

Leaching of inorganic and organic substances from construction materials and their ecotoxicological impact

vorgelegt von
Dipl.-Ing.
Veronika Märkl
geb. in Landshut

von der Fakultät VI - Planen Bauen Umwelt
der Technischen Universität Berlin
zur Erlangung des akademischen Grades

**Doktorin der Ingenieurwissenschaften
-Dr.-Ing.-**

genehmigte Dissertation

Promotionsausschuss:

**Vorsizender: Prof. Dr. Frank U. Vogdt
Gutachter: Prof. Dr. Dietmar A. Stephan
Gutachter: Prof. Dr. Michael Burkhardt**

Tag der wissenschaftlichen Aussprache: 05. Februar 2018

Berlin 2018

- Vorsitzender: Univ.-Prof. Dr.-Ing. Frank U. Vogdt
Institut für Bauingenieurwesen
Fachgebiet Bauphysik und Baukonstruktionen
Technische Universität Berlin, Berlin, DE
1. Gutachter: Univ.-Prof. Dr. rer. nat. Dietmar Stephan
Institut für Bauingenieurwesen
Fachgebiet Baustoffe und Bauchemie
Technische Universität Berlin, Berlin, DE
2. Gutachter: Prof. Dr. agr. Michael Burkhardt
Institut für Umwelt- und Verfahrenstechnik
Fachgruppe Wasser und Abwassertechnik
Hochschule für Technik Rapperswil, Rapperswil, CH

Tag der Einreichung:	01.09.2017
Tag der wissenschaftlichen Aussprache:	05.02.2018

Ehrenwörtliche Erklärung

Ich erkläre hiermit ehrenwörtlich, dass ich die vorliegende Arbeit ohne unzulässige Hilfe Dritter und ohne Benutzung anderer als der angegebenen Hilfsmittel angefertigt habe. Die aus anderen Quellen direkt oder indirekt übernommenen Daten und Konzepte sind unter Angabe der Quelle gekennzeichnet.

Bei der Auswahl und Auswertung folgenden Materials haben mir die nachstehend aufgeführten Personen in der jeweils beschriebenen Weise unentgeltlich geholfen:

- Die Messungen zur Ermittlung der Polycarboxylatethergehalte in den Eluaten wie in [Kapitel 7](#) beschrieben wurden bei der SIKA Deutschland GmbH unter Leitung von Herrn Dr. Oliver Blask durchgeführt.

Weitere Personen waren an der inhaltlich-materiellen Erstellung der vorliegenden Arbeit nicht beteiligt. Insbesondere habe ich hierfür nicht die entgeltliche Hilfe von Vermittlungs- bzw. Beratungsdiensten (Promotionsberater oder anderer Personen) in Anspruch genommen. Niemand hat von mir unmittelbar oder mittelbar geldwerte Leistungen für Arbeiten erhalten, die im Zusammenhang mit dem Inhalt der vorgelegten Dissertation stehen. Die Arbeit wurde bisher weder im In- noch im Ausland in gleicher oder ähnlicher Form einer anderen Prüfungsbehörde vorgelegt.

Ich versichere ehrenwörtlich, dass ich nach bestem Wissen die reine Wahrheit gesagt und nichts verschwiegen habe.

Mirskofen, 01.09.2017

Acknowledgements

I wish to express my sincere appreciation to those who have contributed to this thesis and supported me in whichever way during this adventurous journey.

First, I would like to express my profound gratitude to my supervisor Prof. Dr. Dietmar Stephan for his support and guidance as well as the good and trustful working relationship.

Additionally, I sincerely thank Prof. Dr. Michael Burkhardt for his helpful discussions and support of my doctoral research.

My sincere thanks are extended to my colleagues at the Chair of Building Materials and Construction Chemistry as well as the Chair of Ecological Impact Research and Ecotoxicology at TU Berlin.

Furthermore I want to thank Dr. Anton Reichert for his support, guidance and helpful discussions.

The past few years have also been challenging to my family and my dearest love, who supported me during all situations. My very special thanks go to you!

Danke!

Abstract

In the last few years a growing environmental awareness in the field of construction materials can be observed. This has been, and continues to be, exacerbated since the Construction Products Regulations entered into force in 2013. In general construction products are in direct contact with the surrounding environment such as groundwater and soil. Especially grouting materials that often contain significant amounts of organic/chemical admixtures are used to modify the properties of the ground or to fill voids in order to seal the ground against moisture and water ingress. A broad variety of such grouting materials that can be used for different applications is available on the market. Due to the direct contact with soil and/or groundwater inorganic and organic constituents may be leached and released into the environment.

This work reports about leaching behaviour and mechanisms of three different grouting materials, namely polyurethane, cement and a cement-polyurethane hybrid material. Cement paste and mortar samples were prepared with different superplasticisers, either polycarboxylate ether or a mixture of melamine and naphthalene sulphate condensate. In addition the water-to-cement ratio, pre-storage time and the type of eluent were varied. In case of the polyurethane material the behaviour of three different catalysts was investigated as well as different dosages thereof. Different fractions of cement were replaced by ground granulated blast-furnace slag in case of the cement-polyurethane hybrid material to simulate commonly used slag cements. Leaching was performed with the tank leaching test and the batch test. In case of the polyurethane and cement-polyurethane hybrid material the leaching tests were adopted to gain more information about the leaching behaviour whilst curing. The gained eluates were analysed for general parameters (pH-value and electric conductivity) as well as inorganic constituents (Al^{3+} , Ca^{2+} , Cl^- , SO_4^{2-} , Na^+ and K^+) via IC and ICP-AES. Organic constituents have been analysed as sum parameter (TOC and/or DOC) and wherever possible as single parameter via liquid chromatographic methods or UV-Vis spectrometry. To study their environmental impact the eluates were analysed with different aquatic and terrestrial ecotoxicological assays.

The results showed that the aggressiveness (pH-value and the electrical conductivity) of the eluent plays a key role in leaching. The pH-value of the polyurethane systems stayed constant at pH 7, while for the cementitious systems the pH stays constantly at high values around 12. In general, the leached inorganic ions decrease rapidly over time in case of polyurethane systems. For cementitious systems Ca^{2+} is leached constantly. In addition K^+ and Na^+ were identified as counterion of the superplasticiser. The TOC of all samples is constantly decreasing within the first few leaching steps. The main leaching mechanism for the total organic carbon was identified as wash-off effect for all the samples. It was also possible to detect superplasticiser traces in the cement leachates with HPLC-MS or UV-Vis spectrometry. Statistical data analysis of the ecotoxicological assays showed that time is a significant factor controlling the leaching process. The superplasticiser dosages play a subordinate role in the cementitious systems while the catalyst dosage is a significant factor for the polyurethane systems. With this thesis an insight is given in the complex topic of leaching of building materials and their environmental impact. However, further research needs to be done to gain better and in-depth understanding of the leaching process and the interaction of the leachates with the environment.

Kurzfassung

Seit einigen Jahren kann ein wachsendes Umweltbewusstsein im Bausektor festgestellt werden. Dieses wird noch verstärkt seit die neue Bauproduktenverordnung im Jahr 2013 in Kraft getreten ist. Im Allgemeinen stehen Bauprodukte im direkten Kontakt mit der umgebenden Umwelt, wie beispielsweise dem Grundwasser und Boden. Speziell wasserabdichtende Stoffe die oft einen erheblichen Anteil an organischen/chemischen Additiven enthalten werden verwendet um die Eigenschaften des Bodens zu modifizieren oder um Hohlräume gegen eindringendes Wasser oder Feuchtigkeit abzudichten. Ein breites Spektrum solcher wasserabdichtender Stoffe, die für verschiedene Anwendungen eingesetzt werden können, ist auf dem Markt erhältlich. Durch den direkten Kontakt zu Boden und/oder Grundwasser können anorganische und organische Stoffe aus Baustoffen ausgelaugt werden und in die Umwelt gelangen. Diese Arbeit berichtet über das Auslaugverhalten von drei verschiedenen wasserabdichtenden Stoffen (Polyurethan, Zement und ein Zement-Polyurethan-Hybrid). Zementpasten und Mörtel wurden mit unterschiedlichen Fließmitteln (ein Polycarboxylatether oder eine Mischung aus Naphthalin- und Melaminsulfonatformaldehydkondensat) hergestellt. Der Wasser-Zement-Wert, die Vorlagerungszeit und der Eluent wurden variiert. Bei den Polyurethanen wurde das Verhalten von drei Katalysatoren in drei verschiedenen Dosierungen untersucht. Bei dem Zement-Polyurethan-Hybrid wurden verschiedene Zusammensetzungen von Zement und Hüttensand getestet um übliche Hüttensandzemente nachzustellen. Als Auslaugversuche wurden Standtests und Schütteltests verwendet. Im Falle der Polyurethane und der Zement-Polyurethan-Hybride wurden die Tests angepasst um mehr Informationen über das Auslaugverhalten während des Abbindens zu erhalten. Die so erhaltenen Eluate wurden auf allgemeine Parameter wie pH-Wert und elektrische Leitfähigkeit und ebenfalls auf anorganische Bestandteile untersucht. Die enthaltene Organik wurden in Summe erfasst und wenn möglich mittels flüssig-chromatographischer oder spektroskopischer Verfahren auf deren Einzelbestandteile untersucht. Um den Umwelteinfluss der Eluate zu untersuchen wurden verschiedene aquatische und terrestrische ökotoxikologische Tests durchgeführt. Die Ergebnisse zeigten, dass die Zusammensetzung des Eluenten eine Schlüsselrolle beim Auslaugen spielt. Der pH-Wert der Polyurethansysteme blieb konstant bei pH 7, während der pH-Wert der zementären Systeme bei Werten um etwa 12 deutlich höher lag. Im Allgemeinen nahm die Konzentration der anorganischen Ionen bei den Polyurethansystemen über die Zeit ab. Hingegen blieb die Ca^{2+} -Auslaugung konstant für zementäre System. Weiterhin konnten K^{+} und Na^{+} als Gegenion der Fließmittel identifiziert werden. Während der ersten Auslaugschritte nahm der TOC bei allen Systemen ab. Der Auslaugmechanismus des TOC konnte der Oberflächenauswaschung zugeordnet werden. Weiterhin konnten die verwendeten Fließmittel der zementären Systeme mittels flüssigchromatographischer und spektroskopischer Verfahren in den Eluaten nachgewiesen werden. Die statistische Auswertung der ökotoxikologischen Daten zeigte, dass die Zeit ein signifikanter Parameter ist, der den Auslaugprozess wesentlich beeinflusst. Die Fließmitteldosis spielte bei zementären Systemen eine untergeordnete Rolle, jedoch war die Katalysatormenge bei den Polyurethanen ein signifikanter Faktor.

Mit dieser Arbeit wurde ein Einblick in die komplexen Zusammenhänge des Auslaugens von Baustoffen und deren Einwirkung auf die Umwelt gegeben. Allerdings sind weitere Untersuchungen nötig um ein besseres und noch tieferes Verständnis der Auslaugprozess zu erlangen und um die Wechselwirkungen von Eluaten mit der Umwelt zu verstehen.

Contents

Abstract	ix
Kurzfassung	xi
1 Introduction	1
1.1 Background and motivation	1
1.2 Research objectives	4
1.3 Structure of the thesis	4
2 Leaching of construction materials: A State-of-the-art review	7
2.1 Waterproofing materials	7
2.2 Leaching mechanisms and transport processes	18
2.3 Factors controlling and influencing the leaching behaviour	25
2.4 Overview of leaching methods and their evaluation	29
2.4.1 Percolation tests	29
2.4.2 Tank leaching tests	30
2.4.3 Immersion tests	31
2.4.4 Irrigation and outdoor tests	31
2.4.5 Batch tests	31
2.5 Ecotoxicological data of constituents of waterproofing materials and their environmental risk	32
2.5.1 Cement and its constituents	32
2.5.2 Polyurethane	33
2.5.3 Risk of pollution	33
3 Experimental	35
3.1 Materials, mix design and sample preparation	35
3.1.1 Eluents	35
3.1.2 Polyurethane leaching study	36
3.1.3 HIS leaching study	36
3.1.4 Cement leaching studies	38
3.1.5 Concluding overview of the materials and mix design	41
3.2 Methods	42
3.2.1 Leaching tests	42
3.2.1.1 Polyurethane leaching study	42
3.2.1.2 HIS leaching study	43

Contents

3.2.1.3	Cement leaching studies	44
3.2.2	Analytical methods	45
3.2.2.1	pH and electric conductivity measurements	45
3.2.2.2	Ion chromatography	45
3.2.2.3	Inductively coupled plasma atomic emission spectroscopy	45
3.2.2.4	Total and dissolved organic carbon	46
3.2.2.5	UV-Vis spectrometry	46
3.2.2.6	High performance liquid chromatography mass spectrometry	49
3.2.2.7	Liquid chromatography - organic carbon detection	51
3.2.3	Ecotoxicological measurements	52
3.2.3.1	Algal growth inhibition test with <i>Desmodesmus subspicatus</i>	52
3.2.3.2	Mortality assay with <i>Enchytraeus albidus</i>	53
3.2.3.3	Primary root growth test of cress (<i>Lepidium Sativum</i>) and white mustard (<i>Sinapis Alba</i>)	54
3.2.3.4	Genotoxicity determination with umuC-assay	55
3.2.3.5	Mutagenicity determination with Ames-assay	55
3.2.3.6	Statistical analysis of the ecotoxicological assays	56
4	Leaching of polyurethane systems for waterproofing purpose whilst curing	59
4.1	Experimental	59
4.2	Results and discussion	60
4.2.1	Sum parameters and electrolytes	60
4.2.2	Organic parameters	62
4.2.3	Ecotoxicological aspects	65
4.2.4	Algal growth inhibition assays with <i>Desmodesmus subspicatus</i>	65
4.2.5	Mortality assays with <i>Enchytraeus albidus</i>	68
4.3	Conclusions	70
5	Leaching behaviour of a novel cement-polyurethane hybrid material	71
5.1	Experimental	71
5.2	Results and discussion	72
5.2.1	Batch test	72
5.2.2	Tank test	74
5.2.2.1	Sum parameters, inorganic and organic species	74
5.2.2.2	Ecotoxicological Assay with <i>Enchytraeus Albidus</i>	80
5.2.3	Conclusions	83
6	Release behaviour of major elements and superplasticiser from cement suspensions	85
6.1	Experimental	85
6.2	Results and discussion	85
6.2.1	General parameters	85
6.2.2	Inorganic species	87
6.2.3	Organic species	91
6.3	Conclusions	97
7	Leaching of PCE-based superplasticiser from micro fine cement	99
7.1	Experimental	99

7.2 Results and discussion	100
7.2.1 General parameters and inorganic species	100
7.2.2 Organic species	102
7.2.3 Phytotoxicity assays	105
7.2.4 Genotoxicity and mutagenicity	108
7.3 Conclusions	110
8 Phytotoxicity of cement paste leachates	113
8.1 Experimental	113
8.2 Results and discussion	114
8.2.1 Relative root growth	114
8.2.2 Relative seed germination and germination index	119
8.3 Conclusions	121
9 General summary and conclusions	123
9.1 Leaching of inorganic ions from waterproofing materials	123
9.2 Leaching of organic species from waterproofing materials	125
9.3 Ecotoxicological effects of waterproofing materials	126
10 Outlook and suggestions for future work	129
References	131
List of Figures	152
List of Tables	154
Glossary	158
Appendices	A 1

Introduction

1.1 Background and motivation

Modern society requests high flexibility and mobility where fast travelling is a permanent and crucial component. Consequently current infrastructure has to be maintained and further development needs to be implemented whenever necessary. Construction projects in this vein are often prestigious but at the same time mandatory. Several tunnel constructions are currently under construction in the European Alps as well as in the smaller mountain ranges in Europe, but also urban tunnel constructions are realised e.g. for underground or train routes. Examples of this nature are the Brenner Base Tunnel [[BBT-Brenner Basistunnel, 2017](#)] or Stuttgart main station called Stuttgart 21 [[Deutsche Bahn-Bahnprojekt Stuttgart-Ulm, 2017](#)]. Prior to realization of such projects in-depths investigations on the surrounding geological conditions, the strength and composition of the existing rock formation as well as on the aquifer system need to be carried out. If aquiferous rock layers are detected the tunnel construction needs to be protected from water ingress. This can be done by material injection into the soil before drilling the tunnel or into the surrounding soil layer after completion of a tunnel segment (see [Figure 1.1](#)). However, not only huge prestigious constructions need to be protected from water ingress, but also houses, historical and public buildings. This plight can be circumvented by profound, durable and sustainable engineering solutions using high efficient waterproofing materials which need to be customised according to the respective application.

A typical material used for injections is cement in form of cement suspensions, mortar or concrete¹. Since Roman times concrete is an essential material. Modern construction and buildings would not be possible without this material, because it is low priced and at the same time nearly limitless available. In addition it gives architects a huge flexibility in design of buildings due to the casting possibilities of concrete. Although modern cement and concrete is used since two centuries, a tremendous development has been made by the invention of chemical admixtures. Since about 1970 chemical admixtures like plasticisers, superplasticisers and retarders are commonly used to improve the properties, the processing and the workability of concrete [[Pacheco-Torgal, 2016](#)]. Modern concreting for example in winter, would not be possible without chemical admixtures. Especially in wintertime the use of special concrete

¹ Cement is an inorganic binder that sets and hardens in a hydraulic reaction in contact with water. It is typically used to bind aggregates in order to produce mortars (aggregate size <4 mm) and concretes (aggregate size >4 mm).

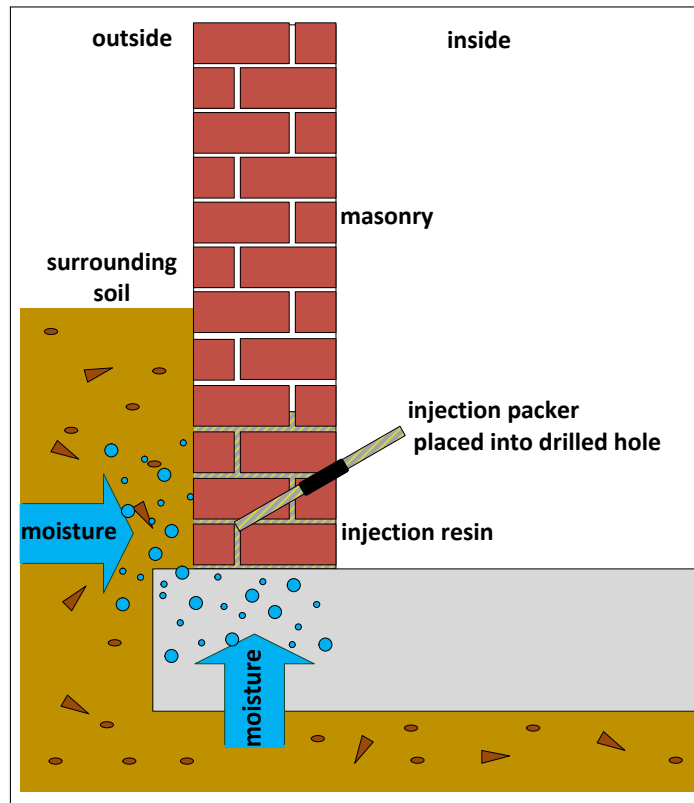


Figure 1.1: Schematic picture of injection of waterproofing materials.

mixtures including air-entraining agents in combination with accelerators or water reducers, shortens the time of initial setting, such that finishing can be accomplished quicker and high strength can be gained [Kosmatka et al., 2011, Ramachandran, 1997]. Furthermore in modern concrete systems like self-compacting concrete (SCC) or ultra high performance concrete (UHPC) chemical admixtures play a key role. A wide range of different chemical admixtures is available such that concrete compositions can be affected in whichever way needed.

