg/g	<1.00	<1.00	<1.00	<1.00		<1.00	<1.00	<1.00
Vanadium	µg/g	47.10	212.0	112.0	39.4		38.7	58.70	57.50
Zink	µg/g	35.80	77.7	143.0	318.0		15.9	192.00	61.50
Barium	µg/g	175.00	460.0	245.0	120.0		675.0	1402.00	184.00
Molybdän	µg/g	1.45	<1.00	2.1	<1.00		<1.00	3.15	<1.00
Kohlendioxid	%							0.37	1.75
Wasser	%	0.63	0.4	0.8	1.1		1.5	1.04	1.23
Chromat nach TR	Ppm	1.98	2.9	4.4	5.5		1.4	11.69	5.53
Kohlendioxid gravi.		1.05	0.8	1.8	0.3		2.2		
TOC									
Silizium(IV)-oxid	%	30.29	30.4	24.3	25.8		27.6	21.78	24.22
Aluminiumoxid	%	10.20	9.8	6.8	5.5		9.7	6.20	7.52
Titandioxid	%	0.47	0.8	0.4	0.3		0.4	0.43	0.35
Phosphor(V)-oxid	%	0.07	0.1	0.2	0.0		0.1	0.09	0.09
Eisen(III)-oxid	%	1.53	1.2	2.2	2.3		1.4	2.71	2.03
Mangan(III)-oxid	%	0.33	0.2	0.1	0.4		0.5	0.22	0.12
Calciumoxid	%	44.12	48.6	56.5	56.8		47.8	58.45	56.05
Magnesiumoxid	%	7.25	5.7	2.9	4.1		5.4	4.04	3.03
Sulfat als SO3	%	2.73	0.9	3.1	2.4		2.6	3.25	2.32
Kaliumoxid	%	0.71	0.3	0.4	0.7		0.4	0.91	0.94
Natriumoxid	%	0.29	0.3	0.3	0.4		0.2	0.35	0.18
Natriumaequivalen	%	0.76	0.6	0.5	0.9		0.5	0.95	0.80

ECRICEM II : Chemical Composition of Test Cements   FLY ASH CEMENTS

Type		**Fly Ash Cements**		**Pozzolan**	**Limestone Cements**	
Identification		**CEM II/B-V 32.5 N (33% FA)**	**CEM II/A-V 42.5 N (10% FA)**	**CEM II/B-Q (32% P)**	**CEM II/B-L (28% LS)**	**CEM II/A-L 32.5 R (13% LS)**
Production period		**17/07/2002**	**26/04/2002**	**01/05/2002**	**09/05/2002**	**ND**
Reception date		**26/07/2002**	**14/05/2002**	**16/05/2002**	**24/05/2002**	**03/06/2002**
Ecricem Code		**HOL-7**	**HOL-8**	**HOL-9**	**HOL-10**	**HOL-11**
DTA Code		**021428**	**020887**	**020895**	**020959**	**021015**
<u>1. Chemical Composition</u>						
1.4 Trace elements						
Arsen	µg/g		10.20	12.60	4.07	4.32
Beryllium	µg/g		1.70	0.67	0.50	0.76
Cadmium	µg/g		0.28	0.31	0.11	0.52
Kobalt	µg/g		9.48	5.09	10.70	8.53
Chrom	µg/g		45.30	25.90	39.20	50.60
Kupfer	µg/g		15.00	25.20	11.80	15.90
Quecksilber	µg/g		0.09	0.05	0.04	0.12
Mangan	µg/g		516.00	456.00	317.00	234.00
Nickel	µg/g		22.60	9.89	41.70	24.70
Blei	µg/g		17.10	8.69	9.00	13.30
Antimon	µg/g		2.56	<1.00	<1.00	<1.00
Zinn	µg/g		4.70	2.84	1.57	4.27
Thallium	µg/g		<1.00	<1.00	<1.00	<1.00
Vanadium	µg/g		65.00	86.10	139.00	64.20
Zink	µg/g		36.30	26.90	26.00	60.30
Barium	µg/g		425.00	195.00	95.50	110.00
Molybdän	µg/g		2.87	4.01	1.65	1.51
Kohlendioxid	%		0.75			
Wasser	%		1.32	2.16	1.53	0.83
Chromat nach TRGS 613 (Rühr	Ppm		2.83	0.41	6.12	7.78
Kohlendioxid gravi.				0.47	10.58	6.09
TOC			1.01			
Silizium(IV)-oxid	%		22.57	35.71	15.16	18.10
Aluminiumoxid	%		7.53	7.65	4.50	4.45
Titandioxid	%		0.40	0.28	0.24	0.27
Phosphor(V)-oxid	%		0.26	0.08	0.04	0.18
Eisen(III)-oxid	%		3.51	2.90	1.94	2.28
Mangan(III)-oxid	%		0.10	0.10	0.04	0.03
Calciumoxid	%		58.03	43.74	59.18	61.62
Magnesiumoxid	%		1.40	2.05	2.77	1.74
Sulfat als SO3	%		2.59	2.23	2.85	3.22
Kaliumoxid	%		0.27	1.30	1.06	1.07
Natriumoxid	%		0.24	1.31	0.10	0.11
Natriumaequivalent	%		0.42	2.17	0.80	0.81

ECRICEM II : Chemical Composition of Test Cements

COCKTAIL CEMENTS

Type			**Cocktail Cements**					**CEM II/B-M 32.5 R (14% GBFS+12% LS+5% FA)**
Identification			**CEM V/A 32.5 N (32% GBFS+20% FA)**	**CEM V/A 32.5 N (23% GBFS+22% FA)**	**CEM II/B-M 32.5 R (33% GBFS+9% LS)**	**CEM IV/A 32.5 R (15% FA+17% P)**	**CEM II/B-M 32.5 R (14% GBFS+12% LS+5% FA)**	**Ecricem II B**
Production period			**03/05/2002**		**01/05/2002**	**06/05/2002**	**06/05/2002**	**ND**
Reception date			**28/06/2002**	**02/07/2002**	**21/05/2002**	**16/05/2002**	**16/05/2002**	**20/06/2002**
Ecricem Code			**HOL-12**	**HOL-13**	**HOL-14**	**HOL-15**	**HOL-16**	**VDZ-2**
DTA Code			**021233**	**021262**	**020933**	**020914**	**020913**	**021171**

1. Chemical Composition

1.4 Trace elements

Arsen	µg/g		46.60	11.70	7.37	7.59	4.22	9.06
Beryllium	µg/g		4.32	2.86	4.35	2.55	2.12	1.05
Cadmium	µg/g		1.91	0.30	0.10	0.53	0.51	1.00
Kobalt	µg/g		15.10	15.80	6.27	12.60	11.00	13.10
Chrom	µg/g		114.00	125.00	55.30	155.00	90.90	49.50
Kupfer	µg/g		41.00	31.90	8.14	80.40	71.50	33.40
Quecksilber	µg/g		0.09	0.09	0.03	0.08	0.08	0.04
Mangan	µg/g		1499.00	1466.00	1558.00	334.00	1257.00	395.00
Nickel	µg/g		37.90	44.60	26.60	67.60	41.10	44.30
Blei	µg/g		169.00	36.40	4.56	11.80	13.90	12.30
Antimon	µg/g		3.27	1.56	<1.00	3.66	3.07	<1.00
Zinn	µg/g		5.44	3.35	1.20	6.99	5.09	2.38
Thallium	µg/g		<1.00	<1.00	<1.00	<1.00	<1.00	**1.81**
Vanadium	µg/g		138.00	71.40	69.40	131.00	88.40	95.80
Zink	µg/g		268.00	372.00	26.80	99.30	82.10	239.00
Barium	µg/g		425.00	510.00	435.00	430.00	480.00	156.00
Molybdän	µg/g		4.09	2.91	<1.00	8.57	6.78	14.20
Kohlendioxid	%			0.81		1579.00	0.49	2.76
Wasser	%		1.25	1.12	1.16	2.01	1.51	0.47
Chromat nach TRGS 613 (Rühren)	Ppm		7.62	15.10	3.94	13.16	12.47	3.53
Kohlendioxid gravi.			0.75		4.15			
TOC				0.36		2.45	4.06	
Silizium(IV)-oxid	%		32.25	28.72	22.60	28.68	23.64	23.30
Aluminiumoxid	%		11.44	10.34	6.91	8.33	7.36	7.37
Titandioxid	%		0.68	0.44	0.31	0.35	0.32	0.35
Phosphor(V)-oxid	%		0.13	0.22	0.10	0.11	0.08	0.18
Eisen(III)-oxid	%		3.04	3.48	2.14	3.33	2.27	3.79
Mangan(III)-oxid	%		0.24	0.23	0.26	0.06	0.20	0.07
Calciumoxid	%		40.43	44.03	56.09	46.82	53.08	54.13
Magnesiumoxid	%		5.56	5.10	3.15	1.90	3.33	1.94
Sulfat als SO3	%		2.73	3.12	2.01	2.74	2.31	4.03
Kaliumoxid	%		1.07	1.56	0.64	1.18	0.85	1.35
Natriumoxid	%		0.32	0.31	0.28	0.44	0.36	0.20
Natriumaequivalent	%		1.02	1.34	0.70	1.22	0.92	1.09

ECRICEM II : Chemical Composition of Test Cements

PORTLAND CEMENTS

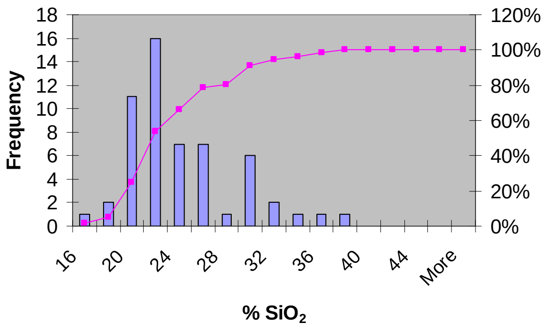
Type		VDZ Cements					Norcem Cements			
Identification		Ecricem II A	CEM II/B-M 32.5 R (6% GBFS+5% LS+10% FA)	Ecricem II C	Ecricem II D	Ecricem II E	CEM I without LD slag in raw mix	CEM I with LD slag in raw mix	CEM I 42.5 R with chromate reduction	CEM II/A-V R (FA) with chromate reduction
Production period		ND	ND	ND	ND	ND	ND	ND	07/06/02	07/06/02
Reception date		20/06/2002	20/06/2002	20/06/2002	20/06/2002	20/06/2002	12/06/2002	12/06/2002	12/06/2002	12/06/2002
Ecricem Code		VDZ-1	VDZ-2	VDZ-3	VDZ-4	VDZ-5	NOR-1	NOR-2	NOR-3	NOR-4
DTA Code		021170	021171	021172	021173	021174	021085	021084	021082	021083
1. Chemical Composition										
1.4 Trace elements										
Arsen	µg/g	5.61	9.06	2.68	3.96	4.54	12.60	5.37	5.87	6.95
Beryllium	µg/g	0.96	1.05	0.37	1.27	1.27	0.90	0.56	1.30	1.89
Cadmium	µg/g	0.86	1.00	0.22	0.35	0.75	0.21	0.30	0.36	0.47
Kobalt	µg/g	7.27	13.10	3.75	8.73	3.45	14.10	13.30	16.30	23.10
Chrom	µg/g	69.30	49.50	29.10	94.10	32.00	79.70	147.00	151.00	122.00
Kupfer	µg/g	59.90	33.40	108.00	35.70	8.30	37.20	17.80	82.10	144.00
Quecksilber	µg/g	0.03	0.04	0.05	0.08	0.02	0.04	0.05	0.04	0.11
Mangan	µg/g	559.00	395.00	283.00	1341.00	688.00	1245.00	2780.00	445.00	375.00
Nickel	µg/g	25.50	44.30	18.90	40.10	16.20	31.60	117.00	44.50	53.50
Blei	µg/g	34.40	12.30	11.50	11.40	20.10	14.10	12.60	23.00	43.30
Antimon	µg/g	23.10	<1.00	3.47	4.97	<1.00	5.74	5.36	2.28	3.01
Zinn	µg/g	3.79	2.38	5.30	3.23	1.37	4.22	4.87	5.57	5.99
Thallium	µg/g	<1.00	1.81	<1.00	<1.00	<1.00	<1.00	<1.00	<1.00	<1.00
Vanadium	µg/g	41.80	95.80	24.50	58.70	57.50	31.70	774.00	53.60	71.00
Zink	µg/g	170.00	239.00	80.90	192.00	61.50	115.00	53.50	102.00	123.00
Barium	µg/g	235.00	156.00	208.00	1402.00	184.00	380.00	345.00	460.00	460.00
Molybdän	µg/g	2.05	14.20	<1.00	3.15	<1.00	4.26	10.20	2.32	3.89
Kohlendioxid	%	1.56	2.76	6.09	0.37	1.75				0.45
Wasser	%	2.64	0.47	0.53	1.04	1.23	0.60	0.68	0.83	0.84
Chromat nach TRGS 613 (Rühren)	Ppm	5.57	3.53	2.41	11.69	5.53	0.52	2.86	1.69	<0.1
Kohlendioxid gravi.							0.96	0.15	1.55	
TOC										0.20
Silizium(IV)-oxid	%	29.01	23.30	20.53	21.78	24.22	22.09	22.26	19.90	25.55
Aluminiumoxid	%	8.11	7.37	3.36	6.20	7.52	3.44	3.22	4.90	9.06
Titandioxid	%	0.33	0.35	0.21	0.43	0.35	0.27	0.31	0.28	0.42
Phosphor(V)-oxid	%	0.26	0.18	0.12	0.09	0.09	0.09	0.13	0.20	0.34
Eisen(III)-oxid	%	3.31	3.79	1.14	2.71	2.03	3.92	3.81	3.15	4.01
Mangan(III)-oxid	%	0.10	0.07	0.05	0.22	0.12	0.20	0.46	0.06	0.07
Calciumoxid	%	48.52	54.13	63.61	58.45	56.05	64.13	64.53	62.14	52.06
Magnesiumoxid	%	1.00	1.94	0.71	4.04	3.03	1.08	1.36	2.37	2.50
Sulfat als SO3	%	2.28	4.03	2.88	3.25	2.32	2.45	2.38	3.07	2.68
Kaliumoxid	%	1.70	1.35	0.53	0.91	0.94	0.64	0.61	1.07	1.27
Natriumoxid	%	1.14	0.20	0.18	0.35	0.18	0.11	0.08	0.46	0.52
Natriumaequivalent	%	2.26	1.09	0.53	0.95	0.80	0.53	0.48	1.16	1.36

APPENDIX E. DISTRIBUTION OF ELEMENT CONTENT BETWEEN THE CEMENTS

1. CEMENT COMPOSITION - MAJOR CONSTITUENTS

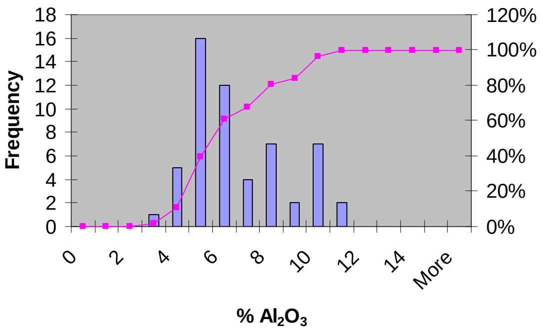
The data of concentrations of major constituents that have been gathered (VDZ 2000, 2001, 2002, ECRICEM I (2001) and II (in preparation 2005) are graphically displayed in histograms (Figure 1). The descriptive statistics of the data are summarized in Table 2.

Figure 1 Histograms of major constituents in ECRICEM world-wide cements



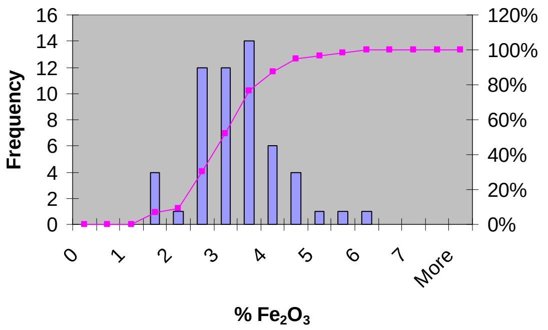
Histogram of SiO_2

in ECRICEM World Wide Cements (median = 21.8 %)



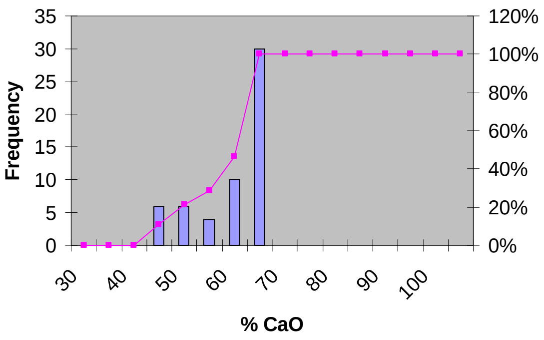
Histogram of Al_2O_3

in ECRICEM World Wide Cements (median = 5.2 %)



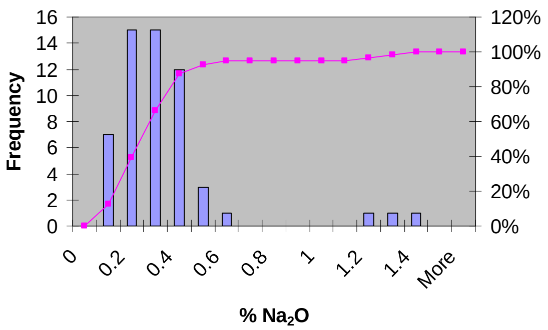
Histogram of Fe_2O_3

in ECRICEM World Wide Ce,ments (median = 3.0%)



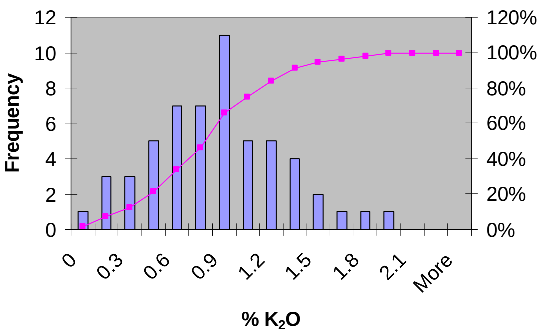
Histogram of CaO

in ECRICEM World Wide Cements (median = 60.7%)



Histogram of Na_2O

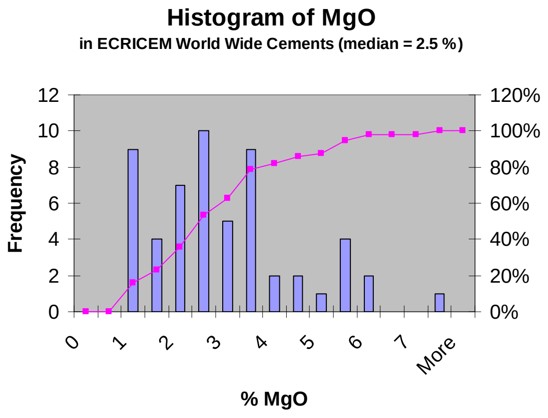
in ECRICEM World Wide Cements (median = 0.24%)

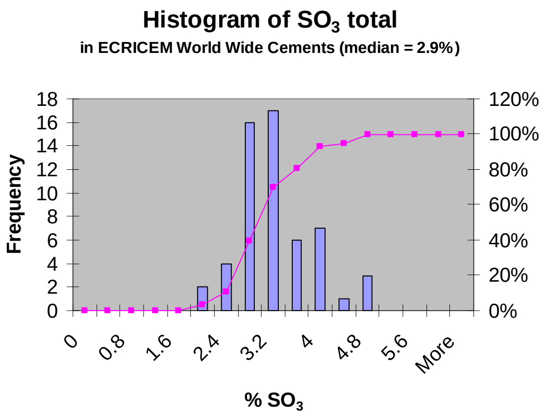


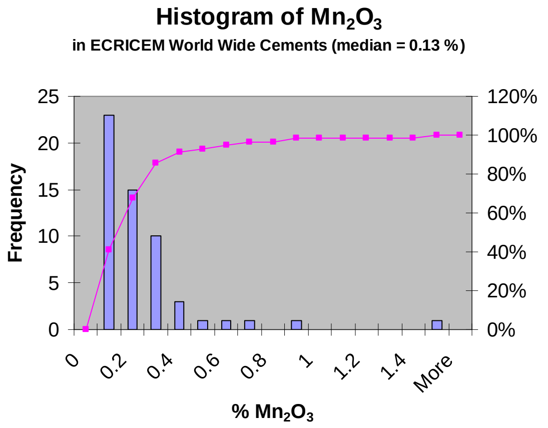
Histogram of K_2O

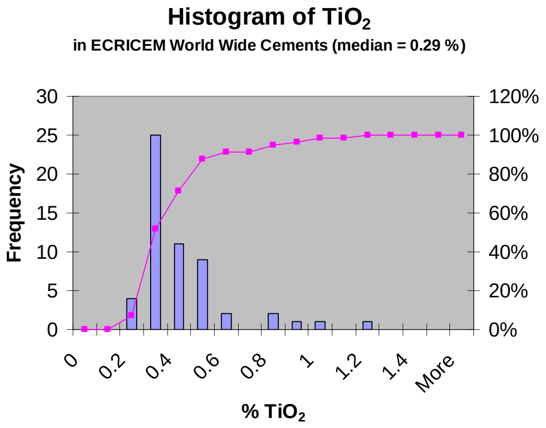
in ECRICEM World Wide Cements (median = 0.79%)

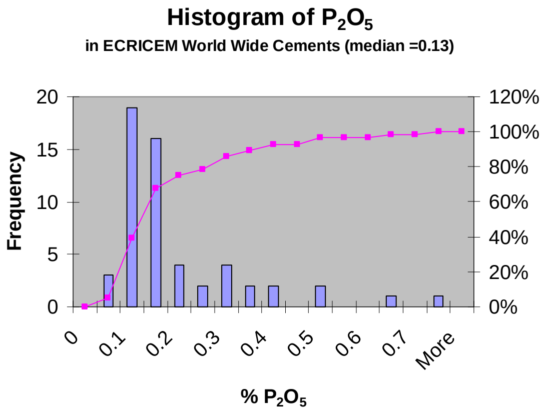
Figure 1 (*continued*) Histograms of major constituents in ECRICEM world wide cements

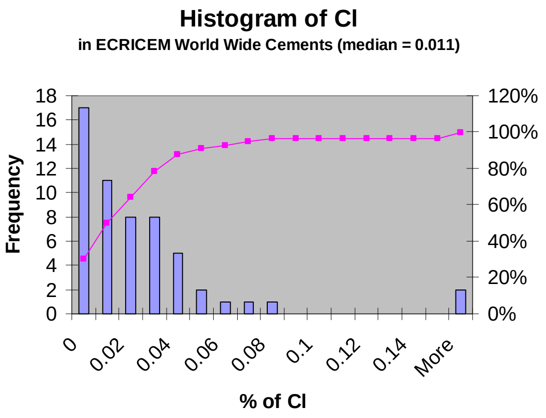








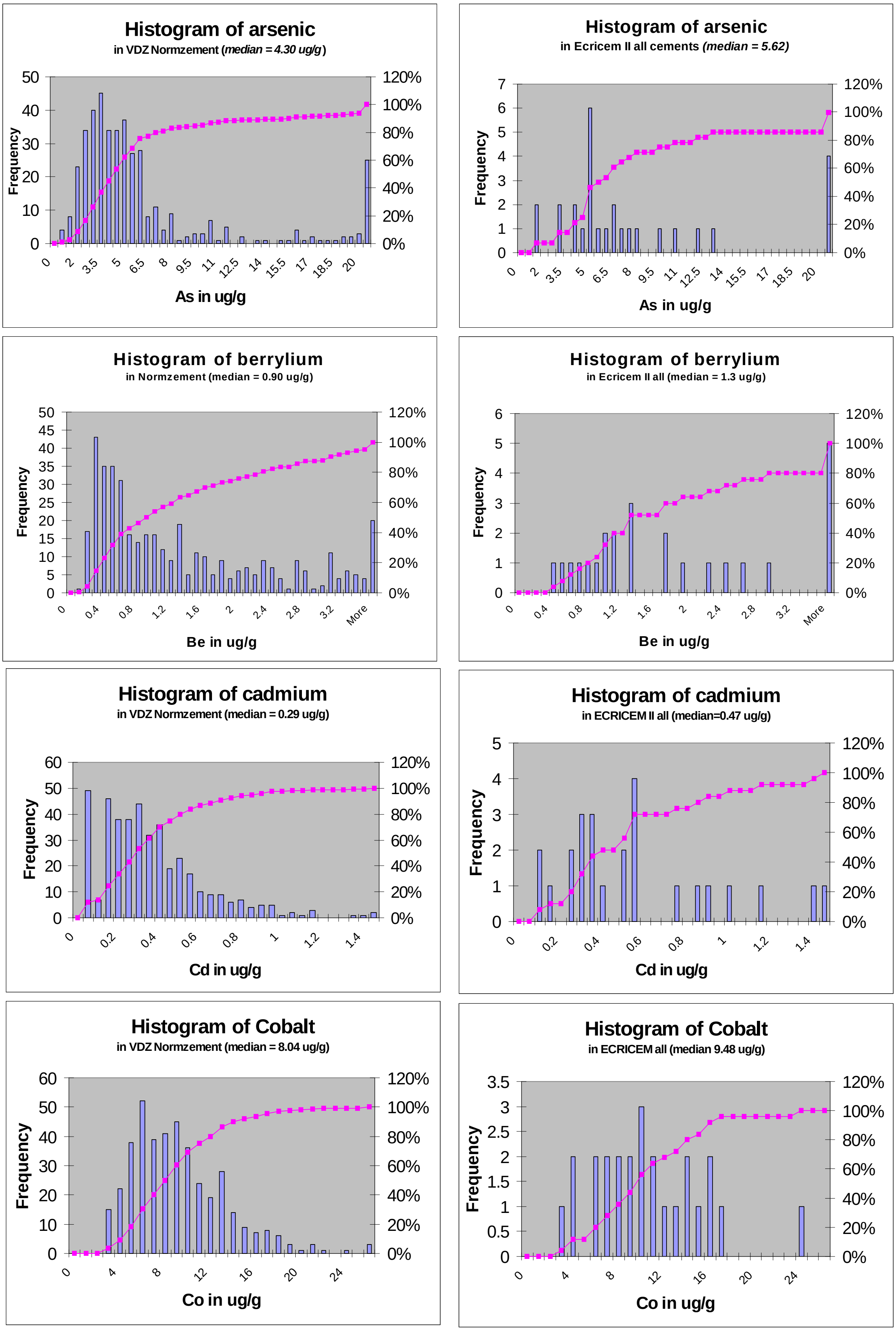


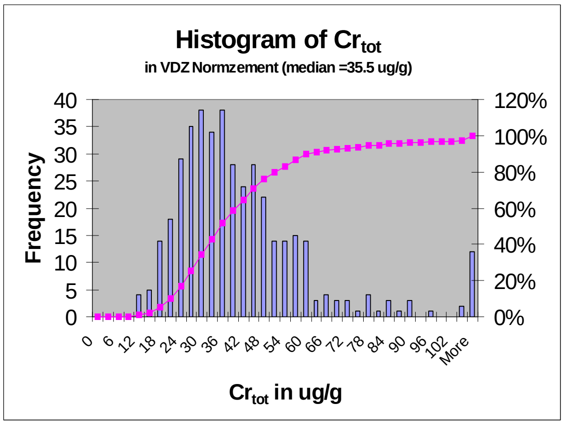


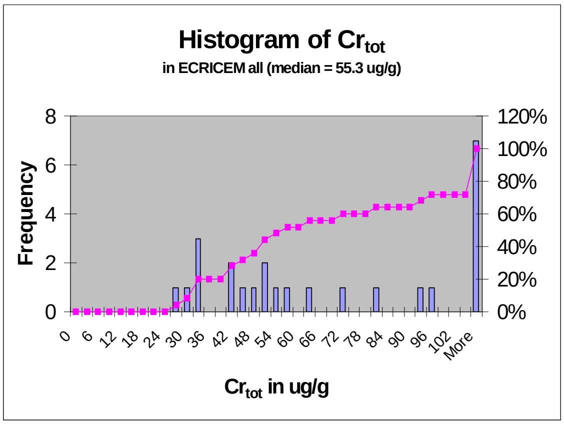
2. CEMENT COMPOSITION - TRACE ELEMENTS

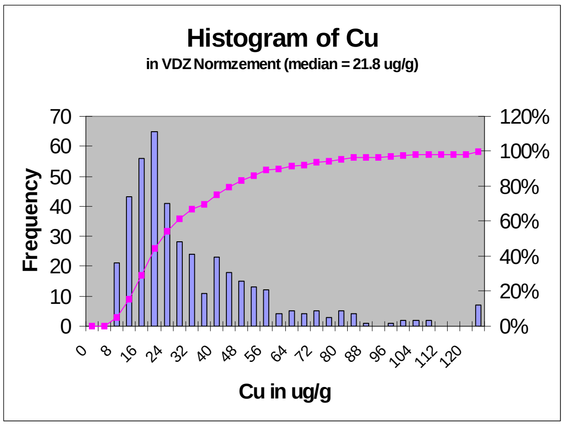
Trace element concentrations in ECRICEM World wide cements are compared to the extensive data of the Verein Deutscher Zementwerke (VDZ). The data are given in figure 2. The concentrations that were reported as lower than the detection limit have been replaced by half the value of the detection limit for purposes of data analysis.