There is a constantly rising global demand of concrete and according to Aitkin and Flatt [Aitkin and Flatt, 2015] some countries like Japan and Canada use at least a water reducer and an air-entraining agent in almost 100 % of every concrete mix processed. As a result the demand of chemical admixtures is constantly rising as well. In contrast to ordinary concrete mixtures cement suspensions which are used as waterproofing material exhibit water-to-cement-ratios from 0.5 to 6.0 [Girmscheid, 2012, Huth, 1996, DIN 12715, 2000, Schulze, 2002b, Schulze, 2002a] and considerably higher amounts than 5 wt.% of chemical admixtures can be used to obtain homogeneous suspensions.

Another typical material used for injections are polyurethanes. As the materials properties can be customised to the application a nearly endless variety of polyurethane products is available nowadays. In the construction sector the main fields of implementation are adhesives and sealants, floor and wall coatings, sealing membranes and thermal insulation. Quality requirements are increasing and environmental legislations are getting more stringent such that the consumption of low-solvent, solvent-free, waterborne and radiation-curing formulations of polyurethane systems is increasing [Meier-Westhues, 2007, Clemitsen, 2008].

Also composite materials made of both materials can be applied as waterproofing. These

composites may be used for special purposes with special properties utilising characteristics of the single components. In case a aquiferous rock layers is not detected before or during the tunnel construction, protection from water ingress needs to be ensured. This can be realised by material injection into the soil before drilling the tunnel or by injections into the surrounding soil layer after completion of a tunnel segment. In a worst case an aquiferous water vein is not detected in the soil investigation. As a consequence massive water ingress possess a risk to the often high-priced drilling machines and may derange the strict timetable of the construction site [Font-Capó et al., 2011, Butscher, 2012]. Due to these circumstances it is necessary to seal the water vein immediately with fast reacting, elastic but at the same time mechanically strong material.

Most constructions are in direct contact to soil and the included water or ground water. Chemical admixtures are often soluble in water and potentially leachable from the construction material. Another crucial point is the injection of polyurethane directly in the construction or in the surrounding soil, [Figure 1.1](#). As long as the chemical reaction is in progress leaching of water soluble constituents might be possible. Further reactions with the surrounding soil and water cannot be excluded. The impact on flora and fauna as well as on the ground water can just be estimated at present. Toxicological and hazardous effects on the environment cannot be excluded or avoided.

The high requirements which are set to construction materials and constructions themselves by technical regulations are getting stricter and stricter. Especially the leaching mechanisms of inorganic compounds from construction materials are repeatedly examined in scientific studies [Andac and Glasser, 1999, Barbir et al., 2012, Berger et al., 2013, Butera et al., 2014, Duong et al., 2013, Engelsen et al., 2009, Faucon et al., 1997, Faucon et al., 1996, Hernández et al., 1997]. However, investigations that cover both, leaching of inorganic and organic components are rare. Still this is a significant aspect in particular with respect to the environmental impact of corresponding leachates.

1.2 Research objectives

As illustrated above, the interest in waterproofing materials against the background of the lack of information concerning such systems form the basis for corresponding studies. To contribute to this purpose, different potential materials, namely a polyurethane, cement pastes and mortars as well as an innovative cement-polyurethane hybrid material were investigated. Leachates were obtained from these materials and further analysed based on three general research objectives as defined below:

- (i) Some knowledge on the leaching behaviour and leaching mechanisms of inorganic compounds and ionic species (Ca^{2+} , K^+ , Na^+ , Si^{4+} , Al^{3+} , Cl^- , SO_4^{2-}) has been generated in recent years. Often real concrete systems (including aggregates and supplementary cementitious materials such as fly ash and ground granulated blast-furnace slag) are used to describe and simulate the leaching behaviour and leaching mechanisms of inorganic ions. These systems are complex and the origin of ions is extremely difficult to determine. This difficulty is further enhanced as the leaching behaviour of neat Portland cement systems is rarely reviewed. Similar leaching behaviour as present in neat or blended Portland cements can be expected in cement-polyurethane hybrid materials as long as only inorganic compounds are considered. To examine this aspect in greater detail a new cement-polyurethane hybrid as developed in the course of this study is investigated using neat Portland cement as well as binary Portland cement-based binders where Portland cement is stepwise substituted by ground granulated blast-furnace slag resulting in binder compositions comparable to CEM III systems (cf. [\[DIN EN 196-1, 2005\]](#)).
- (ii) The leaching mechanisms and behaviour of inorganic species from building materials are well investigated and described while this does not apply for organic species. Besides the detection of total and dissolved organic carbon (TOC and DOC) in the leachates as sum parameters the description of the leaching behaviour of inorganic species as well as the single parameter detection (which means the single organic compound detection with e.g. liquid chromatography) needs to be conducted.
- (iii) As waterproofing materials are often in direct contact with soil and ground water the environmental effects of leachates from these materials are a crucial point. While ecotoxicological effects are often investigated using aquatic bio-assays there is a lack of information on terrestrial bio-assays. Corresponding tests are applied and evaluated with respect to hazardous and toxic impacts on the environment.

1.3 Structure of the thesis

The investigation of the leaching behaviour and the impact of waterproofing materials leachates on the environment is a challenging task due to the complexity of such systems. In order to allow for this aspect a multi-method approach was chosen. Different water proofing materials like polyurethane, hardened cement pastes and mortars and a cement-polyurethane hybrid material were investigated in order to cover a wide range of potential materials. The structure of this thesis that takes account for the above described key aspects is outlined in the flowchart presented in [Figure 1.2](#).

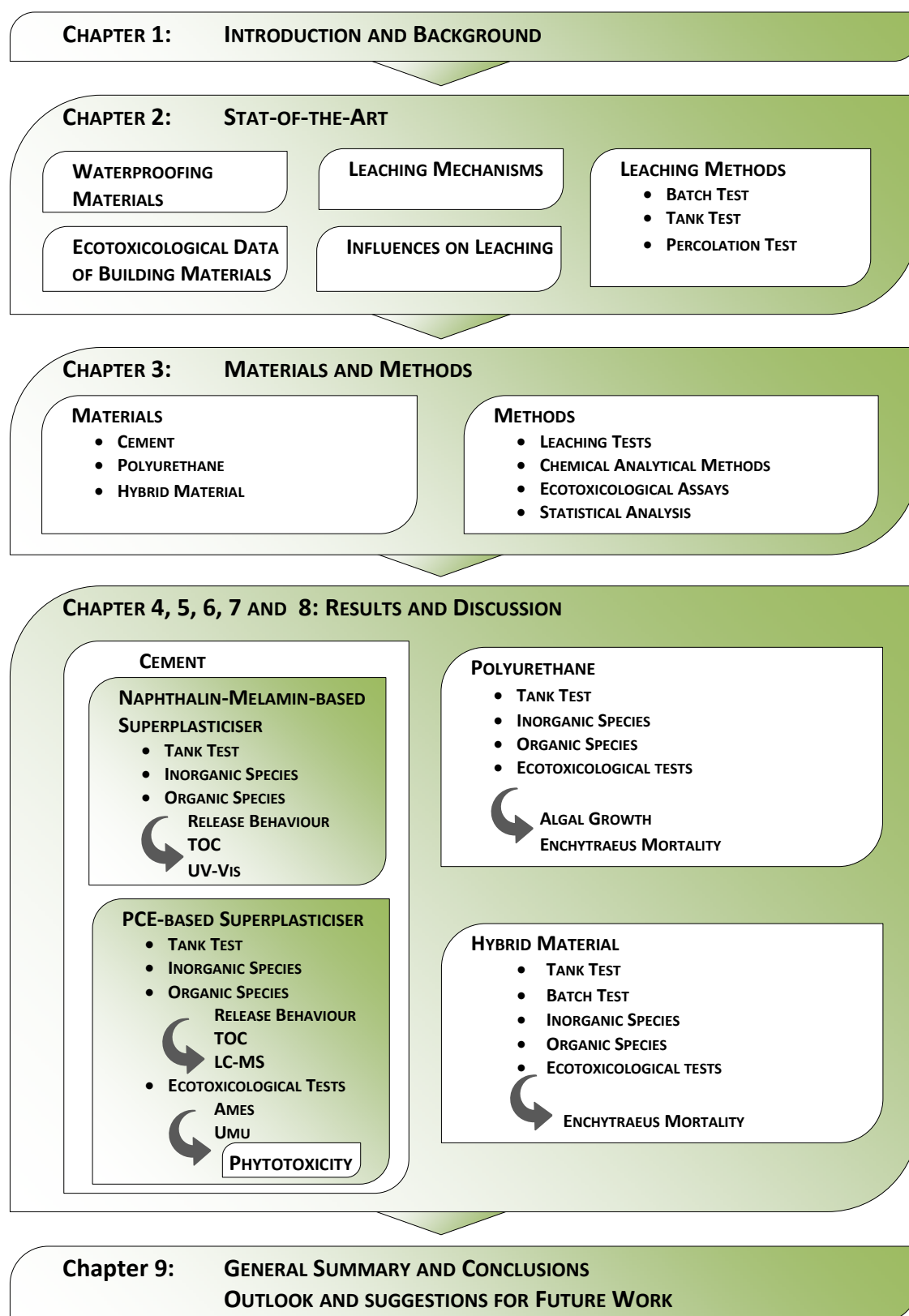


Figure 1.2: Structure of the thesis.

Leaching of construction materials: A state-of-the-art review

This chapter contains a brief summary of research into grouting materials relevant for the present thesis, namely cement and polyurethane. Leaching mechanisms and transport processes are discussed as well as factors influencing the leaching behaviour. An overview of the different leaching methods is provided as well as ecotoxicological data of the relevant grouting materials. With regard to the numerous studies available on relevant topics this overview does not claim to be complete. It is referred to appropriate specialised literature whenever possible.

2.1 Waterproofing materials

Historical background

The first public acquainted injection into a building site was performed in 1802 by Charles Bérigny, who used a suspension of water and puzzolanic cement to repair a sluice. However, he reported the injection not before 1832 [Bérigny, 1832] when he and other engineers used the method repeatedly to repair water-work buildings. One major step forward was the invention of highly hydraulic lime and the invention of Portland cements in 1824 [Haegermann, 1970]. Especially for water-work buildings and in the mining sector the demand for injections was rising. Engert [Engert, 1915] and Neumann [Neumann, 1972] summarise reports about injections in underground, mining and tunnel construction in Germany, e.g. the Schacht Rheinpreußen I in 1864 and the Forst Tunnel of the Black Forest Railway in 1872. In 1864 the English engineer Kinipple invented injection concretes and popularised the term “grouting” [Karol, 2003]. In 1887 a patent was issued to Jeziorski for a sodium silicate-based formulation which could be injected, however the chemicals reacted fast after mixing and restricted their application [Warner, 2004]. The beginning of the 20th century was marked by further development of injection techniques and the used machines. High pressure pumps driven by pressurised air and steam were developed. The possibility of high and adjustable injection pressures was given. First packers were used and according to Saclier the injection procedure and success was controlled by pressure recorders [Saclier, 1908]. In the year 1914 specified grouting of joints and seams in the ground of the Most dam (Brüx dam) in Czech Republic was performed. However, the limitation of injections at that time was given by

the comparably low grain fineness of the cement particles. Only bigger clefts down to the range of middle and coarse grained gravel were possible to fill with injections [Kutzner, 1991]. A broadened field of application was opened by the invention of chemical injections, when Lemair and Dumont injected diluted water glass in combination with diluted acid [Kutzner, 1991, Karol, 2003]. However, the gained gel was not robust and durable. In 1911 François invented a method to seal highly porous sand stone. Further development of chemical injections was done by Joosten in 1926 [Joosten, 1953], when he injected highly concentrated water glass and calcium chloride one by one to obtain a dense silicate gel. The so called Joosten-method was extensively used in 1930 when the Berlin underground was built and can be applied till the middle sand range. After 1950 chemical injections with low viscosity were invented, thus it was possible to inject into fine grained sands with low proportions of silt. Further development of injection techniques was achieved by investigations on the mechanical properties of soils and injections thereof. With the help of valve pipes it was possible to calculate statically the stabilised area [Kutzner, 1985]. In 1951 it was reported about injections of cement suspensions in drilled holes with packers and continuous pressure control [Koenig, 1951]. In addition the cement grain fineness was increased to inject into clefts of 0.08 to 0.1 mm while also injections into coarse sand were possible. Since the second half of the 20th century acrylate gel resins, epoxy resins and polyurethanes are used as injection materials [Kutzner, 1991, Martens, 1998, Warner, 2004]. Using these materials enabled for the first time injections down to silty fine sand. Ever since injection techniques were continuously developed and jet grouting is broadly applied nowadays [Croce et al., 2014].

Grouting materials

Grouting materials are used as sealings or to stabilise the soil of building sites. The main fields of application are dam projects, tunnel constructions, geological drill holes and waterproofing of buildings. A grouting material should be liquid and pumpable, while after an adjustable amount of time the grouting material starts to cure to form a firm bond with the surrounding material. A crucial parameter is the materials viscosity and for suspensions the yield point as well as the speed of sedimentation. The field of application depends on a large number of parameters such as length and the aperture of the clefts, the diameter of the voids, the state of stress in the injection area, the permeability of the rocks or soil, the chemical composition of the surrounding ground water, the desired penetration depth, equipment-specific parameters, workability, costs and environmental sustainability. Figure 2.1 demonstrates the dependence of the grouting material and the surrounding building site.

Nowadays a broad variety of grouting materials like cement-based materials, bitumen, water glass, acrylamide, polyacrylamide, acrylate resins, lignosulfonate resins, phenolic resins, aminoplast resins, epoxy resins, polyurethanes and composite materials is available on the market [Ahmed et al., 2015, Martens, 1998].

In the following grouting materials relevant for this thesis are described in detail.

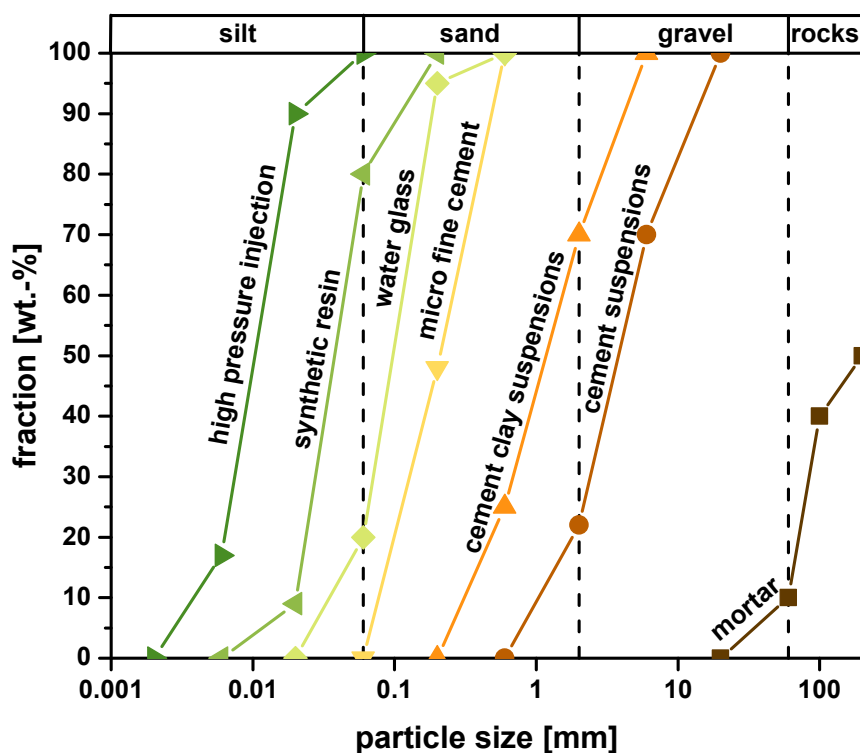


Figure 2.1: Application of soil injection materials [Wagner, 2011, Stein et al., 1992, Osebold, 2008, Martens, 1998].

Cement-based suspensions

In Figure 2.2 the global cement production is depicted [USGS, 2017] along with estimations of the global annual concrete admixture demand which have been assumed due to a lack of reliable data. The first estimation (green dots) is based on German data on sales of chemical admixtures in general in Germany [Deutsche Bauchemie e.V., 2016] and extrapolated to the global demand. The second estimation is based on standard European concrete recipes according to [DIN EN 206, 2017] where a maximum of 5 wt.% of chemical admixture with regard to the cement amount is assumed to be contained in every concrete mix (red squares). Both estimations cannot claim to be thorough, however, they show that the large quantities of chemical admixtures processed are directly related to the amount of concrete produced such that an increase of the demand is likely in future years. Cementitious grouts are the most economical and cost effective injection material and therefore most commonly used. Nearly all cement types including Portland cements and calcium aluminate cements can be used for injections [Newman and Choo, 2003]. There is a wide range of applications like grouted repairs for off-shore structures, geotechnical grouting for groundwater control and contact grouting behind tunnel linings during tunnel construction to fill the remaining voids [Raymond and Nathan, 2010]. However, the application of cementitious systems is depending on the grain size distribution, the maximum grain size and the chemical (mineralogical) composition. Cementitious grouting systems are characterised by their hydraulic reaction in contact with water. To reduce the carbon footprint of such systems the cement fraction is partially replaced by fillers (sand, clay, lime stone, activated bentonite, etc.) and supplementary cementitious materials (SCM) (ground granulated blast-furnace slag, fly

ash, etc.)². The properties of cement-based suspensions are adjusted using stabilisers (bentonite) [Smoltczyk, 2003], plasticisers and superplasticisers, accelerators (sodium silicate), air-entraining agents (alkyl sulphates), retarders (sodium phosphate, sodium gluconate) and expanding agents (aluminium powder).