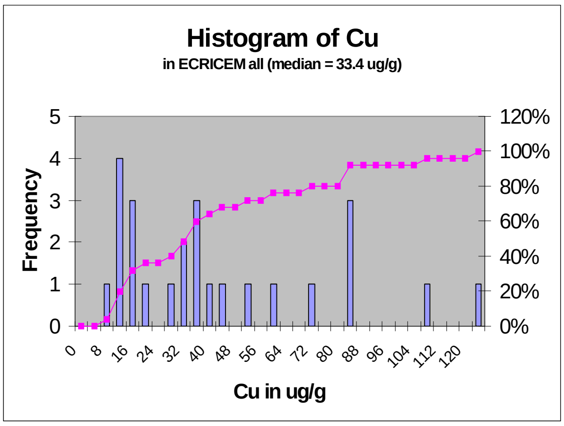
Figure 2 Histograms of trace constituents in ECRICEM world wide cements

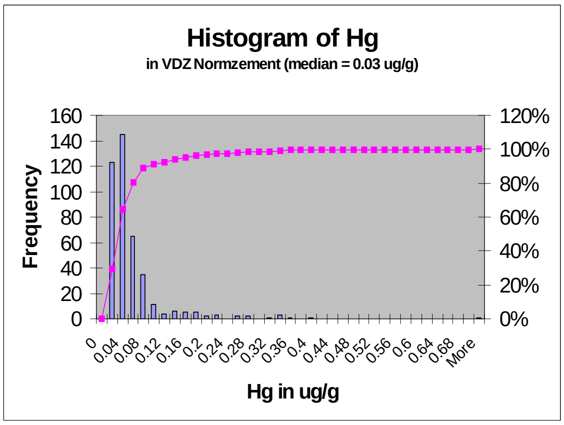


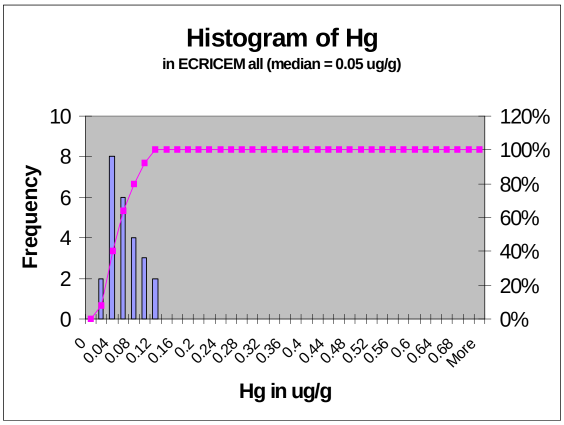

Histogram of Cr_{tot}
in VDZ Normzement (median =35.5 ug/g)
Frequency
0
5
10
15
20
25
30
35
40
0%
20%
40%
60%
80%
100%
120%
0
6
12
18
24
30
36
42
48
54
60
66
72
78
84
90
96
102
More
Cr_{tot} in ug/g

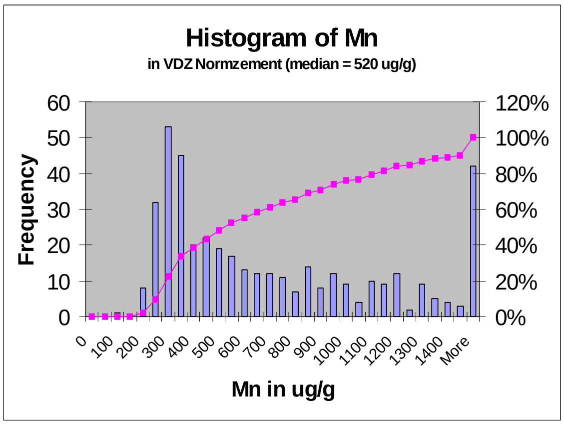

Histogram of Cr_{tot}
in ECRICEM all (median = 55.3 ug/g)
Frequency
0
2
4
6
8
0%
20%
40%
60%
80%
100%
120%
0
6
12
18
24
30
36
42
48
54
60
66
72
78
84
90
96
102
More
Cr_{tot} in ug/g

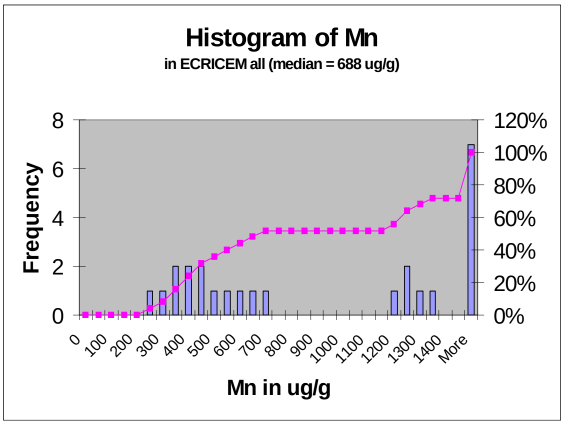

Histogram of Cu
in VDZ Normzement (median = 21.8 ug/g)
Frequency
0
10
20
30
40
50
60
70
0%
20%
40%
60%
80%
100%
120%
0
8
16
24
32
40
48
56
64
72
80
88
96
104
112
120
Cu in ug/g

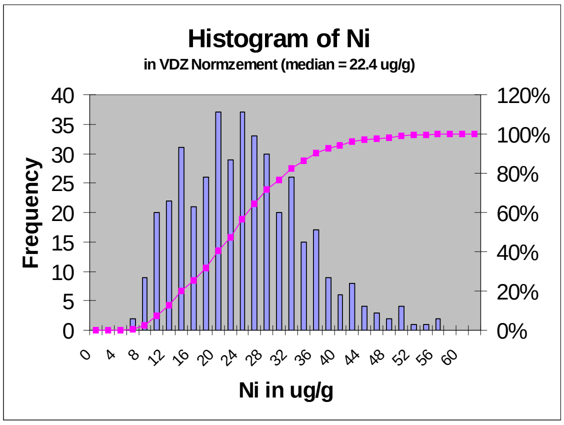

Histogram of Cu
in ECRICEM all (median = 33.4 ug/g)
Frequency
0
1
2
3
4
5
0%
20%
40%
60%
80%
100%
120%
0
8
16
24
32
40
48
56
64
72
80
88
96
104
112
120
Cu in ug/g


Histogram of Hg
in VDZ Normzement (median = 0.03 ug/g)
Frequency
0
20
40
60
80
100
120
140
160
0%
20%
40%
60%
80%
100%
120%
0
0.04
0.08
0.12
0.16
0.2
0.24
0.28
0.32
0.36
0.4
0.44
0.48
0.52
0.56
0.6
0.64
0.68
More
Hg in ug/g


Histogram of Hg
in ECRICEM all (median = 0.05 ug/g)
Frequency
0
2
4
6
8
10
0%
20%
40%
60%
80%
100%
120%
0
0.04
0.08
0.12
0.16
0.2
0.24
0.28
0.32
0.36
0.4
0.44
0.48
0.52
0.56
0.6
0.64
0.68
More
Hg in ug/g

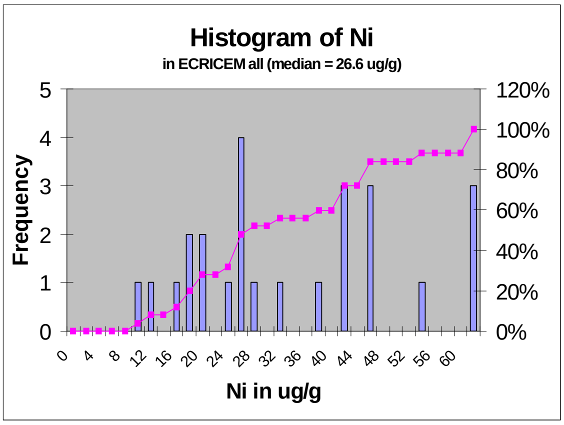

Histogram of Mn
in VDZ Normzement (median = 520 ug/g)
Frequency
0
10
20
30
40
50
60
0%
20%
40%
60%
80%
100%
120%
0
100
200
300
400
500
600
700
800
900
1000
1100
1200
1300
1400
More
Mn in ug/g


Histogram of Mn
in ECRICEM all (median = 688 ug/g)
Frequency
0
2
4
6
8
0%
20%
40%
60%
80%
100%
120%
0
100
200
300
400
500
600
700
800
900
1000
1100
1200
1300
1400
More
Mn in ug/g



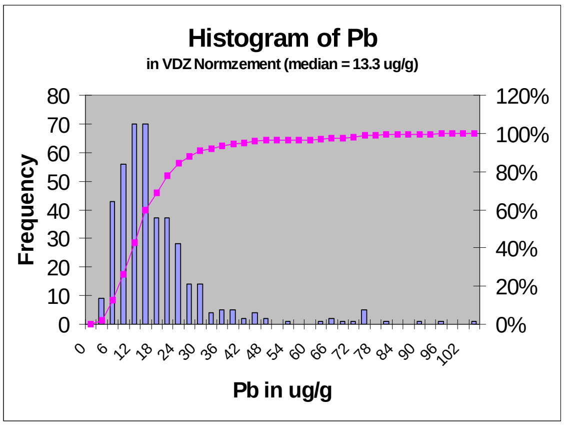
Histogram of Ni

in VDZ Normzement (median = 22.4 ug/g)



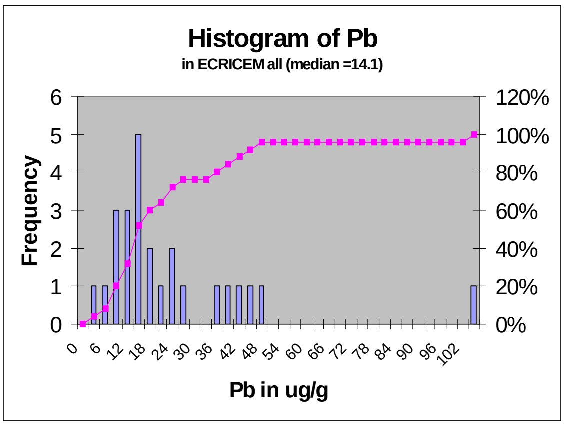
Histogram of Ni

in ECRICEM all (median = 26.6 ug/g)



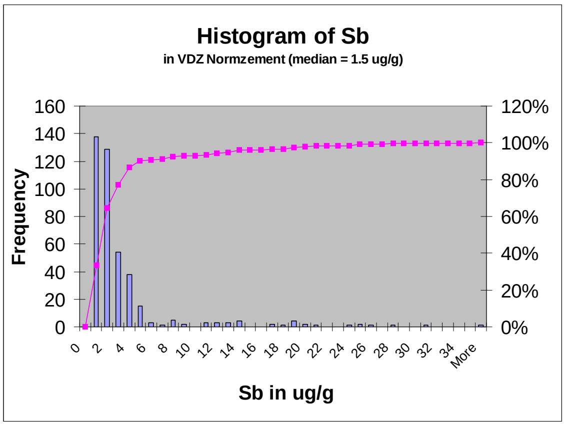
Histogram of Pb

in VDZ Normzement (median = 13.3 ug/g)



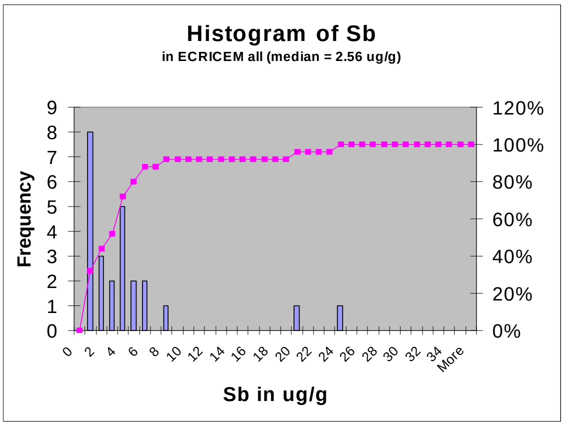
Histogram of Pb

in ECRICEM all (median =14.1)



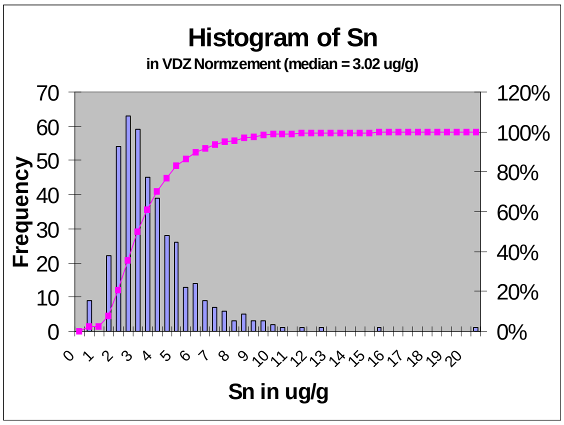
Histogram of Sb

in VDZ Normzement (median = 1.5 ug/g)



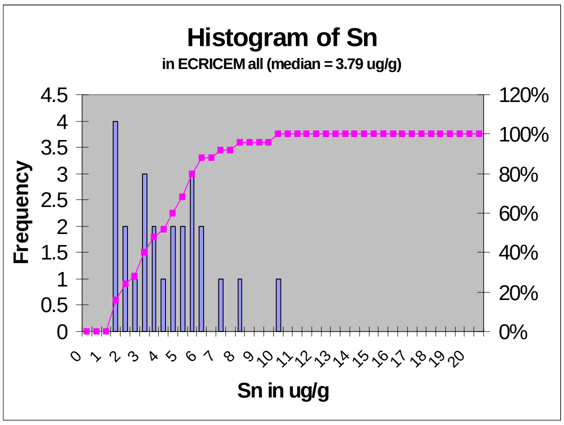
Histogram of Sb

in ECRICEM all (median = 2.56 ug/g)



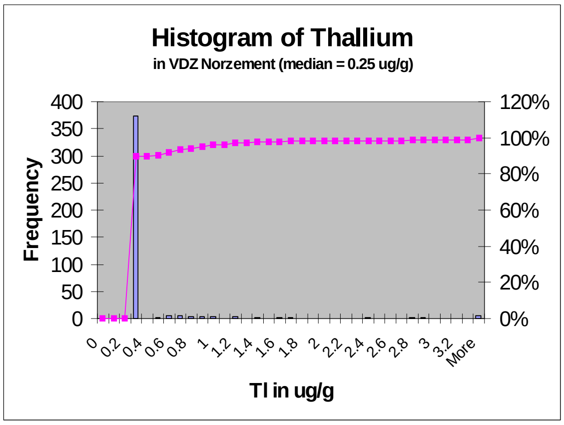
Histogram of Sn

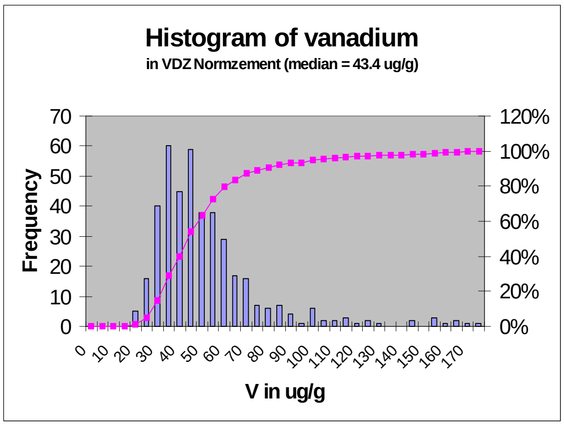
in VDZ Normzement (median = 3.02 ug/g)

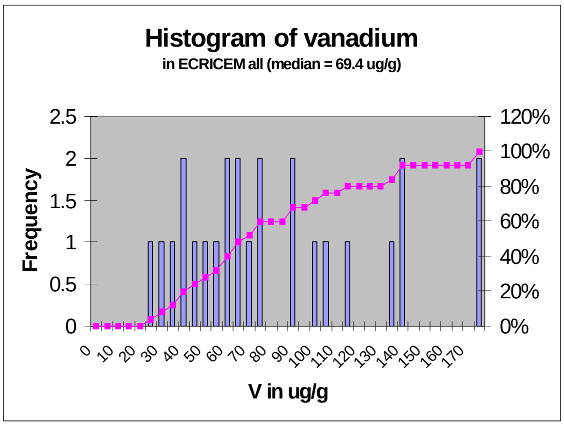


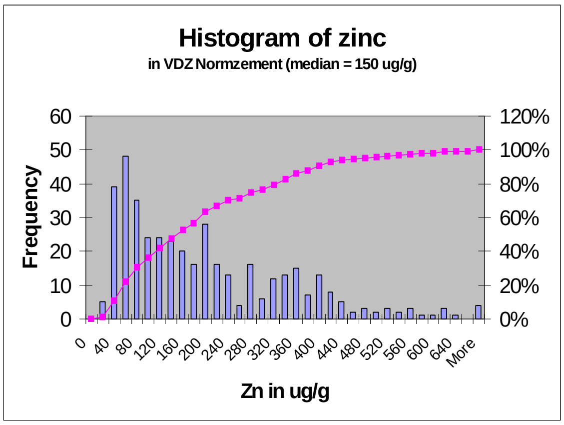
Histogram of Sn

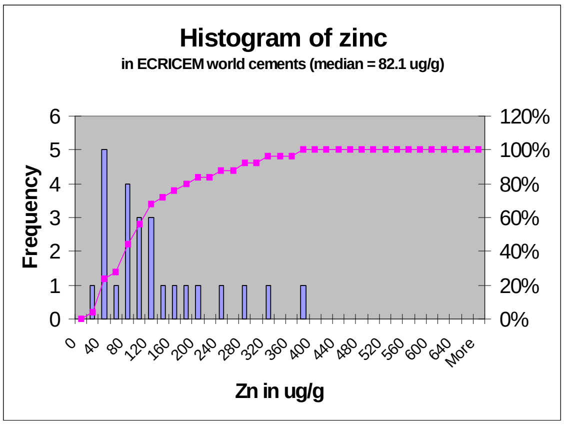
in ECRICEM all (median = 3.79 ug/g)


Histogram of Thallium
in VDZ Norzement (median = 0.25 ug/g)
Frequency
400
350
300
250
200
150
100
50
0
120%
100%
80%
60%
40%
20%
0%
0
0.2
0.4
0.6
0.8
1
1.2
1.4
1.6
1.8
2
2.2
2.4
2.6
2.8
3
3.2
More
Tl in ug/g


Histogram of vanadium
in VDZ Normzement (median = 43.4 ug/g)
Frequency
70
60
50
40
30
20
10
0
120%
100%
80%
60%
40%
20%
0%
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
V in ug/g


Histogram of vanadium
in ECRICEM all (median = 69.4 ug/g)
Frequency
2.5
2
1.5
1
0.5
0
120%
100%
80%
60%
40%
20%
0%
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
V in ug/g


Histogram of zinc
in VDZ Normzement (median = 150 ug/g)
Frequency
60
50
40
30
20
10
0
120%
100%
80%
60%
40%
20%
0%
0
40
80
120
160
200
240
280
320
360
400
440
480
520
560
600
640
More
Zn in ug/g


Histogram of zinc
in ECRICEM world cements (median = 82.1 ug/g)
Frequency
6
5
4
3
2
1
0
120%
100%
80%
60%
40%
20%
0%
0
40
80
120
160
200
240
280
320
360
400
440
480
520
560
600
640
More
Zn in ug/g

APPENDIX F. MICROSCOPY INVESTIGATION

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TITLE OF REPORT

MICROSCOPY INVESTIGATION OF 10 MORTAR BARS WITH DIFFERENT TYPES OF CEMENT.

ECRICEM II

DATE
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NO OF PAGES / ENCL.
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KEY WORD

ABSTRACT

Concerning the project ECRICEM II, 10 bars of mortar have been investigated by means of optical microscope. The quality of the mortars, porosity and the distribution of sand, paste and air were of particular interest. This is important for further exposure and leaching test.

The microscopy investigation of 10 samples shows:

- The air content in the samples varies from 1 to 4 %. Thin sections no. 3 and 6 have only 1 % air voids in the mortar. No. 4 and 8 have the highest content with 4 % air voids. The normal air content is up to 4 %.
- Most of the samples are homogeneous.
- The porosity of the samples are different. The measured capillary porosity indicates that the thin section number 1 and 8 have highest porosity. Number 2, 6 and 7 have the densest paste.
- The differences in the mortar bars are caused by differences of the cement type and not casting. Difference in homogeneity, content and size of the air voids and porosity can influence the results in the leaching test.

TABLE OF CONTENTS

ENCLOSURE

- Explanation of the photos of the thin section: Encl. 1.
- Photos, optical microscope: Encl. 2-11.

1.0 INTRODUCTION

Concerning the project ECRICEM II, 10 bars of mortar have been investigated by means of optical microscope. Norcem R&D received the samples 16. January 2003.
The quality of the mortars, capillary porosity and the distribution of sand, paste and air were of particular interest. This is important for further exposure and leaching test.

2.0 SAMPLES AND METHODS

2.1 Samples

We have received 2x10 samples of mortar, size 40x40x160 mm^3 from Patricia Dath, Holcim. The mortars were marked with number and producer. The number, the reference number and the type of the samples are seen in table1. The name of the producers is not given.
Each sample consists of two mortar bars. One of the mortar bars was cut in two pieces (length of 6 and 10 cm). The mortar bars were cast at nearly the same time (18-21.November. 2002). The hydration time is about 2 months.

Table 1. Summary of the samples:

Number	**Reference no.**	**Preparation date**	**Type of cement**	
1	021001	19.11.2002	Slag	CEM III/B (80%GBFS)
2	020949	18.11.2002	‘’	CEM III/B 32,5N (66%GBFS)
3	020948	‘’	‘’	CEM II/B-S 32,5R (29%GBFS)
4	021377	‘’	‘’	CEM II/A-S 32,5R (20%GBFS)
5	021173	19.11.2002	‘’	CEM II/A-S 32,5R
6	021428	‘’	Fly ash	CEM II/B-V 32,5N (33%FA)
7	021083	‘’	‘’	CEM II/A-V (chromate reduction)
8	021170	‘’	Pozzolan	CEM II/B-P 32,5R (26%trass)
9	021233	21.11.2002	Cocktail	CEM V/A 32,5N (32%GBFS + 20%FA)
10	021084	’’	Portland Cement	CEM I (with LD slag in raw mix)

2.2 Thin section analysis

The thin section analysis is a method to estimate the structure of the concrete with very thin section in an optical microscope.
The cut samples are first impregnated in fluorescence epoxy to prevent loss of paste. Then it is ground plane at one side, dried at 30°C and evacuated in about 0,25 mbar. The sample is impregnated again in fluorescence epoxy and polished. A glass-slide is glued on the polished surface. The sample is cut in about 0,5 mm thickness and ground down to a thin section with a thickness of 0,025 mm. The thin section is sprayed with a lacquer and investigated in a polarization microscope.
The size of the thin section is about 25x45 mm.

2.3 Quantitative analysis of the air voids and the composition of the samples

The amount of aggregates, paste and air voids is determined with help of a point counter with a distance between the points of 0,167 mm and an even distribution of 2000 points in each thin section. The air voids are quantified with different size of diameter: < 0,12 mm, [0,12-0,25 mm], [0,25-1,35 mm] and > 1,35 mm. The total air of the paste content and the mortar are decided.

The calculation is done by using density of the cement, water and sand as follow: 3.12, 1.00 and 2.69 kg/dm^3. Because the cement types are different with different density the air content will be approximately determined.

2.4 Capillary porosity

The capillary porosity of the cement is measured with a spotlight-meter in the optical microscope. The transmission of the fluorescence light is measured in several points (40-45 points). The transmission of the air voids is used as ”zero”. The intensity of the fluorescence light from the impregnated paste of cement is about proportional with the water/cement-ratio.
The degree of hydration and amount of filler (for example silica) influence the porosity of the cement.
Usually we compare an unknown sample with a reference sample with known hydration and type of cement. The reference sample should preferably be of the same type as the unknown sample. However, we have no reference samples suitable for this investigation. Therefore, the result from the spotlight-measuring has to be used in the comparison between the ten samples.

3 RESULT

3.1 Quantitative analysis of the air voids and the composition of the samples.

Table no.2

Sample no.	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**
Reference code / Type of cement	021001/ CEM III/B	020949/ CEM III/B 32,5N	020948/ CEM II/B-S 32,5R	021377/ CEM II/A-S 32,5R	021173/ CEM II/A-S 32,5R	021428/ CEM II/B-V 32,5N	021083/ CEM II/A-V	021170/ CEM II/B-P 32,5R	021233/ CEM V/A 32,5N	021084/ CEM I
% Cement paste in the thin section	43,6	44,7	42,2	44,3	43,5	46,9	43,0	43,9	43,9	41,8
% Aggregates in the thin section	54,4	52,6	57,1	51,4	53,7	52,0	55,0	52,3	54,1	56,6
% Air voids < 0,12 mm in the thin section	0,1	0	0,1	0,2	0,3	0	0,1	0,1	0	0,1
% Air void [0,12-0,25 mm] in the thin section	0,2	0,2	0,2	0,1	0,2	0,1	0,2	0,2	0,1	0,2
% Air voids [0,25-1,35 mm] in the thin section	1,0	2,3	0,5	2,6	1,5	1,1	1,6	1,5	0,3	1,3
% Air voids >1,35 mm in the thin section	0,7	0,3	0	1,4	0,8	0	0,2	2,0	1,6	0
% Total air voids in the thin section	**2,0**	**2,8**	**0,8**	**4,3**	**2,8**	**1,2**	**2,1**	**3,8**	**2,0**	**1,6**
% Air voids < 0,12 mm in the paste	0,2	0	0,2	0,6	0,7	0	0,2	0,2	0	0,2
% Air void [0,12-0,25 mm] in the paste	0,4	0,4	0,4	0,3	0,5	0,2	0,4	0,5	0,2	0,4
% Air voids [0,25-1,35 mm] in the paste	2,3	5,1	1,3	5,9	3,5	2,2	3,7	3,4	0,6	3,1
% Air voids >1,35 mm in the paste	1,6	0,7	0	3,2	1,7	0	0,4	4,6	3,6	0
% Total air voids in the paste	**4,5**	**6,2**	**1,90**	**10,0**	**6,4**	**2,4**	**4,7**	**8,6**	**4,4**	**3,7**
% Total air voids of the mortar	**2**	**3**	**1**	**4**	**3**	**1**	**2**	**4**	**2**	**2**

3.2 Microscopy analysis of the samples

Table no. 3

Sample no.	**1**	**2**	**3**	**4**	**5**
Reference code / Type of cement	021001/ CEM III/B	020949/ CEM III/B 32,5N	020948/ CEM II/B-S 32,5R	021377/ CEM II/A-S 32,5R	021173/ CEM II/A-S 32,5R
Cement paste	Very porous, with only few dens areas.	Inhomogeneous with dens and porous areas	Normal porous paste with some denser areas. Quite homogeneous	Normal porous paste with some denser areas. Quite homogeneous	Homogeneous and normal paste with only a few denser areas.
Air voids	The air voids are rounded and oval, even distributed**.** An area with small irregular pores.	As number 1	Rounded. Few and even distributed.	Rounded and even distributed.	Rounded. Fairly even distributed. Some small irregular pores are seen.
Aggregates	Rounded and edged. Some with fine cracks within the particle. A couple are porous. Even distributed: Aggregates: Mostly with fine- and coarser crystalline form of quartz. A few particles of sandstone.	As number 1	As number 1	As number 1	As number 1
Various	Very little $Ca(OH)_2$ are seen in the cement paste. Edged particles of slag are seen.	$Ca(OH)_2$ are seen. Particles of slag are seen.	$Ca(OH)_2$, some coarse particles of cement and slag are seen	More $Ca(OH)_2$ are seen than in no.1,2 and 3. Particles of slag are seen.	A lot of $Ca(OH)_2$ are seen. Particles slag are seen.
The measured transmission of the fluorescence light	**75,9**	**57,3**	**67,8**	**66,2**	**68,0**

Table no. 4

Sample no.	**6**	**7**	**8**	**9**	**10**
Reference code / Type of cement	021428/ CEM II/B-V 32,5N	021083/ CEM II/A-V	021170/ CEM II/B-P 32,5R	021233/ CEM V/A 32,5N	021084/ CEM I
Cement paste	Dens paste. Only a few areas with porous paste.	Dens paste. Some inhomogeneous areas.	Porous paste. Quite homogeneous.	Normal/dens. Quite homogeneous.	Dens and quite homogeneous.
Air voids	Rounded and even distributed. A small area with tiny irregular pores.	Rounded and even distributed. Area with small irregular pores is seen.	Rounded and quite even distributed.	Rounded and even distributed.	Rounded. An area with some small irregular air voids. Less even distributed.
Aggregates	As number 1	As number 1	As number 1	As number 1	As number 1
Various	Less $Ca(OH)_2$ than no.4 and 5. Some coarse unhydrated particles of cement are seen, and particles of fly ash are seen.	$Ca(OH)_2$ are seen. Some coarse particles of cement, but finer ground cement than no.6. Particles of fly ash are seen.	A lot of small $Ca(OH)_2$ are seen. Some coarse particles of cement are seen. Particles of slag and fly ash are seen.	$Ca(OH)_2$ are seen. A few unhydrated particles of cement are seen. Particles of slag and fly ash are seen.	Coarse $Ca(OH)_2$ are seen. A lot of unhydrated particles of cement are seen.
The measured transmission of the fluorescence light	**59,9**	**59,7**	**70,2**	**67,2**	**61,8**

Photos of the air voids and pasta are sees in encl. 2-11.

4.0 DISCUSSION

The microscopy investigation of the air content in the 10 samples varies from 1 to 4 % (table no. 2). Thin section no. 3 and 6 has only 1 % air voids in the mortar. No. 4 and 8 have the highest content with 4 % air voids. The normal air content is up to 4 %.
Number 4 and 8 have the highest content of coarse air voids (>0,25 mm).
The air voids are rounded and even distributed in most of the thin sections. Only in thin section number 10 the air voids are less even distributed.

The microscopy investigation of the quality of the mortars shows that most of the samples are homogeneous, only no. 2 and 7 have inhomogeneous paste (table no. 3 and 4).
The measurement of transmission of fluorescence light is proportional with the capillary porosity. The result of the measurements of the 10 samples indicates a difference in porosity. The age is quite equal, and the water/cement-ratio is identical. The difference in porosity is probably caused by the different types of cement and is not unexpected.
The measured capillary porosity indicates that the thin section number 1 and 8 have highest porosity. Number 2, 6 and 7 have the densest paste.

More or less unhydrated cement particles are seen in the samples. In the fly ash and the slag cements the particles might be “covered” with a diffuse paste in the light microscope or the particles are finer than in cement with little or no fly ash or slag. It is not unusual to see unhydrated particles in paste. Even in old concrete particles of unhydrated cement are seen.
The content of $Ca(OH)_2$ vary in the different samples. A lot $Ca(OH)_2$ has been registered in mortars with little or no fly ash or slag. Less $Ca(OH)_2$ is seen in mortars with a lot of fly ash or slag, because of the pozzolan effect. $Ca(OH)_2$ react with the pozzolan to CSH (calsium-silicahydrate).

The differences we see in the mortar bars are caused by differences of the cement type and not casting. Difference in homogeneity, content and size of the air voids and porosity can influence the results in the leaching test.

The results of this microscopy investigation show much better casting than the first one (Norcem report no.9D4/R02059). In that investigation inhomogeneous paste with porous areas produced a lot of irregular air during preparation. This time Norcem R&D prepared the thin sections, and we tried to preserve the porous paste better. However, some areas in some of the samples show small irregular air. This can be due to poor compaction or preparation. These areas and the air voids are small and will hardly affect the leaching test.

If we compare the result in this investigating with the result in Norcem report no. 9D4/R02059 the mortar bars are more homogeneous this time. The content of air voids (normal, rounded pores) is almost the same: Samples with high air content in this investigation also had high content last time (ex. no. 4 and 8 in this report correspond with no. 5 and 17 in report 9D4/R02059), when it was up to 6 % rounded air voids (excluded the irregular air voids).
The porosity is also almost the same if the samples in this investigation are compared with the same samples last time.

5.0 CONCLUSION

The microscopy investigation of 10 samples shows:

- The air content in the samples varies from 1 to 4 %. Thin sections no. 3 and 6 have only 1 % air voids in the mortar. No. 4 and 8 have the highest content with 4 % air voids. The normal air content is up to 4 %.
- Most of the samples are homogeneous.
- The porosity of the samples are different. The measured capillary porosity indicates that the thin section number 1 and 8 have highest porosity. Number 2, 6 and 7 have the densest paste.
- The differences in the mortar bars are caused by differences of the cement type and not casting. Difference in homogeneity, content and size of the air voids and porosity can influence on the results in the leaching test.

Enclosure 1
Explanation of the photos of the thin section.

The green/yellow photos are taken with fluorescence light and show:

- The air voids are yellow, rounded area.
- Thin lines are cracks.
- The aggregates are dark area.
- The paste of cement is green/yellow area. The darkness of the colour is an expression of the capillary porosity. Darker green/yellow colour mean less porous and denser paste.

The multi coloured photos are taken in polarized light and a filter of gypsum.

- The air voids are read.
- The paste of cement is dark coloured, brown/violet colour.
- The aggregates are multi coloured, single or a number of colours.
- The carbonated area is light brown to yellow/brown.
- $Ca(OH)_2$ is yellow or turquoise small area in the paste.
- The gel of silica and alkali-silica are dark pink.
- Particles of slag are dark pink.
- Particles of fly ash are often dark and rounded.

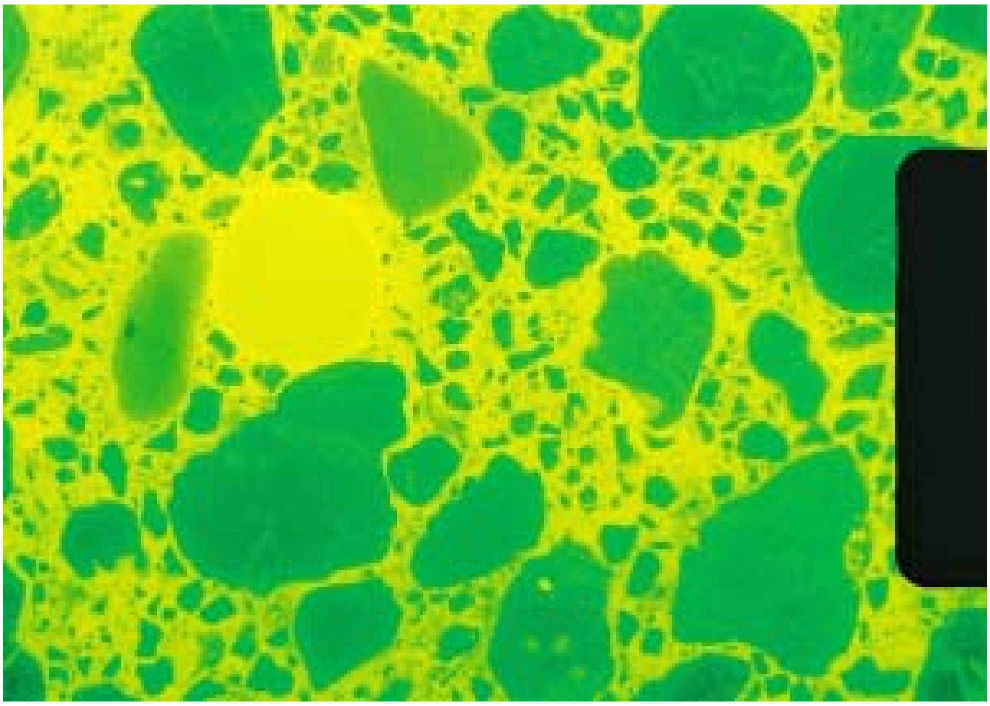
Explanation of the magnification and size of the photos:

25 X: 2,75 cm in the photo is equivalent to 1 mm in reality.

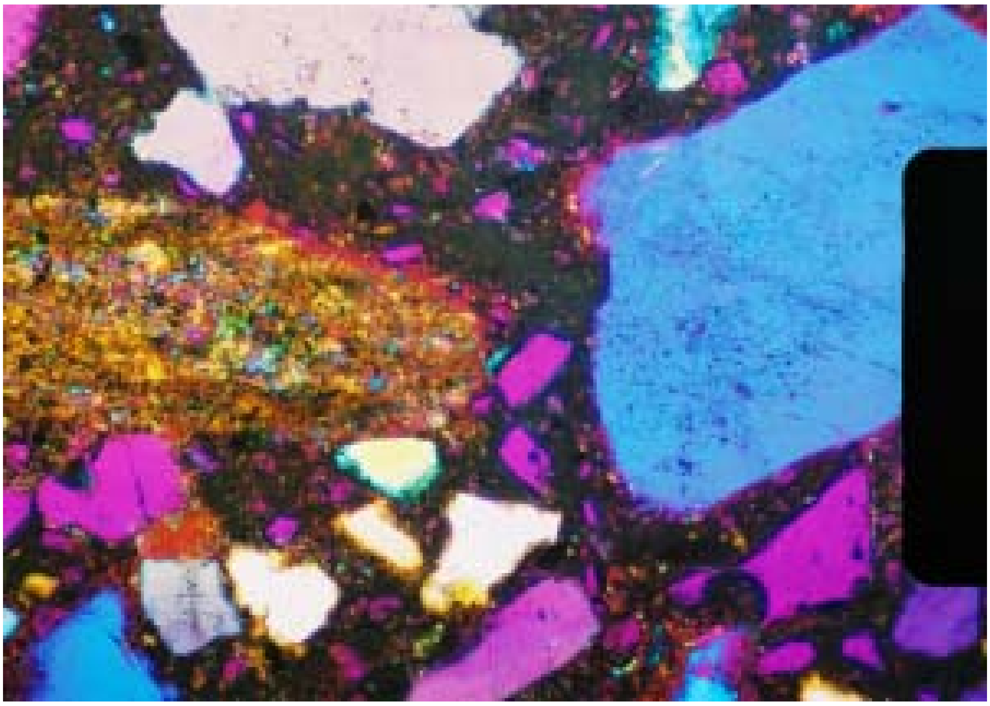
100 X: 1,1 cm in the photo is equivalent to 0,1 mm in reality.