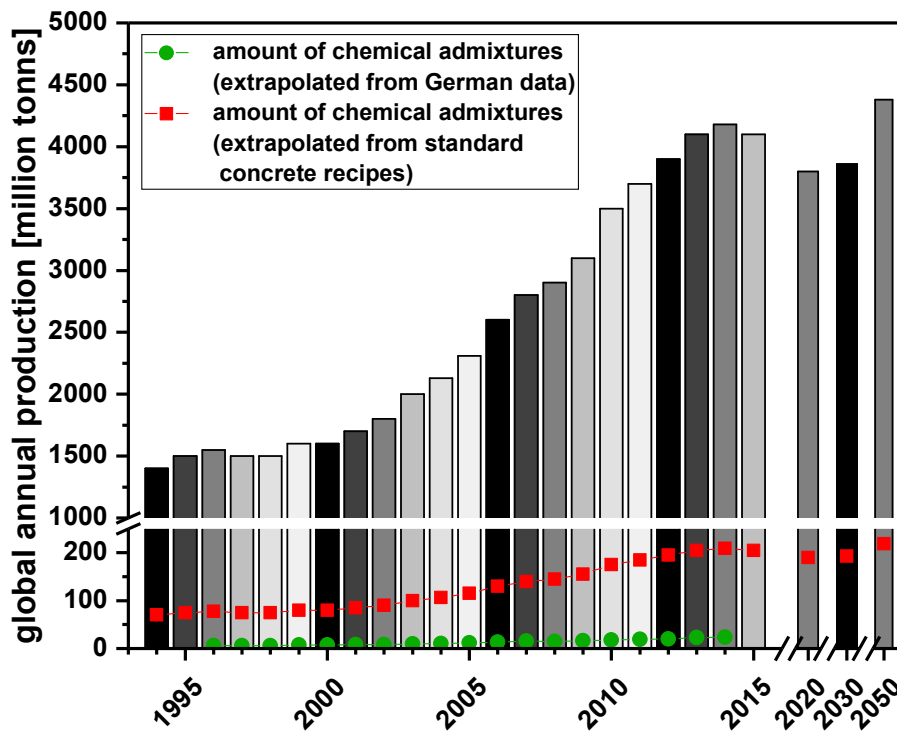


Figure 2.2: Global cement production [Khatib, 2016, Schneider et al., 2011, USGS, 2017] and the amount of used chemical admixtures extrapolated from German data and from standard concrete recipes.

The following requirements should be fulfilled by (micro fine) cement-suspensions:

- Formation of a stable suspension
- Low viscosity (and possibly thixotropic)
- Adequate working time at low and high temperatures
- Rapid setting and hardening
- Low segregation
- Low shrinkage
- Good adhesion
- Sufficient tensile and compressive strength

²The production of cement clinker causes 5–8 % of the global man made CO₂ emissions [Schneider et al., 2011, Damtoft et al., 2008]. In addition SCM affect the reaction of Portland cement by acting initially as (quasi-)inert addition and at later stage due to their chemical reaction, which depends on the type, fineness and composition of the SCM [Schöler et al., 2017].

Compressive strength of cement grouts is located in a range from 0.2 N mm^{-2} to 80 N mm^{-2} [Dhir and Henderson, 1999]. This wide range corresponds to the water-to-cement ratio which can range from 0.5 to 6.0 [Schulze, 2002a]. The utilisation of normal cements is limited to pore sizes or voids in the soil or masonry $>200 \mu\text{m}$ and a soil permeability of $> 10^{-3} \text{ m s}^{-1}$. To broaden the scope of application of cementitious grouts microfine and ultrafine cements which exhibit a high grain fineness can be utilized [Huth, 1996, Schulze, 2002a]:

- ordinary Portland cement $d_{95} > 40 \mu\text{m}$
- microfine cement $20 \mu\text{m} < d_{95} \leq 40 \mu\text{m}$
- ultrafine cement $d_{95} \leq 20 \mu\text{m}$

Despite this clear classification with respect to the grain fineness the term microfine cement is used differently [Pantazopoulos et al., 2012, Perret et al., 2000, Littlejohn, 2003, Henn and Soule, 2010] by various institutions:

- International Society for Rock Mechanics: $d_{95} < 16 \mu\text{m}$ [Widmann, 1996, Hemphill, 2012]
- American Concrete Institute Committee 552: $d_{\text{max}} < 15 \mu\text{m}$ [Henn, 1996, Hemphill, 2012]
- Portland Cement Association: $d_{\text{max}} < 10 \mu\text{m}$ [Kosmatka et al., 2002, Hemphill, 2012]

Microfine and ultrafine cements can be manufactured by grinding of Portland cement, slag or a combination of these [Henn et al., 2003]. Compared with ordinary cement grouts microfine cement grouts exhibit a finer grain size distribution, better flow properties and bleed characteristics [Mollamahmutoglu and Avcı, 2015] at an initial setting time of four to five hours [Reuben et al., 2003]. Yet, grinding to high grain fineness is an energy-intensive process such that microfine cements are comparatively expensive.

Concrete is often falsely attributed to only contain cement, water and aggregates. Its composition changed in the last decades from a ternary system to a multi-component system by adding SCMs like fly ash, ground granulated blast-furnace slag and various organic additives like superplasticisers, retarders, accelerators etc. In the following relevant materials for this thesis are further described.

Figure 2.3 presents an overview of different cementitious materials and their composition according to [Lothenbach et al., 2011]. Relevant for this thesis is only blast-furnace slag, which is a by-product of the pig iron production. According to [RILEM TC 73-SBC, 1988] blast-furnace slag is a non-metallic product consisting essentially of silicates, aluminosilicates, calcium and of other bases. In the blast-furnace a mixture of iron oxide ore, coke and limestone (fluxing agent) is heated/molten at temperatures of about 1500°C . Thereby the iron oxide is reduced to metallic iron due to the presence of coke while a slag is formed on top of the molten iron which consists of silicates and alumina originating from the iron ore and oxides from the limestone. When the blast furnace is tapped, the liquid slag is cooled by use of high pressure water jets. The rapid quenching results in a wet and sandy granular material. Due to the high rate of cooling the formation of larger crystals is suppressed such that contents of amorphous/glassy phases (calcium aluminosilicates) of up to 100 wt.% are obtained. This granular material is further processed by drying and milling, hence its denotation 'ground granulated blast-furnace slag' [E DIN EN 197-1, 2014].

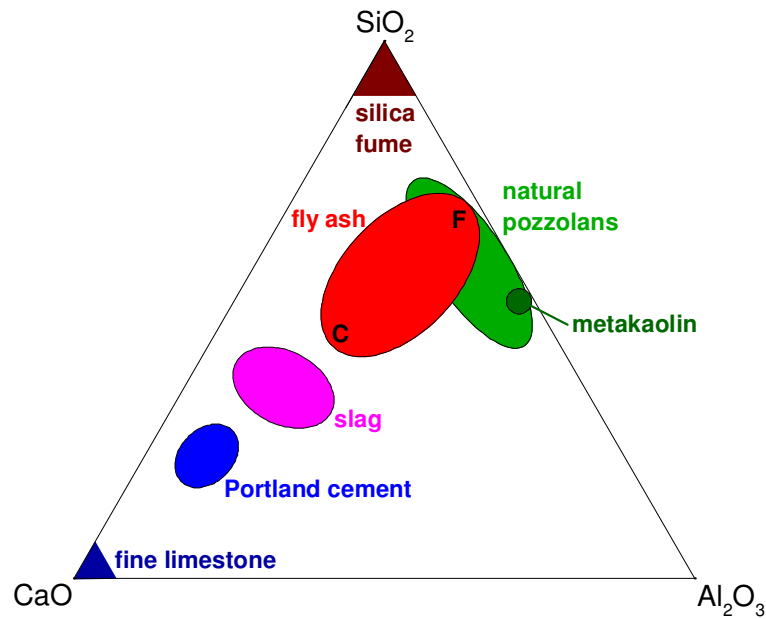
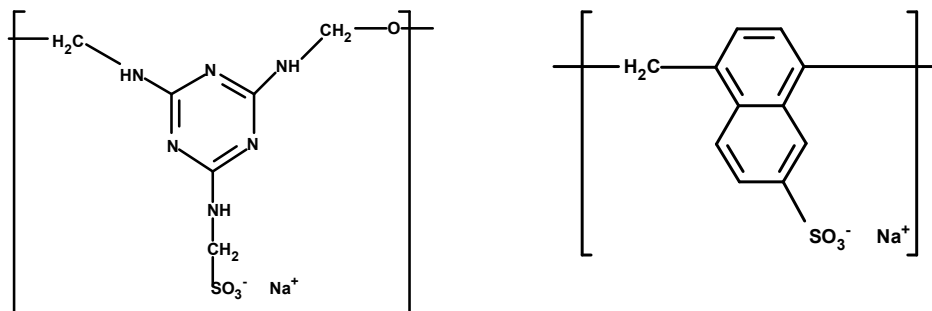


Figure 2.3: $\text{CaO}-\text{Al}_2\text{O}_3-\text{SiO}_2$ ternary diagram of cementitious materials. Reproduced from [Lothenbach et al., 2011].

For grouting materials used to strengthen the ground or an existing concrete structure the strength of a grouting material is important. When using cementitious materials the strength can be influenced by the water-to-cement ratio, i.e. the lower the w/c-ratio the higher the resulting strength. However, for cementitious grouting materials the w/c-ratio is higher because of different reasons like higher water demand of micro fine cements or the soil absorbs water during grouting. As the workability is dramatically reduced with decreasing w/c-ratio the use of chemical admixtures is necessary to influence and adjust the adequate physical properties (c.f. Table 2.1).



Melamine sulfonate formaldehyde condensate

Naphthalene sulfonate formaldehyde condensate

Figure 2.4: Chemical structure of melamine sulfonate formaldehyde condensate (left) and naphthalene sulfonate formaldehyde condensate (right).

Plasticisers and superplasticisers are the most important groups to adjust the cement workability without increasing the water-to-cement ratio. Plasticisers like lignosulfonate were first introduced in the construction sector in the 1920s [Plank, 2005, Lou et al., 2013]. In the 1960s superplasticisers like melamine and naphthalene sulfonate formaldehyde condensates (MFS and NFS) were introduced in the building materials sector (c.f. Figure 2.4).

During the polycondensation production process of melamine and naphthalene sulfonate formaldehyde condensates resinous polymers with a variable degree of cross-linking are manufactured. The main component of NFS is repeated 3 to 7 times. Commercially available products include an amount of active component from 30 wt.% to 50 wt.%. Compared to lignosulphonates they show an improved influence on the physical properties of cement pastes while at the same time their retarding effect is lower. In addition they are compatible with other chemical admixtures. MFS are also produced in a polycondensation reaction while its main components are repeated 4 to 10 times.

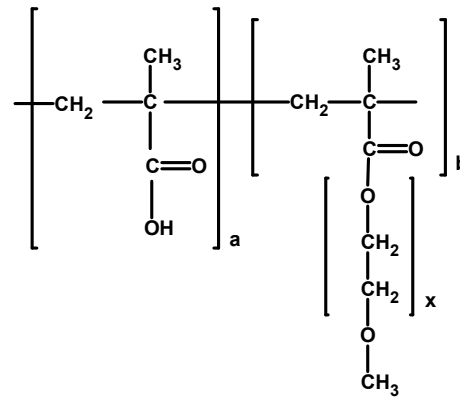
Table 2.1: Concrete admixtures by classification. Partially reproduced from [Aïtcin and Flatt, 2015].

effect	classification
increase flowability of concrete, reduce w/c-ratio	sulfonated mealmine formaldehyde condensates, sulfonated naphthalene formaldehyde condensates, lingnosulfonate materials, polycarboxylates
reduce water content at least 5%	lingnosulfonates, hydroxylated carboxylic acids, carbohydrates
retard setting time improve pumpability	lignin, borax, sugars, tartaric acid and salts organic and synthetic polymers, organic flocculants
decrease permeability	latex, calcium stearate
accelerate setting and early strength development	calcium chloride, triethanolamine, sodium thiocyanate, calcium formate, calcium nitrate, calcium nitrite
decrease air content	tributyl phosphate, dibutyl phthalate, actyl alcohol, silicones
improve durability in freeze/thaw	salts of wood resins, synthetic detergents,
improve workability	salts of sulfonated lignin, etc.
reduce alkali-aggregate reactivity expansion	barium salts, lithium nitrate, etc.
cohesive concrete for underwater placement	cellulose, acrylic polymer
increase bond strength	styrene copolymeres, polyvinyl chloride, polyvinyl acetate, acrylics, butadiene
coloured concrete	modified carbon black, iron oxide, phthalocya- nine, chromium oxide, titanium oxide, cobalt blue
retard moisture penetration into dry concrete	soaps of calcium, ammonium stearate, oleate butyl stearate, petroleum products
control bacterial and fungal growth	polyhalogenated phenols, copper compounds, etc.
cause expansion before setting	aluminium powder

The MFS based superplasticisers exhibit an amount of active component of 20 wt.% to 40 wt.%. As cement particles are mostly positive charged³, the negative charged sulphonic acid group SO_3^{2-} of the polycondensates are adsorbed on the cement particles. This results in a negative charged surface of the cement particles such that the resulting repulsive electrostatic forces between the particles cause a dispersing effect. However, the dispersing effect is short in time and limited at low w/c-ratios [Lei and Plank, 2012, Plank et al., 2008, Benedix, 2008].

³Cement is a so called patched-particle, which means that the surface of the particle is positively and negatively charged depending on the underlying clinker phase.

In the middle of the 1980s superplasticisers based on polycarboxylates were introduced [Plank et al., 2008]. These comb-shaped polycarboxylates (PCE) (see Figure 2.5) consist of an adsorptive backbone and a hydrophilic polyethylene-oxide (PEO) side chain [Zingg, 2008, Puertas et al., 2005, Ferrari et al., 2010, Ferrari et al., 2011].



Polycarboxylate ether

Figure 2.5: Chemical structure of comb-shaped PCE [Aïtcin and Flatt, 2015].

Side chain density and length can be varied during the production process to take control of the adsorption behaviour and the dispersion ability. According to [Winnefeld et al., 2007] two main process routes of comb-shaped PCEs are known.

1. Radical polymerization of (meth)acrylic acid and optional other comonomers to form the backbone followed by polymer analogue linking of mono end-capped polyethylene glycoles ('alkyl-PEG').
2. Preformation of mono unsaturated 'teeth' via linking of (meth)acrylic acid units with alkyl-PEGs followed by radical copolymerization of these macromonomers with additional (meth)acrylic acid and optional other comonomers.

In general the negatively charged carboxyl groups (COOH) of the backbone adsorb on the positively charged cement particles. In addition to electrostatic forces the side chains stabilise the binder suspension with the help of steric/repulsive forces [Anagnostopoulos, 2014]. Depending on the flexibility of the PCE different kinds of adsorption phenomena such as loops, trains and tails can occur (see Figure 2.6).

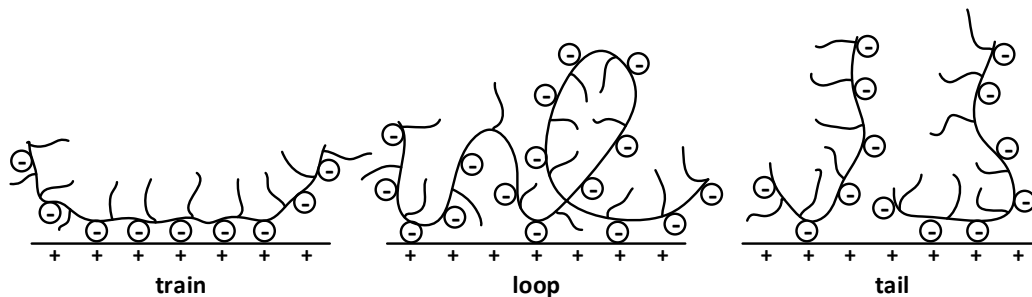


Figure 2.6: Adsorption phenomena of PCEs on particle surfaces. Reproduced from [Benedix, 2008].

In general the dispersing effect of PCEs is higher compared to NFS and MFS. A summarised comparison of polycondensates and polycarboxylates is given in [Figure 2.7](#).

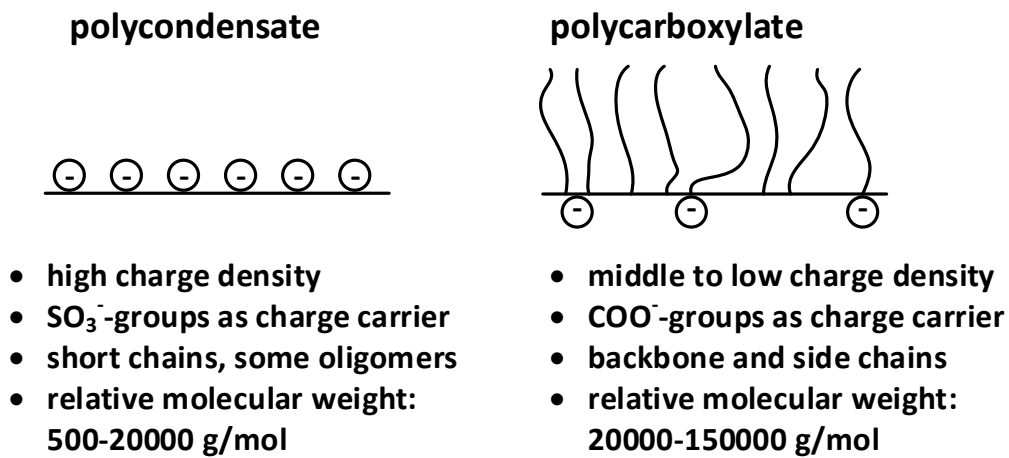


Figure 2.7: Comparison between polycondensate and polycarboxylate superplasticisers [[Benedix, 2008](#), [Ferrari et al., 2011](#), [Ferrari et al., 2010](#)].

Polyurethane resins

Polyurethane is relatively new on the construction sector as first sealants were introduced in the markets in the mid-1960s [[Mittal and Pizzi, 2009](#)]. In 1937 Heinrich Rinke produced 1,6-hexamethurethanes (DHI) and Otto Bayer discovered the diisocyanate polyaddition process [[Meier-Westhues, 2007](#), [Szycher, 2012](#)]. Ever since polyurethanes were developed further for a broad range of applications such as wood finishing, coatings, construction or corrosion protection and can be manufactured as foams, fibres, coatings etc. The different market shares for 2015 are depicted in [Figure 2.8A](#), which do not differ much over the years.

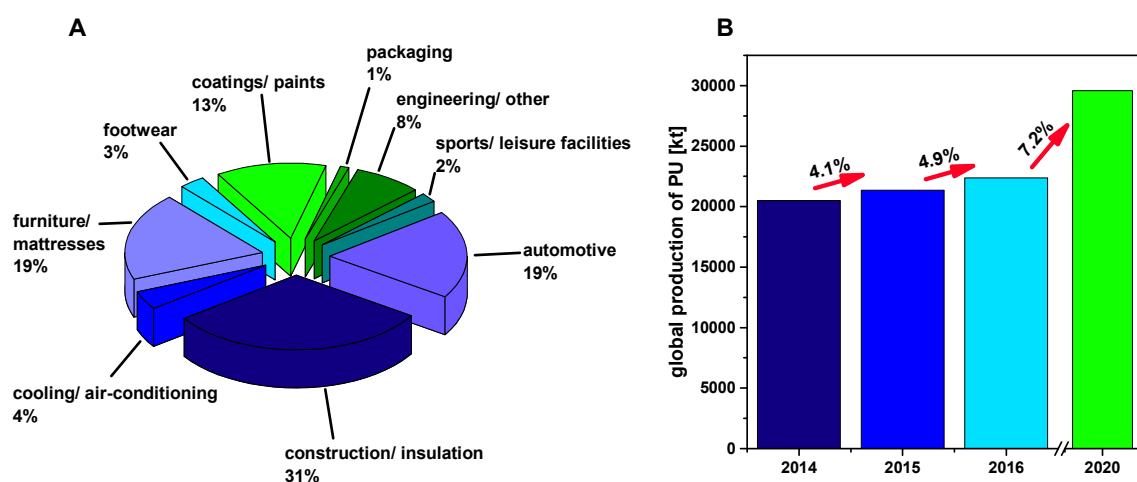
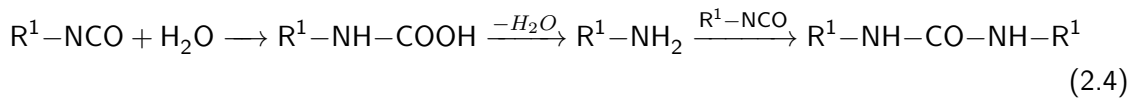
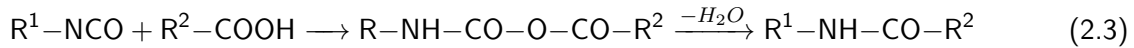
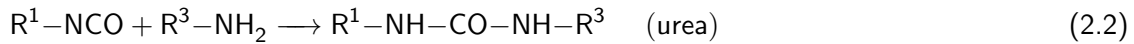
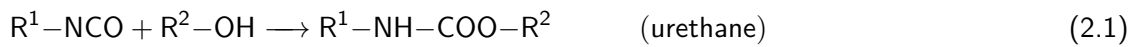


Figure 2.8: Global PU market segments 2015 (A) and global annual PU production with average annual growth rate indicated with arrows (B) [[Austin and Hicks, 2016](#), [IAL consultants, 2017](#), [FSK, 2017](#)].

However, the global annual polyurethane production is rising constantly (Figure 2.8B) with an average annual growth rate of up to 5 % per year [Austin and Hicks, 2016, IAL consultants, 2017, FSK, 2017]. Polyurethane grouting materials are cost-intensive such that they are used only for special applications like filling, sealing and waterproofing of (aquiferous) joints as well as for injection plugs in karst cavities. The material results from a polyaddition reaction, where component A (a polyalcohol or a hydroxylgroup containing component) and component B (1,1'-Methylenebis(4-isocyanatobenzene) MDI, homologes, isomeres) are the reactants. Component A can be polyether polyols, polyester polyols or glycols. It has to be noted that one-component PU resins are also available, but handling is difficult. Depending on the type of isocyanate used different reactions can proceed to form PU. The reaction of the isocyanate with alcohols, amines, carbon acids and water [Leppkes, 1996] is depicted in equations (2.1), (2.2), (2.3) and (2.4).



The main reaction partners of isocyanates are polyalcohols and OH-functional esters. Carbon acids are involved when polyesterpolyols are used as component A and the carboxyl group is not fully esterified. Amines and/or tin salts are used as catalysts to promote and adjust the reaction. Reactions with water or air humidity, which are used as blowing agents, lead to CO₂ release and expansion. The bubble size is controlled by surface active agents. Depending on the reaction with water PU grouts can be divided into hydrophilic and hydrophobic [Joyce, 1992].

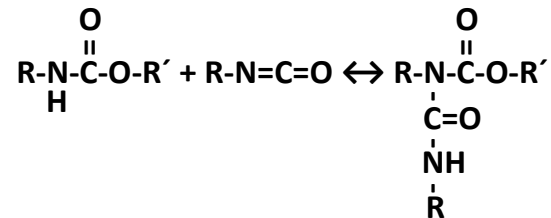
According to [Joyce, 1992] PU seals in three ways:

- Formation of chemical bond to the concrete/mortar/rock surface
- Formation of a mechanical anchor by entering the pores and voids
- Formation of a compression seal within the crack, joint or void to act as a waterstop

Due to azide hydrogen atoms in the compounds, the formed urethane and urea are able to react further with isocyanates to form biuret and allophanate (see Figure 2.9). Isocyanates are able to react in oligomeric reactions, which is depicted in Figure 2.10. In general all listed reactions are possible during polyurethane production, but with the help of catalysts some reactions can be promoted or suppressed [Becker et al., 1993, Oertel and Abele, 1983]. PU occupies the most important position in the chemical grouting materials area due to its adjustable properties. The material possesses good mechanical properties [Yang et al., 2017],

is easy to adjust to the building site conditions and the viscosity which can be adjusted with e.g. acetone [Jiacai et al., 1982] is located in a range from 10 Pas to 1000×10^{-3} Pas. PU is excellent abrasion resistant and features both properties of plastics and elastomers [Xiang et al., 2006]. The gel time can be adjusted by the catalyst dosage and is in the range of seconds to several minutes or hours [Bodi et al., 2012].

biuret formation



allophanate formation

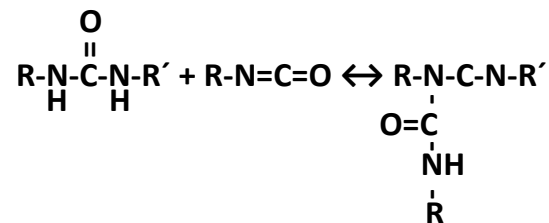


Figure 2.9: Consecutive reactions of urethane chemistry [Clemitsen, 2008, Becker et al., 1993, Leppkes, 1996].

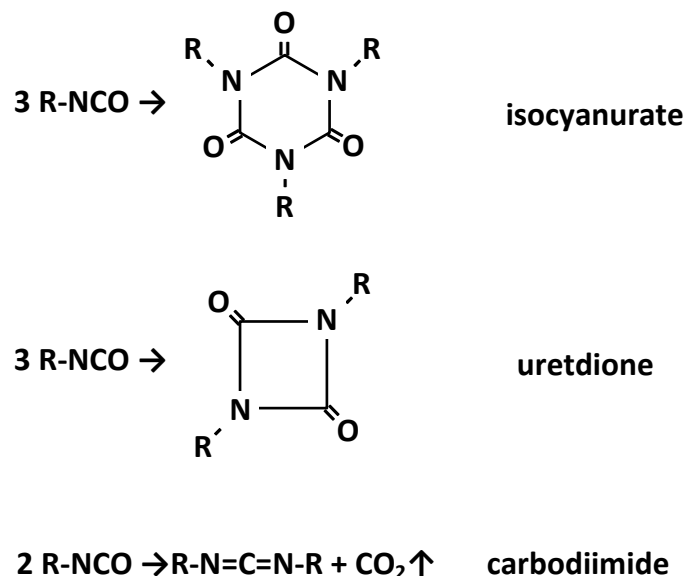


Figure 2.10: Oligomerisation reactions of isocyanates [Clemitsen, 2008, Becker et al., 1993, Leppkes, 1996].

Composite materials

Composite materials are made from at least two constituents with different physical and/or chemical properties. The combination of grouting materials can limit the disadvantages and favours the advantages. For example inorganic grouting materials like cement shrink during curing and exhibit unsatisfactory elasticity, which can result in insufficient grouting performances. In addition the poor penetration of inorganic materials into the soil leads to short length of grouting. Organic grouting materials are high in price and inflammable. A combination of inorganic and organic grouting materials might reduce the costs and enhance the materials properties. A wide variety of material combinations is possible and listed in Table 2.2.

Table 2.2: Material combinations for composite grouting materials.

component 1	component 2	reference
polyurethane	waterglass	[Yang et al., 2017, He et al., 2016], [Starovoitova et al., 2009], [Shan and Liu, 2011, Guan et al., 2012] [Hong et al., 2015]
cement	asphalte	[Pei et al., 2016]
inorganic particles	polyurethane	[Xiang et al., 2006]
epoxy resin	inorganic particles	[Pinto et al., 2015b, Pinto et al., 2015a], [Keivani et al., 2014]
epoxy resin	cement	[Anagnostopoulos et al., 2016], [Shamsuddoha et al., 2013], [Issa and Debs, 2007], [El-Hawary and Abdul-Jaleel, 2010], [Perfilov et al., 2016]
cement	hollow glass spheres	[Hussain et al., 2014, Hussain et al., 2013]
polyurethane	cement	[Duan et al., 2012, Faramarzi et al., 2016]
urea-formaldehyde	cement	

The main goal of these composites is to enhance the unique properties of the material and to combine the advantages of organic and inorganic grouting materials. Special designed composite grouting materials are used for applications like Stuttgart main station (Stuttgart 21) [Deutsche Bahn-Bahnprojekt Stuttgart-Ulm, 2017] taking into account the kind of surrounding soil or rock, the kind of water ingress, etc.

2.2 Leaching mechanisms and transport processes

Different processes and properties, either of chemical or physical nature, control the leaching and/or binding mechanisms of building materials. Chemical processes can be e.g. changes in pH-value, incorporation of ions in more or less soluble phases as well as precipitation of hydrate phases. Physical parameters are e.g. temperature, permeability and porosity. Solubility is an important parameter which determines the kind of transport process [de Groot et al., 1999] such that distinguishing of ions according to their solubility is possible [Moszkowicz, 1998, Moszkowicz et al., 1997, de Groot et al., 1999]:

1. Elements that remain soluble at any pH-value e.g. Na^+ and K^+ .
2. Elements that are soluble in acid solutions but precipitate in alkaline solutions e.g. Cd^{2+} .

3. Elements that are similar to (2) except for partial or total re-dissolution in highly alkaline solutions ($\text{pH} > 10$) e.g. Al^{3+} , Cu^{2+} , Zn^{2+} , Pb^{2+} (amphoteric character) (see [Figure 2.11](#)).
4. Elements that are present in solution in oxo-anionic form e.g. CrO_4^{2-} , $\text{Cr}_2\text{O}_7^{2-}$.

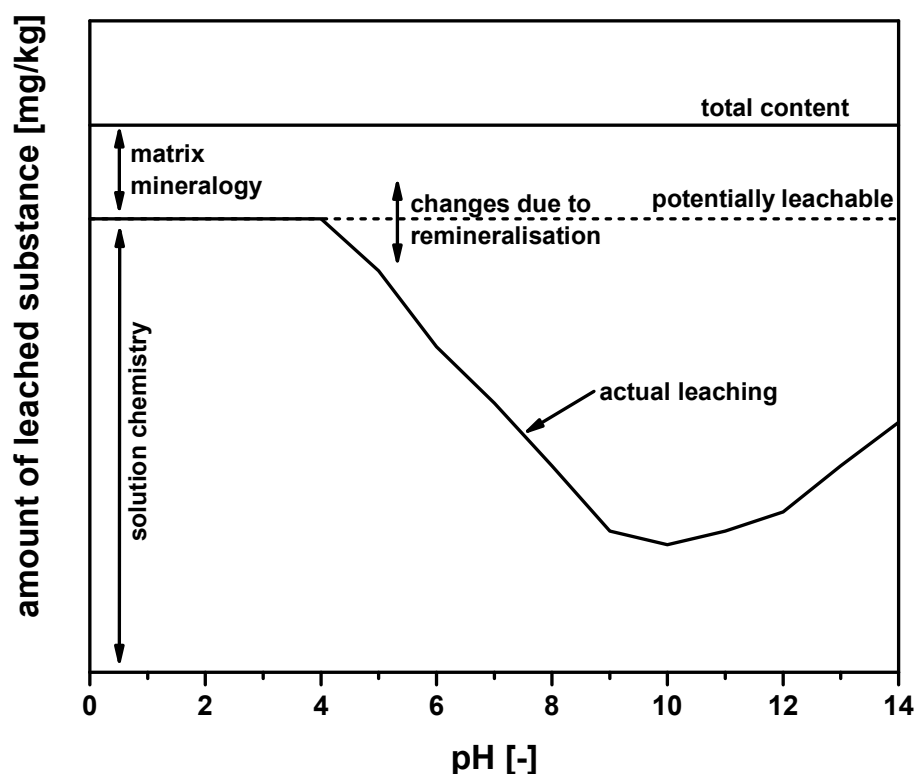


Figure 2.11: Influence of pH on bound and available fractions of a component with amphoteric character [van der Sloot and Dijkstra, 2004, de Groot et al., 1999].

So far it is unclear which are the dominating binding mechanisms for many compounds. For example [Hinsenveld, 1992] discussed controversially whether metal ions are physically adsorbed in the pore structure or chemically bound in the matrix.

In addition the availability of substances may also play a role in leaching. Availability describes the quantity of a component which is part of the total concentration that ultimately can leach from a material under certain conditions. Basically three different transport processes can be distinguished when a grouting material is in contact with an eluent [Hohberg, 2002]:

- Adsorbed or loosely bound compounds e.g. soluble salts can be removed from the sample surface during the first contact with the eluent. This process is called “wash-off effect” and ends after a short period of time.
- Continuous dissolution takes place when a component is soluble in the eluent. This process occurs from the outside to the inside of the sample.
- Diffusion is depending on the concentration of species in the sample and the eluent. This process can take place from the sample into the eluent and vice versa. In cementitious samples diffusion takes mainly place from the sample to the pore solution.

Depending on changes in the pH-value precipitation and dissolution can occur. At the sample surface adsorption and absorption can be found [de Groot et al., 1999].

Leaching can be described with the leaching rate $J(t)$ or the cumulative leached amount of substance $\Sigma E(t)$ (see (2.5)). The leaching rate is defined as the amount of substance, which is leached per volume/surface of the sample in function of time (see (2.6)). In close to reality leaching tests (see tank tests in Subsection 2.4) the concentration of the substances of interest is detected in each leaching step and the leaching rate can be calculated [Côté et al., 1987]. The dominant leaching mechanism can be determined by plotting the leaching rate in function of the time intervals in a double logarithmic diagram (see Figure 2.12). The nature of the prevailing leaching mechanism can be read from the slope of the resulting straight line. Thereby different mechanisms can exist for one substance at different times which results in a bend of the straight line [DAfStb-Richtlinie, 2005, DIN CEN/TS 16637-2, 2014, NEN 7341, 1995].

$$\Sigma E(t) = J(t) \cdot A \cdot dt \quad (2.5)$$

$$J_i = \sum_{n=1}^N (c_n - c_0) \frac{V_E}{A \cdot t} \quad n = 1, 2, \dots, N \quad (2.6)$$

- $\Sigma E(t)$ – cumulative leached substance [mg]
- $J(t)$ – leaching rate [$\text{mol m}^{-2} \text{s}^{-1}$] or [$\text{mg m}^{-2} \text{s}^{-1}$]
- A – sample surface [m^2]
- J_i – leaching rate per interval [$\text{mol m}^{-2} \text{s}^{-1}$]
- c_n – concentration of substance in leachate per interval [mol m^{-3}]
- c_0 – blank; concentration of substance in eluent [mol m^{-3}]
- V_E – volume of the eluent [m^3]
- t – contact time [s]
- N – amount of intervals [-]

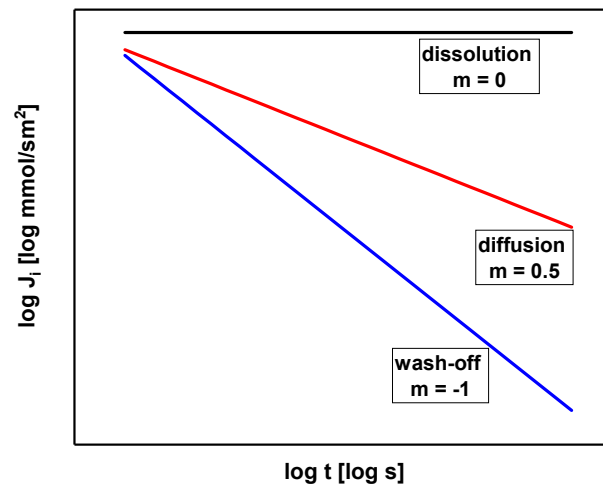


Figure 2.12: Determination of the dominating leaching mechanism (m = slope of the straight line).

Leaching models

Pure diffusion

A simple but reliable leaching model is pure diffusion, which is based on Brownian Motion. The driving force for diffusion is a concentration gradient between the sample and the surrounding which can be described by the first and second Fick's law. The first Fick's law describes steady state diffusion where the concentration gradient stays constant over time (2.7). The second Fick's law describes unsteady state of diffusion, where concentration is a function of position and time (2.8). However, to use the pure diffusion model the sample has to be saturated with water from the beginning and no chemical or physical interactions should occur [Hohberg, 2002, Beddoe and Dörner, 2005].

$$J = -D \frac{\partial c}{\partial x} \quad (2.7)$$

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} \quad (2.8)$$

J – diffusion flux [$\text{mol m}^{-2} \text{s}^{-1}$]
 D – diffusion coefficient [$\text{m}^2 \text{s}^{-1}$]
 $\frac{\partial c}{\partial x}$ – concentration gradient [mol m^{-4}]

Diffusion model for leaching processes

A simple diffusional model is often used to describe the leaching process like in the tank tests. Equations (2.9) and (2.10) are valid if the leached substances are transported fast enough away from the sample and the surface concentration is negligible. Furthermore it is assumed that the substances of interest are homogeneously distributed, the effective diffusion coefficient is constant, no chemical reactions take place and the leached substances are sufficiently soluble in the eluent [Crank, 1975, Amarantos et al., 1985, Batchelor, 1990, Barna et al., 1994, Barna et al., 1997, Tiruta-Barna et al., 2006, Jackson, 2005, Godbee et al., 1980].

$$J(t) = -D_e \left. \frac{\partial c}{\partial x} \right|_{x=0} = c_{0,mo} \cdot \sqrt{\frac{D_e}{\pi \cdot t}} \Rightarrow D_e = \pi \cdot t \left(\frac{J}{c_{0,mo}} \right)^2 \quad (2.9)$$

integrated as a function of time:

$$\Sigma E(t) = 2 \cdot A \cdot c_{0,mo} \sqrt{\frac{D_e \cdot t}{\pi}} = k_3 \cdot t \quad (2.10)$$

$J(t)$ – leaching rate [$\text{mol m}^{-2} \text{s}^{-1}$] or [$\text{mg m}^{-2} \text{s}^{-1}$]
 $\Sigma E(t)$ – cumulative leached substance [mg] or [mmol]
 A – sample surface [m^2]
 D_e – effective diffusion coefficient [$\text{m}^2 \text{s}^{-1}$]
 t – contact time [s]
 $V_{c_{0,mo}}$ – mobilised concentration of substance i in sample at time $t=0$ [mmol m^{-3}]
 k_3 – empirical constant [$\text{mmol s}^{-0.5}$]

However, chemical and physical interaction processes such as hindered diffusion and fixed substances in the matrix are not considered [Togerö, 2004]. Two major cases can be differentiated:

1. Fast reaction compared to diffusion; a constant chemical equilibrium between solved and unsolved substances [Côté et al., 1987, Godbee et al., 1978, Godbee and Joy, 1974] (2.11).
2. Slow reaction [Côté et al., 1987, Godbee et al., 1978, Godbee and Joy, 1974] (2.12).