→ The colour of the photos should not be compared because of automatic production of the photos.

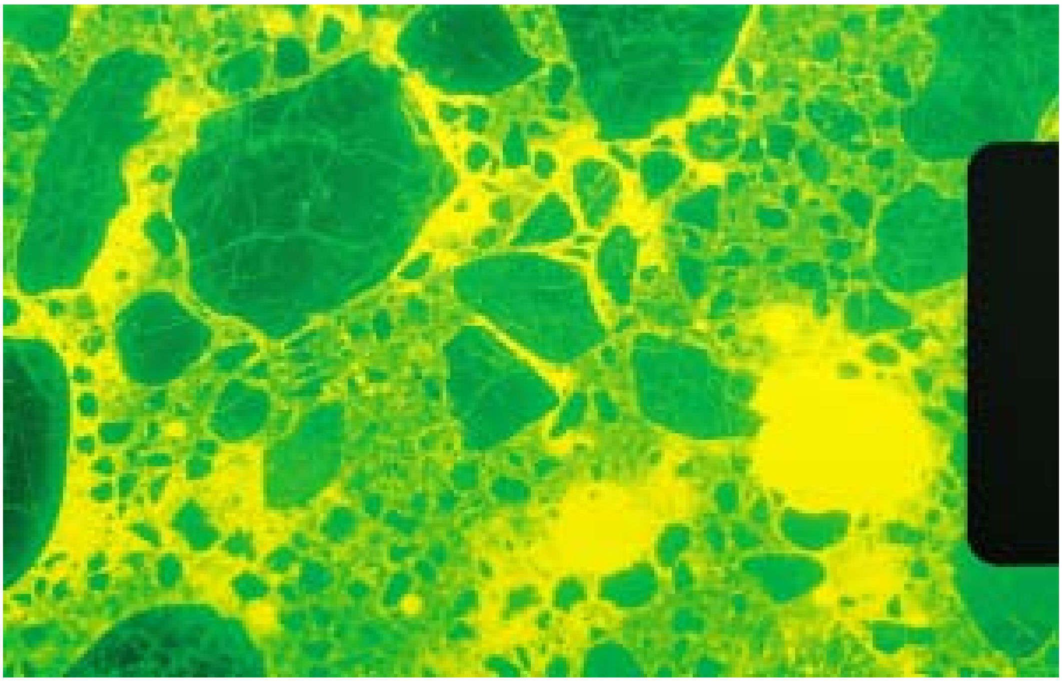
The photo is taken in fluorescence light Magnification: 25X.



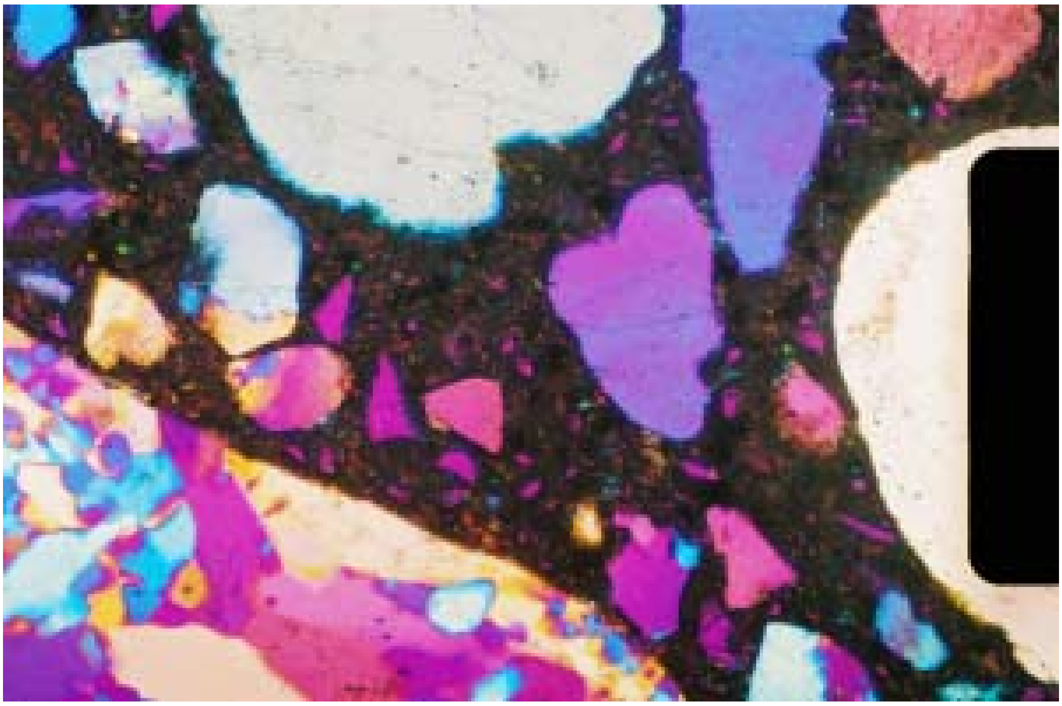
The photo is taken in polarized light and a filter of gypsum. Magnification: 100X.



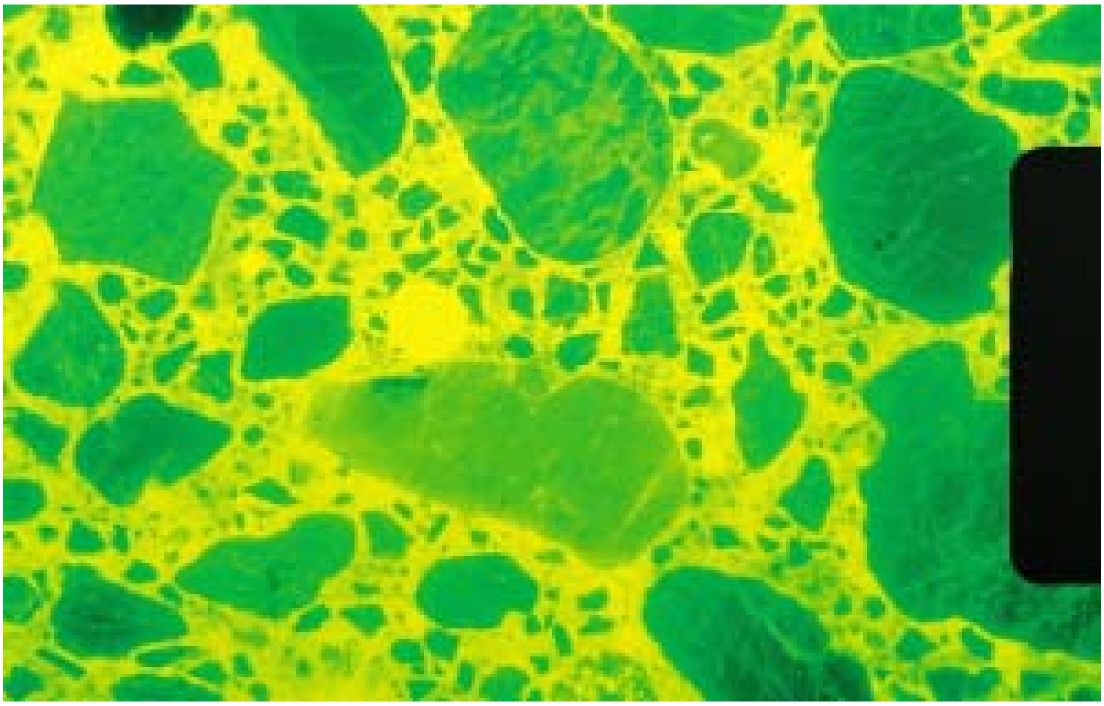
The photo is taken with fluorescence light   Magnification: 25X.



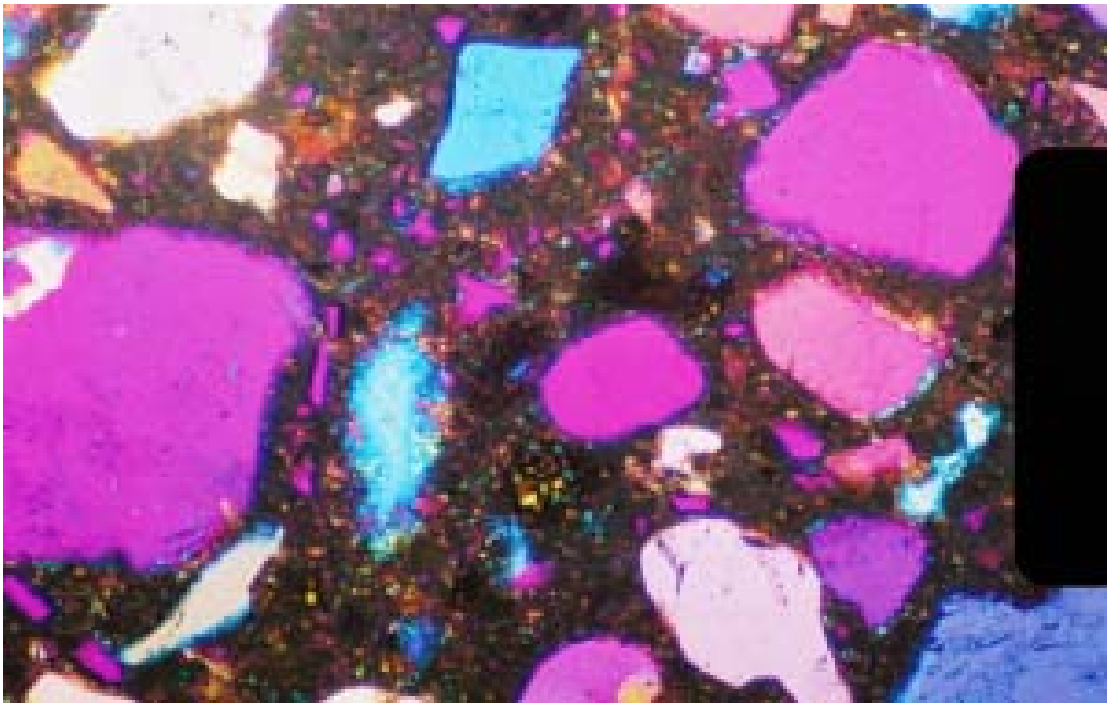
The photo is taken in polarized light and a filter of gypsum. Magnification: 100X.



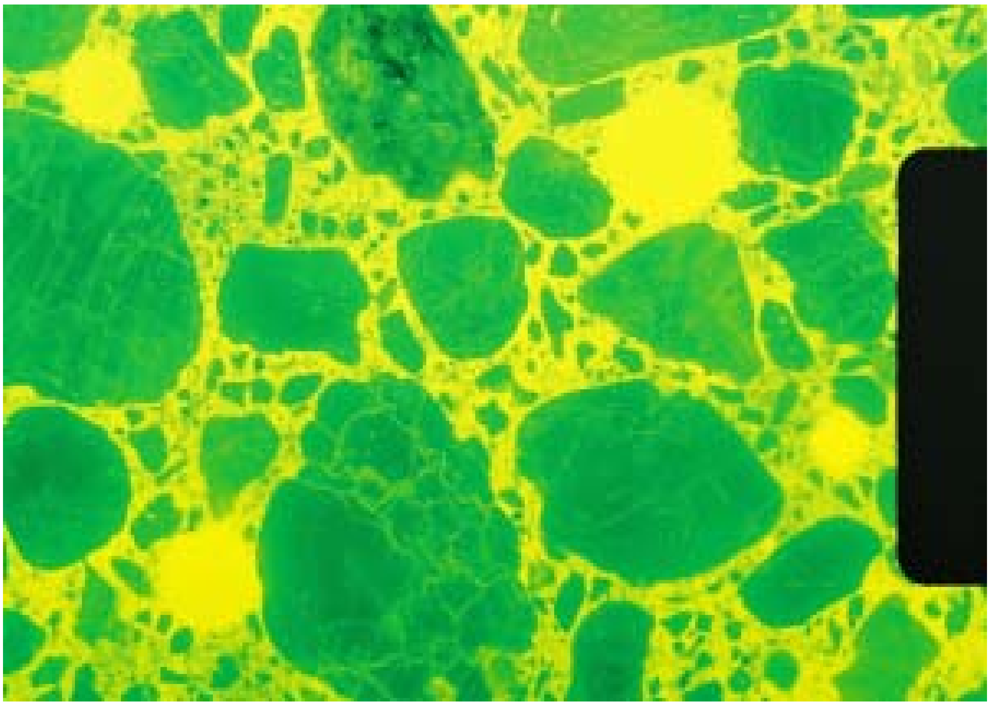
The photo is taken with fluorescence light   Magnification: 25X.



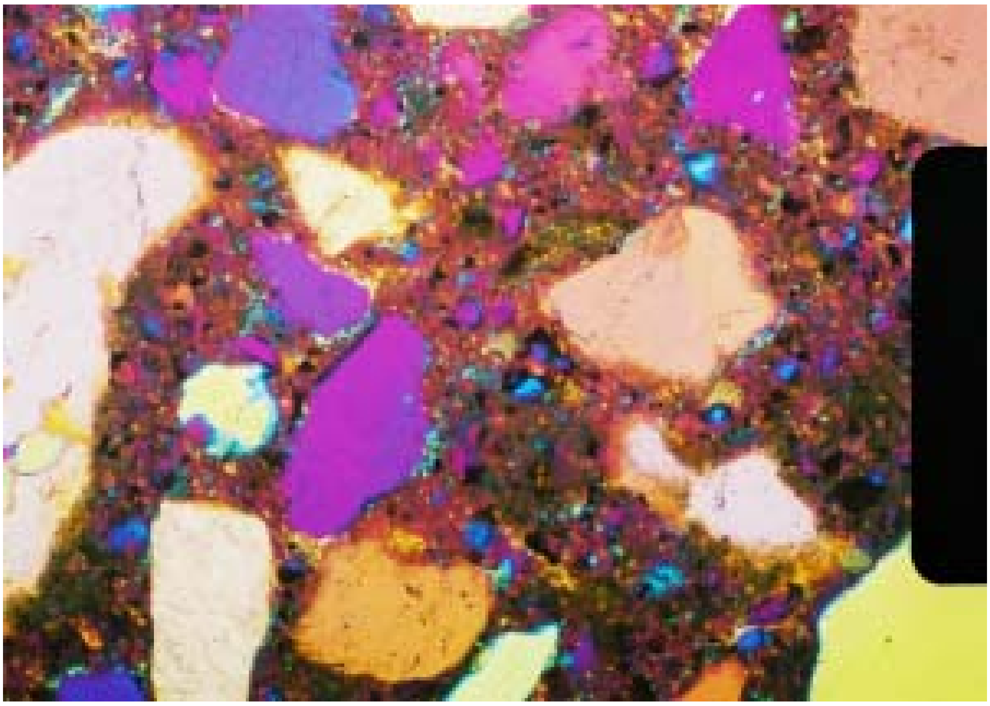
The photo is taken in polarized light and a filter of gypsum. Magnification: 100X.



The photo is taken with fluorescence light Magnification: 25X.

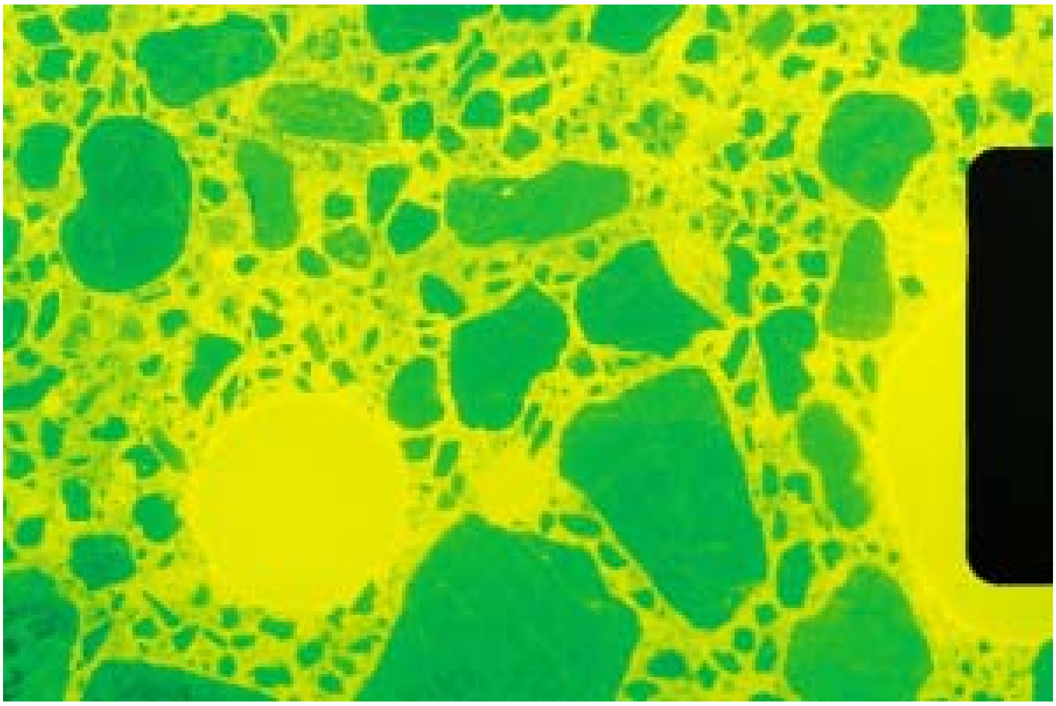


The photo is taken in polarized light and a filter of gypsum. Magnification: 100X.

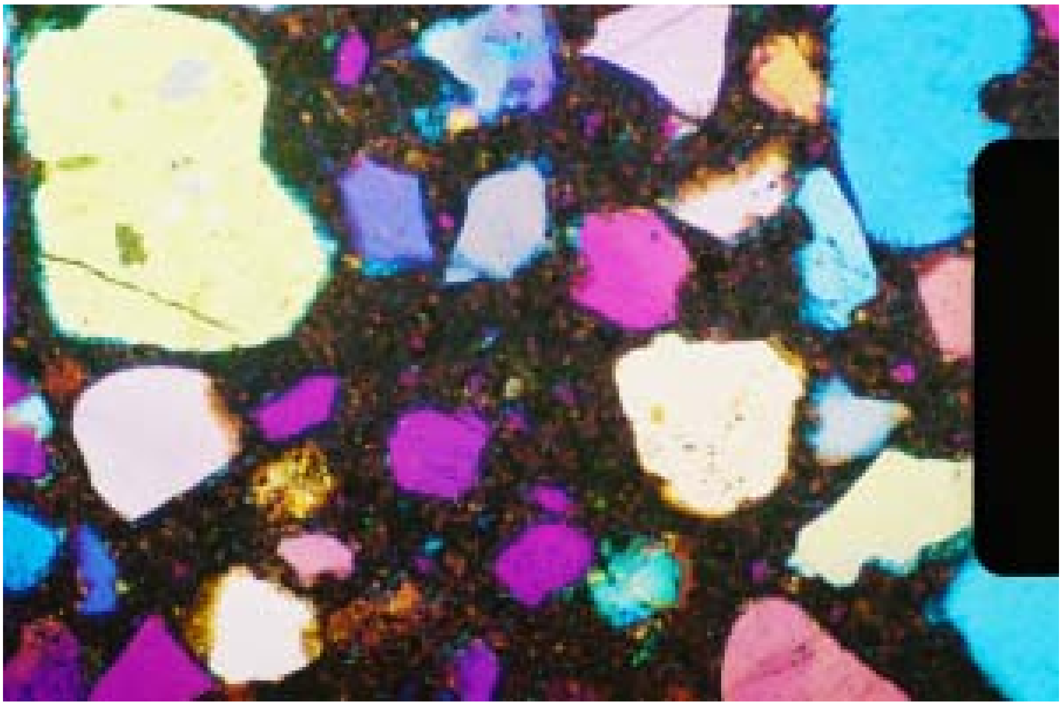


Sample No.5 **Encl.6**

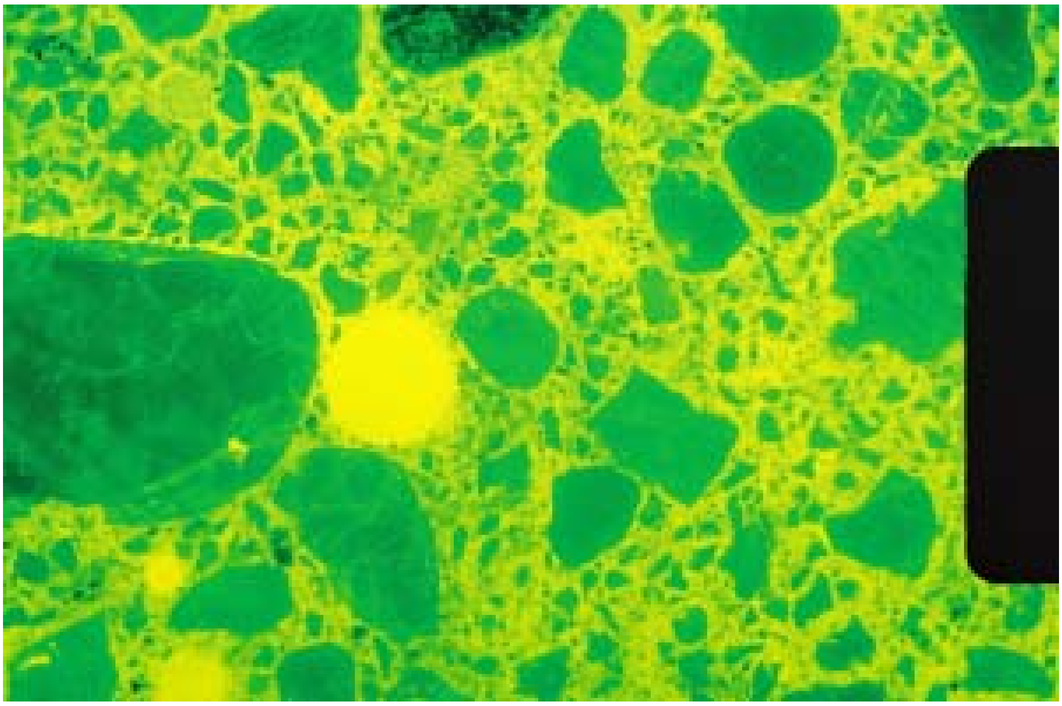
The photo is taken with fluorescence light Magnification: 25X.



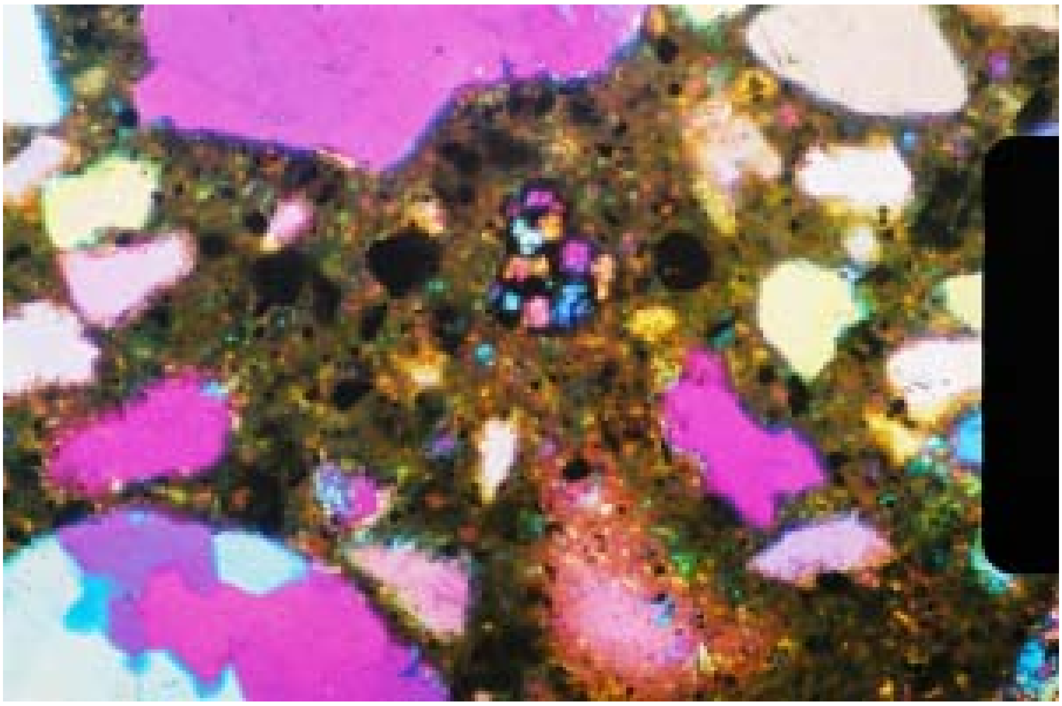
The photo is taken in polarized light and a filter of gypsum. Magnification: 100X.



The photo is taken with fluorescence light   Magnification: 25X.

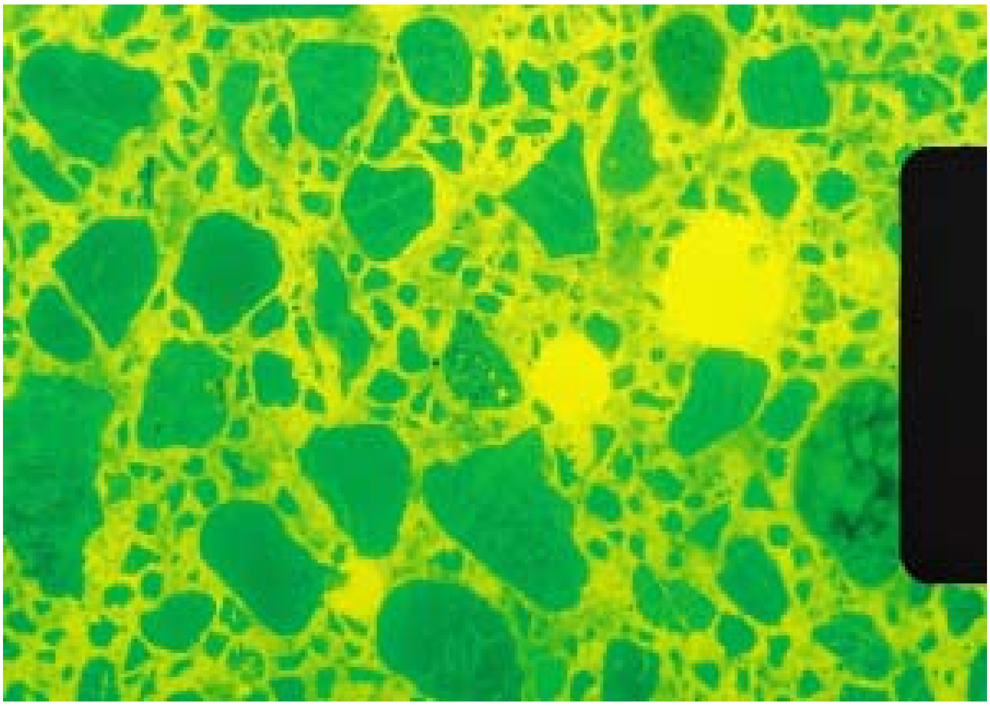


The photo is taken in polarized light and a filter of gypsum. Magnification: 100X.

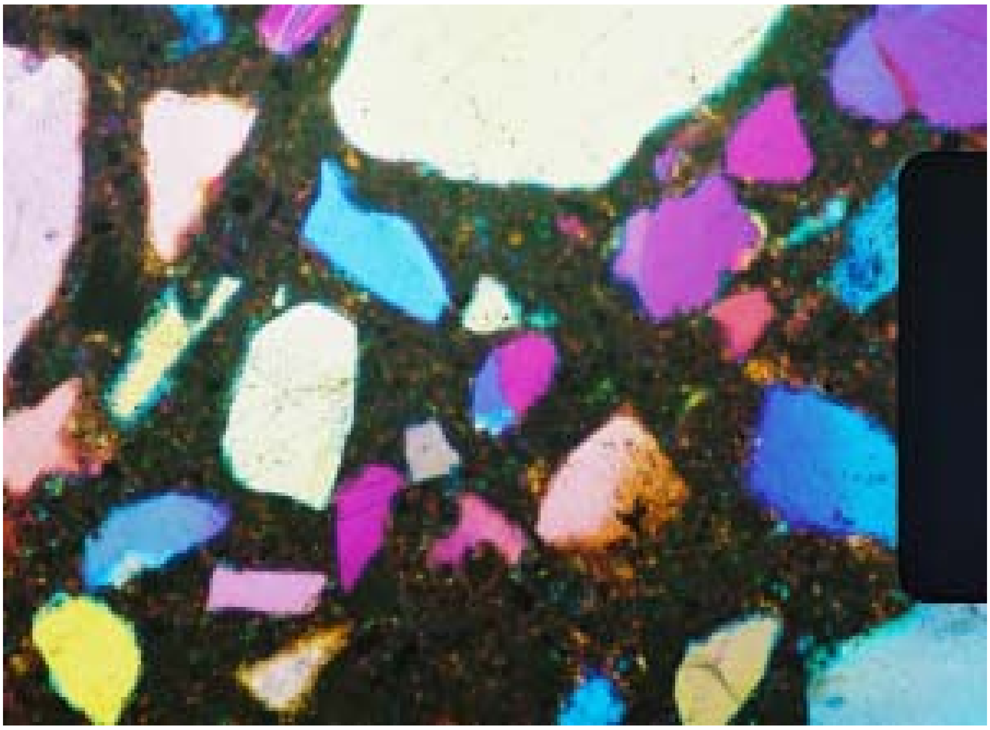


Sample No.7 **Encl.8**

The photo is taken with fluorescence light   Magnification: 25X.

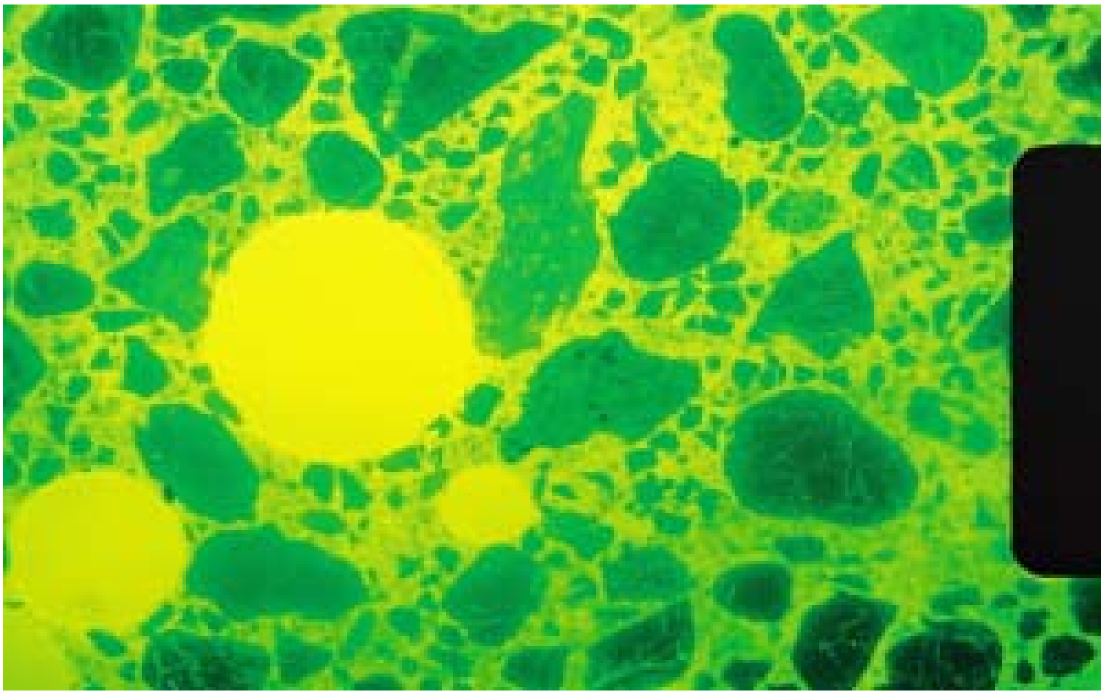


The photo is taken in polarized light and a filter of gypsum. Magnification: 100X.



Sample No.8 **Encl.9**

The photo is taken with fluorescence light   Magnification: 25X.



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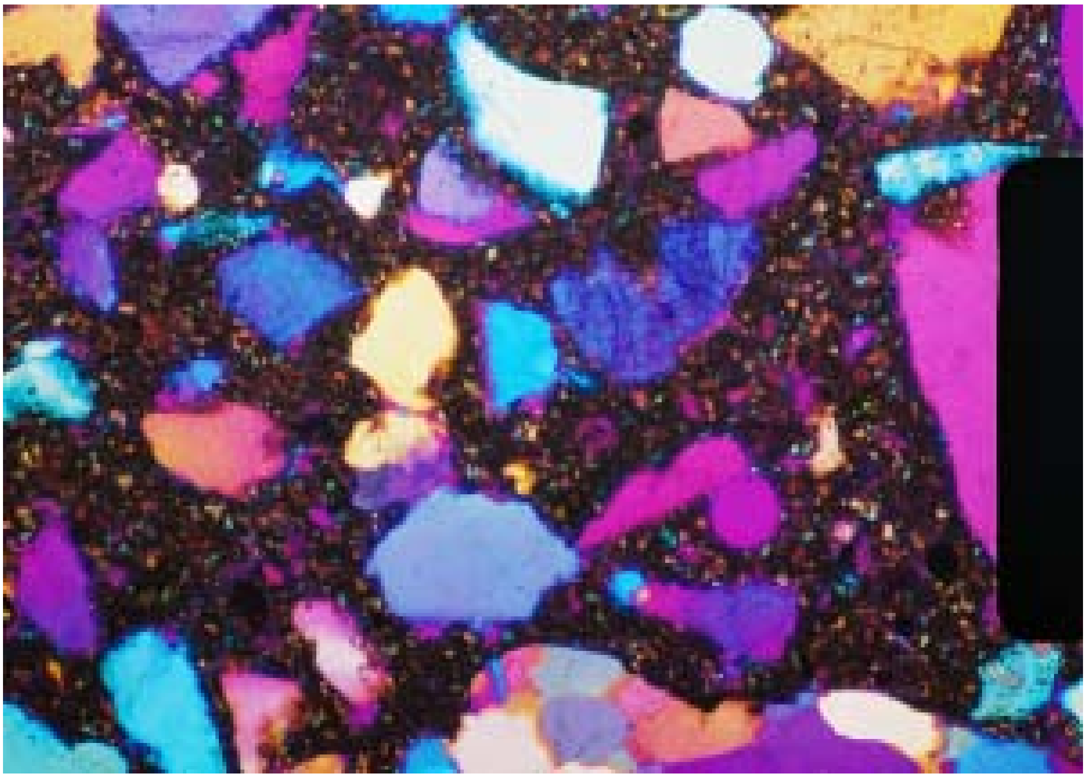

Sample No.9 **Encl.10**

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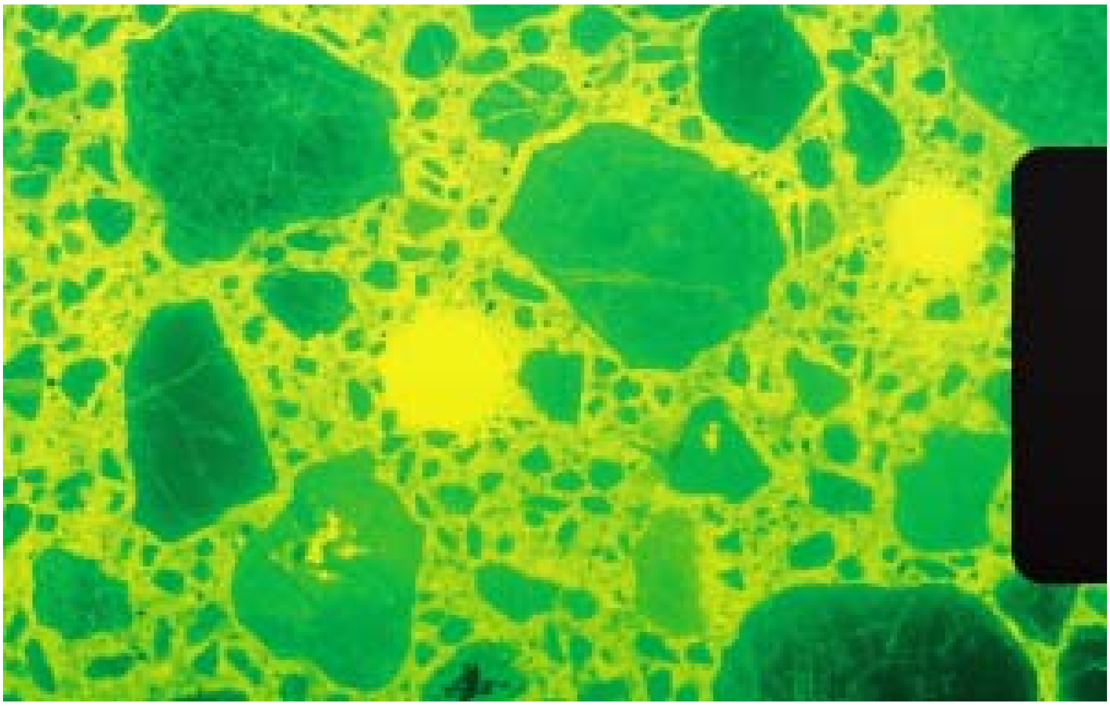
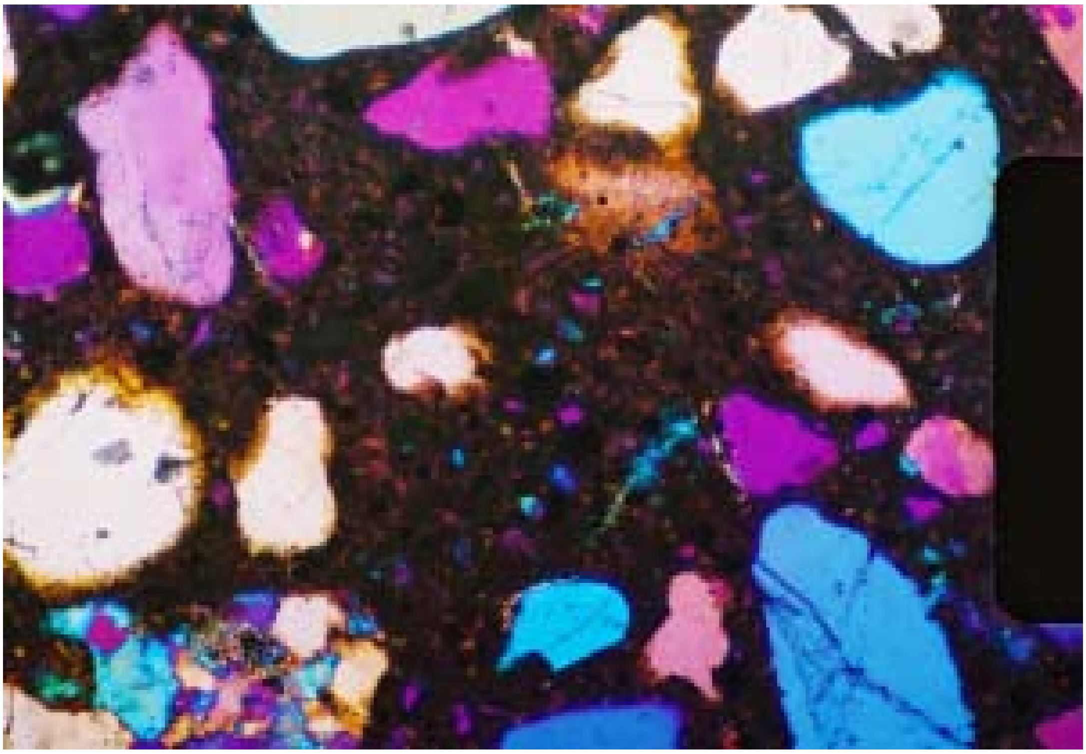
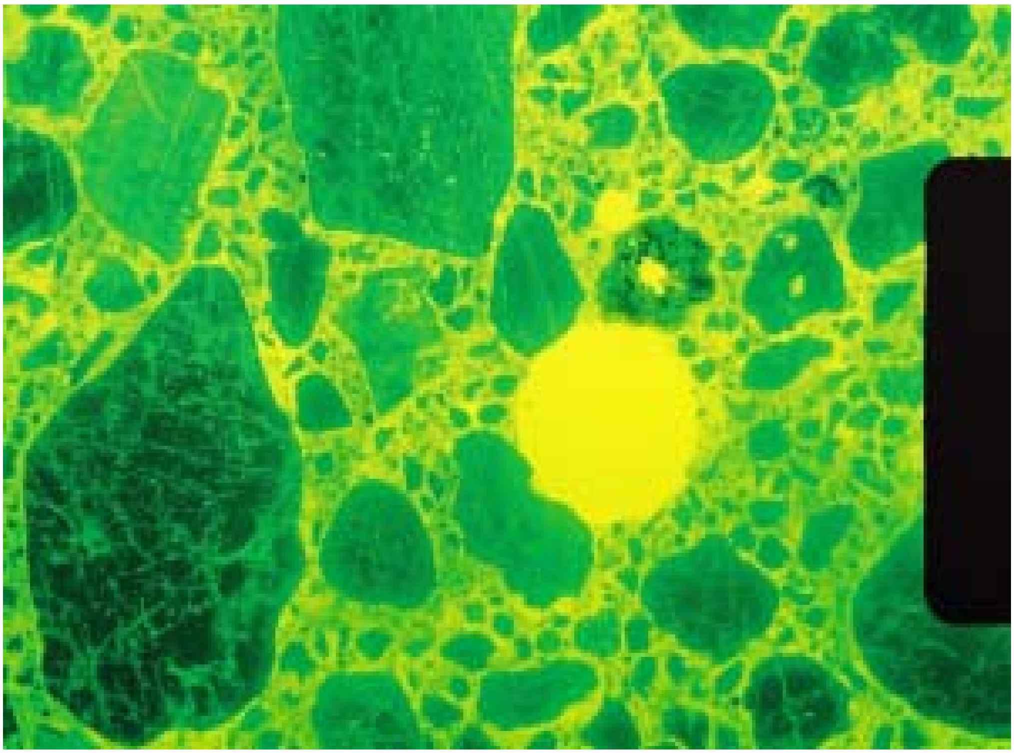


The photo is taken in polarized light and a filter of gypsum. Magnification: 100X.



Sample No.10 **Encl.11**

The photo is taken with fluorescence light   Magnification: 25X.



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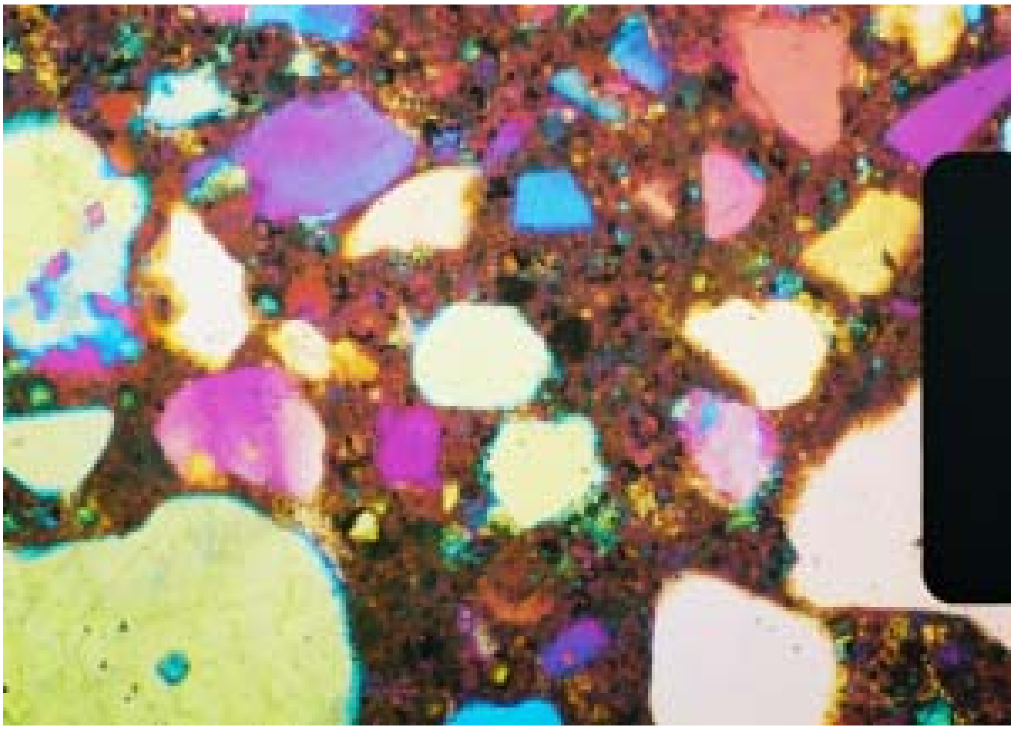


APPENDIX G. CHARACTERISATION LEACHING TESTS

World wide many leaching tests are used (Environment Canada, 1990). Several of these methods have been used in the studies listed in the previous sections. Many of the different leaching tests largely address the same aspects of leaching under slightly different conditions. In recent years, attempts have been made to harmonise leaching tests (van der Sloot et al, 1997). Recently a framework has been developed (Kosson et al, 2002), which combines different test results in an encompassing evaluation that allows conclusions on a range of aspects relevant to long term environmental impact of alternative materials. A few of the most promising tests in this context are described below.

pH dependence leaching test

Based on a comparison of methods and test data the pH dependence test (PrEN 14429, 2003; pH stat, 2004) has been identified before as a method that allows mutual comparison of several different test methods (van der Sloot et al., 1997). Here the properties of the method to quantify the acid neutralisation capacity and to use the data for geo-chemical speciation modelling are most relevant. Fresh concrete is known to exhibit changing chemical properties over time, of which the most important is pH, due to the uptake of CO_2 from the atmosphere. In turn, pH strongly affects leaching properties. The element specific leaching curve (metals, oxy-anions, major and minor elements) obtained with the pH dependence test can be seen as a material characteristic, a “geo-chemical fingerprint” of the material under study.

Features of the pH dependence leaching test (TS14429)
- Applicable to almost any material
- In initial acid base addition mode very easy and anywhere to perform
- Identification of sensitivity of leaching to small pH changes
- Provides acid neutralization capacity information
- Provides information on release under pH conditions imposed by external influences
- Basis for comparison of international leaching tests
- Basis for geochemical speciation modelling
- Mutual comparison of widely different materials to assess similarities in leaching behaviour
- Tool for recognition of factors controlling release
- Identification of solubility limitation in a tank test or DMLT by comparing eluate data with pH dependence test data
- For non-interacting species provides possibilities to assess the sub-sampling error

Percolation test

For the percolation behaviour of (granular) materials the presentation of release and concentration as a function of the liquid to solid (L/S) ratio is the most suitable form of data presentation (van der Sloot et al , 1997), as it allows comparison with data from larger scale experiments (e.g. lysimeter) and field data (van der Sloot et al, 2003). The latter does require an estimate on the amount of liquid that has passed through the material. The release behaviour as obtained in a percolation type test can be used to derive parameters for long-term prediction. A relatively simple approach for granular materials is the CSTR (Continuously Stirred Tank Reactor, a first order decay function) model, which provides a first crude estimate of release:

$C_{L/S} = C_0 * e^{-\kappa L/S}$

In the above CSTR equation, C_0 is the initial concentration (as obtained in the lowest L/S fraction) and κ is a first-order release factor. Obviously, more mechanistic models provide more accurate predictions (Dijkstra et al, 2002; Dijkstra et al, 2003). This can be seen as a hierarchy in the use of models: sophisticated when needed and simple when sufficient discrimination can be obtained. Both column leaching tests and the more simple batch leaching tests may be classified as percolation tests.

Features of the percolation test (TS14405)
- Applicable to many materials.
- Limited or not applicable to clayey soils and sediments (due to low permeability).
- Identification of solubility control versus wash out
- Quantification of pore water concentrations relevant to field leachate from low L/S data
- Local equilibrium established quite rapidly under the specified conditions
- Basis for geochemical speciation and transport modelling
- Allows comparison with lysimeter and field data provided L/S value can be obtained from such measurements
- Prediction towards long term behaviour possible on the basis of either solubility controlled release or wash-out of non-interacting species

Tank leaching test

In this test the release is related to the surface area of the specimen to be tested. In Europe the Dutch standard tank leaching test (NEN 7345, 1996) has been widely used. The specimen is subjected to leaching in a closed tank. The leachant is renewed after regular time intervals roughly related to the square root of time and generally up to around 64 days at a specified leachant to product volume ratio (L/V). The results are expressed in 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). This method can be applied as long as the product maintains its integrity. To assess the behaviour after disintegration or demolition of monolithic forms, the information obtained in the pH dependence leaching test is very relevant, as in this situation the pH is likely to change to more neutral conditions. Dynamic leaching tests for monolithic materials are now subject of standardisation in CEN TC 292 (DMLT, 2004), both for basic characterisation and compliance purposes. The tests under development are intended to be able to describe both the situation where the components on the surface of the material are in equilibrium with the same components dissolved in the water phase and a more dynamic situation where the release of components from the monolith is controlled by diffusion.

Features of dynamic monolith leach test (in development)
- Relevant for materials with monolithic character (durable materials) or materials behaving as monolith (low permeability soil and sediments)
- Identification of solubility control versus dynamic leaching possible
- Quantification of the tortuosity of the matrix
- Identification and quantification of surface wash-off effects
- Quantification of intrinsic release parameters
- Basis for reactive/transport modelling
- Prediction towards long term behaviour possible

APPENDIX H. LEACHING OF MONOLITHIC PRODUCTS

Characterisation data for 50 cement mortars is given in figure VIII 1 - 11. Results gathered for pH dependence leaching test data and tank leaching test data are given. In the tank test results also data obtained with pH control using CO_2 are given and where relevant indicated.

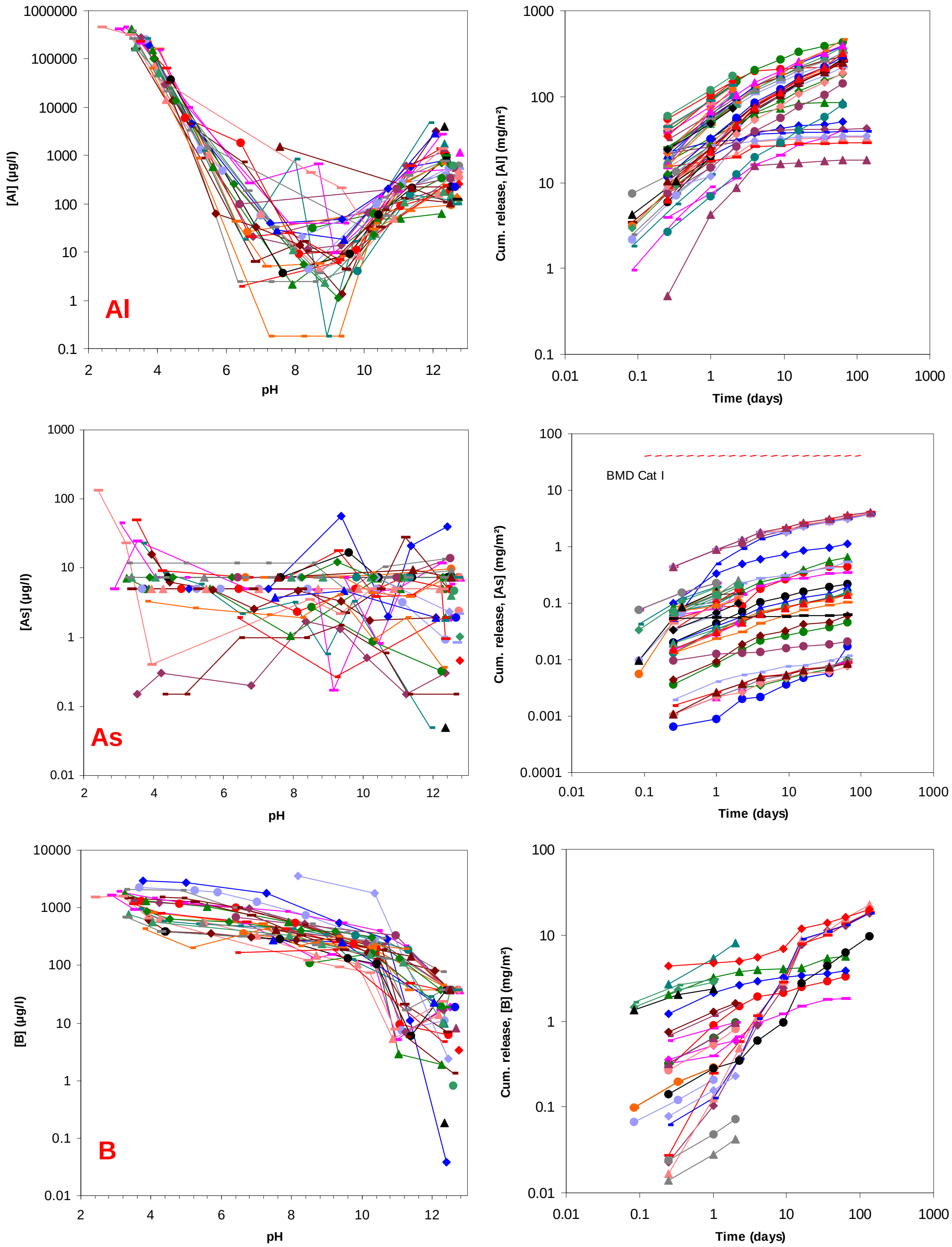


Figure VIII-1 Leaching of Al, As and B from cement mortar as a function of pH (PrEN14429; crushed mortar) and as cumulative leached amount as a function of time (NEN 7345). pH as a function of time is given in figure 18.

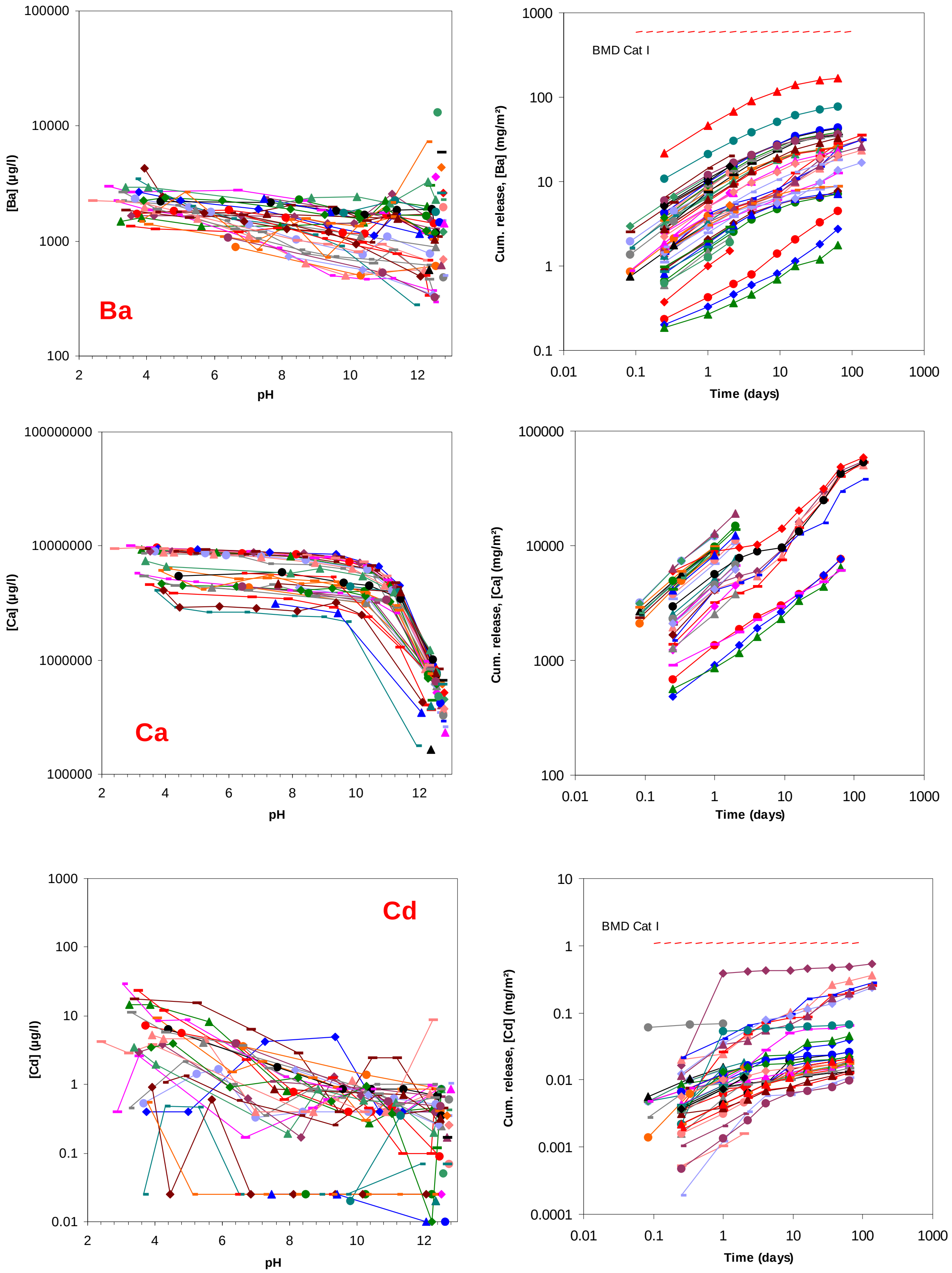


Figure VIII_2 Leaching of Ba, Ca and Cd from cement mortar as a function of pH (PrEN14429; crushed mortar) and as cumulative leached amount as a function of time (NEN 7345). pH as a function of time is given in figure 18.

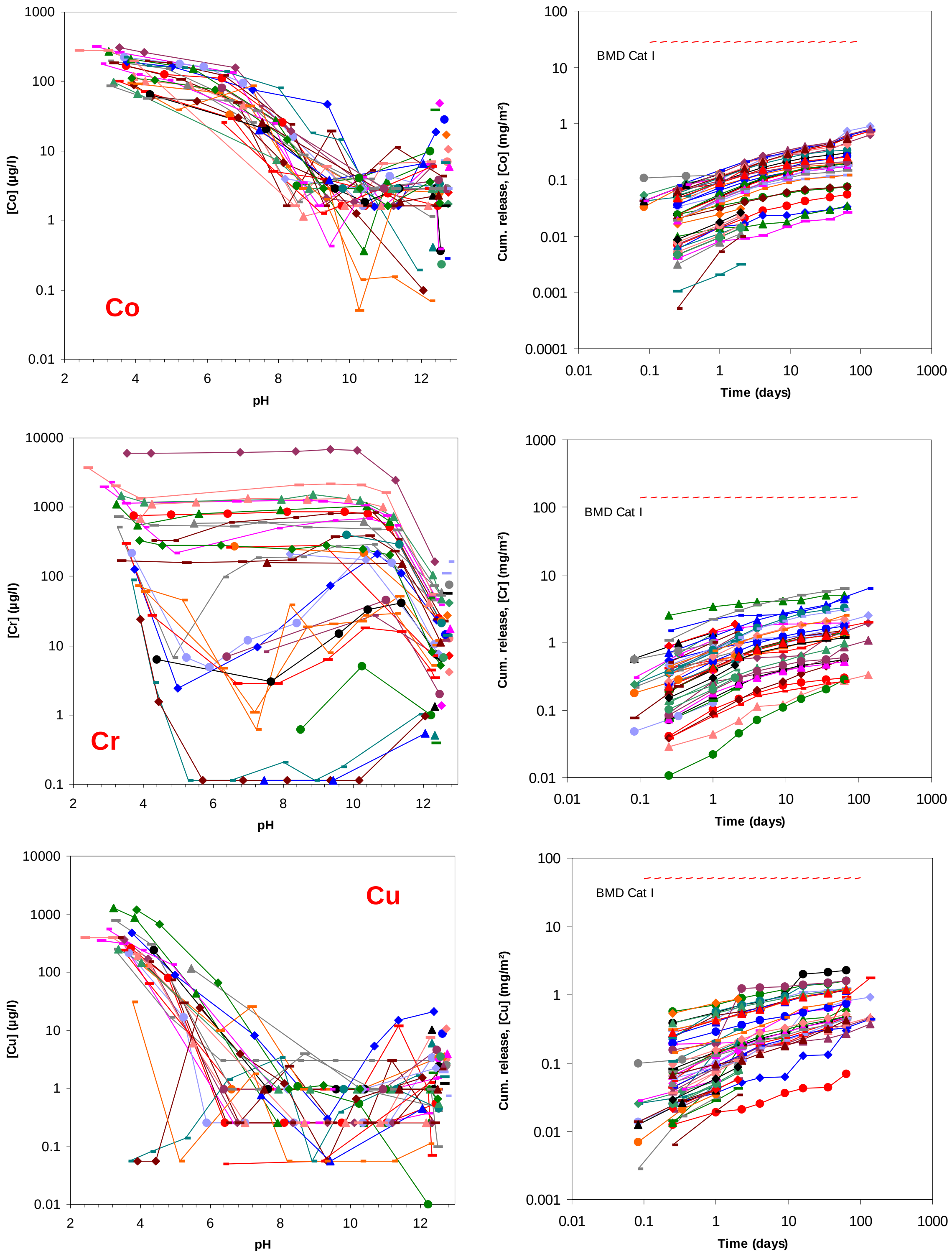


Figure VIII-3 Leaching of Co, Cr and Cu from cement mortar as a function of pH (PrEN14429; crushed mortar) and as cumulative leached amount as a function of time (NEN 7345). pH as a function of time is given in figure 18.

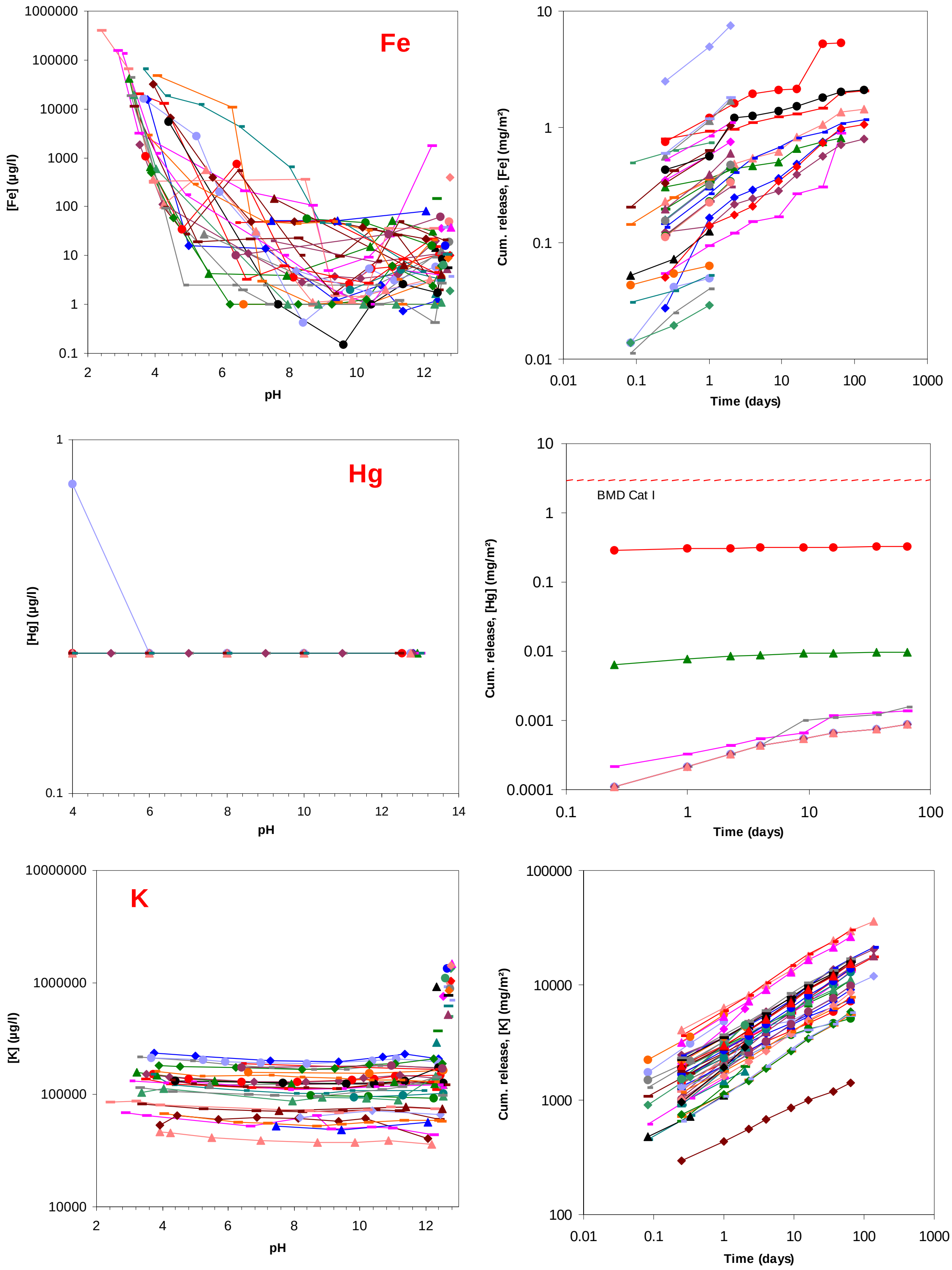


Figure VIII_4 Leaching of Fe, Hg and K from cement mortar as a function of pH (PrEN14429; crushed mortar) and as cumulative leached amount as a function of time (NEN 7345). pH as a function of time is given in figure 18.