$$J(t) = (c_{mo} - c_{im}) \cdot \left(\frac{D_e}{(1 + K_d) \cdot \pi \cdot t} \right)^{0.5} \quad (2.11)$$

$$J = c_T \cdot \sqrt{D_e^1 \cdot k} \cdot \left(\operatorname{erf} \sqrt{k \cdot t} + \frac{\exp(-k \cdot t)}{\sqrt{\pi \cdot k \cdot t}} \right) \quad \text{with} \quad D_e^1 = \frac{D_e}{\frac{c_T}{c_e}} \quad (2.12)$$

$$J(t) = c_T \cdot \sqrt{\frac{D_e^1}{\pi \cdot t}} \quad \text{if the elution time is short} \quad (2.13)$$

$$J = c_T \cdot \sqrt{D_e^1 \cdot k} \quad \text{if the elution time is long} \quad (2.14)$$

$J(t)$ – leaching rate $[\text{mol m}^{-2} \text{s}^{-1}]$ or $[\text{mg m}^{-2} \text{s}^{-1}]$
 D_e^1 – effective diffusion coefficient $[\text{m}^2 \text{s}^{-1}]$
 c_{mo} – mobilised concentration of substance $[\text{mmol m}^{-3}]$
 c_{im} – immobilised concentration of substance $[\text{mmol m}^{-3}]$
 t – contact time $[\text{s}]$
 K_d – adsorption isotherme with $K_d = \frac{c_{im}}{c_{mo}} [-]$
 c_T – $(c_{mo} + c_{im})$ $[\text{mmol m}^{-3}]$
 c_e – c_{mo} at time 0 = $f \cdot c_T = c_{mo}$ $[\text{mmol m}^{-3}]$
 f – mobilised fraction $[\%]$
 D_e – cumulative leached substance $[\text{mg}]$
 k – reaction rate constant $[\text{s}^{-1}]$

The cumulative leached amount of a substance can also be empirically determined via (2.15).

$$\Sigma E(t) = k_1 \cdot (1 - \exp(-k_2 \cdot t)) + k_3 \cdot \sqrt{t} + k_4 \cdot t \quad (2.15)$$

$\Sigma E(t)$ – cumulative leached substance $[\text{mg}]$ or $[\text{mmol}]$
 k_1 – empirical constant $[\text{mmol}]$
 k_2 – empirical constant $[\text{s}^{-1}]$
 k_3 – empirical constant $[\text{mmol s}^{-0.5}]$
 k_4 – empirical constant $[\text{mmol s}^{-1}]$
 t – contact time $[\text{s}]$

Shrinking core model

The shrinking core model is similar to the diffusion model but more realistic in terms of the assumption that the ion is present in the matrix in the solid phase [Moszkowicz, 1998]. In other words this model takes into account physico-chemical effects, e.g. ion exchange, which can disturb diffusion. It considers direct solubilisation of the species present in the solid phase of the porous matrix saturated with water and its diffusional transport in the pore solution [Moszkowicz et al., 1997]. The shrinking core model involves a dissolution front, which is inside the sample, to the leaching behaviour [Moszkowicz et al., 1997] (see Figure 2.13) such that sample/particle properties as depicted in Figure 2.14 may prevail. According to [Moszkowicz et al., 1997] on the leachant side, but still in the sample, the substance is completely dissolved and on the other side of the dissolution front the concentration of the substance equals the saturation concentration.

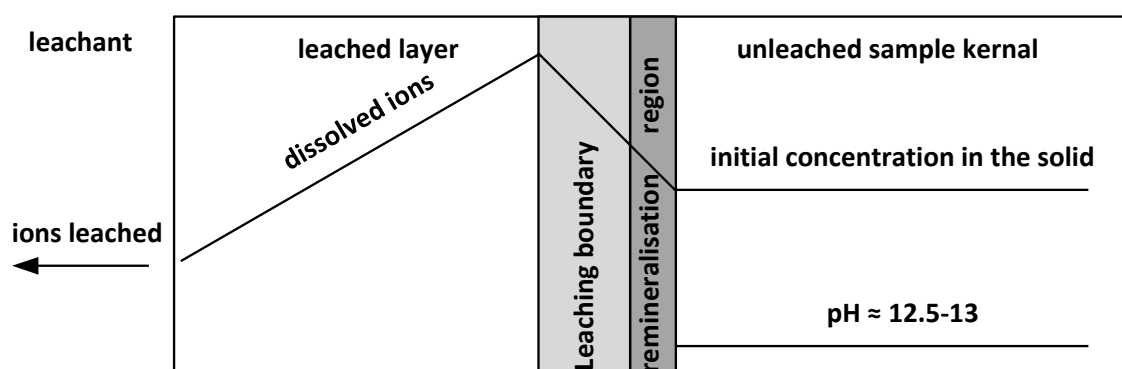


Figure 2.13: Principles of the shrinking unreacted core model according to [Baker and Bishop, 1997, Gilliam and Wiles, 1996, Hinsenveld and Bishop, 1996, Arendt et al., 2012].

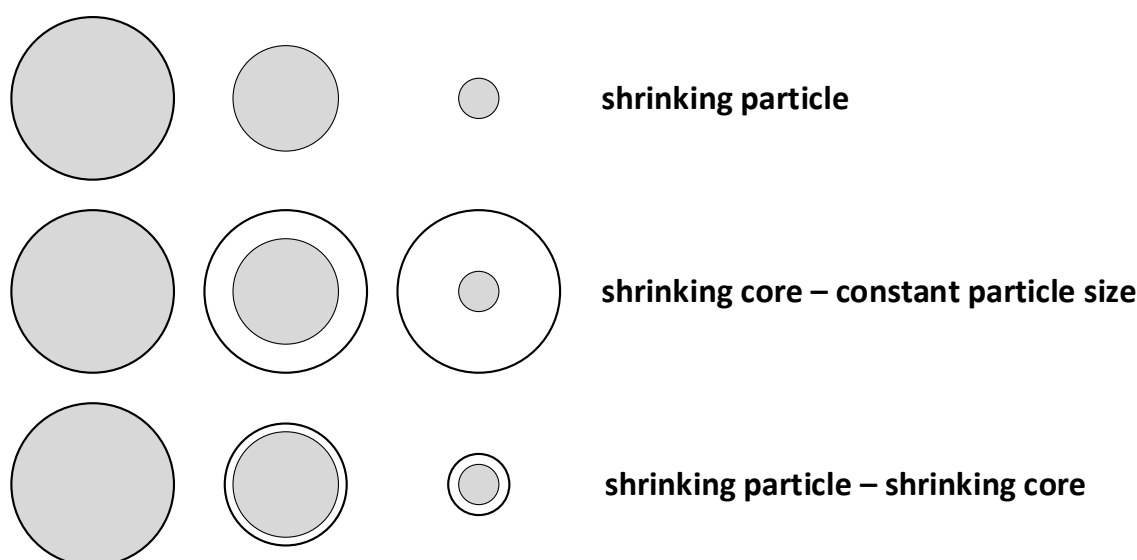


Figure 2.14: Different shrinking core models according to [Safari et al., 2009].

The main hypotheses of the model are:

1. At $t=0$ the concentration C_0 [kg m^{-3}] in the solid is homogenous.
2. The solution is saturated with respect to the solute with a constant concentration gradient (aqueous phase in the porous matrix is in equilibrium with the solid phase).

The solid core can be described as a “shrinking” core. Between the liquid interface and the dissolution front, the substance is dissolved and transported in the pore water to the surrounding leachant by diffusion which can be expressed in (2.16), (2.17) and (2.18) [Moszkowicz et al., 1997].

$$\frac{\partial c}{\partial t} = \frac{\partial^2 c}{\partial x^2} \quad \text{if } 0 < x < X(t) \quad (2.16)$$

$$-D \left. \frac{\partial c}{\partial x} \right|_{x=X(t)} = C_0 \frac{\partial x}{\partial t} \quad \text{if } x = X(t) \quad (2.17)$$

$$c = c_{sat}; C = C_0 \quad \text{if } x > X(t) \quad (2.18)$$

C_0 – initial concentration in the solid sample [kg m^{-3}]
 C_{sat} – concentration in the pores when saturated [kg m^{-3} liquid]
 X – position of the dissolution front [m]

According to [Baker and Bishop, 1997, Togerö, 2004] a simplified solution of the equations under the assumption that the amount of substance between the front and the surface is marginal ($C_{sat} \ll C_0$) is given in (2.19) and (2.20).

$$X = \sqrt{\frac{2 \cdot D \cdot C_{sat}}{C_0}} \cdot \sqrt{t} \quad (2.19)$$

$$Q(t) = X(t) \cdot C_0 = \sqrt{2 \cdot D \cdot C_{sat} \cdot C_0} \cdot \sqrt{t} \quad (2.20)$$

The shrinking core model is extended and further developed by [Sanchez et al., 2003, Safari et al., 2009, Homma et al., 2005, Segura et al., 2013, Beddoe and Dorner, 2005, Beddoe, 2016]. Faucon et al. were one of the first who used the shrinking core model to explain the leaching behaviour of cement [Faucon et al., 1996, Faucon et al., 1997, Faucon et al., 1998a, Faucon et al., 1998b].

2.3 Factors controlling and influencing the leaching behaviour

The release of ions is controlled and influenced by material specific factors as well as environmental factors, which is shown in [Figure 2.15](#). A key role in the release or leaching is played by:

1. Chemical processes e.g. dissolution of mineralogical phases, adsorption, availability, precipitation, etc. [[van der Sloot and Dijkstra, 2004](#), [de Groot et al., 1999](#)].
2. Physical processes e.g. advection, diffusion, surface wash-off, etc.

There is always a combination of both factors accountable for leaching into the aqueous phase. Also the surrounding of the material influences the release behaviour of building materials. These “external” factors are especially important for field scenarios. Among those factors are the water flow rate, the water flow path ways, degradation of (organic) substances, influences of light, buffering function of soil, temperature, etc. [[van der Sloot and Dijkstra, 2004](#)].

Inorganic as well as organic substances can be leached from building materials. The leaching processes for organic substances may be similar to the ones of inorganic materials, however, only a few studies deal with the leaching of organic substances [[Guerandel et al., 2011](#), [Andersson and Stromvall, 2001](#)].

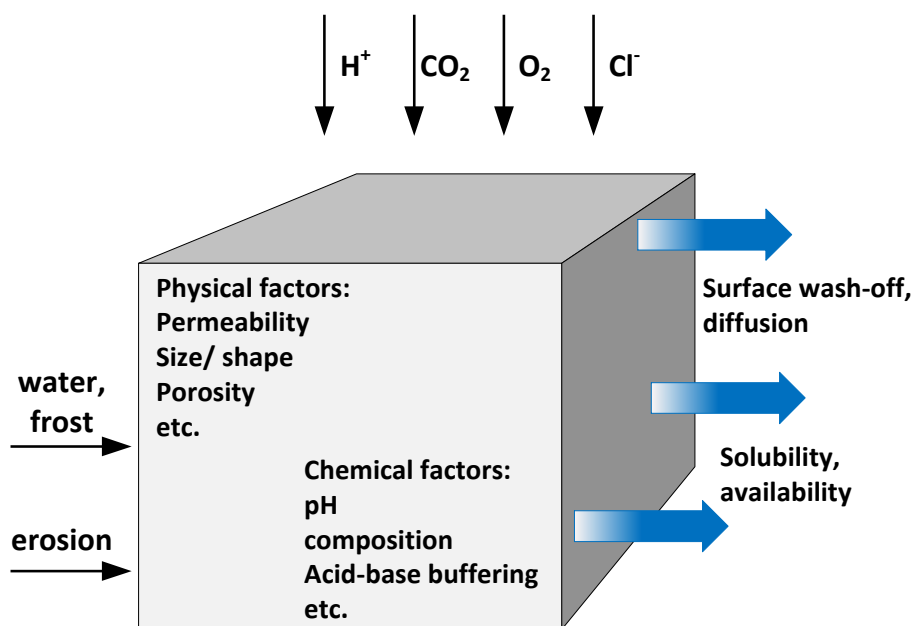


Figure 2.15: Factors influencing the leaching process [[van der Sloot and Dijkstra, 2004](#)].

Physical and chemical processes

Some basics about transport processes whilst leaching, like diffusion and wash-off effects, are discussed in detail in [Subsection 2.2](#). A further transport process is advection, which is the transport of a dissolved or suspended substance in the water flow. This phenomenon is relevant for facades impinged with rainfall [[Scherer, 2012](#)], cement-mortar-lined pipes for drinking water [[Guo, 1997](#)] and granular materials (e.g. waste) which are tested in percolation

tests [Wehrer and Totsche, 2008, van der Sloot et al., 2016]. Advection through a material is only possible for very porous materials like foams or granular material.

According to [van der Sloot and Dijkstra, 2004] leaching is based on solubility, availability and sorption processes. Sorption is an important process influencing the transport of substances during leaching. Sorption can be divided in absorption, adsorption and desorption. Absorption is the uptake of a substance without chemical reaction where the process partners need to have a certain affinity to each other. Adsorption takes place when substances are adhered or bonded at the inner or outer surface of the sample. Desorption takes place when substances are released again from the sample. The binding forces of sorption are based on permanent or temporarily states of charge. The affinities based on physical forces are usually weak and reversible, whereas chemical affinities exhibit higher bonding forces which are only partly reversible [Savric, 2001] (cf. Table 2.3).

Table 2.3: Bond types and bond energies during sorption processes.

bond type	bond energy [kJ mol ⁻¹]
Van-der-Waals-forces	4 to 8
dipole-dipole-interactions	<10
hydrophobic bond	~4
hydrogen bond	2 to 60
chemisorption ^a	125 to 800

^a covalent and coordinative bond as well as ion exchange.

A mathematical description of sorption behaviour is provided by the Henry sorption-isotherm or the Langmuir isotherm, however, both are only valid for low concentrations (see (2.21) and (2.22)).

$$q = K_d \cdot c \quad (2.21)$$

$$q = q_{max} \cdot \frac{K_L \cdot c}{1 + K_L \cdot c} \quad (2.22)$$

For high concentrations the Freundlich isotherm is valid (see (2.23)).

$$q = K_F \cdot c^n \quad (2.23)$$

K_d – partition coefficient [L g⁻¹]
 K_L – sorption constant [L g⁻¹]
 K_F – sorption constant [L g⁻¹]
 n – Freundlich-exponent
 q – absorbed amount of substance per mass unit
 q_{max} – maximum load at mono-molecular layer

Those three equations describe the complex interactions between the sample and the pore solution, where cation and anion exchange are the most relevant sorption mechanisms. An exchange of organic as well as inorganic cations is possible which follow a selective series that is influenced by the sorbent properties like valency and size. The affinity for ion exchange

is higher for smaller, high charged cations. Exchangeable anions are Cl^- , NO_3^- , SO_4^{2-} , PO_4^{3-} , aluminium- and iron oxides, whereby the exchange capacity of the last two is limited by their isoelectrical point and at a pH-value of 8-9 [Savric, 2001]. In general the ion exchange depends on the pH-value which controls the formation of surface charges. Consequently the cation exchange capacity decreases with decreasing pH-value, while the anion exchange capacity increases. The sorption kinetics of organic substances are complex and can be divided into a “slow” and a “fast” sorption (within a short period of time). Sorption of organic substances is based on the assumption that organic substances are sorbed in pores due to concentration gradients. It is believed that organic substances under moist conditions are present as a gel [Savric, 2001, Mikutta, 2006, Höll and Dahlke, 2003]. It is possible that organic substances in narrow pores are attracted from pore walls located opposite each other and thus are strongly adhered. In bottle neck pores organic substances can block the pore such that substances are trapped inside the sample, which inhibits desorption due to possible concentration gradients [Savric, 2001, Mikutta, 2006, Koß, 1997, Sun et al., 2003].

The composition and pH-value of the eluent and the pore solution significantly influence the leaching process of inorganic as well as organic compounds. The pH of the pore solution is influenced by the composition of the material and the leaching environment [Bäverman, 1997]. Depending on dissolution and sorption processes of the material the pH is affected [van der Sloot and Dijkstra, 2004]. The pH of the eluent is influenced by the pH of the material, the pH of the surrounding lechant and the buffering capacity. In general for cement-based materials the pH decreases in the course of leaching, which affects the solubility of pH-dependent constituents like alkalis and hydrates. According to [Gérard and Tang, 1998] alkalis cause a first decrease in pH from approx. 14 down to 12.6 in the eluent for cement-based materials, as they are not firmly bound in the cement matrix. The effect of hydrates on pH depends on the solubility and the diffusivity of interfering ions. For example the leaching of $\text{Ca}(\text{OH})_2$ has a strong impact on pH causing a very slow dissolution of the cement matrix [Togerö, 2004]. According to [Adenot, 1992, Faucon et al., 1996, Faucon et al., 1997, Faucon et al., 1998a, Faucon et al., 1998b] the leaching of hydrates in the cement matrix is equivalent to the deterioration of different main matrix phases, whereby the hydrates dissolve by forming a dissolution front for each hydrate (see Figure 2.16).

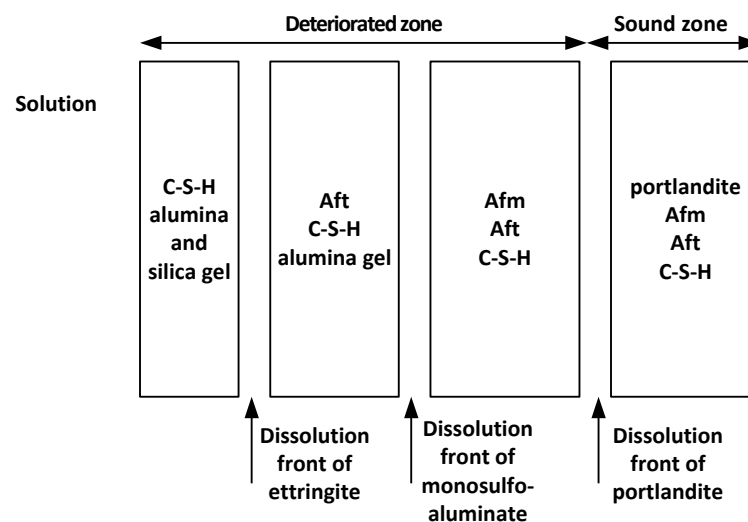


Figure 2.16: Dissolution fronts present in a cementitious material leached by pure water [Adenot, 1992, Faucon et al., 1996].

During leaching the structure of the sample is altered over time. Often an increase in porosity takes place which contributes to a change in the dissolution front. Structural and pH changes will affect the availability and the leaching rate of the constituents [Gérard and Tang, 1998].

In terms of cement-based materials carbonation, a chemical reaction between calcium hydroxide in the cement matrix and carbon dioxide from the surrounding, can occur. Carbonation is present under dry but also under moisturised conditions [Müllauer et al., 2012]. The carbonation reaction favours the formation of calcium carbonate, which will be precipitated under water-saturated conditions [Togerö, 2004]. Carbonation affects the material and the leaching thereof in different ways. For example the composition of the cement matrix will change, the pH-value of the pore solution decreases ($\text{pH} < 9$) and therefore the solubility changes and as the porosity increases due to leaching the structure of the materials changes [Andac and Glasser, 1999, Gerven et al., 2007, Gerven et al., 2004, Kazuko et al., 2005].