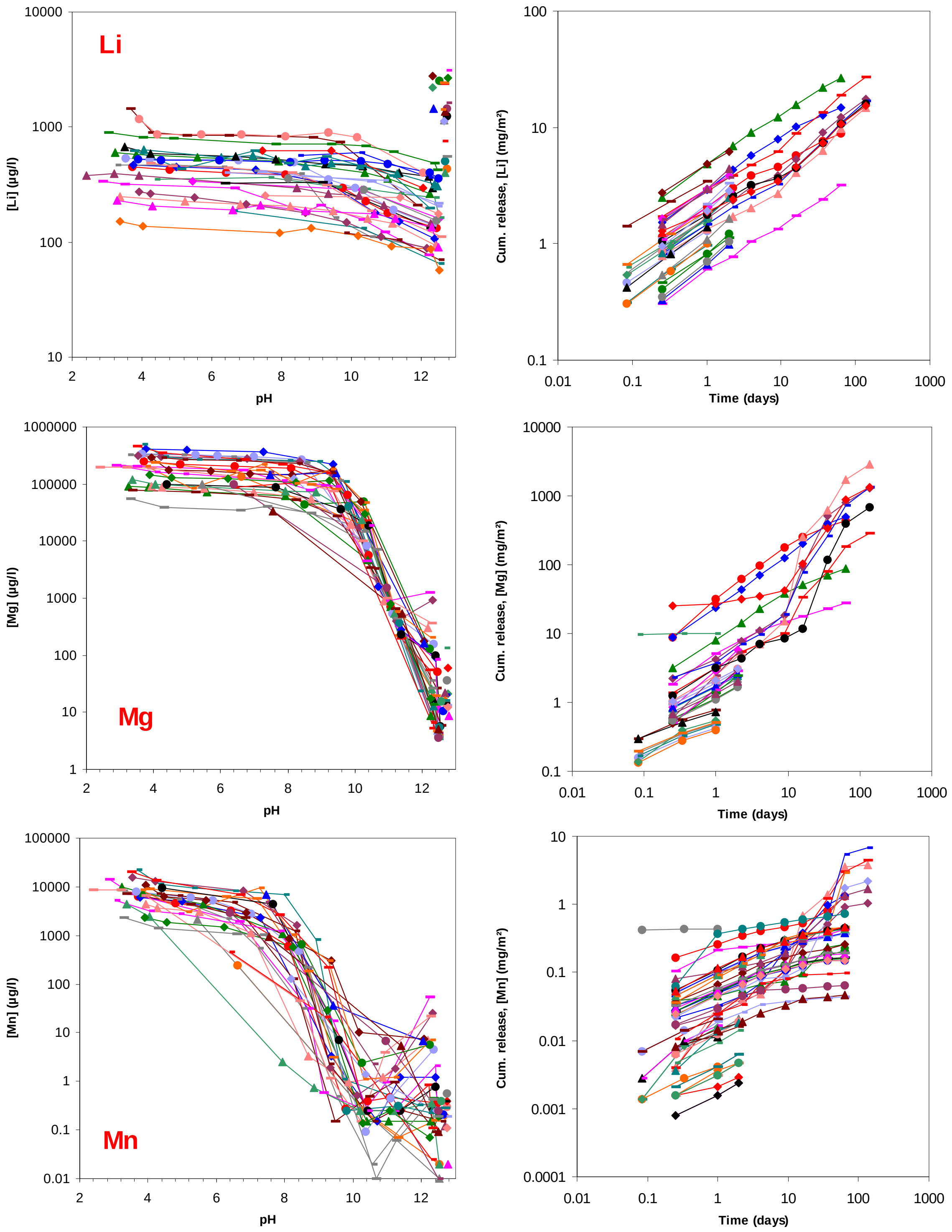


Figure VIII_5 Leaching of Li, Mg and Mn from cement mortar as a function of pH (PrEN14429; crushed mortar) and as cumulative leached amount as a function of time (NEN 7345). pH as a function of time is given in figure 18.

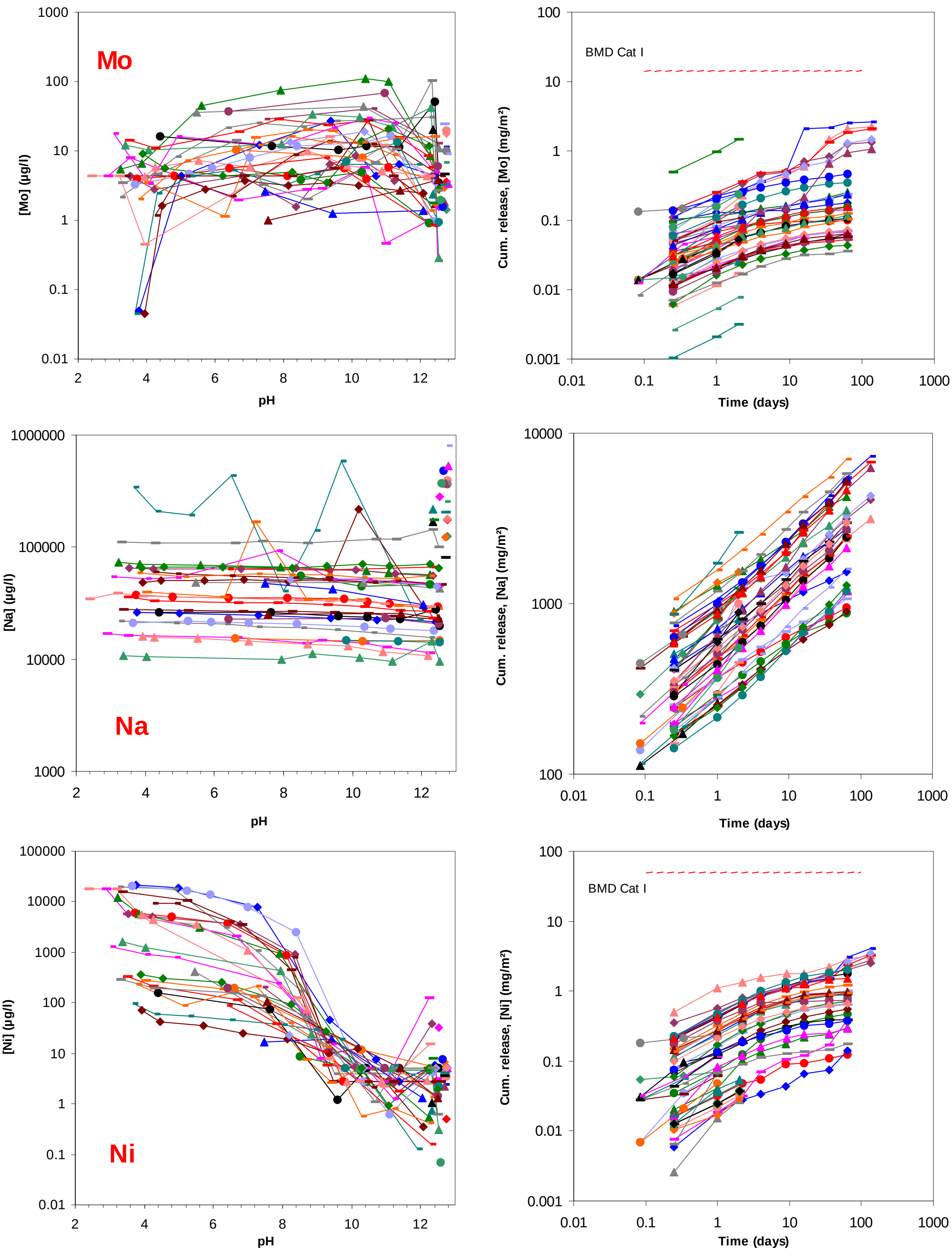


Figure VIII_6 Leaching of Mo, Na and Ni from cement mortar as a function of pH (PrEN14429; crushed mortar) and as cumulative leached amount as a function of time (NEN 7345). pH as a function of time is given in figure 18.

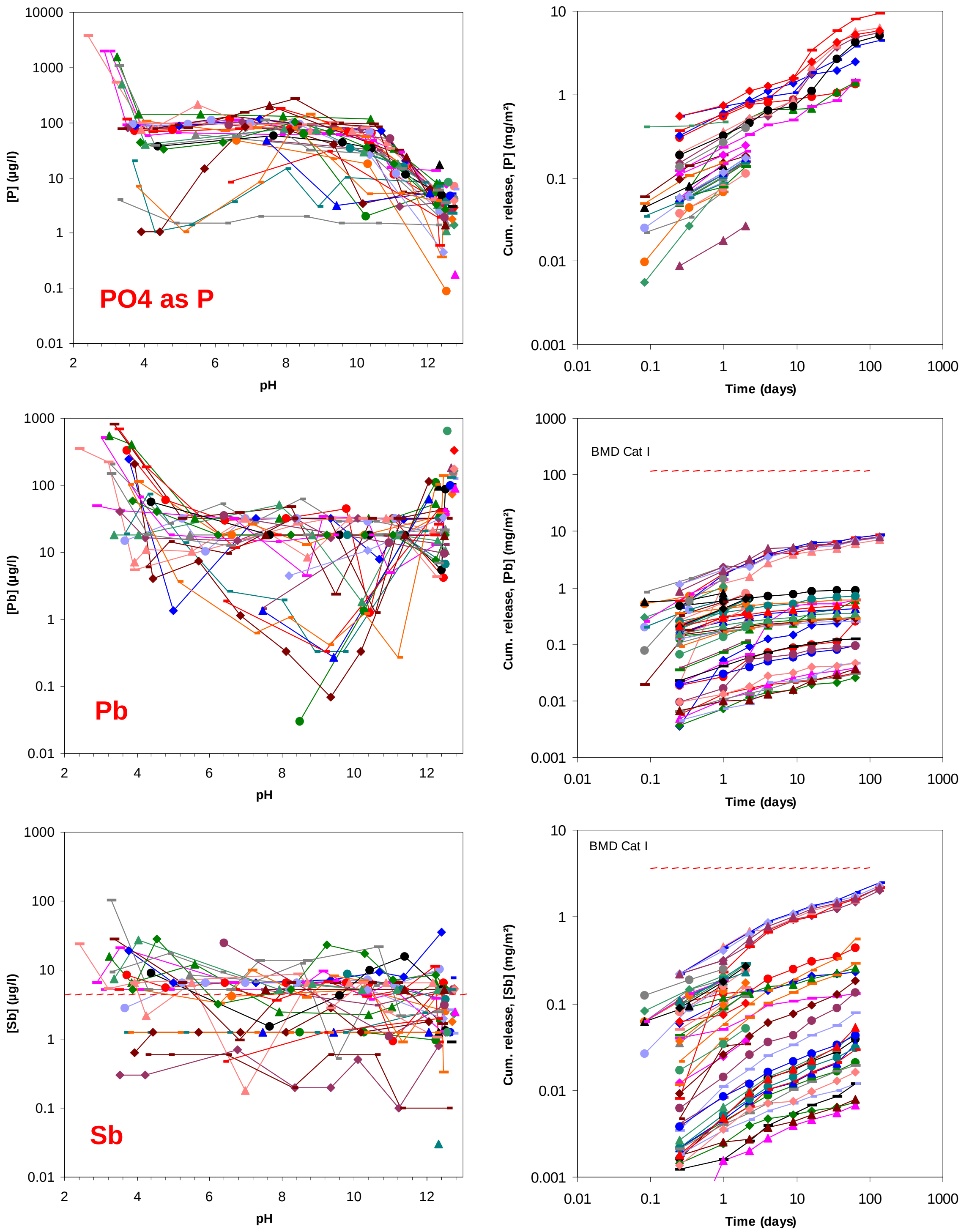


Figure VIII_7 Leaching of PO4 as P, Pb and Sb from cement mortar as a function of pH (PrEN14429; crushed mortar) and as cumulative leached amount as a function of time (NEN 7345). pH as a function of time is given in figure 18.

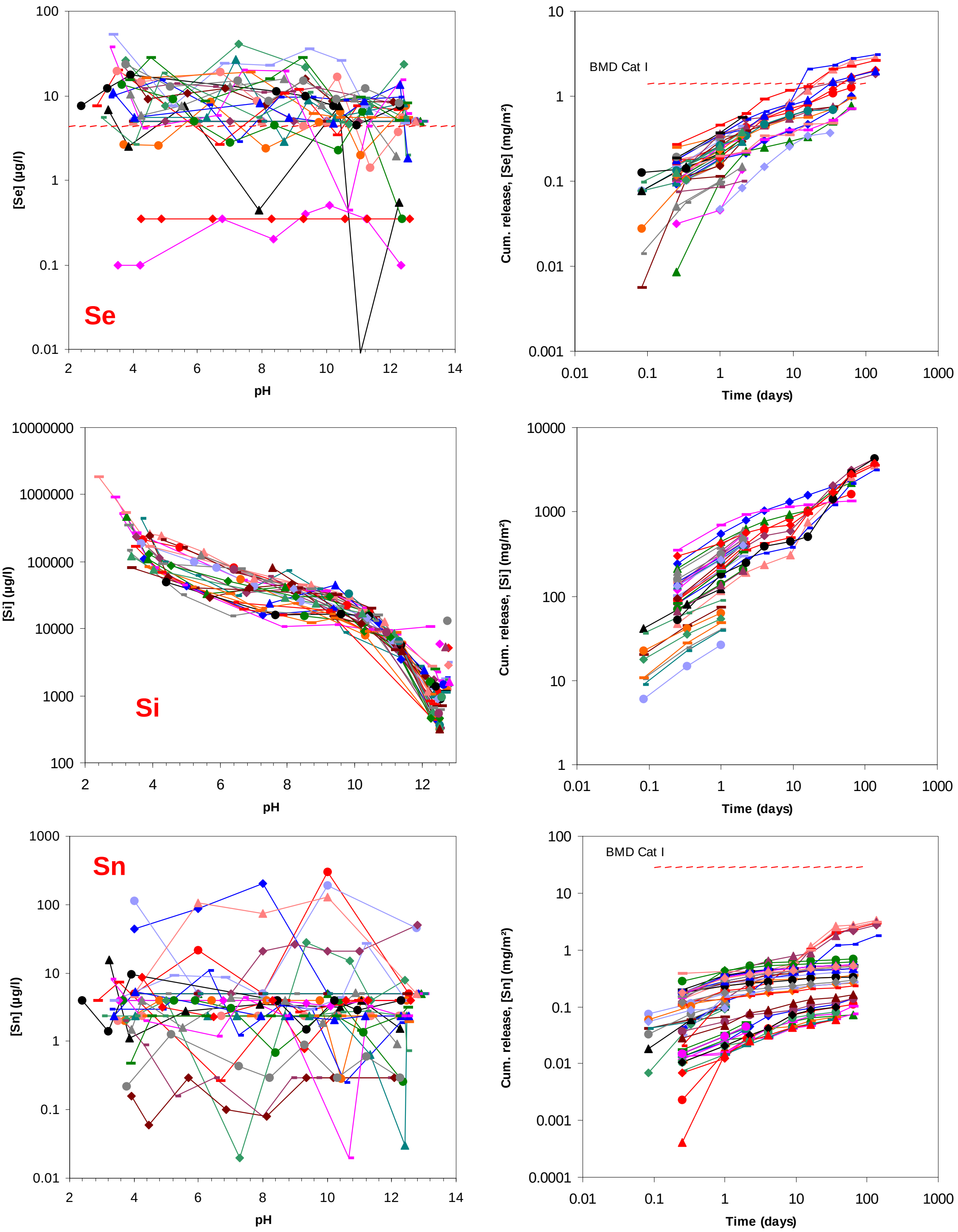


Figure VIII_8 Leaching of Se, Si and Sn from cement mortar as a function of pH (PrEN14429; crushed mortar) and as cumulative leached amount as a function of time (NEN 7345). pH as a function of time is given in figure 18.

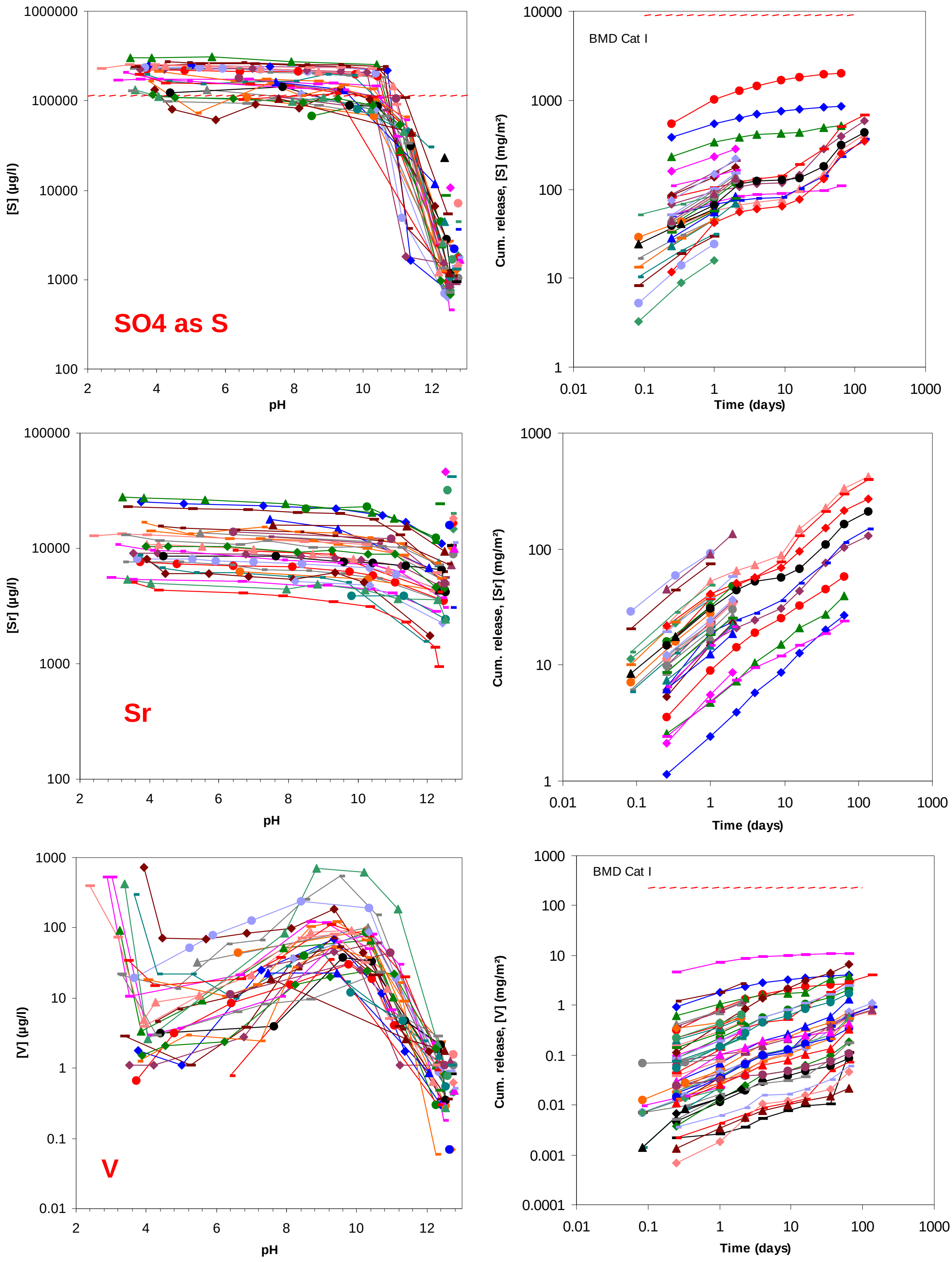


Figure VIII_9 Leaching of SO4 as S, Sr and V from cement mortar as a function of pH (PrEN14429; crushed mortar) and as cumulative leached amount as a function of time (NEN 7345). pH as a function of time is given in figure 18.

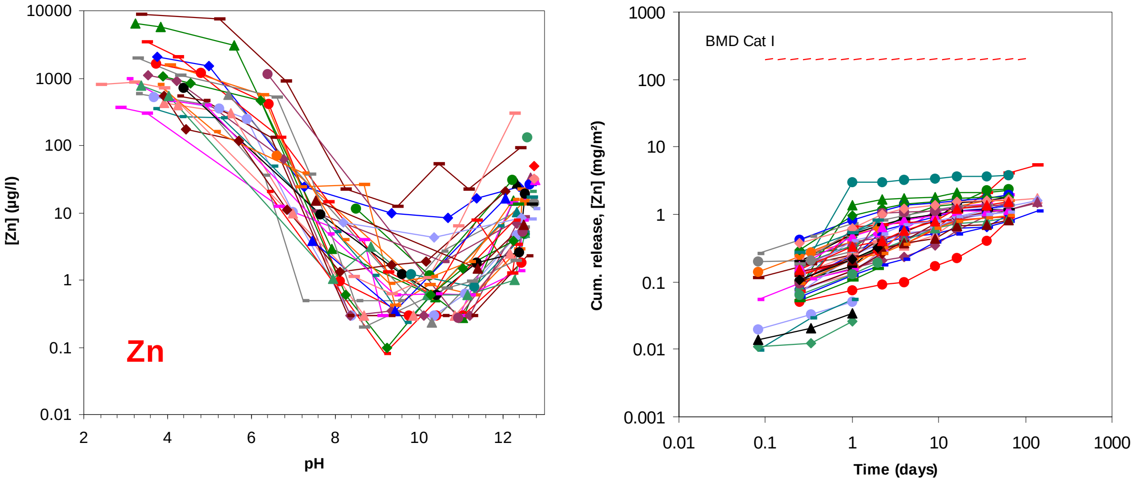


Figure VIII_10 Leaching of Zn from cement mortar as a function of pH (PrEN14429; crushed mortar) and as cumulative leached amount as a function of time (NEN 7345). pH as a function of time is given in figure 18.

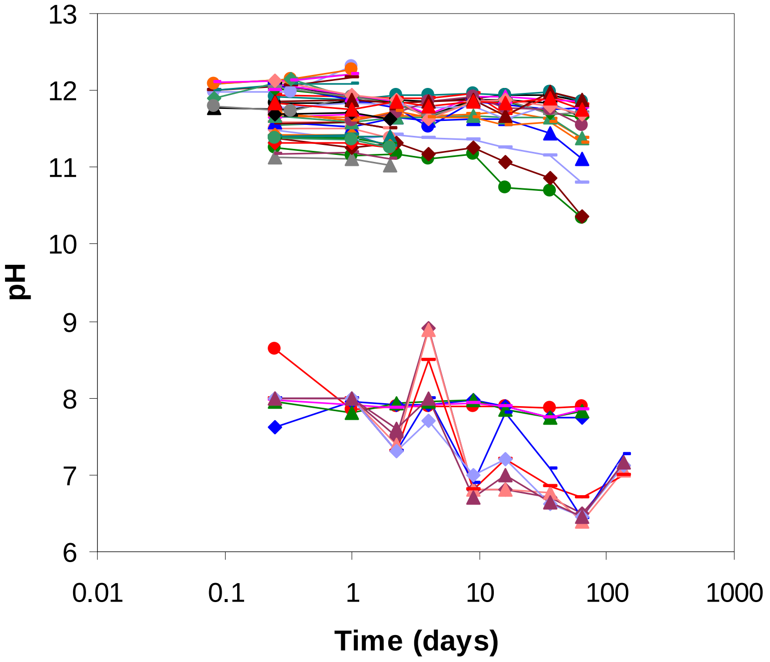


Figure VIII_11 Corresponding pH measurement in tank test data using own pH and pH control using CO_2.

APPENDIX I. REPEATABILITY OF CHARACTERISATION LEACHING TESTS

Tank leach test (NEN 7345, similar to method 1315 US EPA, CEN/TS 15683 and CEN/TC351/TS-2)

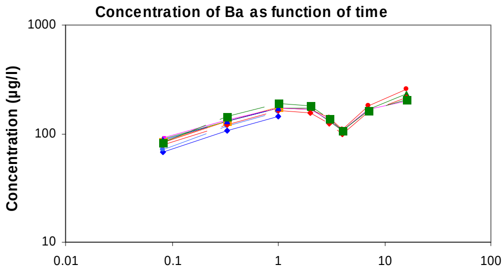
Repeatability comparison for BCR specimen (round robin study 1995)

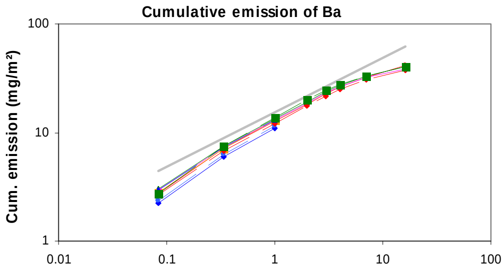
Material: cement stabilised MSWI fly ash with 15% waste loading

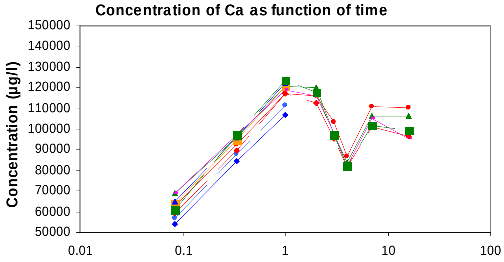
	Element	Ba	Ca	K	Mo	Pb	SO4as S	Zn#
Full characterisation test	Average	174	119599	134711	2.5	18.9	1695	20
n=5	Stdev	10	2678	2747	0.2	3.1	74	7.9
	% var	5.9	2.2	2.0	8.5	16.5	4.3	39
3-Step test	Average	163	115425	136558	2.5	15.0	1708	15.7
n=4	Stdev	14	7374	1117	0.3	1.7	76	4.5
	% var	8.5	6.4	0.8	11.8	11.2	4.5	28

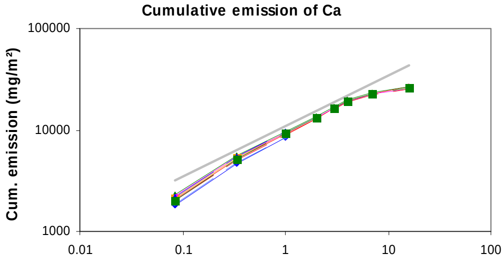
Zn data are close to the detection limit, which leads to higher variability between samples

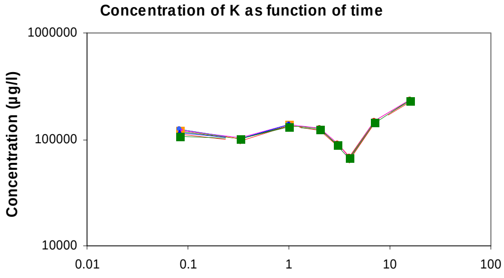
Conclusion: discrepancies between test results not related to test but to material heterogeneity between test samples

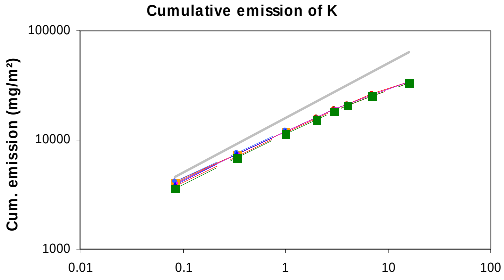


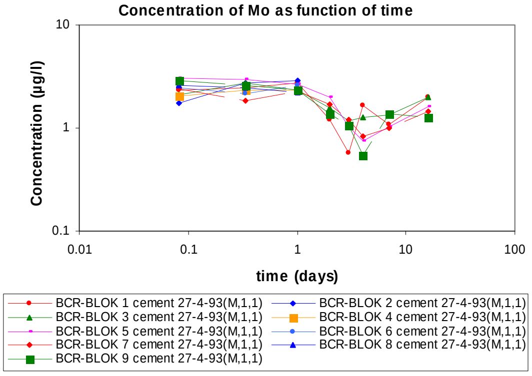


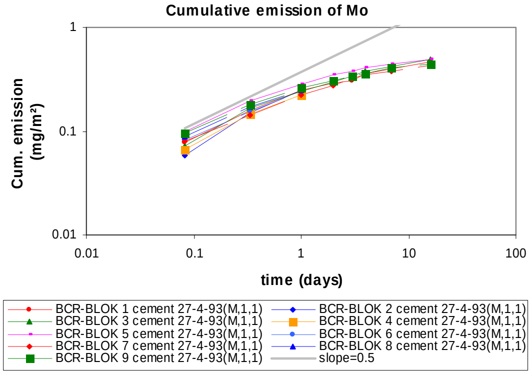






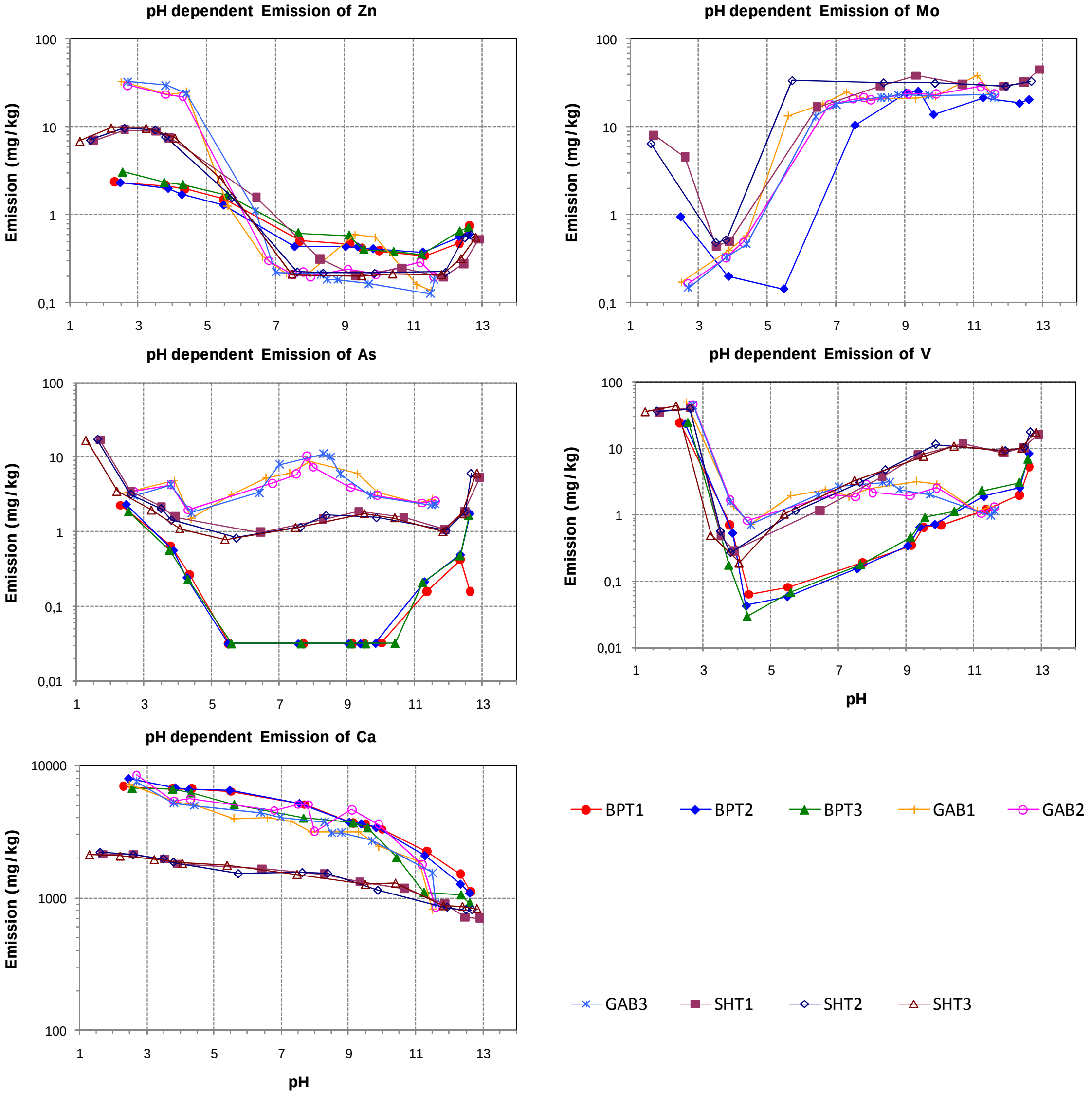






pH dependence leaching test (Method 1313 US EPA similar to CEN/TS14429)

Results below reflect repeatability data for ph dependence leaching tests carried out in triplicate on three different coal fly ash samples, illustrating good repeatability for this method and a clear distinction between ashes with different leaching caharacteristics (EPA study Kosson et al 2009).



Repeatability data for coal fly ash (all measurements in triplicate).

Percolation test NEN 7343 (similar to Method 1314 US EPA and CEN/TS14405 and CEN/TC351 TS-3)

Substances with concentrations close to the limit of detection show larger uncertainties (F, Sb and Cr). It appears there is a strong pH dependence for sulfate, since the extracts with a lower pH show significantly higher sulphate release levels. This is in agreement with observations in the pH dependence test.

Repeatability data for the percolation test according to NEN 7343.

Percolation test at L/S=10 (mg/kg) MSWI B0ttom ash

Sample	Na	K	Br	Cl	F	SO4	Cu	Ba	Cr	Mo	Sb	pH
1	1530	433		2958	2.01	687.0	3.23	0.97	0.05	0.56	0.21	10.2
2	1545	412	3.18	2660	2.01	620.4	3.12	1.01	0.07	0.50	0.11	10.3
3	1623	442	3.32	3158	1.90	837.0	3.73	1.03	0.07	0.59	0.17	10.2
4	1654	458	3.42	3073		868.5	3.78	1.04	0.04	0.60	0.24	10.2
5	1635	461	3.28	2748		916.8	3.81	1.03	0.07	0.60	0.21	10.0
6	1654	491	3.56	3079		1232.1	3.97	0.97	0.05	0.64	0.22	10.2
7	1664	502	3.89	3256		1599.9	4.43	1.14	0.06	0.66	0.15	9.9
8	1713	485	3.47	3130		1252.2	3.95	1.19	0.06	0.67	0.21	10.0
9	1734	468	3.42	3321	1.98	1129.8	4.06	1.10	0.05	0.61	0.23	10.1
10	1652	454	3.05	3144	1.36	1413.0	4.05	1.06	0.02	0.59	0.17	10.0
11	1639	469	3.22	3224	1.99	1087.2	3.84	1.04	0.05	0.61	0.29	10.1
12	1615	449	3.15	3100	1.69	1052.1	3.73	1.05	0.06	0.63	0.29	10.1
13	2168	516	3.10	3121	1.11	854.1	3.67	1.01	0.02	0.61	0.21	10.3
14	1734	469	2.47	2963	0.77	871.8	3.32	1.04	0.02	0.60	0.17	10.3
No	14	14	13	14	9	14	14	14	14	14	14	
Average	1683	465	3.27	3067	1.65	1030	3.76	1.05	0.05	0.61	0.21	
StdDev	152	28	0.33	183	0.46	276	0.35	0.06	0.02	0.04	0.05	
Var %	**9%**	**6%**	**10%**	**6%**	**28%**	**27%**	**9%**	**6%**	**36%**	**7%**	**24%**	

APPENDIX J. SPECIATION MODELLING CEMENT MORTAR (pH dependence)

The input for the chemical speciation modelling using LeachXS-Orchestra is provided in table A1. Organic matter is not considered in this case.