A very important factor that influences leaching is time. Short and long term effects can occur during the whole time scale or life time of the applied building material. The material properties can change over time (due to carbonation, erosion, etc.) and are further influenced by environmental conditions. In addition chemical processes are influenced by reaction kinetics which deal with reaction rates of chemical processes. This time dependency is present for all diffusion models.

An increase in temperature leads to increased solubility, acceleration of chemical reactions and reaction kinetics, which leads to increased transport by diffusion [van der Sloot and Dijkstra, 2004, Engelsens et al., 2012, Engelsens et al., 2017]. The effective diffusion coefficient is influenced by the temperature and can be expressed as an Arrhenius-equation (see (2.24) and (2.25)) [Page et al., 1981]:

$$D_e = a \cdot \exp \frac{-E_D}{R \cdot T} = D_0 \cdot \exp \frac{-E_D}{R \cdot T} \quad (2.24)$$

$$\ln D_e = \ln D_0 - \frac{E_D}{R \cdot T} \quad (2.25)$$

- D_e – effective diffusion constant [$\text{m}^2 \text{s}^{-1}$]
- R – ideal gas constant [$8.314 \text{ J K}^{-1} \text{ mol}^{-1}$]
- T – temperature [K]
- a, D_0 – pre-exponential factors [$\text{m}^2 \text{s}^{-1}$]
- E_D – activation energy of diffusion [J mol^{-1}]

Further physical and chemical aspects influencing the leaching results are summarised in Table 2.4.

Table 2.4: Summarised factors influencing leaching [[van der Sloot and Dijkstra, 2004](#), [Togerö, 2004](#), [Hohberg, 2002](#)].

chemical processes	physical processes	external factors
dissolution	temperature	liquid-to-solid-ratio
pH	time	contact time
chemical form	percolation	pH of environment
availability	diffusion	temperature
redox-state	wash-off	redox-state of environment/eluent
acid-base buffering	sample shape	TOC/DOC in eluent
TOC/DOC	porosity	adsorption
composition of eluent	permeability	water-to-cement-ratio
	tortuosity	chemical composition of eluent
	erosion	aggregates in sample
	sample size	degree of hydration/curing of sample
		homogeneity of sample
		binder content
		particle fineness
		type of binder/material

2.4 Overview of leaching methods and their evaluation

In the following the currently used leaching tests are discussed. Besides parameter variations, the advantages and disadvantages are presented. Depending on the stage of the life cycle of the material, leaching tests can be associated. Percolation tests and fresh-material tank tests are referred to the construction phase. Depending on the application the utilization phase can be simulated with tank tests, immersion tests and irrigation tests. The demolition and recycling phase can be assigned with batch tests.

2.4.1 Percolation tests

The percolation tests or column leaching tests are common methods and are suitable for fragmented, fine grained and shortly cured material. Here columns made of stainless steel or acrylic glass with a length of 0.5 m to 1 m and a diameter from 5 cm to 30 cm are used. The samples can be inserted in different ways, for example with a pressure vessel [[Wagner, 2011](#)] or via packing the column [[DIN 19528, 2009](#)]. In addition the contact to the eluent can be varied:

- Column leaching test with reversed flow direction (inverse percolation test): The eluent is pumped from the bottom up through the column and the material to be tested. The eluent is drained off and collected by an overflow device [[DIN 19631, 2013](#)].
- Column leaching test with direct flow direction: The eluent is guided from top to bottom of the column where it is collected.
- Static elution: The eluate remains in the column during the whole leaching time and is drained at the end of the test.
- Flow-through elution: The eluent is meandering around the sample, is led from top to bottom where it is collected [[Breitenbücher et al., 1992](#)].

With this kind of experimental set-up the L/S-ratio can be varied over a broad range. Leaching conditions can be created, which would otherwise only be possible after extremely long exposure times. Simulation of close to reality flow conditions is also possible. The percolation test is suitable for examining the disposability and the recycling compatibility of building materials such as road construction material, or to research curable materials. These test arrangements are less appropriate to cementitious systems [Wagner and Dumm, 2010] except the flow-through elution [Stein, 2004]. In addition the reproducibility is limited [Wagner, 2011].

2.4.2 Tank leaching tests

Tank leaching tests are currently the most popular leaching tests and are distinguished by national [DAfStb-Richtlinie, 2005] and international standardisation efforts, like in the technical committee CEN/TC 351 [DIN CEN/TS 16637-2, 2014]. In this test procedure monolithic materials are investigated. Besides calculating the release behaviour it is possible to determine the dominating leaching mechanism. Thus the long-term leaching behaviour can be forecasted. The test specimen is placed in a container and completely immersed in an eluent that is fully replaced after certain intervals. The eluent is collected for analysis after each eluent change. However, it is also possible to keep the eluent for the whole exposure period. The following test parameters can be varied and affect directly the concentration of the eluate:

- The ratio of volume respectively mass of eluent to sample volume or sample surface area or sample mass (L/S-ratio).
- The dimensions of the sample and thus the wettable surface.
- The time interval of the eluent replacement.
- The type of eluent.
- The initial pH of the eluent.
- The movement type of the eluent (agitated or not agitated).
- The temperature.

According to the DAfStb-Richtlinie [DAfStb-Richtlinie, 2005] and DIN CEN/TS 16637-2 [DIN CEN/TS 16637-2, 2014] the L/S-ratio is 80 L m^{-2} . The eluate is completely replaced after certain days, filtered and analysed. The cumulative release is summed up over the whole test duration. The empirically determined formula concerning the substance release during the tank leaching test, allows comparison with the de minimis threshold⁴ (DMT) (2.26) [Deutsches Institut für Bautechnik, 2009].

$$\text{val.E}_i = \frac{\text{DMT}}{0.97} \quad (2.26)$$

$$\begin{aligned} \text{val.E}_i & - \text{valid release rate } [\text{mg m}^{-2}] \\ \text{DMT} & - \text{de minimis threshold } [\mu\text{l l}^{-1}] \end{aligned}$$

⁴ The DMT is defined as the concentration at which, despite an increase in the solids content against regional background levels, no relevant ecotoxicological effects occur and at the same time comply with the requirements of the German Drinking Water Ordinance. Implemented by the German Working Group of the Federal States on Water Issues (Bund/Länder-Arbeitsgemeinschaft Wasser (LAWA)) .

2.4.3 Immersion tests

For coatings and paints the immersion tests according to [DIN EN 16105, 2011] are utilised. The test specimens are either covered with water on top of the sample or the eluent is placed under the sample. Here the L/S-ratio is 25 L m^{-2} . Typically for this kind of test procedure is the alternation of submerging and drying the sample, also called immersion cycle. Mixed fractions of two or more eluates are generated and analysed during this test. It is possible to estimate the leaching behaviour depending on the time or the eluent volume. This test can also be adopted to mineral-based systems as has been shown by [Nebel et al., 2012].

2.4.4 Irrigation and outdoor tests

Components that are exposed to rain such as façades and roofs can be tested with irrigation and outdoor experiments. Monolithic panels of the building material are produced and placed in the test device either vertical or in a certain angle whereby they can be treated with simulated rain [Nebel et al., 2012]. Simulation of continuous rain is possible as well as rain intervals with or without drying periods. The eluent quantity and intensity can be adjusted to certain geographical regions using corresponding meteorological data [Vollpracht and Brameshuber, 2010]. [Burkhardt et al., 2011] describe a similar design of a weathering chamber, where also the temperature can be regulated. [Scherer, 2012] described multi-layered mineral plaster samples placed in glass bowls. The samples were oriented heading to the west in outdoor experiments. The exposure time was 3 years and sampling was carried out according to the natural rain conditions. Similar experiments for rendering samples, coatings and paints were described by [Schwerd, 2011]. Outdoor experiments with facade coatings and roof foils were described by [Burkhardt et al., 2007, Burkhardt et al., 2009, Wangler et al., 2012]. Further outdoor experiments, for example with freshly concreted tunnels, were illustrated by [Ruckstuhl, 2001].

2.4.5 Batch tests

Batch tests are characterized by stirring or shaking the sample. Hence the pH-stat-test, the DEV-S4-test, availability tests and cascade tests may be counted to this category. Crushing the sample to a particle size $<10 \text{ mm}$ and eluting it for 24h in distilled water with a liquid-to-solid-ratio (L/S-ratio) of 10 L m^{-2} is standardized for the DEV-S4-test [DIN 38414-4, 1984]. The sample is either turned in an overhead shaker or slowly agitated in a horizontal shaker to guarantee a constant movement of the sample. Further crushing or abrasion should be prevented, which means a horizontal shaker is preferably used [DIN EN 12457-4, 2003]. After the elution time the sample is filtered away from the eluent. The cascade tests repeat the elution procedure several times. Here the eluate can be analysed separately or it can be applied with new sample material [Blankenhorn, 1994]. Availability tests are close to the above mentioned test but the sample is placed in a sieve. The eluent is agitated with a magnetic stirrer such that no mechanical load is put on the sample material and thus no abrasion or further crushing are generated. Further parameters like particle size and composition of the eluent can be varied [Scherer, 2012]. The pH-stat-test has similar test conditions as the DEV-S4-test but is carried out at constant pH-value [Brameshuber and Vollpracht, 2004].

The listed tests are easy to handle, fast, commonly used and hardly time-consuming. In addition the DEV-S4-test is standardized to guarantee a uniform implementation and comparability of different test runs or labs [Blachnik, 2001]. The drawback of these tests is the breakage of the sample and the generated additional/new surface area during overhead

shaking. The overestimation of the surface area and the leached species may be intensified with the mechanical load of the sample. Though it is difficult to predict the leaching behaviour under real conditions or to forecast the long-term leaching behaviour [Hohberg, 2002, Hohberg and Schiessl, 1996].

2.5 Ecotoxicological data of constituents of waterproofing materials and their environmental risk

2.5.1 Cement and its constituents

Cement and cementitious grouting materials are generally referred to be environmentally friendly. According to [EU Parlament und Rat, 2006] Portland cement, Portland-slag cement, Portland-pozzolana cement, Portland-limestone cement, Portland-composite cement, blast-furnace cement, composite cement and masonry cement do not meet the criteria for PBT (persistent, bioaccumulative and toxic) and vPvB (very persistent, very bioaccumulative substances).

However, [Afolabi et al., 2012] state when cement dust from cement plants is washed away with rain, it can also pollute water bodies and affect plant growth [Singh and Rao, 1981, Borka, 1980, Shukla et al., 1990, Czaja, 1960]. According to [Mishra and Siddiqui, 2014] particulate cement emissions contain potentially harmful toxic metals and compounds such as lead, chromium, nickel and barium, which can pose serious health impact on humans. These emissions can be toxic as they carry carcinogens, mutagens, immunotoxins, respiratory toxins and neurological toxins, but the physical properties of such particles define the degree of their effect on human health. Metal ions like barium, lead, vanadium, antimony, chromium, molybdenum were detected in the pore solution and in leachates of cements as has been shown by [Vollpracht and Brameshuber, 2016]. Although these metal ions were detected in low amounts, below the threshold limit of German regulations, so far their impacts on the environment has not been researched in detail yet.

In addition cement contains chromium reducing agents, which reduce the soluble chromium (VI) content to less than 2 ppm (0.0002 wt.%). However, improper storage conditions, e.g. contact with water or air humidity or an extended storage period, reduce the effectiveness of the chromium reducing agent and the cement becomes skin sensitising, which is known as bricklayers' itch (chromate dermatitis) [HSE, 2017]. Also the high alkalinity (pH>13) represents a health hazard.

Studies by [Gollmann et al., 2007] investigated desorption of lead from cement bound matrices with toxicity test with *Daphnia magna*. The results showed that the mortality of *D. magna* was not significantly different from the control. In contrast [Azizian et al., 2003] found that leachates gained from cementitious highway construction and repair materials were toxic for algae (*Selenastrum capricornutum*) and water flea (*Daphnia magna*). An EC₅₀ of 18 % for 24-hour leachate for algae which means a high toxicity and a LC₅₀ of 44 % for 24-hour leachate for water flea which means moderate toxicity was observed by [Azizian et al., 2003]. Investigations by [Lalonde et al., 2011] report a LC₅₀ of 15 cm² l⁻¹ for rainbow trout (*Oncorhynchus mykiss*), LC₅₀ of 25 cm² l⁻¹ for water flea (*Daphnia magna*) and an IC₅₀ of 20 cm² l⁻¹ for bacteria (*Vibrio fischeri*). For leachates gained from concretes containing biomass ashes an EC₂₀ 70 h >80 % for algae (*P. subcapitata*), EC₅₀ >80 % for bacteria (*V. fischeri*), algae (*P. tricornutum*) and crustacean (*A. franciscana*) which is low in toxicity is reported by [Barbosa et al., 2013]. However, the toxicity to water flea (*Daphnia magna*) after 48 hours was in the range of EC₅₀ 35 % to 50 %. Leachates gained from concrete artifacts

were found to show toxic effects for water flea (*D. magna*), earthworms (*E. foetida*) and onion root (*A. cepa*) [Mastella et al., 2014].

Concrete is often falsely attributed to only contain cement, water and aggregates. Its composition changed in the last decades from a ternary system to a multi-component system by adding SCMs like fly ash, ground granulated blast-furnace slag and various organic additives like superplasticisers, retarders, accelerators etc. These constituents can contribute to the environmental pollution as well. Some of these materials are already tested for their ecotoxicological impact (see Appendix 1), however, these materials are only tested alone and not in combination/ compound with cement.

The different and sometimes controversial results gained from cement leachates underline the high complexity of such systems and establish the need for detailed research and investigations.

2.5.2 Polyurethane

Polyurethane grouting materials are often discussed to be environmentally polluting or hazardous. However, [Pusch, 1993, CRC press, 1993] state that for grouting purposes exclusively MDI 1,1'-Methylenebis(4-isocyanatobenzene) is used as component B, which exhibits a low vapour pressure (0.000 005 mmHg (20 °C) [NIOSH, 2017]) such that the threshold limit value (TLV) or maximum workplace concentration (MAK) cannot be reached at normal application temperature. According to [Donel and Feder, 1981] it is possible that long gel times promote the reaction of water with isocyanate to form polyurea. Unbound polyol might reach or migrate into ground water, but, it is seen as biodegradable within 6 days [Martens, 1998]. However, polyurethanes have variable curing times, and the presence of free isocyanates vary accordingly [Riedlich, 2010].

According to [Allport et al., 2003] typically LD₅₀ are several hundred milligrams per kilogram. Despite their relatively low acute toxicities, isocyanates are potentially irritants to the eyes and respiratory tract.

2.5.3 Risk of pollution

Environmental pollution to soil, air, water etc. is caused by the presence of (xenobiotic) chemicals⁵. Hazardous substances, toxic substances and harmful substances have always been present in the environment. However, as Paracelsus [Paracelsus, 2009] stated "Alle Dinge sind Gift, und nichts ist ohne Gift; allein die Dosis macht, daß ein Ding kein Gift sei"⁶.

It is important to know whether substances present in grouting materials are released into the environment or immobilised in the materials. In case substances are released the question is what substance or compound is released in which amount. If substances are released from the grouting materials, it needs to be known whether these substances are harmful to the environment or not. In general pollution from building materials can be air-borne, soil-borne and water-borne. Air-borne emissions from buildings and building materials have been identified during the last decades. Serious health problems like the sick building syndrome can be a result thereof [Levin, 1989, Yu and Crump, 1998, Böhm et al., 2012]. However, air-borne emissions are far beyond the scope of this thesis and are not further discussed here.

⁵A xenobiotic compound is foreign to a living organism. Principal xenobiotics include: drugs, carcinogens and various compounds that have been introduced into the environment by artificial means.

⁶"The dose makes the poison."

Nevertheless, one fact has to be mentioned about plasticisers on the basis of melamine- and naphthalen sulphonate condensates. According to [Togerö, 2004, Andersson and Stromvall, 2001, Togerö, 2006] these plasticisers contain a fraction <0.3 wt.% of formaldehyde, which is hazard to water organisms and humans [ECHA, 2017].

Water-borne and soil-borne emissions are possible during the grouting process, especially when the uncured building material is in contact with water and soil. There is a possible risk that compounds of the building material are leached or migrate to the compartments soil or water. Water- and soil-living animals and organisms like plants will first be affected [Togerö, 2004]. Humans will be affected -if at all- in a second stage, e.g. by pollution of the drinking water or by combining slow degradation and bioaccumulation (in fish or fish-eating mammals) [Togerö, 2004]. In addition, building materials are used for long periods of time and thus are exposed to the surrounding soil and water for a long time. Demolition materials are often reused, e.g. demolition concrete is used for roads, such that it is important to know whether substances could be released from recycling materials [Gallagher et al., 2013].

A brief summary of the ecotoxicological data of commonly used waterproofing/grouting materials and their constituents is presented in [Appendix 1](#). It has to be mentioned that most components listed were tested as delivered and not evaluated during leaching experiments. At realistic conditions there is always an interaction of the components in the waterproofing material with the surrounding compartments air, soil and water. This means that testing the neat material does not take into account the complex interaction mechanisms such that different results may be obtained during leaching experiments.

Experimental

3.1 Materials, mix design and sample preparation

3.1.1 Eluents

The eluents were either demineralised water (DI)⁷ or Berlin tap water (BTW). Both eluents were chosen because of their different properties and aggressiveness. In addition DI water fulfils the requirements of different national and international standard procedures, whereas BTW as eluent reflects the leaching behaviour under natural or realistic conditions. The mean ionic content of both eluents refers to an average of over hundred measurements in a time span of six month and is summarised in (Figure 3.1). Correction to the blank value was performed with the exact value of the specific eluent.

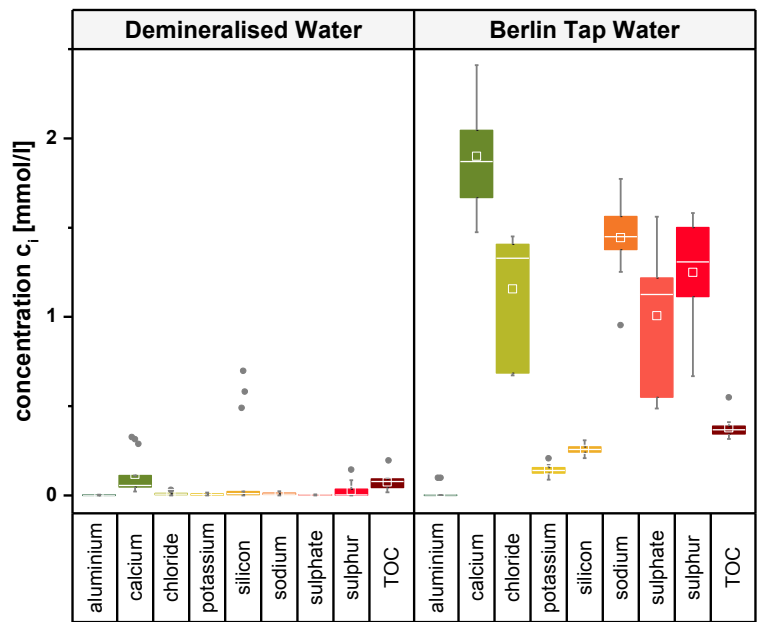


Figure 3.1: Ion concentrations of the eluents measured over a period of six month.

⁷DI is used synonymously for deionised water. The ions of the water are removed in a special ion-exchange process. However, no organic compounds are removed.

Ultrapure water with an electric conductivity of $0.055 \mu\text{S cm}^{-1}$ was used as eluent for the leaching study presented in [Chapter 5](#). This eluent was prepared with a Barnstead MicroPure UV from Thermo Scientific, Germany.

3.1.2 Polyurethane leaching study

The polyurethane leaching study is presented in [Chapter 4](#). The polyurethane system (PU) was supplied by WEBAC-Chemie GmbH, Barsbüttel, Germany, and was used as matrix system. Component A was a mixture of polyester and polyether polyols and component B was a mixture of different isomers of methylene diphenyl diisocyanate (MDI). Three different catalysts were tested: a zinc compound (80 wt.% to 90 wt.%) mixed with an amine (20 wt.% to 10 wt.%) (ZINC), di-n-octyltin di-laurate, $\text{C}_{40}\text{H}_{80}\text{O}_4\text{Sn}$, CAS number 3648-18-8 (DOTL) and triethylene diamine, $\text{N}_2(\text{C}_2\text{H}_4)_3$, CAS number 280 -57-9 (TEDA). As eluent either demineralised water (DI) or Berlin tap water (BTW) was used. The mean electrolyte composition is presented in [Figure 3.1](#). The waterproofing PU was synthesised through a one-step polymerisation process. Three different amounts of catalyst were investigated to examine the full range of workability. The formulation details are summarised in [Table 3.1](#). Polyester and polyether polyols (Component A) were mixed and homogenised with the appropriate amount of catalyst in a polystyrene cup for 30 s. After addition of the mixture of different isomers of MDI (Component B) the whole mixture was homogenised for 3 min. To achieve a best possible homogenisation the mixture was re-potted in a polystyrene cup and mixed again for 30 s. All experiments were carried out under standardised climate conditions (60 % RH and 20°C).

Table 3.1: Formulation of the waterproofing polyurethane.

Materials [g]							
Component A		71.05		Component B		78.95	
Catalyst ^a	low (1)	middle (2)	high (3)	CA ^b	low (1)	middle (2)	high (3)
ZINC	0.0053	0.0830	0.161	ZINC	7.5×10^{-3}	0.117	0.227
DOTL	0.0036	0.0153	0.027	DOTL	5.6×10^{-3}	0.022	0.102
TEDA	0.0040	0.0385	0.073	TEDA	5.0×10^{-3}	0.054	0.038

^a Data given in [g].

^b Comparative amount of catalyst related to component A [wt.%].

3.1.3 HIS leaching study

This study is presented in [Chapter 5](#). Experiments were performed with three different cements and with a substitution of ordinary Portland cement (OPC) by ground granulated blast-furnace slag (GGBFS) using two different slags as shown in [Table 3.2](#). OPC 1 was from the type CEM I 52.5 N-SR 3/NA, CEM III was type CEM III/A 42.5N LH/NA with a proportion of 36 wt.% to 65 wt.% GGBFS and OPC 2 was of type CEM I 42.5 R [[E DIN EN 197-1, 2014](#)]. The chemical composition of the materials determined by means of X-ray fluorescence (XRF) is given in [Table 3.3](#).

The polyurethane system (PU) was supplied by WEBAC-Chemie GmbH, Barsbüttel, Germany. Component A was a polyol and component B an isocyanate, which were mixed in the proportions 1:1 by volume. Different cement slurries were prepared as presented in [Table 3.2](#).

The composition of the PU system was not altered throughout. The cement slurry was mixed according to DIN EN 196-1 [DIN EN 196-1, 2005] with a water-to-binder-ratio of 0.3 and the addition of 0.14 wt.% of dispersing agent and 0.2 wt.% of superplasticiser, both with respect to the binder⁸ content. The PU was mixed freshly for each sample. As eluent ultrapure water (MicroPure UV, Thermo Scientific, Germany) (UPW) was used.

Table 3.2: Mixtures under investigation. Data given in [wt.%].

Mixture	OPC 1	GGBFS 1	CEM III	OPC 2	GGBFS 2
C1-0	100	-	-	-	-
C1-10	90	10	-	-	-
C1-20	80	20	-	-	-
C1-30	70	30	-	-	-
C III	-	-	100	-	-
C2-10	-	-	-	90	10
C2-30	-	-	-	70	30

Table 3.3: Chemical composition and physical properties of the used raw materials. n.d. = not detected.

	OPC 1	GGBFS 1	CEM III	OPC 2	GGBFS 2
Chemical composition [wt.%] ^a					
SiO ₂	16.35	31.02	29.87	20.05	34.91
Al ₂ O ₃	3.40	7.27	9.05	4.40	9.12
Fe ₂ O ₃	5.10	0.90	1.31	2.63	0.33
CaO	64.13	46.73	48.09	64.91	40.51
MgO	1.20	5.74	4.83	1.80	6.11
SO ₃	2.58	2.58	2.84	n.d.	1.33
K ₂ O	0.57	2.15	0.79	0.73	0.97
Na ₂ O	0.13	0.51	0.33	0.10	0.30
TiO ₂	n.d.	0.58	0.58	0.24	0.79
L.O.I. ^b	1.49	2.29	0.00	3.09	3.09
Physical properties					
Blaine [cm ² g ⁻¹]	3437	4364	4532	4429	3592
Density [g cm ⁻³] ^c	3.25	2.88	3.02	3.15	2.95
d ₅₀ [μm]	15	16	19	24	15

^a Determined by means of XRF.

^b Loss on ignition.

^c Determined using a Micrometrics AccuPyc 1330 helium pycnometer.

In the notation used to abbreviate the different systems under investigation C1, C2 and C III refer to the contained type of cement and the number represents the cement substitution by GGBFS (see Table 3.2).

The cement slurries (Table 3.2) and the PU were mixed in the volumetric proportion 5:1 using a co-axial cartridge 380 equipped with a static mixing element. The samples were moulded with a pneumatic 2-K cartridge dispenser COX CCA 380 at 6 bar pressure. Both devices were supplied by Ritter/Innotech, Germany. The equipment is depicted in Figure 3.2.

⁸Binder refers to dry mixture of inorganic materials, here either neat OPC or mixtures of OPC and GGBFS.

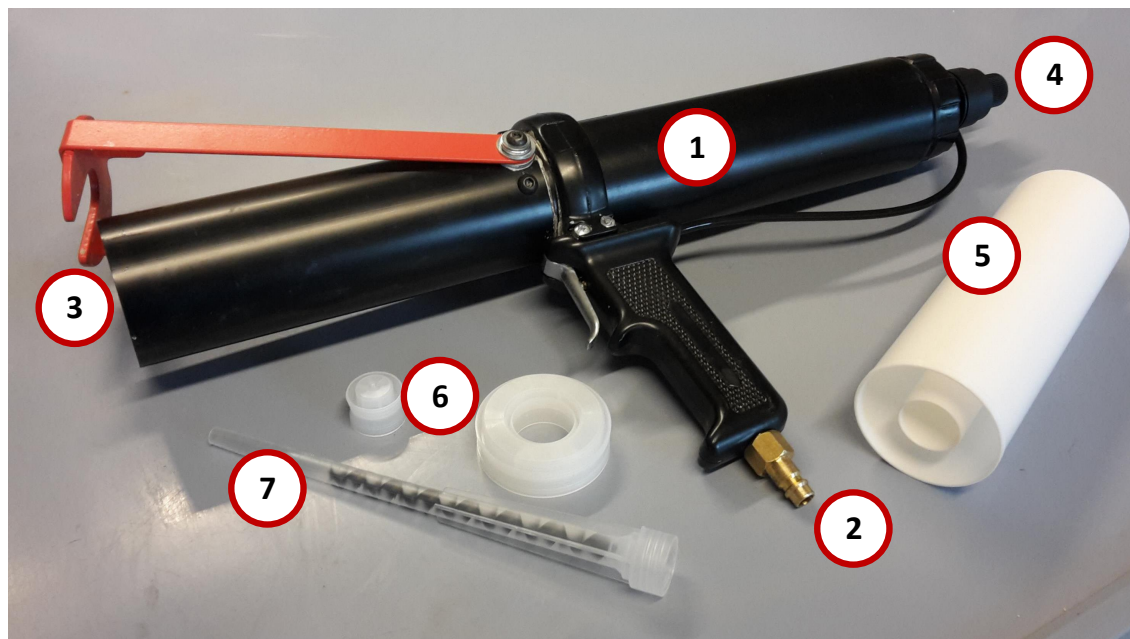


Figure 3.2: Pneumatic 2-K cartridge dispenser COX CCA 380. 1) compressed air pistol 2) compressed air supply 3) safety system of the air pistol 4) compressed air control 5) co-axial cartridge 380 in the ratio 5:1 6) inner and outer cartridge lids 7) static mixing element.

3.1.4 Cement leaching studies

Two different cement leaching studies were carried out in this thesis. The first one is presented in [Chapter 6](#).

All mixtures were prepared using Portland cement-based micro fine cement, with a w/c-ratio of 0.5 and 0.7, respectively. As superplasticiser a commercially available mixture based on a combination of naphthalene sulfonate formaldehyde condensate (NFS) and melamine sulfonate formaldehyde condensate (MFS) was used in the amount of active component of 0.5 and 1.5 wt.% with respect to the amount of cement. Mortar mixtures contained fine quartz sand F 36 (Quarzwerke Frechen, Germany; average grain size 0.16 mm) in the amount of 750 kg m^{-3} . The mixtures were prepared with an Ultra Turrax T50 to guarantee breakage of the agglomerates. First demineralised water was mixed with the superplasticiser for 30 s at 7000 rpm, followed by the addition of the cement and mixing for 3 min at the same speed. Detailed compositions of the mixtures, the eluent and pre-storage times are listed in [Table 3.4](#).

The sample notation as given in [Table 3.4](#) refers to either pastes (P) or mortars (M), followed by the w/c-ratio (0.5 or 0.7), the pre-storage time (1 or 56 d), the superplasticiser content (0.0, 0.5 or 1.5 wt.%) and the eluent, either demineralised water (DI) or Berlin tap water (BTW). The chemical composition of the initial material measured with XRF is given in [Table 3.5](#).

The second leaching study dealing with cementitious materials is presented in [Chapter 7](#) and [Chapter 8](#).

Experiments were performed with cement pastes using Portland cement-based microfine cement. The chemical composition measured with XRF is given in [Table 3.5](#). As superplasticiser a commercially available polycarboxylate ether (PCE) with a back bone of about 5000 g mol^{-1} and side chains of about 1000 g mol^{-1} was used in this investigation. Further

Table 3.4: Matrix under investigation. DI = demineralised water, BTW = Berlin tap water.

mixture	w/c	prestorage time [d]	superplasticiser content [wt.%]	eluent
P 0.5-1-0.0-DI	0.5	1	0.0	DI
P 0.5-1-0.5-DI	0.5	1	0.5	DI
P 0.7-1-0.5-DI	0.7	1	0.5	DI
P 0.5-56-0.5-DI	0.5	56	0.5	DI
P 0.7-56-0.5-DI	0.7	56	0.5	DI
P 0.5-1-1.5-DI	0.5	1	1.5	DI
P 0.5-1-0.0-BTW	0.5	1	0.0	BTW
P 0.5-1-0.5-BTW	0.5	1	0.5	BTW
P 0.5-1-1.5-BTW	0.5	1	1.5	BTW
M 0.5-1-0.5-DI	0.5	1	0.5	DI
M 0.7-1-0.5-DI	0.7	1	0.5	DI
M 0.5-56-0.5-DI	0.5	56	0.5	DI
M 0.7-56-0.5-DI	0.7	56	0.5	DI
M 0.5-1-1.5-DI	0.5	1	1.5	DI
M 0.5-1-0.5-BTW	0.5	1	0.5	BTW
M 0.5-1-1.5-BTW	0.5	1	1.5	BTW

Sample notation: P=paste, M=mortar, digit 1=w/c , digit 2=pre-storage time [d] , digit 3 = superplasticiser content [wt.%].

Table 3.5: Chemical and mineralogical composition of the used raw materials.

Chemical analysis ^a			Mineralogical analysis ^b		Physical properties		
	Cement	Sand		Cement		Cement	Sand
SiO ₂	22.66	99.30	C ₃ S	75.5	L.O.I. ^c	0.9	0.2
Al ₂ O ₃	4.08	0.50	β-C ₂ S	11.0	Density [g/cm ³] ^d	3.10	2.65
Fe ₂ O ₃	1.50	0.06	C ₃ A	8.6	Blaine [m ² /g]	1200	n.d.
CaO	66.46		C ₄ AF	1.0	SA [cm ² /g] ^e	n.d.	144
MgO	0.87		Gypsum	0.4	d ₅₀ [mm]	n.d.	160
SO ₃	2.58		Bassanite	3.4			
K ₂ O	0.85		Christobalite	0.1			
Na ₂ O	0.02						
TiO ₂	0.21						

^a Determined by XRF analysis [wt.%].

^b Determined by XRD Rietveld [wt.%].

^c Loss on ignition (1000 °C).

^d Determined with a Micrometrics AccuPyc 1330 helium pycnometer.

^e Surface area.

information on the micro fine cement and the PCE based on the suppliers technical or safety data sheet can be found in [Table 3.6](#). The eluent was either demineralised water (DI) or Berlin Tap Water (BTW). The mean electrolyte composition of the eluents can be found in [Figure 3.1](#). The mixtures were prepared with a water-to-cement-ratio (w/c) of 0.5. The superplasticiser dosage was 0.5 wt.% of active component with respect to the amount of cement. The mixtures were prepared with an Ultra Turrax T50 to guarantee breakage of the agglomerates. First demineralised water was mixed with the superplasticiser for 30 s at 7000 rpm, followed by the addition of the cement and mixing for 3 min at the same speed.

Table 3.6: Information on the used materials. n.d. = not detected/ not relevant.

		cement	Polycarboxylate Ether
Information on the ingredients	Classification of the substance	■ H315 ■ H318 ■ H335 ■ skin irritation 2 ■ serious eye damage/ eye irritation 1 ■ Specific target organ toxicity single ■ exposure respiratory tract irritation 3	EUH208, Contains 1,2-benzisothiazol-3(2H)-one, mixture of 5-Chloro-2-methyl-1,2-thiazol-3(2H)-one [EG Nr. 247-500-7] and 2-Methyl-1,2-thiazol-3(2H)-one [EG Nr. 220-239-6] (3:1), Triisobutyl phosphate. May produce an allergic reaction.
	Composition	hydraulic binder (CAS 65997-15-1)	mixture
Information on basic physical and chemical properties	pH	(T = 20 °C in water, water-solid ratio 1:2): 11 to 13.5	~ 4
	Solubility in water	slight (0.1 g l ⁻¹ to 1.5 g l ⁻¹)	soluble
Ecological information	Aquatic toxicity	not hazardous The addition of large amounts of cement to water may, however, cause a rise in pH and may, therefore, be toxic to aquatic life under certain circumstances.	n.d.

Different mixtures and eluents were used for this study, which are listed in [3.7](#).

Table 3.7: Mixtures used for cement leaching experiments presented in [Chapter 7](#) and [Chapter 8](#).

Mixture	w/c-ratio	superplasticiser content [wt.-%]	eluent ^a
REF-DI	0.5	0.0	DI
PCE-DI	0.5	0.5	DI
REF-BTW	0.5	0.0	BTW
PCE-BTW	0.5	0.5	BTW

^a DI = demineralised water, BTW = Berlin tap water.

3.1.5 Concluding overview of the materials and mix design

Figure 3.3 summarises the used materials and mix designs.

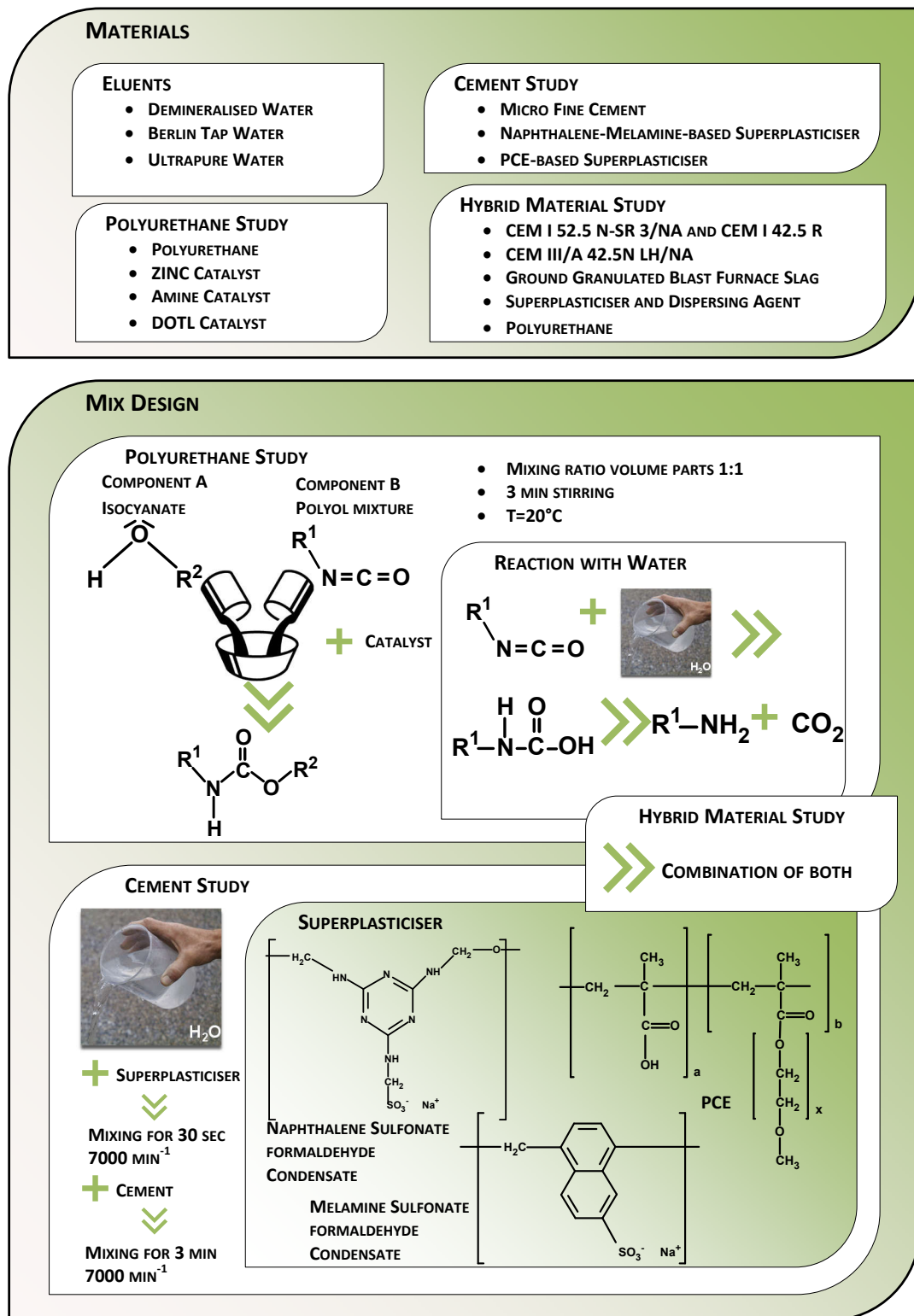


Figure 3.3: Concluding overview of the used materials and the mix design.