Table A1. Input data for chemical speciation modelling

		Input specification
Prediction case	CEM NOR 2	

Solved fraction DO	0.2	
Sum of pH and pe	15.00	
L/S	10.0000	
Clay	0.000E+00	**kg/kg**
HFO	2.000E-04	**kg/kg**
SHA	0.000E+00	**kg/kg**

DOC/DHA data	**pH**	**[DOC] (kg/l)**	**DHA fraction**	**[DHA] (kg/l)**	**Polynomial coeficients**	
	1.00				**C0**	0.000E+00
	3.37	0.000E+00	1.00	0.000E+00	**C1**	0.000E+00
	4.04	0.000E+00	1.00	0.000E+00	**C2**	0.000E+00
	7.94	0.000E+00	1.00	0.000E+00	**C3**	0.000E+00
	8.85	0.000E+00	1.00	0.000E+00	**C4**	0.000E+00
	10.21	0.000E+00	1.00	0.000E+00	**C5**	0.000E+00
	11.17	0.000E+00	1.00	0.000E+00		
	12.30	0.000E+00	1.00	0.000E+00		
	12.52	0.000E+00	1.00	0.000E+00		

Reactant concentrations

Reactant	**mg/kg**
Ag+	not measured
Al+3	1.855E+03
H3AsO4	7.626E-02
H3BO3	8.026E+00
Ba+2	3.299E+01
Br-	not measured
Ca+2	7.572E+04
Cd+2	3.638E-02
Cl-	5.000E+01
CrO4-2	1.577E+01
Cu+2	2.599E+00
F-	5.000E+01
Fe+3	2.045E+02
H2CO3	5.000E+03
Hg+2	not measured
I-	not measured
K+	1.251E+03
Li+	1.568E+00
Mg+2	1.249E+03
Mn+2	4.562E+01
MoO4-2	4.197E-01
Na+	1.250E+02
NH4+	not measured
Ni+2	1.665E+01
NO3-	5.000E+01
PO4-3	5.108E+00
Pb+2	5.194E+00
SO4-2	1.363E+03
Sb[OH]6-	9.102E-02
SeO4-2	1.347E-01
H4SiO4	1.231E+03
Sr+2	5.570E+01
Th+4	not measured
UO2+	not measured
VO2+	7.312E+00
Zn+2	8.093E+00

Selected Minerals

AA_2CaO_Al2O3_SiO2_8H2O[s]
AA_2CaO_Fe2O3_8H2O[s]
AA_2CaO_Fe2O3_SiO2_8H2O[s]
AA_3CaO_Al2O3[Ca[OH]2]0_5_[CaCO3]0_5_11_5H2O[s]
AA_3CaO_Al2O3_6H2O[s]
AA_3CaO_Al2O3_CaCO3_11H2O[s]
AA_3CaO_Al2O3_CaSO4_12H2O[s]
AA_3CaO_Fe2O3[Ca[OH]2]0_5[CaCO3]0_5_11_5H2O[s]
AA_3CaO_Fe2O3_6H2O[s]
AA_3CaO_Fe2O3_CaCO3_11H2O[s]
AA_3CaO_Fe2O3_CaSO4_12H2O[s]
AA_4CaO_Al2O3_13H2O[s]
AA_4CaO_Fe2O3_13H2O[s]
AA_Al[OH]3[am]
AA_Anhydrite
AA_Brucite
AA_Calcite
AA_CaO_Al2O3_10H2O[s]
AA_CO3-hydrotalcite
AA_Fe[OH]3[microcr]
AA_Gibbsite
AA_Gypsum
AA_Jennite
AA_Magnesite
AA_Portlandite
AA_Silica[am]
AA_Syngenite
AA_Tobermorite-I
AA_Tobermorite-II
AA_Tricarboaluminate
Cd[OH]2[A]
Cr[OH]3[C]
Fe_Vanadate
Manganite
Ni[OH]2[s]
Pb[OH]2[C]
Pb2V2O7
Pb3[VO4]2
PbCrO4
PbMoO4[c]
Rhodochrosite
Strontianite
Tenorite
Willemite

For a few elements proper thermodynamic stability data are either missing or not too well defined. Such white spots can be identified readily and subsequently be resolved. Ettringite solid-solution is incorporated for B, As, Mo, V, Cr, SO4, PO4, Sb, Ba, Sr, Se.

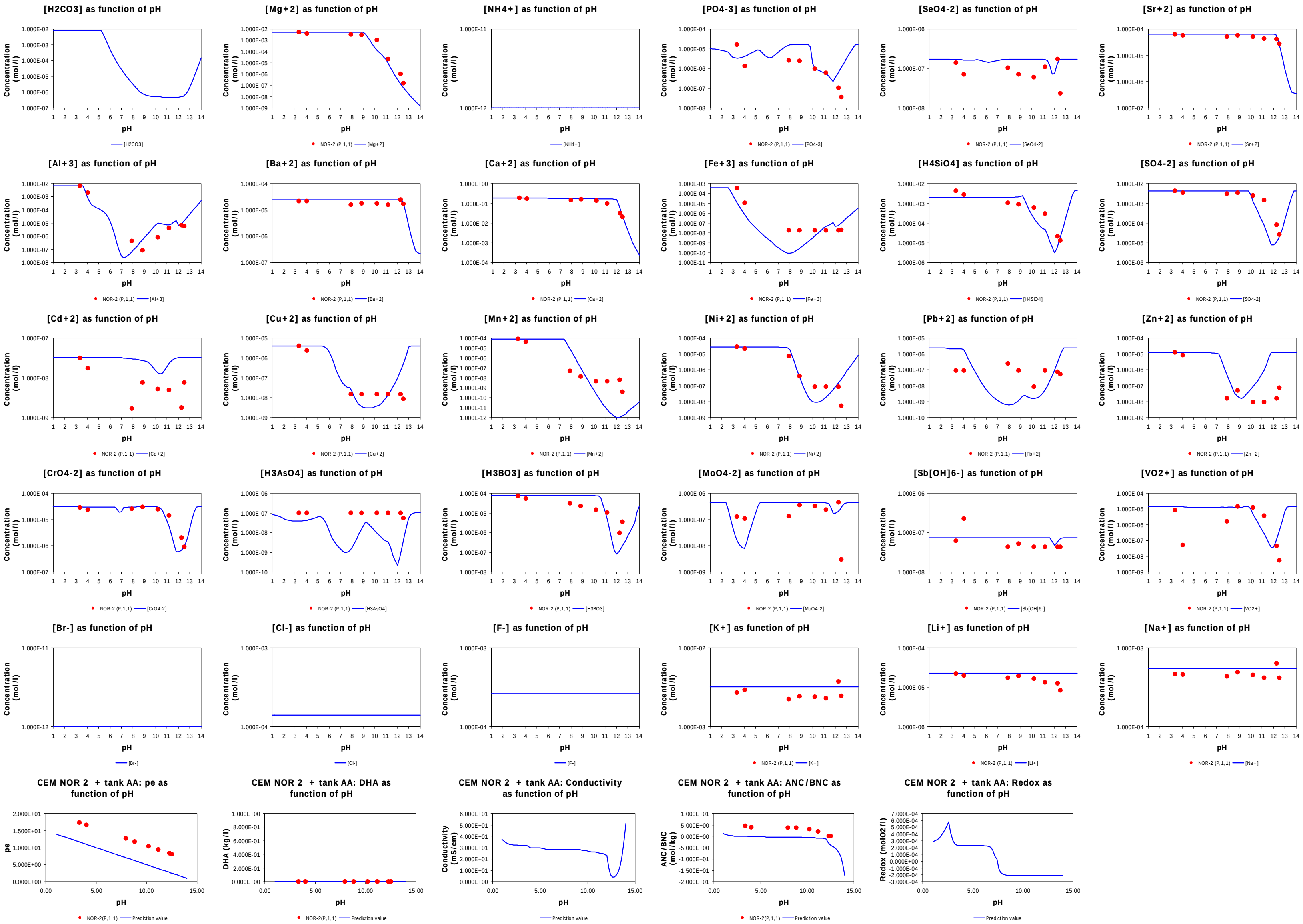


Figure X-1. Comparison of pH dependence leaching test data for cement mortar NOR 2 with full mechanistic model results based on input of table 1.

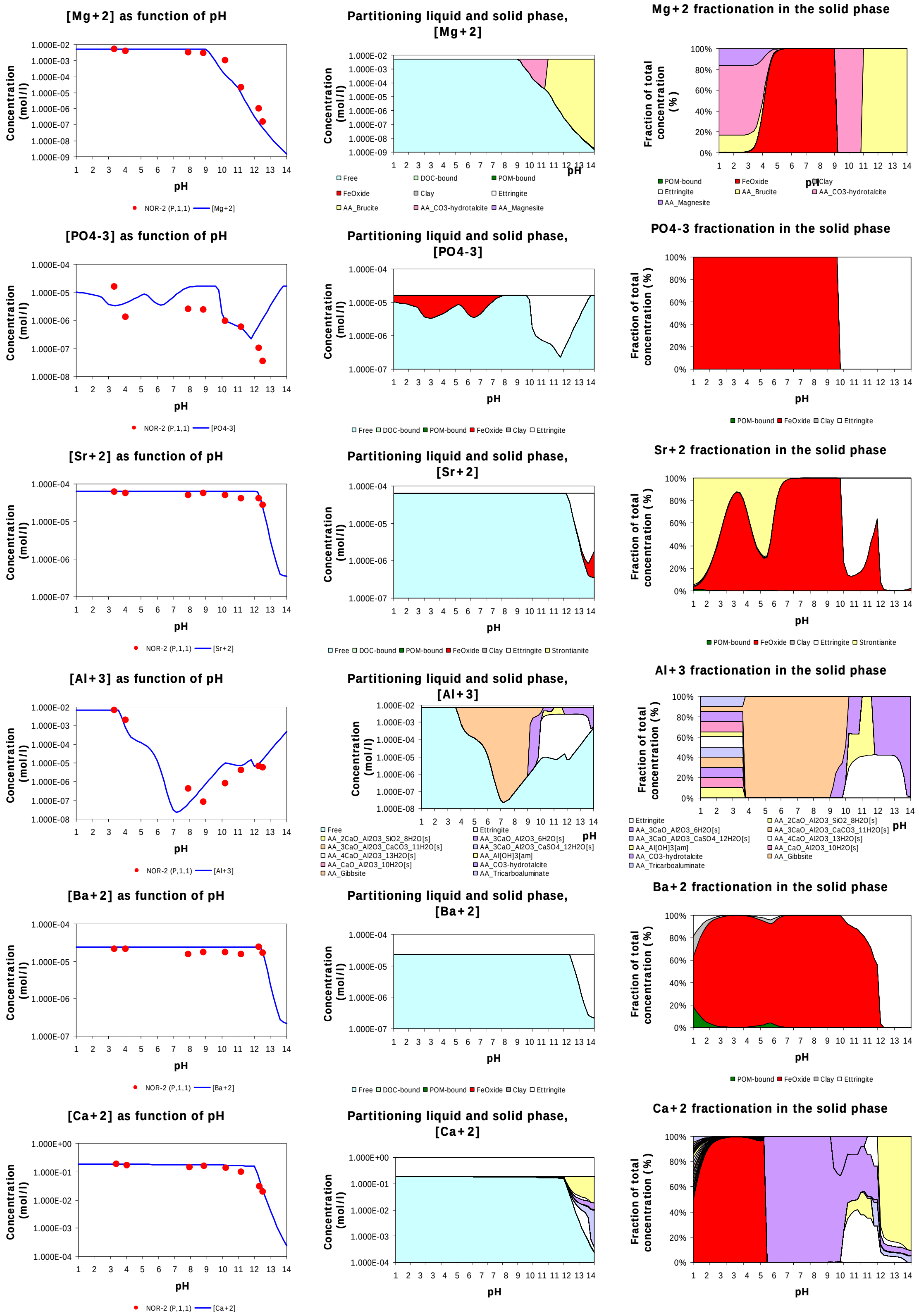


Figure III-2. Partitioning of elements in cement mortar leaching between dissolved and particulate phases. Left: pH dependence test data with model prediction. Middle: partitioning. Right: Distribution of solubility controlling phases

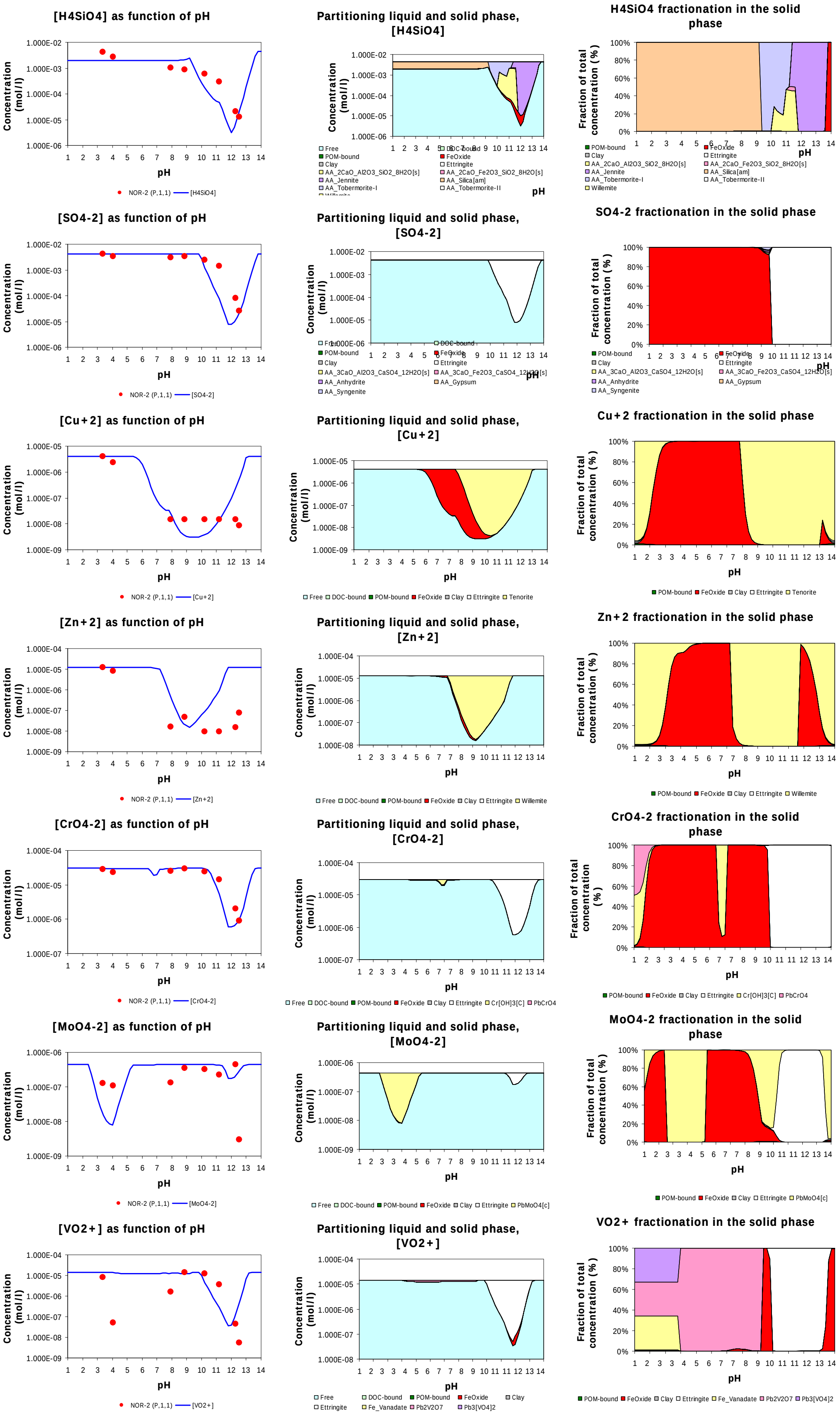


Figure III-3. Partitioning of elements in cement mortar leaching between dissolved and particulate phases. Left: pH dependence test data with model prediction. Middle: partitioning. Right: Distribution of solubility controlling phases.

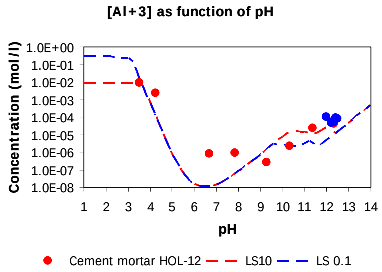
APPENDIX K. GENERIC CHEMICAL SPECIATION FINGERPRINT FOR CEMENT MORTARS.

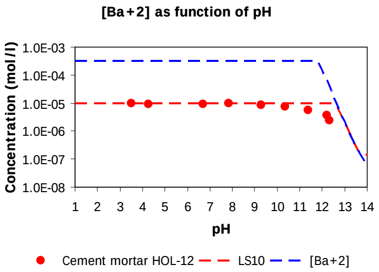
The modeling results for a range of cement mortars shown below have been generated with a single mineral assemblage as specified below. The carbonate level has been set at 5000 mg/kg for all specimen. The solid organic matter was set at 2.10-5 kg/kg and the DOC at 1.10-7 kg/l with a 20 % reactive fraction. The hydrated iron oxide quantity for sorption was set at 2.10-4 kg/kg. The element availability for interaction was taken as the maximum release observed in the pH dependence test. Those numbers vary from one cement mortar to another. The other factor that is different between the mortars is the redox state in the paste. For regular Portland cement the pE+pH is set at 17, for the mildly reducing cements it is set at 10 and for the strongly reducing blend with 80 % ground blast furnace slag (GBFS) a value of 8 is used. This condition is important to match the Fe and Cr release behaviour. A solid solution of ettringite containing besides the main components Al, Ca and SO4, the elements Ba, Sr, Mo, V, Sb, Se, B, Cr, As and P as substitutions for respectively Ca and sulfate. Leaving phases out results in a poor match for some or several substances in this multi element model run.

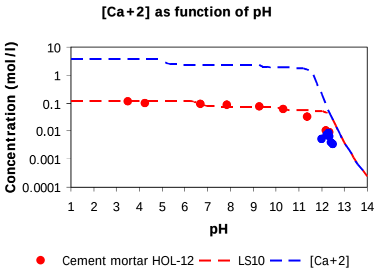
AA_2CaO_Al2O3_8H2O[s]
AA_2CaO_Al2O3_SiO2_8H2O[s]
AA_2CaO_Fe2O3_8H2O[s]
AA_2CaO_Fe2O3_SiO2_8H2O[s]
AA_3CaO_Al2O3_6H2O[s]
AA_3CaO_Al2O3_CaCO3_11H2O[s]
AA_3CaO_Al2O3_CaSO4_12H2O[s]
AA_3CaO_Fe2O3_6H2O[s]
AA_Al[OH]3[am]
AA_Anhydrite
AA_Brucite
AA_Calcite
AA_CaO_Al2O3_10H2O[s]
AA_Fe[OH]3[microcr]
AA_Gibbsite
AA_Gypsum
AA_Jennite
AA_Magnesite
AA_Portlandite
AA_Syngenite
AA_Tobermorite-I
AA_Tobermorite-II
Analbite
Ca2Cd[PO4]2
Cd[OH]2[C]
Cr[OH]3[A]
Fe_Vanadate
Magnesite
Manganite
Ni[OH]2[s]
Pb[OH]2[C]
Pb2V2O7
Pb3[VO4]2
PbCrO4
PbMoO4[c]
Rhodochrosite
Strontianite
Tenorite
Willemite

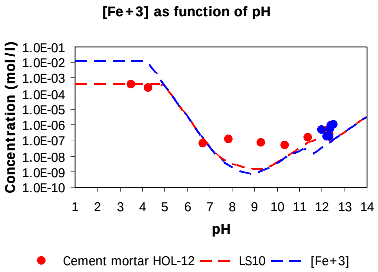
All graphs consist of the following data: red dots – pH dependence test data (CEN/TS14429); blue dots – percolation test data at low L/S reflecting pore water conditions (CEN/TS14405); red broken line – description of release by LeachXS-ORCHESTRA using the chemical speciation fingerprint as described above; blue broken line – prediction of release at low L/S (0.2) using LeachXS-ORCHESTRA using the same chemical speciation fingerprint.

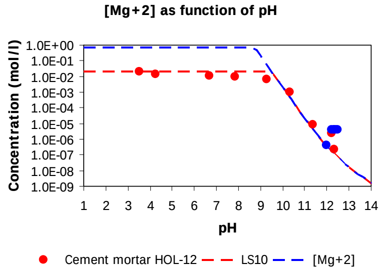
Model results for HOL 12 – blended cement mortar (32% GBFS + 20% FA)

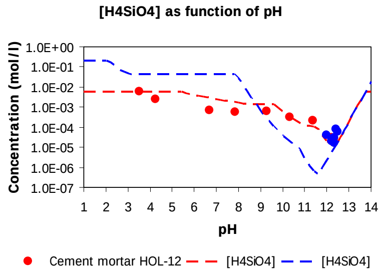


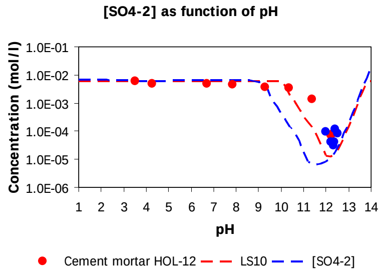


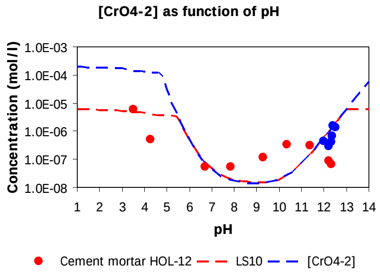




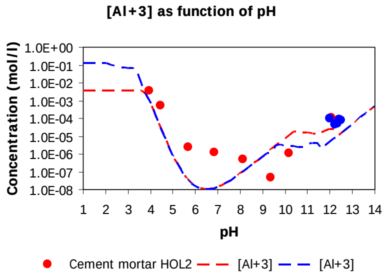


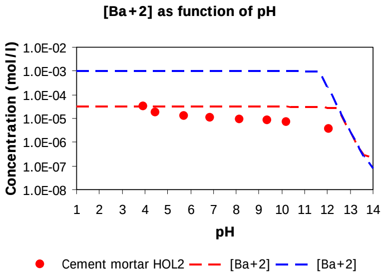


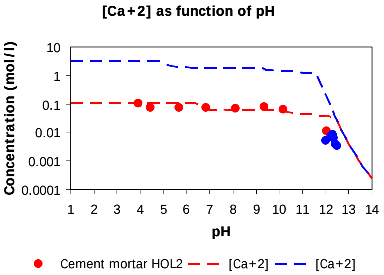


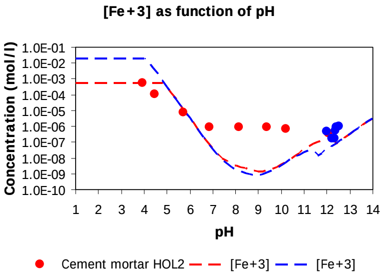


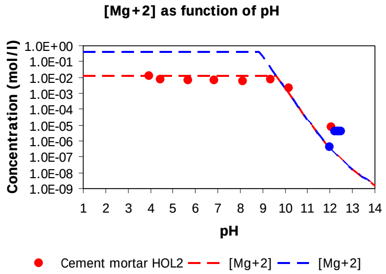
Model results for HOL 2 – blended cement mortar (66% GBFS)

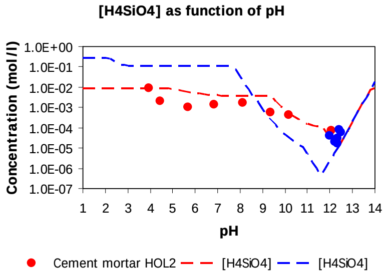


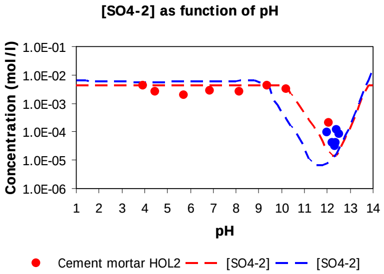


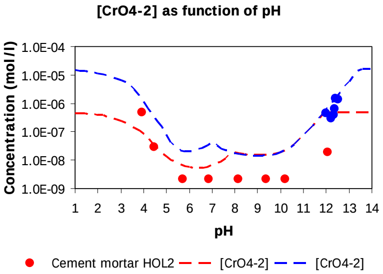






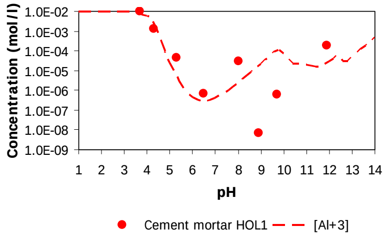




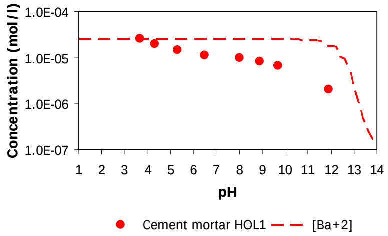


Model results for HOL 1 – blended cement mortar (80% BFS)

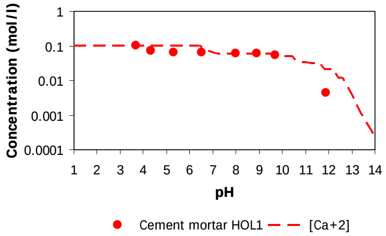
[Al+3] as function of pH



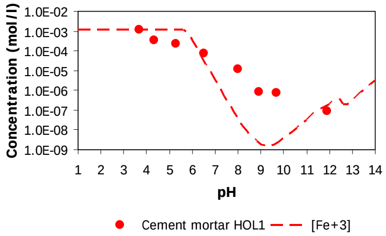
[Ba+2] as function of pH



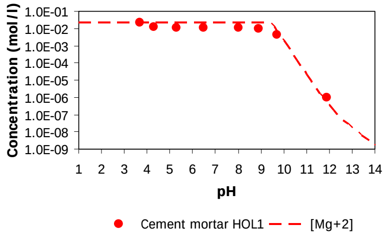
[Ca+2] as function of pH



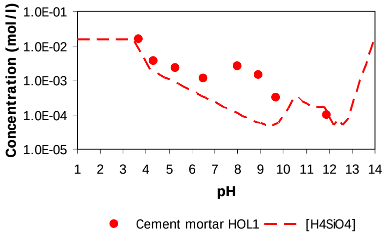
[Fe+3] as function of pH



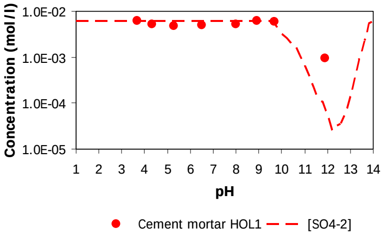
[Mg+2] as function of pH



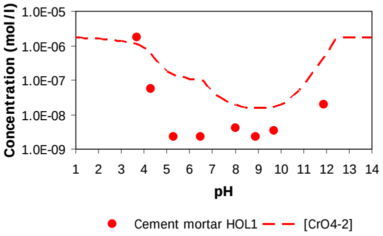
[H4SiO4] as function of pH



[SO4-2] as function of pH

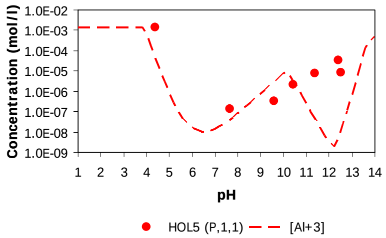


[CrO4-2] as function of pH

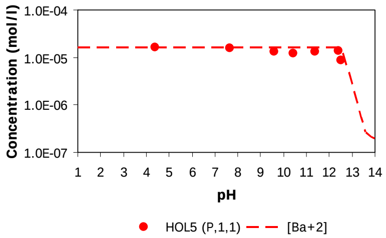


Model results for HOL 5 – blended cement mortar (20% GBFS)

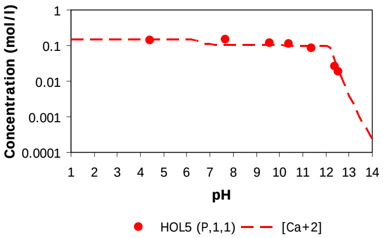
[Al+3] as function of pH



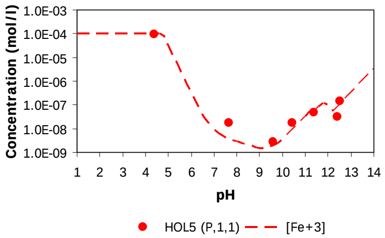
[Ba+2] as function of pH



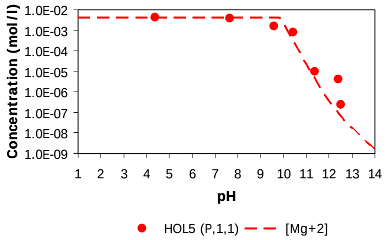
[Ca+2] as function of pH



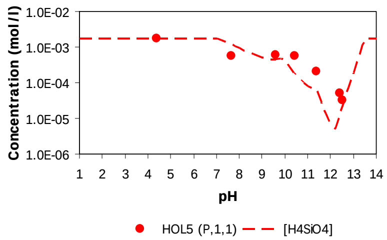
[Fe+3] as function of pH



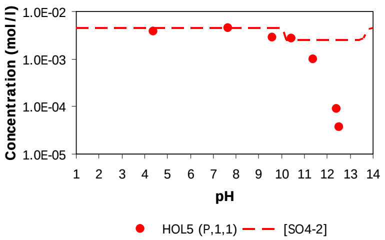
[Mg+2] as function of pH



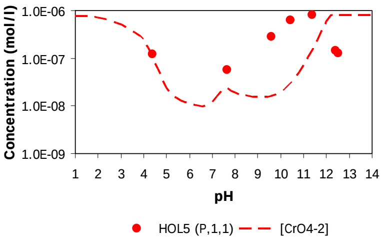
[H4SiO4] as function of pH



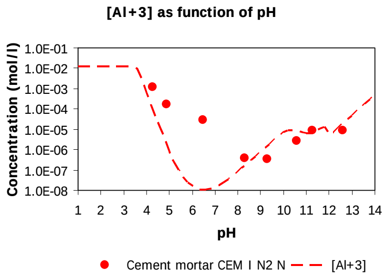
[SO4-2] as function of pH

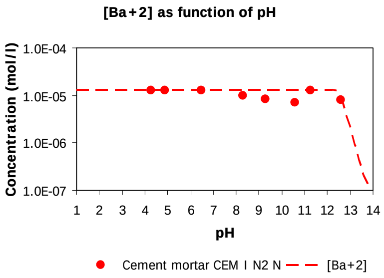


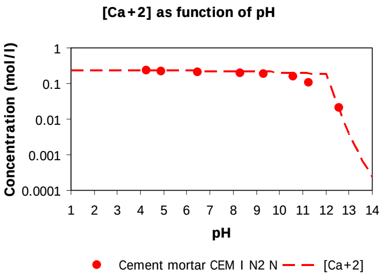
[CrO4-2] as function of pH

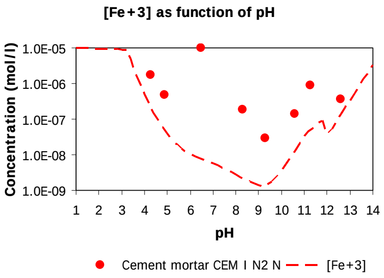


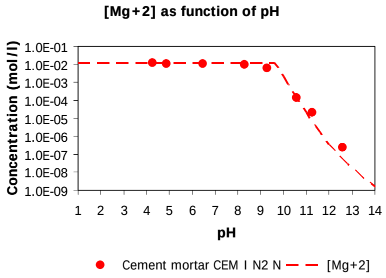
Model results for N2 – CEM I cement mortar

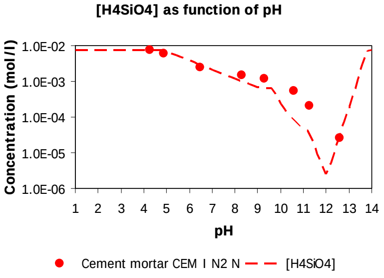


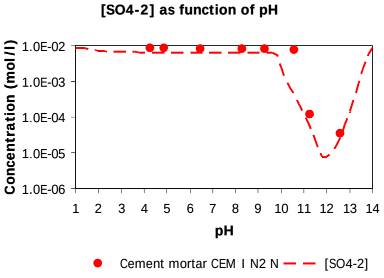


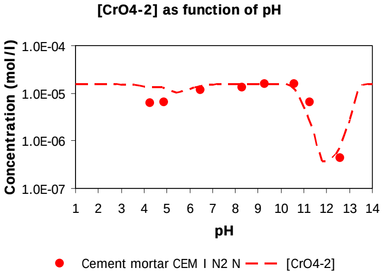




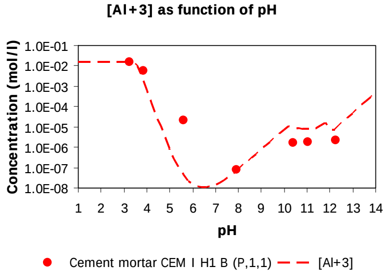


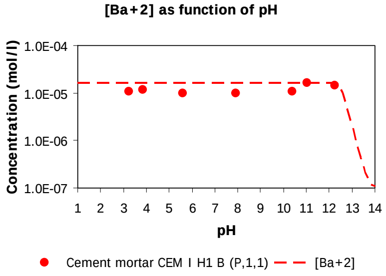


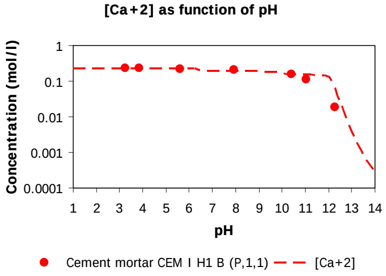


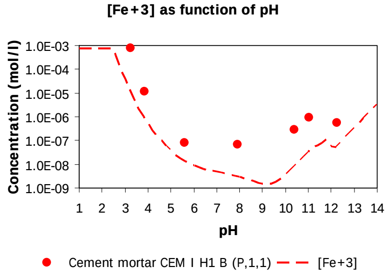


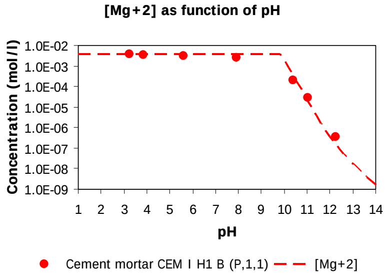
Model results for H1 – CEM I cement mortar

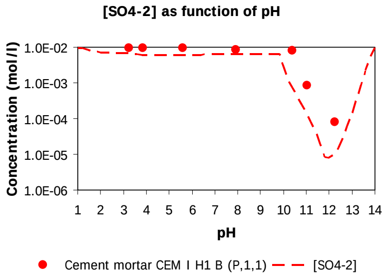


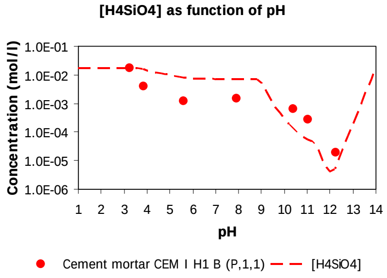


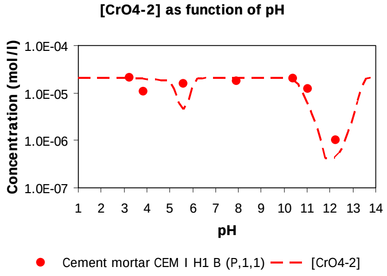




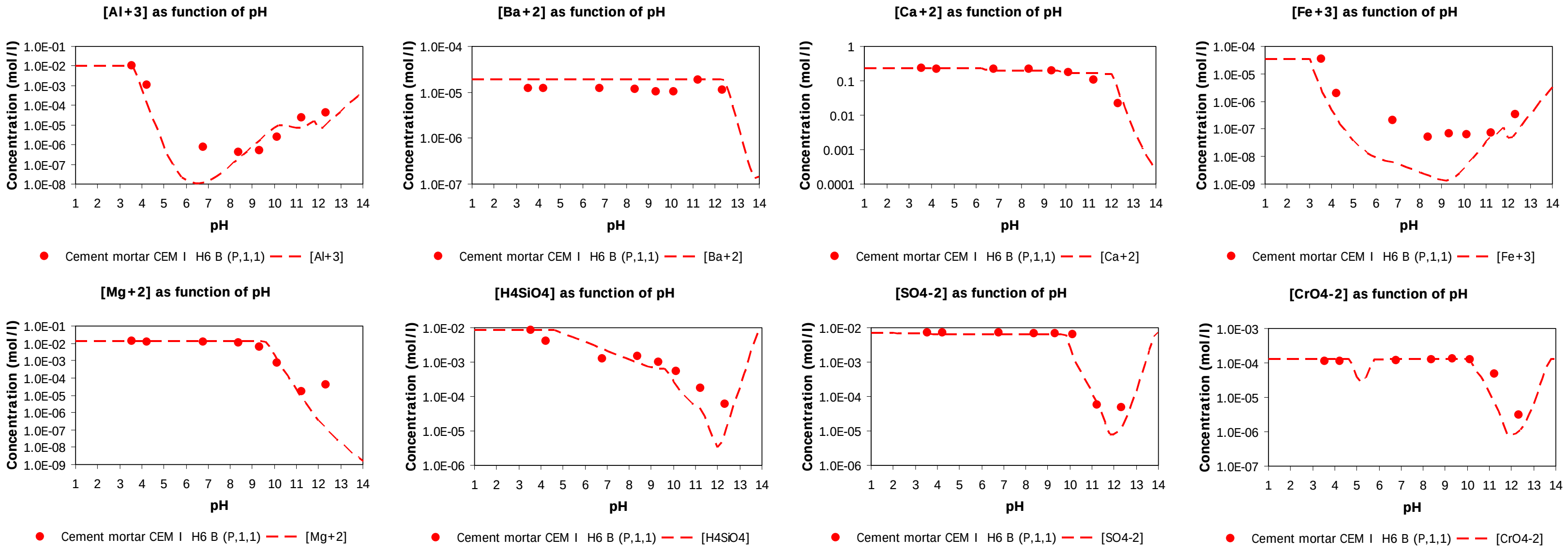




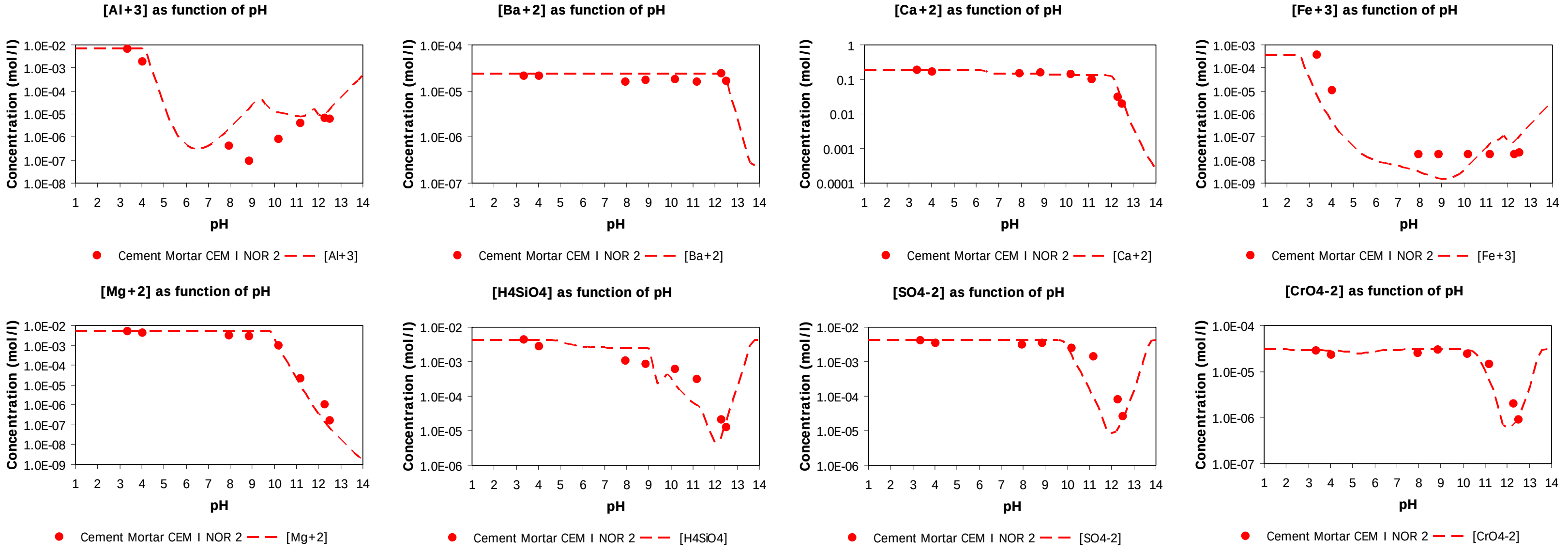




Model results for H6 – CEM I cement mortar



Model results for NOR2 – CEM I cement mortar



APPENDIX L. FULL MECHANISTIC MODELLING OF RELEASE FROM INTACT CEMENT MORTAR

The input for the chemical reaction/transport modelling using LeachXS-Orchestra is provided in the table below.

Input specification

Prediction case	CEM NOR 2	
Solved fraction DO	0.2	
Sum of pH and pe	15.00	
L/S	10.0000	
Clay	0.000E+00	**kg/kg**
HFO	2.000E-04	**kg/kg**
SHA	0.000E+00	**kg/kg**

DOC/DHA data	**pH**	**[DOC] (kg/l)**	**DHA fraction**	**[DHA] (kg/l)**	**Polynomial coeficients**	
	1.00				**C0**	0.000E+00
	3.37	0.000E+00	1.00	0.000E+00	**C1**	0.000E+00
	4.04	0.000E+00	1.00	0.000E+00	**C2**	0.000E+00
	7.94	0.000E+00	1.00	0.000E+00	**C3**	0.000E+00
	8.85	0.000E+00	1.00	0.000E+00	**C4**	0.000E+00
	10.21	0.000E+00	1.00	0.000E+00	**C5**	0.000E+00
	11.17	0.000E+00	1.00	0.000E+00		
	12.30	0.000E+00	1.00	0.000E+00		
	12.52	0.000E+00	1.00	0.000E+00		

Reactant concentrations

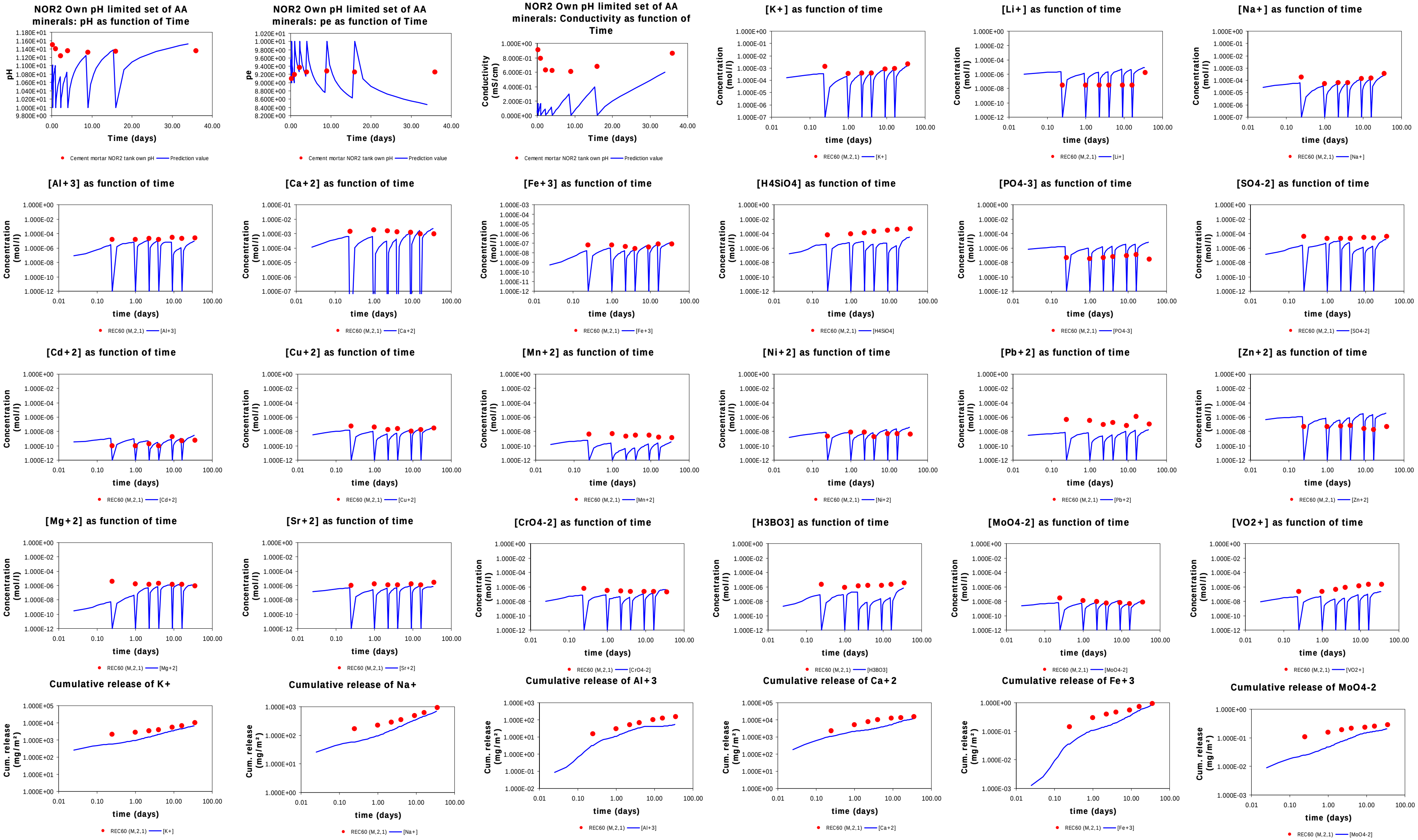
Reactant	**mg/kg**
Ag+	not measured
Al+3	1.855E+03
H3AsO4	7.626E-02
H3BO3	8.026E+00
Ba+2	3.299E+01
Br-	not measured
Ca+2	7.572E+04
Cd+2	3.638E-02
Cl-	5.000E+01
CrO4-2	1.577E+01
Cu+2	2.599E+00
F-	5.000E+01
Fe+3	2.045E+02
H2CO3	5.000E+03
Hg+2	not measured
I-	not measured
K+	1.251E+03
Li+	1.568E+00
Mg+2	1.249E+03
Mn+2	4.562E+01
MoO4-2	4.197E-01
Na+	1.250E+02
NH4+	not measured
Ni+2	1.665E+01
NO3-	5.000E+01
PO4-3	5.108E+00
Pb+2	5.194E+00
SO4-2	1.363E+03
Sb[OH]6-	9.102E-02
SeO4-2	1.347E-01
H4SiO4	1.231E+03
Sr+2	5.570E+01
Th+4	not measured
UO2+	not measured
VO2+	7.312E+00
Zn+2	8.093E+00

Selected Minerals

AA_2CaO_Al2O3_SiO2_8H2O[s]
AA_2CaO_Fe2O3_8H2O[s]
AA_2CaO_Fe2O3_SiO2_8H2O[s]
AA_3CaO_Al2O3[Ca[OH]2]0_5_[CaCO3]0_5_11_5H2O[s]
AA_3CaO_Al2O3_6H2O[s]
AA_3CaO_Al2O3_CaCO3_11H2O[s]
AA_3CaO_Al2O3_CaSO4_12H2O[s]
AA_3CaO_Fe2O3[Ca[OH]2]0_5[CaCO3]0_5_11_5H2O[s]
AA_3CaO_Fe2O3_6H2O[s]
AA_3CaO_Fe2O3_CaCO3_11H2O[s]
AA_3CaO_Fe2O3_CaSO4_12H2O[s]
AA_4CaO_Al2O3_13H2O[s]
AA_4CaO_Fe2O3_13H2O[s]
AA_Al[OH]3[am]
AA_Anhydrite
AA_Brucite
AA_Calcite
AA_CaO_Al2O3_10H2O[s]
AA_CO3-hydrotalcite
AA_Fe[OH]3[microcr]
AA_Gibbsite
AA_Gypsum
AA_Jennite
AA_Magnesite
AA_Portlandite
AA_Silica[am]
AA_Syngenite
AA_Tobermorite-I
AA_Tobermorite-II
AA_Tricarboaluminate
Cd[OH]2[A]
Cr[OH]3[C]
Fe_Vanadate
Manganite
Ni[OH]2[s]
Pb[OH]2[C]
Pb2V2O7
Pb3[VO4]2
PbCrO4
PbMoO4[c]
Rhodochrosite
Strontianite
Tenorite
Willemite

Additional properties are:

pe + pH 15 0.56 kg
initial pH : 12 2.289 kg/dm3
Tortuosity : 10 1.3 (facto for layer thickness
Porosity 0.1
Dimensions: 16x4x4 cm


NOR2 Own pH limited set of AA minerals: pH as function of Time

NOR2 Own pH limited set of AA minerals: pe as function of Time

NOR2 Own pH limited set of AA minerals: Conductivity as function of Time

[K+] as function of time

[Li+] as function of time

[Na+] as function of time

[Al+3] as function of time

[Ca+2] as function of time

[Fe+3] as function of time

[H4SiO4] as function of time

[PO4-3] as function of time

[SO4-2] as function of time

[Cd+2] as function of time

[Cu+2] as function of time

[Mn+2] as function of time

[Ni+2] as function of time

[Pb+2] as function of time

[Zn+2] as function of time

[Mg+2] as function of time

[Sr+2] as function of time

[CrO4-2] as function of time

[H3BO3] as function of time

[MoO4-2] as function of time

[VO2+] as function of time

Cumulative release of K+

Cumulative release of Na+

Cumulative release of Al+3

Cumulative release of Ca+2

Cumulative release of Fe+3

Cumulative release of MoO4-2

Figure XII-1. Release prediction (all 30 elements simultaneously) in the monolith leach test (renewal mode) in comparison with test data for cement mortar NOR 2 (ECRICEM project).

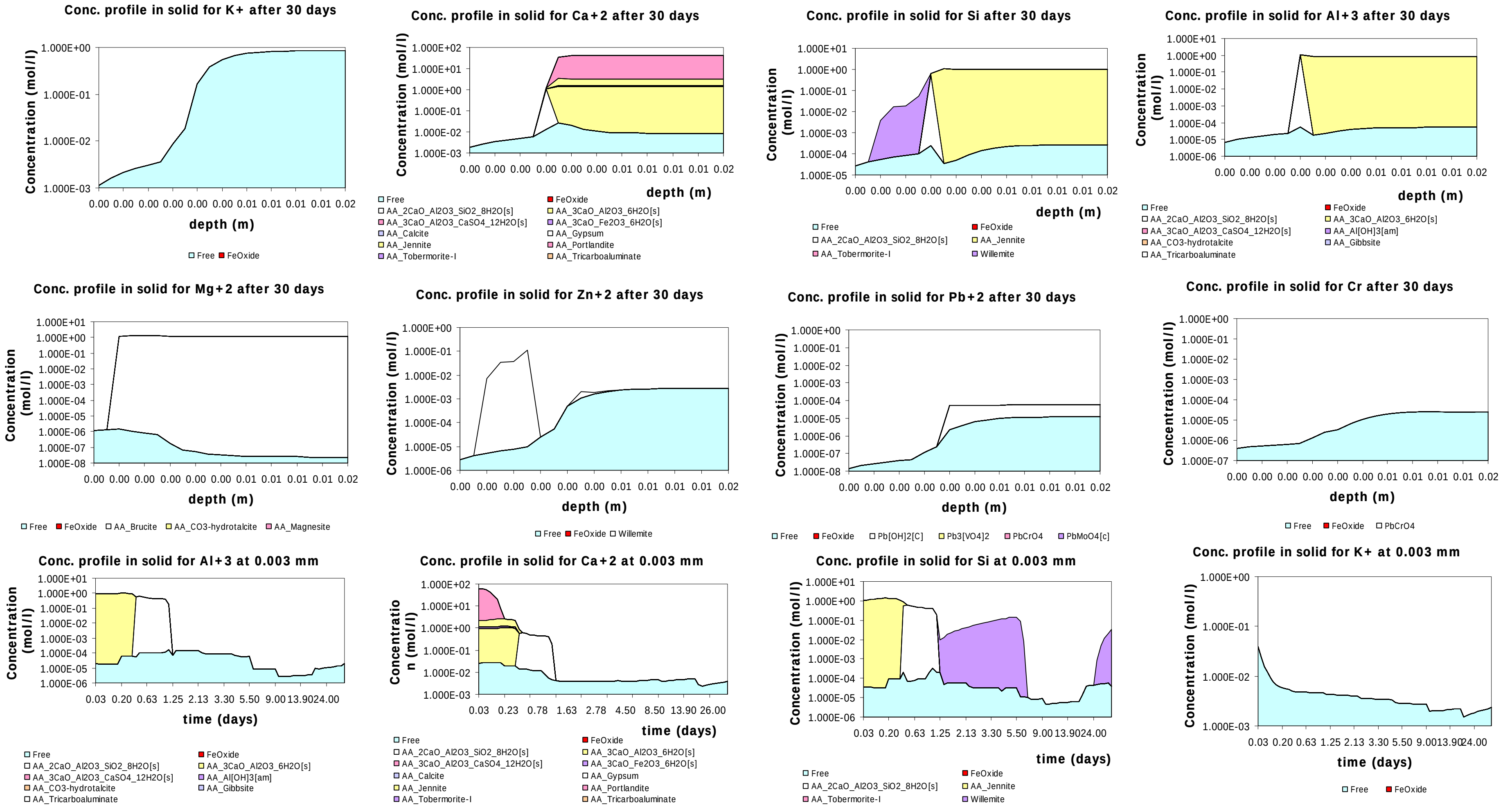


Figure XII-2. Profiles of dissolved concentrations in porewater and solubility controlling minerals as a function of depth in the mortar at a specified time and as a function of time at a specified depth (from the surface of the specimen). Note x axis is not numeric.

PROFILES IN CASE OF CARBONATION

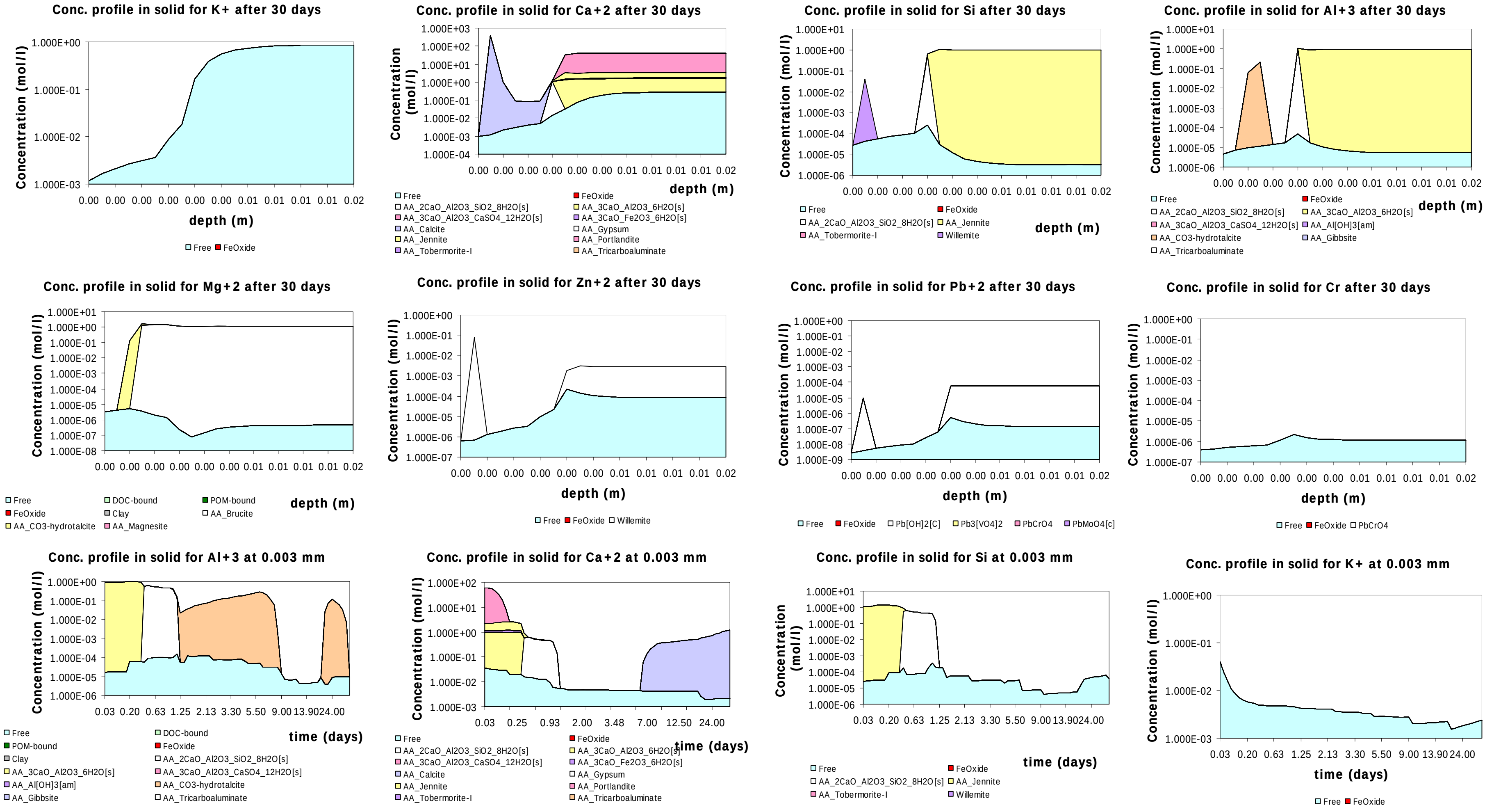
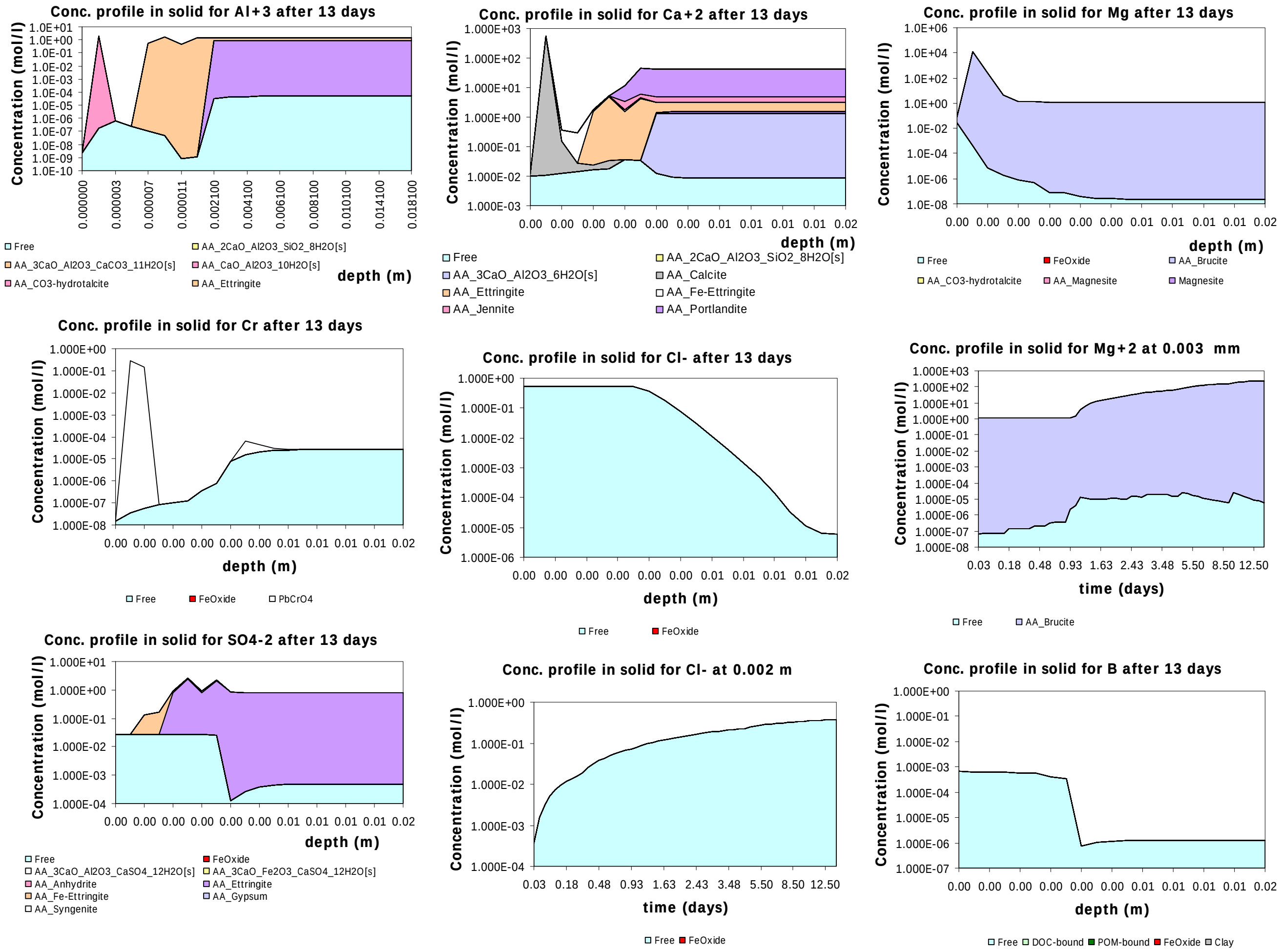


Figure XII-3. Profile of concentration as a function of depth at a specified time and as a function of time at a specified depth in a tank test after carbonation

PROFILES IN CASE OF SEWATER EXPOSURE



Conc. profile in solid for Al+3 after 13 days

Conc. profile in solid for Ca+2 after 13 days

Conc. profile in solid for Mg after 13 days

Conc. profile in solid for Cr after 13 days

Conc. profile in solid for Cl- after 13 days

Conc. profile in solid for Mg+2 at 0.003 mm

Conc. profile in solid for SO4-2 after 13 days

Conc. profile in solid for Cl- at 0.002 m

Conc. profile in solid for B after 13 days

Figure XII-4. Profile of concentration as a function of depth at a specified time and as a function of time at a specified depth in a tank test with seawater as a contact solution. Note precipitation of Al, Ca (calcite) , Mg (brucite) and Cr at interface.

Appendix M. Cement based products: guidance in testing for environmental impact assessment, treatment evaluation and regulatory compliance aspects example: cement mortars and concrete (M/100, M/114, M128)

The judgement of environmental aspects of cement mortars and concrete requires different information on the environmental characteristics for different purposes. Examples of such needs are: the development of criteria to assess impact from cement mortar and concrete use in different construction scenarios and the quality control to verify compliance with the specified limit values.

For an assessment of impact in different scenarios of application the range of exposure conditions, which may occur, is relevant. In addition, the material will undergo changes with time (e.g. carbonation). To take these changes into account an assessment of other conditions is required than when evaluating a fresh sample. This may involve pH and, possibly, redox changes resulting from carbonation, weathering and remineralisation.

In all impact scenarios the degree of contact with water will be the key aspect determining the release. This calls for insight in changes of leaching behaviour as a function of time. The difficult part is that a pH change resulting from carbonation in the field does not necessarily keep pace with the exposure in a lab test (too short relative to field). Therefore a tank test in the lab will never reflect precisely what will happen in practice. Only through modelling a prediction can be made based on understanding the relevant processes.

A hierarchy in testing can provide the necessary detail required to answer some specific questions as well as the simple straightforward testing needed to verify compliance with previous characterisation data and subsequently with derived criteria based on characterisation test results. A well-defined link between characterisation test and compliance procedures is essential to be able to make the inferred relation.

Initial Type Testing ITT of monolithic materials will generally consist of:

- *Composition*. In case of construction materials this is not a preferred means of judgement, but may be required for other regulations and other purposes
- *pH static test data* (TS14429/TS14997) These test results provide insight in the chemical speciation of substances and form the basis for full mechanistic chemical reaction/transport modelling
- *tank test* (e.g., NEN 7375) and compliance options (preferred first fraction of the elaborate method) The tank test reflects many aspects that are relevant for the translation from lab to field. This relates in particular to the tortuosity of the product (measure for the pore structure).
- *physical characteristics* (not covered here) e.g. strength, porosity, permeability, density. Several physical parameters are relevant for modelling transport in field scenarios.
- *ecotoxicity* – At present there are no regulations addressing ecotoxicity. However, extracts from the above mentioned test could be used. In the waste field EN 14735 has been standardised. For assessing ecotoxicity under intended use

conditions, the laboratory leaching methods seem unsuitable, as the release in the lab test does not relate to intended use conditions and unlike leaching is more difficult to translate from extreme exposure conditions.

Questions arise with respect to:

- Variability in production (between facilities and in time within one facility) and variability between different countries
- Behaviour of material in reuse/recycling options in a size reduced form

Approach to address multiple questions related to a material (in line with EN 12920 Methodology)

- Evaluation of the question to be answered
- Perform the proper testing to assess the relevant properties
- Evaluate possible critical substances
- Model the release in the scenario under consideration
- Verify the outcome against field observations
- Adjust model when needed
- Develop criteria by comparison of impact against target objectives or identify compliance with regulatory targets
- Identify key controlling factors and based on the understanding select a suitable test condition for compliance purposes
- Draw conclusion on acceptance or rejection.

Verification against regulatory criteria will allow

- determination of crucial substances (reduction of number of parameters to be tested in compliance testing, if needed) and
- frequency of testing (less frequent testing when values sufficiently far from the critical limit).

Method of evaluation of a scenario

Define exposure window in terms of pH and time (identify relevance of redox, atmospheric exposure and dissolved organic carbon - DOC)
Define conditions (wet / dry cycles, temperature, etc)

Check substances based on this against limit values
    if more than 5 times lower (to be decided elsewhere) - non critical
Check for variability in production

General remark: very consistent leaching behaviour when judged based on characterisation leaching tests between cements produced at different locations worldwide.
Very good repeatability possible for tank test (BCR reference sample tested over a period of several years and in a repeatability study of 10 tests on the same specimen, ECN, 2007)

Judgement of critical parameters based on characterisation (Building Materials Decree, 1995 as example) for both the intact specimen (product in use phase) and as recycling material for unbound application is given in table G.1. In figure G.1 it is indicated how the factor between the regulatory limit and the observed behaviour is derived.

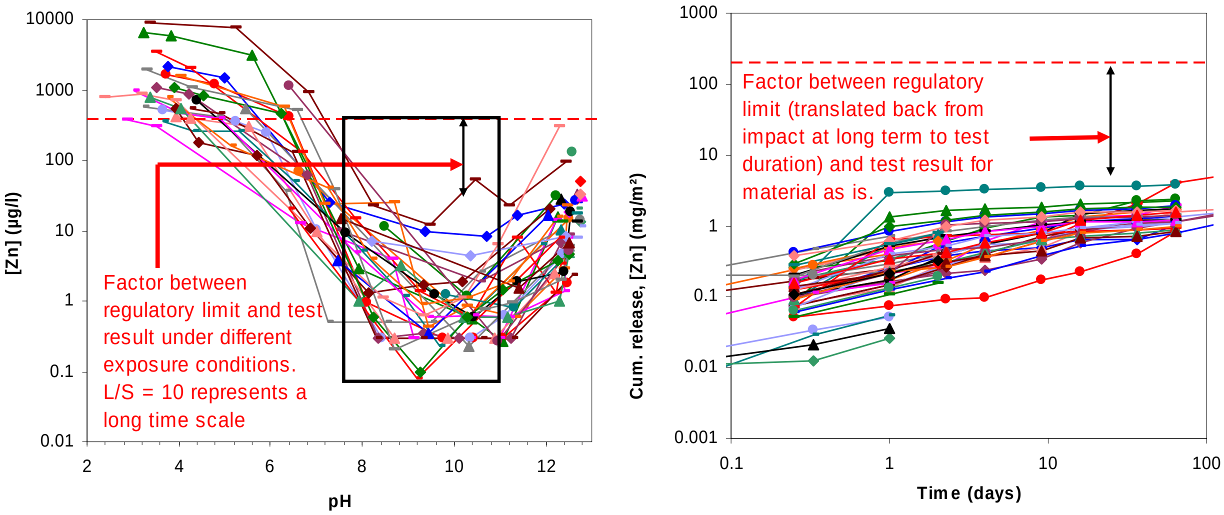


Figure G.1. Judgement of cement based products and recycled concrete aggregate based on characterisation test data.

Table xx.1. Judgement of cement mortar in use and unbound recycled concrete aggregate.

Substance	Service life: Cat 1 BMD tank test data at 64 days	Factor#	Recycling: Cat 1 BMD fresh and after carbonation pH stat (L/S=10; neutral pH; < 2mm)	Factor#	Remarks
Al					Consistent data. After carbonation decrease in release.
As	Pass	10	Pass	30	
B					After carbonation increase in leachability from pH 12 to 10.5
Ba	Pass	5	Fail	5	Ba release strongly related to sulphate leachability.
Ca					Very consistent data
Cd	Pass	3	Pass	3	At pH 7.8 full carbonation close to limit
Cl	Pass		Pass		Very limited data

Substance	Service life: Cat 1 BMD tank test data at 64 days	Factor#	Recycling: Cat 1 BMD fresh and after carbonation pH stat (L/S=10; neutral pH; < 2mm)	Factor#	Remarks
Cr	Pass	OPC 23 Bl C 60	OPC Fail BFS and slag blended Pass	30	Maximum in selected pH range
Cu	Pass	100	Pass	30	
Fe					Consistent
Hg	Pass	10	Pass		
K					Consistent
Li					Consistent
Mg					Consistent, very pH sensitive
Mn					Consistent
Mo	Pass	10	Fail	5	
Na					Consistent, all ww cements within a factor 10
Ni	Pass	50	Fail (pH 8-9) Pass (pH 9-12)	10 10	
P					Consistent
Pb	Pass	30 - 100*	Pass	4	
SO4 as S	Pass	10	Fail	2	After carbonation increase in leachability
Sb	Pass	2-100*	Fail	10	Maximum at pH 7.8 (full carbonation)
Si					Consistent
Sn	Pass	100			Poor analysis
Sr					Consistent
V	Pass	20 - 1000	Fail	0 - 7*	
Zn	Pass	100	Pass	5-50*	

A factor in connection with pass or fail indicates the factor below the limit for pass and the factor above for fail
* A range in the factors presented for the granular material implies that there is a significant difference in the pH domain. A range in the factors for service life indicates the bandwidth

Conclusion (applies to materials falling in the "normal" range of cement mortars, not special blends or additives):

Factory Production Control FPC:
First steps of the tank test possibly combined to one fraction for analysis
For recycling an optimal controlled pH condition for size reduced material (< 4 mm) at L/S=10 is recommended (for mortar and concrete this will be a pH condition between pH 9 and 10)

Potentially critical substances based on leaching:
Service life (64 day tank test): None
Recycling unbound (L/S=10): Ba, Cr, Mo, Ni, SO4, Sb, V

Frequency of testing (service life):
WT for all substances after demonstration once that the production on the site matches with the existing worldwide database.

Frequency of testing (recycling):
WFT for several substances from cement mortar derived aggregate based on non critical leaching (source materials non critical).
FT for Cr, SO4 for all OPC derived aggregates and Mo, Sb and V depending on the nature of the (alternative) raw materials used.

Note: judgement of recycling based on size reduced material (< 2 mm). Judgement on other size fractions will show less critical conditions for several parameters. This aspect requires a further evaluation. As testing different particle sizes for compliance purposes is cumbersome (how to define the contribution of fine particles?) a modelling approach is in preparation.

Strength of this combination of characterisation and compliance:
Potential to recognise deviations in leaching behaviour on a single data point
Potential to assess changes in process conditions

In figure xx.2 and xx.3 below the judgment underlying the conclusions in table xx.1 is illustrated for Cr and Zn from cement mortars.

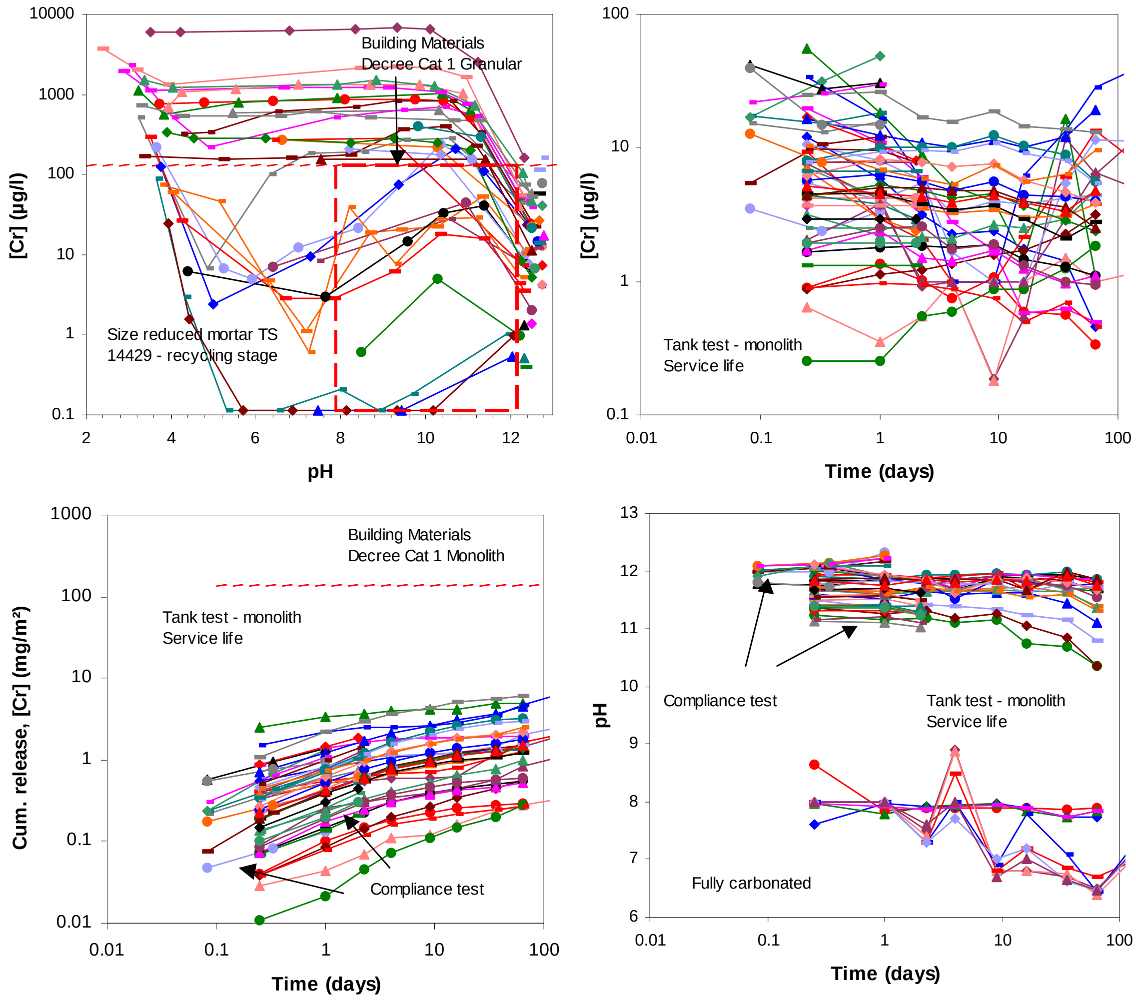


Figure xx.2. Initial type testing for Cr in cement mortars according to EN-197. Top left: pH dependence leaching (TS14429) data of OPC and blended cements with a box denoting the relevant pH domain for judging release (initial pH – full carbonation). The upper limit is the regulatory criterion (here BMD cat I for granular materials); the lower limit represents the analytical detection limit. All three other graphs show data as obtained in the tank leach test (NEN 7345 or the like). Top right: concentration as a function of time; bottom left: cumulative release with regulatory limit (here BMD Cat I for monolithic materials); bottom right pH as measured in the test illustrating the difference between uncontrolled (own pH) and testing under imposed carbonating conditions. FPC test results are given for comparison.

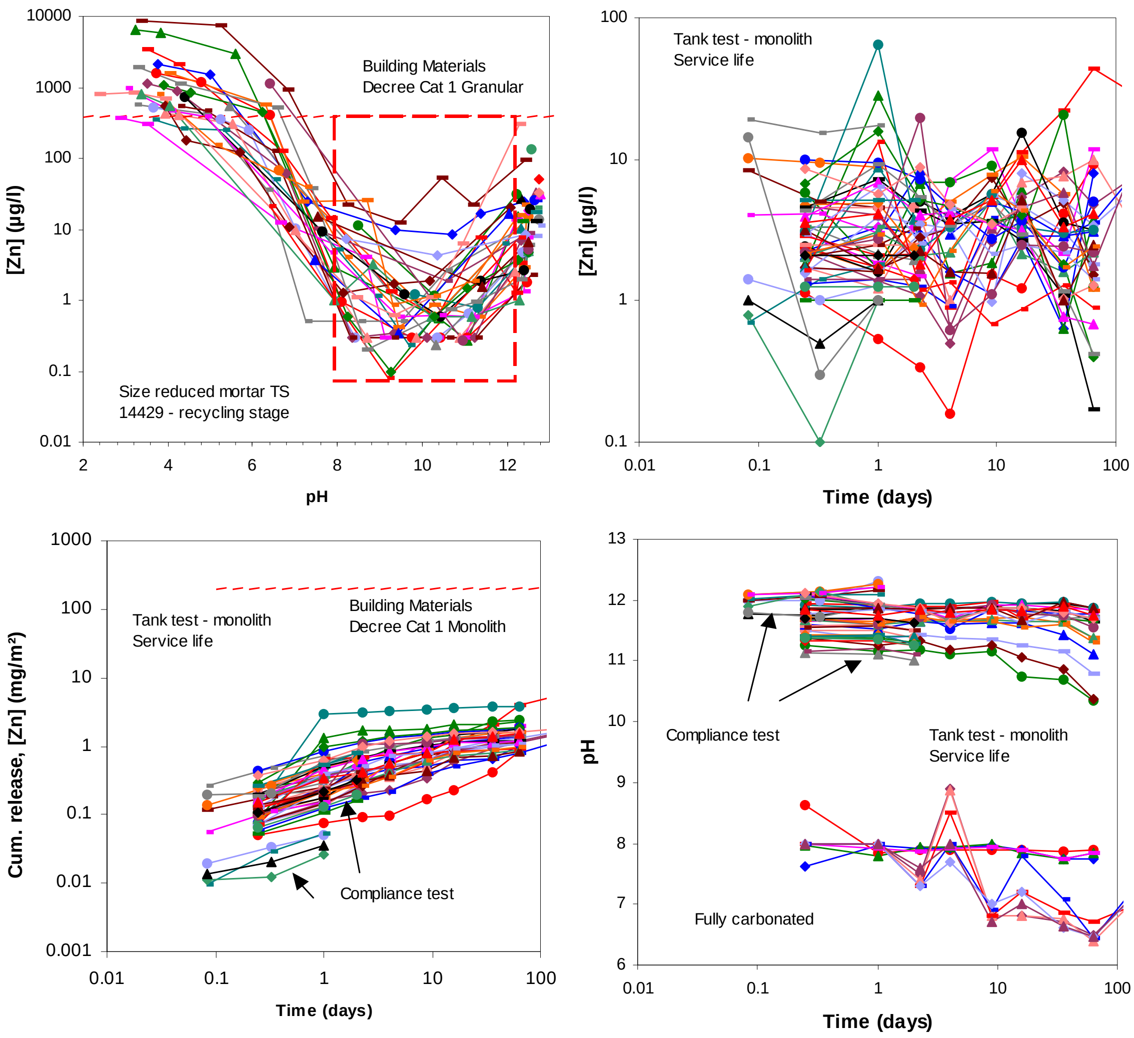


Figure G.3. Initial type testing for Zn in cement mortars according to EN-197. Top left: pH dependence leaching (TS14429) data of OPC and blended cements with a box denoting the relevant pH domain for judging release (initial pH – full carbonation). The upper limit is the regulatory criterion (here BMD cat I for granular materials); the lower limit represents the analytical detection limit. All three other graphs show data as obtained in the tank leach test (NEN 7345 or the like). Top right: concentration as a function of time; bottom left: cumulative release with regulatory limit (here BMD Cat I for monolithic materials); bottom right pH as measured in the test illustrating the difference between uncontrolled (own pH) and testing under imposed carbonating conditions. FPC test results are given for comparison.

Assessment for utilisation or disposal based on different scenario conditions

relevant pH domain in use phase
degree of water contact
exposure to atmosphere
site/application layout
....

Development of criteria, if needed can be based on forward modelling using a scenario approach targeted to a unsaturated (above soil) or saturated exposure scenario. For this full mechanistic modelling is envisaged. This implies understanding the release controlling factors

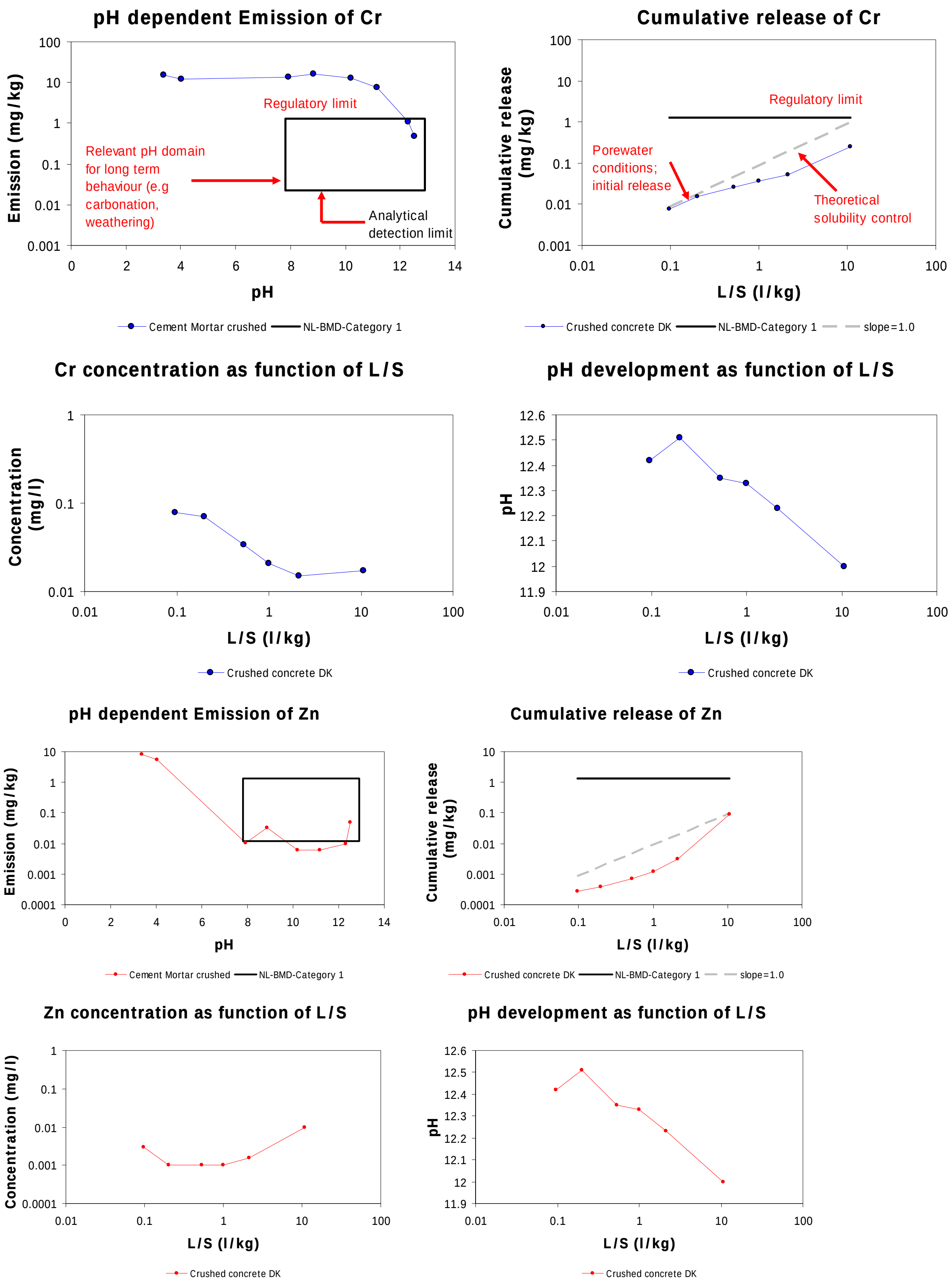


Figure G.4. Judgement of Cr and Zn in recycled concrete aggregate against criteria illustrating acceptance at own pH of the material and exceeding of limits upon carbonation. Particle size in the test is 4 mm. Correction for particle size needed to relate lab data to practice.

in sufficient detail to allow prediction of the laboratory test data. For field impact evaluation the source term obtained this way will only have to be extended with site specific exposure conditions, like degree of water contact, tortuosity of the material to be judged, temperature, dimensions, etc.

Statistics

With sufficient data in the database now a proper evaluation of product performance can be made. In figure G.5 the statistics are given for the cumulative release of Zn from cement mortars.

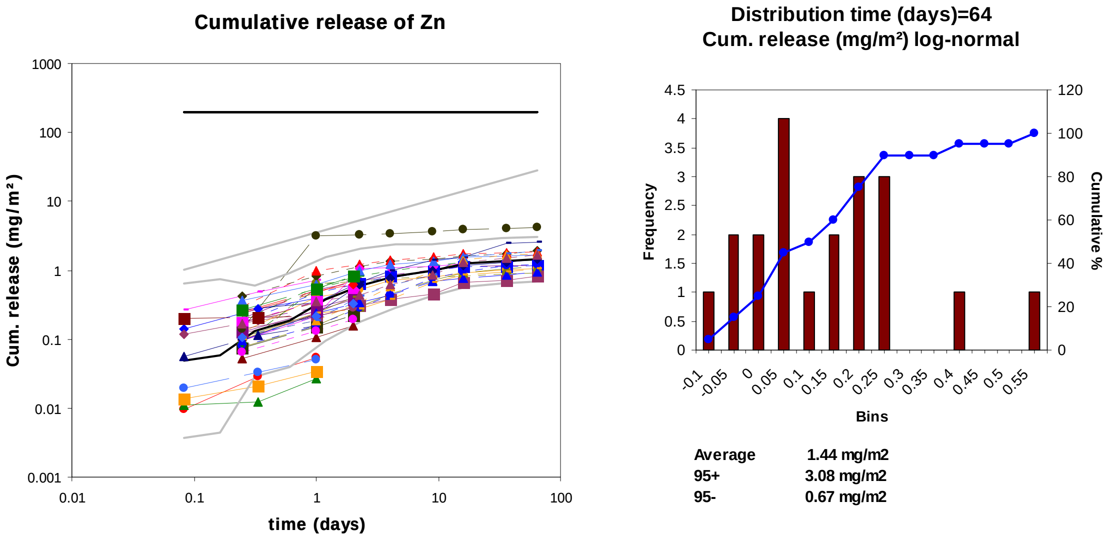


Figure G.5. Statistics on cumulative release curves for Zn at 64 days as obtained in ITT (tank leach test, n=20).

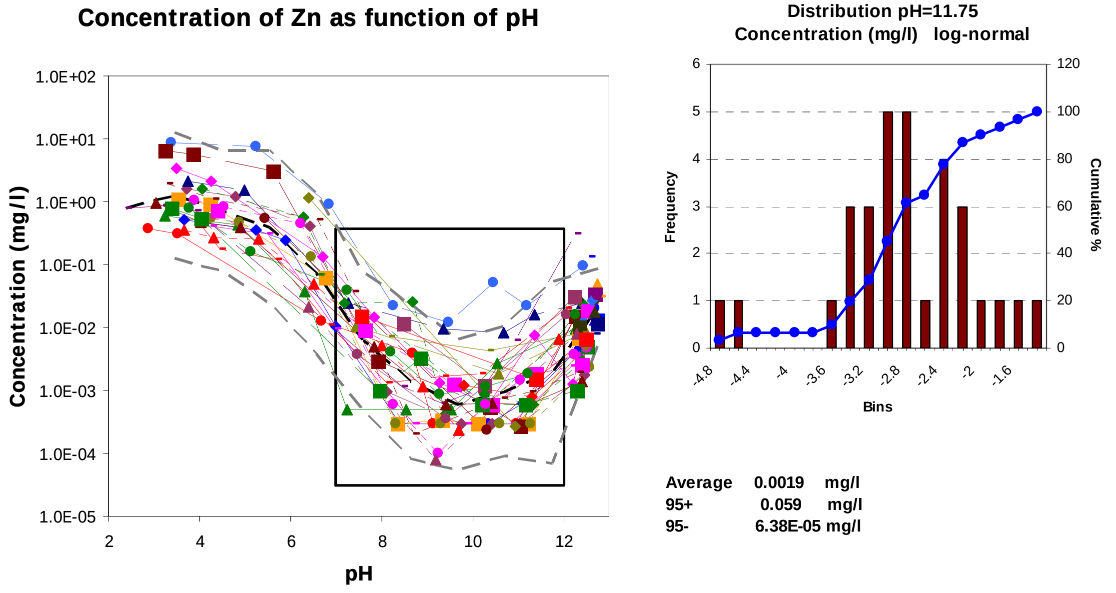


Figure G.6. Statistics on pH dependent release curves for Zn at pH 11.75 as obtained in ITT (TS14429, n=31).

The leaching data need to be judged in a log-normal distribution as a linear scale would overrate the higher concentrations.

Decision criterion for WT/WFT and FT based on statistics

Following the concept of log normal distributions, the present number of data allow statistics to be applied, in which the risk on non-compliance (RNC) can be calculated for a given number of observations. In table .. the values for the RNC are given for k-values as defined below for a specified number of observations.

k-value = log (regulatory limit) – $\mathrm{Y}_{\text{average of log normal data}}$/ $\mathrm{Stdev}_{\text{log normal data}}$

The risk of non-compliance can be linked to an interpretation in terms of product or substance qualification as WFT or FT with a certain testing frequency.

Table.. RNC values derived from k-values and their possible interpretation in terms of product of substance qualification.

K-value N=5	K-value N=10	Chance of compliance	Risk of non-compliance	Testing frequency	Parameter relevance
> 6.12	> 4.63	> 99.9 %	< 0.1%		WFT
4.67 -6.12	3.53 -4.63	99% -99.9%	0.1% -1%	Every year	FT
2.74 -4.67	2.07 -3.53	90% -99%	1% -10%	Every 10 batches	FT
1.46 -2.74	1.07 -2.07	70% -90%	10% -30%	Every 4 batches	FT
0.69 -1.46	0.44 -1.07	50% -70%	30% -50%	Every other batch	FT
< 0.69	< 0.44	< 50%	> 50%	Every batch	FT

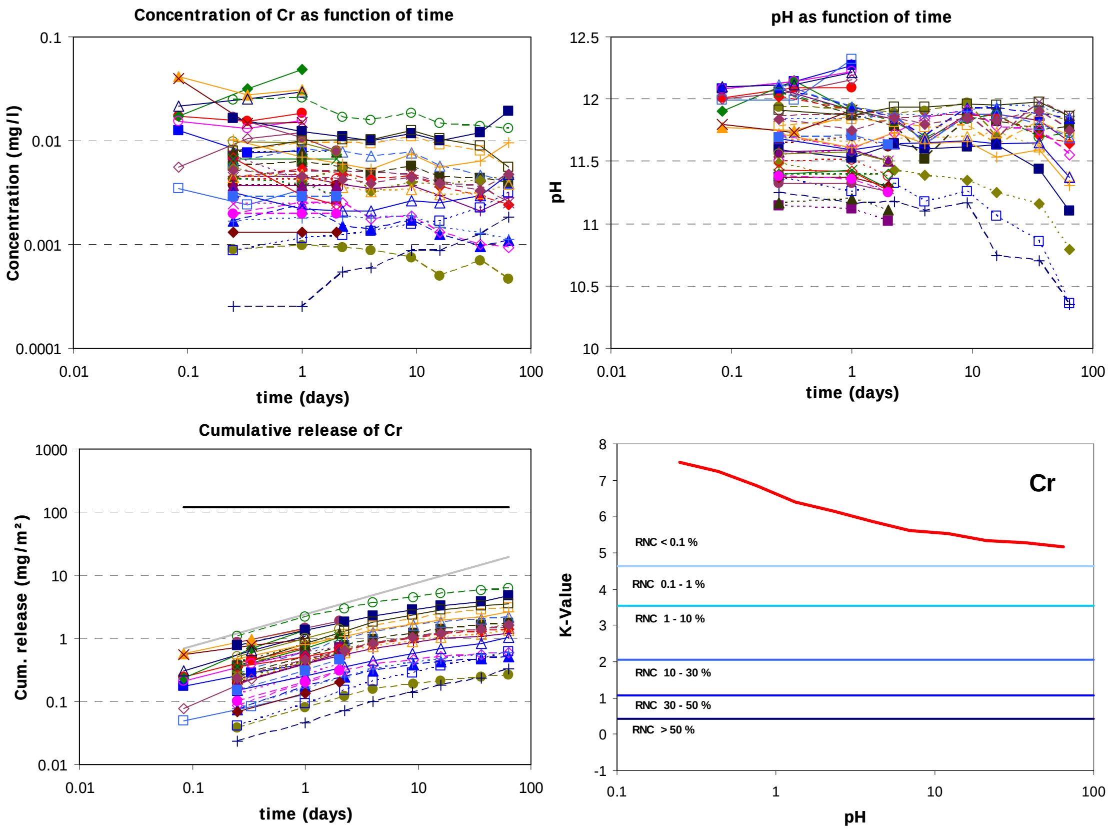


Figure.. The release of Cr from cement in a tank test. The cumulative release data are transformed into k-values with the associated RNC ranges to judge WFT or FT performance.

In table.. the k values and associated ranges for risk of non-compliance are given for cement mortars for the elements assessed assording to the Soil Quality Decree.

Table.. Evaluation of cement mortar based on k-value against the Soil Quality Decree (follow up from the Building Materials Decree)

	Average release (mg/m2)	Regulatory limit	K-Value for N=10	RNC	Classification
As	0.036	260	8.9	< 0.1%	WFT
Ba	29.530	1500	4.8	< 0.1%	WFT
Cd	0.035	3.8	16.8	< 0.1%	WFT
Co	0.231	60	13.0	< 0.1%	WFT
Cr	1.327	120	5.2	< 0.1%	WFT
Cu	0.665	98	9.4	< 0.1%	WFT
Mo	0.120	144	11.1	< 0.1%	WFT
Ni	0.764	81	7.3	< 0.1%	WFT
Pb	0.170	400	6.7	< 0.1%	WFT
Sb	0.040	8.7	4.3	0.1% -1%	WFT#
SO4	550.166	165000	6.0	< 0.1%	WFT
Sn	0.460	50	15.4	< 0.1%	WFT
V	0.351	320	4.7	< 0.1%	WFT
Zn	1.422	800	14.9	< 0.1%	WFT

RNC = risk of non-compliance

For the number of observations (N=20) k value is lower and WFT is secured

Table xx shows that an integration of leaching behaviour, statistics, WFT and FT classification of substances is quite well feasible.

For service life, cement mortar and concrete meet criteria of Dutch Soil Quality Decree for all regulated substances

Judgement of FPC test data

FPC test data can be compared in tables, but much more effectively in terms of decision power is a judgement in the context of the more detailed testing information in the already existing database. By identifying the data set against which data are compared, the new data can be placed in proper perspective with respect to pH and time dependent release. In figure G.7 the conformity evaluation is given for a assessment based on leaching.

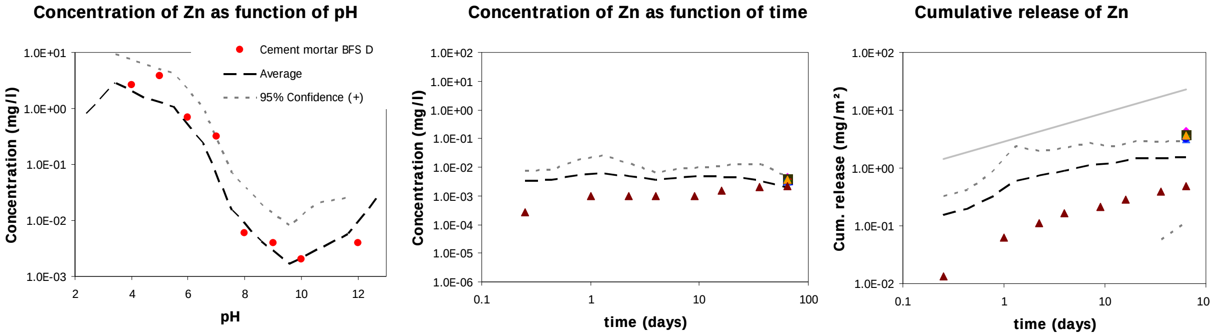


Figure G.7. FPC test data in relation to performance data based on a worldwide dataset.

To evaluate the changes in release for a production process with time, a presentation mode has been developed that allow data to be judged on this aspect. In figure G.8 the variation with time is given for concrete mortars tested over a period of 7 years.

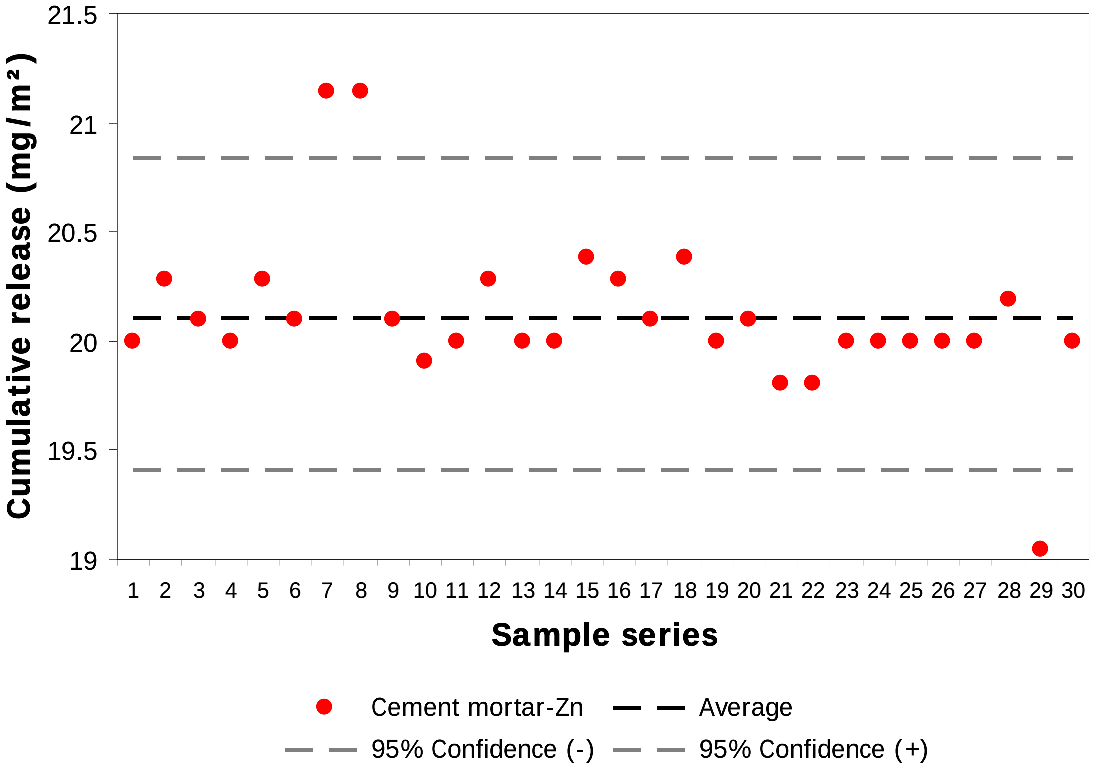


Figure G.8. Time series variation in cement production assessed on leaching of mortar specimen

Impact evaluation

Based on intrinsic parameters obtained from the pH dependence test (pH change due to carbonation) and tank leach test (time evolution) a scenario description can be developed for different applications of concrete. The same basic information can be used for these different applications. Main parameters that need to be varied in an intended use scenario are: mode and intensity of contact with water, mode and intensity of contact with the atmosphere, type of leachant, temperature in intended use (rate of diffusion), surface area exposed.

Examples of scenarios are:

- drinking water pipe with continuous flow and stagnant conditions at times
- concrete in groundwater

Referenties

– ECN, personal communication, 2007, data available upon request)

– ECRICEM I en II

– Engelsen, C. J., Fidjestøl, P., van der Sloot, H. A., Justnes, H., Mulugeta, M. Recent advances in modelling of the constituent release from recycled concrete aggregates with different degree of carbonation. In Sustainable Concrete Construction; India Chapter of the American Concrete Institute: Mumbai, India, 2008, pp 109-116

– Van der Sloot H.A. (2000): Comparison of the characteristic leaching behaviour of cements using standard (en 196-1) cement-mortar and an assessment of their long-

term environmental behaviour in construction products during service life and recycling. Cement & Concrete Research 30, 1 – 18
- Building Materials Decree. Staatsblad van het Koninkrijk der Nederlanden, 1995, 567.