3.2 Methods

3.2.1 Leaching tests

Figure 3.4 provides a short overview of the used leaching methods.

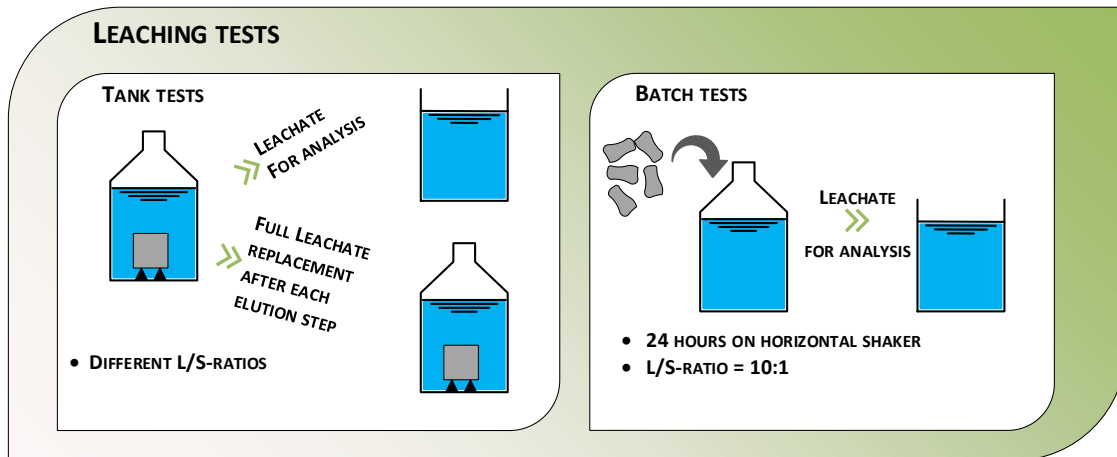


Figure 3.4: Schematic overview of the used leaching tests.

3.2.1.1 Polyurethane leaching study

The leaching test was based on the European Standardised Tank Leaching Test for construction materials [DIN CEN/TS 16637-2, 2014] and the directive of the German Committee for Reinforced Concrete [DAFStb-Richtlinie, 2005] which was adjusted for leaching the polyurethane systems whilst curing. 25 g of the polyurethane was placed in a polyethylene beaker and gently overlaid with 100 mL of the eluent. The ratio of initial sample surface to volume eluent was set to 47 L m^{-2} . Complete eluent exchange was carried out after 10, 30, 70, 150, 310 and 1440 min. Further details of the eluate exchanges are listed in Table 3.8. Note that all exchange times were doubled, just the last was exceeded. Leaching tests were performed with DI for all catalyst dosages and additionally with BTW for low and high catalyst dosages. The results were corrected to the blank value and represent the average of two parallel tests.

Table 3.8: Schedule of the tank leaching test for polyurethane material.

interval	interval length [d]	Δt_i [d]	summarised elution time t_i [d]
Δt_1	0 to 10	10	10
Δt_2	10 to 30	20	30
Δt_3	30 to 70	40	70
Δt_4	70 to 150	80	150
Δt_5	150 to 310	160	310
Δt_6	310 to 1440	1130	1440

3.2.1.2 HIS leaching study

The HIS leaching study is presented in [Chapter 5](#). In order to determine the environmental impact assessment, leaching tests were performed based on the European tank leaching test [[DIN CEN/TS 16637-2, 2014](#)] with cubes $20 \times 20 \times 20 \text{ mm}^3$. As release agent PTFE-spray was used to ensure a minimum of influence from the mould. The cubes were demoulded after 30 min and directly leached. Experiments were conducted in triplicate. As eluent ultrapure water (MicroPure UV, Thermo Scientific, Germany) was used. Each cube was immersed in the eluent with a liquid-to-surface-ratio of 80 l m^{-2} in an amber glass bottle and stored at $20^\circ\text{C}/99\% \text{ RH}$. A full exchange of the eluent took place according to the eluate changes listed in [Table 3.9](#).

Table 3.9: Schedule of the HIS tank leaching test. Note that the test procedure is very similar to the European Standardised Tank Leaching Test for construction materials [[DIN CEN/TS 16637-2, 2014](#)].

interval	interval length [d]	Δt_i [d]	summarised elution time t_i [d]
Δt_1	0 to 0.083	0.083	0.083
Δt_2	0.083 to 0.25	0.16	0.25
Δt_3	0.25 to 2.25	0.75	1
Δt_4	2.25 to 4	1.75	4
Δt_5	4 to 9	5	9
Δt_6	9 to 16	7	16
Δt_7	16 to 36	20	36
Δt_8	36 to 64	28	64

Each eluate was taken for chemical analysis and the cumulative release rate $E_{64,i}$ was calculated using equations (3.1) and (3.2), where c_i is the concentration of the ion after each elution step [mmol l^{-1}], V is the volume of the eluent [l] and S is the surface area at the beginning of the leaching test [m^2].

$$E_i = c_i \cdot \frac{V}{S} \quad (3.1)$$

$$E_{64,i} = \sum_{i=1}^8 E_i \quad (3.2)$$

To obtain a worst-case scenario further leaching tests were conducted in triplicate according to the batch test described in [[DIN 38414-4, 1984](#)] and [[NEN 7341, 1995](#)]. After curing for 1 d the sample was manually ground with a mortar and pestle and dry sieved $<250 \mu\text{m}$. Without further drying the sample was leached with a solid-liquid-ratio of 1:10 for 24 h. For analysis ultrapure water was used. This test was conducted in duplicate. All results were corrected to the blank values.

3.2.1.3 Cement leaching studies

The first cement leaching study presented in [Chapter 6](#) used the test procedure based on the German Tank leaching test according to the guidelines of the German Committee for Reinforced Concrete [[DAfStb-Richtlinie, 2005](#)]. Paste and mortar cubes with the dimensions $20 \times 20 \times 20 \text{ mm}^3$ were prepared. To guarantee no influence from the mould PTFE was used as release agent. To get information during the very early curing of the cementitious system the test was adapted. Therefore the sample was cured and hardened for 1 d and the leaching procedure started immediately after demoulding. Comparisons were made to samples prestored for 56 d. For this purpose the samples were wrapped in foil to minimize carbonation and stored at $20^\circ\text{C}/99\% \text{ RH}$. Average values of two parallel tests are presented. Each cube was immersed in the eluent with a liquid-to-solid-ratio of 80 l m^{-2} in an amber glass bottle. A full exchange of the eluent took place after the times presented in [Table 3.10](#). The eluate was taken for chemical analysis.

Table 3.10: Schedule of the tank leaching test for the cement study according to the German Committee for Reinforced Concrete [[DAfStb-Richtlinie, 2005](#)].

interval	interval length [d]	Δt_i [d]	summarised elution time t_i [d]
Δt_1	0 to 1	1	1
Δt_2	1 to 3	2	3
Δt_3	3 to 7	4	7
Δt_4	7 to 16	9	16
Δt_5	16 to 32	16	32
Δt_6	32 to 56	24	56

The second cement leaching study is based on the European Standardised Tank Leaching Test for construction materials [[DIN CEN/TS 16637-2, 2014](#)] and is presented in [Chapter 7](#) and [Chapter 8](#). Paste samples with the dimensions $20 \times 20 \times 20 \text{ mm}^3$ were prepared and the pre-storage time was 1 d. Leaching started immediately after demoulding. Average values of two parallel tests are presented. Each cube was immersed in the eluent with a liquid-to-solid-ratio of 80 l m^{-2} in an amber glass bottle. A full exchange of the eluent took place after the times presented in [Table 3.11](#). All eluate fractions were taken for chemical analysis.

Table 3.11: Schedule of the tank leaching test for the cement study according to the European Standardised Tank Leaching Test for construction materials [[DIN CEN/TS 16637-2, 2014](#)].

interval	interval length [d]	Δt_i [d]	summarised elution time t_i [d]
Δt_1	0 to 0.25	0.25	0.25
Δt_2	0.25 to 1	0.75	1
Δt_3	1 to 2.25	1.25	2.25
Δt_4	2.25 to 4	1.75	4
Δt_5	4 to 9	5	9
Δt_6	9 to 16	7	16
Δt_7	16 to 36	20	36
Δt_8	36 to 64	28	64

3.2.2 Analytical methods

3.2.2.1 pH and electric conductivity measurements

The pH and electric conductivity were measured on the neat eluate with a SevenGo Duo Pro SG78 (Mettler Toledo) equipped with a Expert Pro-ISM IP67 electrode for pH and a 738-ISM electrode for electric conductivity. The two electrodes were calibrated against buffer solutions of known concentrations.

3.2.2.2 Ion chromatography

The sulphate (SO_4^{2-}) and chloride (Cl^-) concentrations were measured using a 761 Compact IC ion chromatograph from Metrohm equipped with an autosampler Rainin Varian Pro Star AI-3. Calibration was performed with an anion multi-elemental standard obtained from Merck, Germany at 10, 20, 30, 40, 50, 60, 70, 80, 90, 100 and 200 ppm. Measurement parameters are listed in [Table 3.12](#).

Table 3.12: Operation conditions for IC.

Parameter	Condition
Pre-Column	Shodex IC SI-50G, (4 mm × 10 mm)
Column	Shodex IC SI-50 4E, (4 mm × 250 mm), 5 μm
Eluent	1.5 mmol l ⁻¹ NaHCO ₃ / 4.8 mmol l ⁻¹ Na ₂ CO ₃
Flow rate	0.70 $\mu\text{l min}^{-1}$
Injection volume	20 μl
Suppressor	Metrohm Suppressor Module «MSM»
Suppressor solvent	100 mmol l ⁻¹ H ₂ SO ₄ / 20 mmol l ⁻¹ C ₂ H ₂ O ₄ , DI water
Column temperature	25 °C
Detection	Conductivity
Determination mode	Peak area

Prior to measurement the sample was vacuum filtered with a 0.45 μm acetate filter. If necessary the sample was diluted prior to measurement by Milli-Q water⁹. Standards with 0.1 and 50 mg l⁻¹ were used for all ions of interest to define the lower (l.d.l.) and upper (u.d.l.) detection limit. The relative uncertainty is $\pm 10\%$.

3.2.2.3 Inductively coupled plasma atomic emission spectroscopy

The simultaneous multi-element determination of the cations (Al^{3+} , Ca^{2+} , K^+ , Na^+ , Si^{4+} , Zn^{2+} and Sn^{4+}) was performed by ICP-AES (Ciros Vision from SPECTRO). During this procedure the sample is nebulised and ionised in a plasma flame (6000 to 10 000K) such that the excited atoms and ions emit electromagnetic radiation at a characteristic wavelength for a particular element. Operating parameters used in these experiments are summarised in [Table 3.13](#).

⁹Milli-Q water refers to ultrapure water typically 18.2 mS cm at 25 °C.

Table 3.13: Operational parameters for determination of cations by ICP-AES. Atomic (I) and ionic (II) emission lines.

Parameter	ICP-AES	Analyte	Emission line [nm]	
			Atomic (I)	Ionic (II)
Radio frequency power [W]	1400	Al	167.078	396.152
Plasma flow gas rate [L min ⁻¹]	12.0	Ca	396.847	393.366
Auxiliary gas flow rate [L min ⁻¹]	1.0	K	766.491	n.d.
Nebuliser gas flow rate [L min ⁻¹]	1.0	Na	589.592	588.995
Nebuliser	Concentric	S	180.731	178.287
		Si	251.612	152.672
		Bi	223.061	n.d.
		Zn	213.856	206.191
		Sn	189.991	147.516

The measurement was performed in triplicate followed by a flushing cycle for 70 s with a 2% HNO₃ solution. Argon (purity 99.999% from Air Liquide) was used to purge the optics and to generate the plasma. Calibration was performed at 0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 10 and 200 mg/L with a multi-element standard obtained by Merck, Germany. The standard deviation of the measured elemental concentrations ranged between 5 and 10%. 20 ml undiluted eluate sample was vacuum filtered with a 0.45 µm acetate filter and acidified to pH 2 with hydrochloric acid to prevent any precipitation of solids and to ensure stabilisation. If necessary the sample was diluted prior to measurement with ultrapure water.

3.2.2.4 Total and dissolved organic carbon

A Shimadzu TOC-L analyser was used for TOC and DOC¹⁰ measurements operated with the so called direct technique, which requires an acidified sample prior to measurement where the inorganic proportion of carbon is converted to carbon dioxide. This technique uses a combustion catalytic oxidation method at 700 °C in an oxygen-rich environment. Therefore a synthetic air (mixture of N₂ and O₂ without CO₂) was used as carrier gas. The generated carbon dioxide was detected using an infrared gas analyser (NDIR) calibrated at 5, 10, 50, 100, 150, 200, 250, 300, 350, 400, 450 and 500 mg L⁻¹ with a 500 mg L⁻¹ potassium hydrogen phthalate solution. Before and after every injection the injector was flushed twice. The total number of injections was set to 3. In case of a deviation higher than 0.1 and a variation higher than 2.0 % the total number of injections was increased to 5. Stripping time was set to 3 min. For TOC measurements the samples were acidified with hydrochloric acid to pH 2 and vacuum filtration with a 0.45 µm acetate filter and acidification to pH 2 was done for DOC determination.

3.2.2.5 UV-Vis spectrometry

The concentration determination by UV-Vis spectrometry is based on the fact that molecules are able to absorb light energy. Electrons are excited by the radiated light energy and are transferred to a energy-rich state. Ultraviolet (UV) and visible (Vis) light can normally only

¹⁰All measured concentrations of TOC and DOC are referred to the total amount of carbon in the sample.

excite the relatively low-energy π -electrons and the nonbonding electrons. For this kind of analysis all kinds of substances which have multiple bonds or free electron pairs are suitable. The absorbed energy is used for the transfer of the electron into an energy rich state. Since only defined energy states are possible, also a defined amount of energy E is necessary. At the wave length λ of the irradiated light, which corresponds to the Planck's law (with h as the Planck constant and c as the speed of light) this energy amount, a maximum absorption occurs in the spectrum.

$$E = \frac{hc}{\lambda} \quad (3.3)$$

Due to attenuation effects and overlays of other forms of energy transformation, such as excitation of molecule vibrations and molecule rotation, the resulting peak is relatively broad. The absorption maxima in the UV spectrum of a substance are mainly given through the existing chromophoric atomic groups in the molecule which containing π -electrons or free electrons and therefore are able to absorb UV or visible light. Also the respective neighboring atoms are of importance. Free electron pairs of neighboring atoms interact with the electrons of the chromophoric group and thereby influence the level and position of the absorption maximum. Even the solvent can affect the position and intensity of the absorption maximum. With the aid of UV spectroscopy quantitative analysis of chromophore substances can be performed. To determine the concentration of such a substance is the wavelength-dependent absorption is measured. The absorbance A is a level of the difference of intensities I_0 of the incident and of transmitted light I :

$$A = \log \frac{I_0}{I} \quad (3.4)$$

According to the Lambert-Beer law, the absorbance depends on the molar concentration c of the substance, the molar extinction coefficient ε and the optical path length d .

$$A = \sum_{j=1}^n \varepsilon_{ij} \cdot c_j \cdot d \quad (3.5)$$

After calibration measurement, the extinction coefficient is known. Thus knowing the path length through the sample, the concentration of the substance can be determined by the absorption spectrum. Calibration was performed in water basified to a pH of 12 with the pure substance of NFS and MFS, which is illustrated in [Figure 3.5](#). As there are several absorption maxima which overlap each other it is difficult to identify them exactly ([Figure 3.6](#)). This is why for interpretation of MFS the maximum in the range 200 nm to 230 nm and for NFS 270 nm to 300 nm was chosen with the appropriate extinction coefficient [[Andersen et al., 1986](#), [Andersen et al., 1987](#), [Spanka and Thielen, 1995](#)]. For the total NFS-MFS-superplasticiser the maximum in the range 200 nm to 230 nm with its extinction coefficient was chosen. Integration over the peak area is difficult due to the superimposed maxima. However the absolute value of the absorption is used for further calculations. The measurements were performed with a 1650 PC spectrometer from Shimadzu in a wave range from 200 nm to 400 nm and an optical path length of 10 mm. The suspended particles were gently decanted for UV-Vis-measurements.

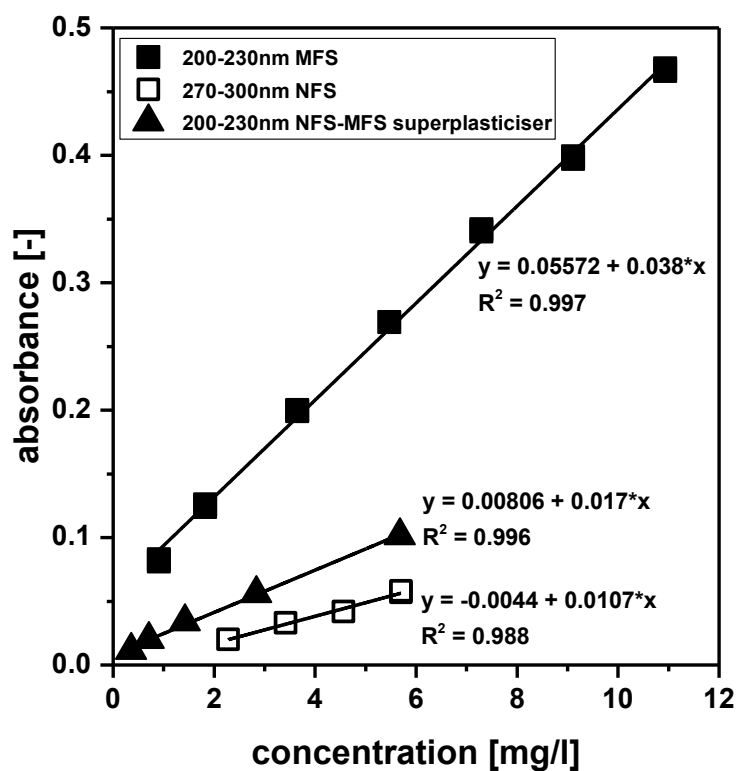


Figure 3.5: Calibration curves of NFS-MFS in water.

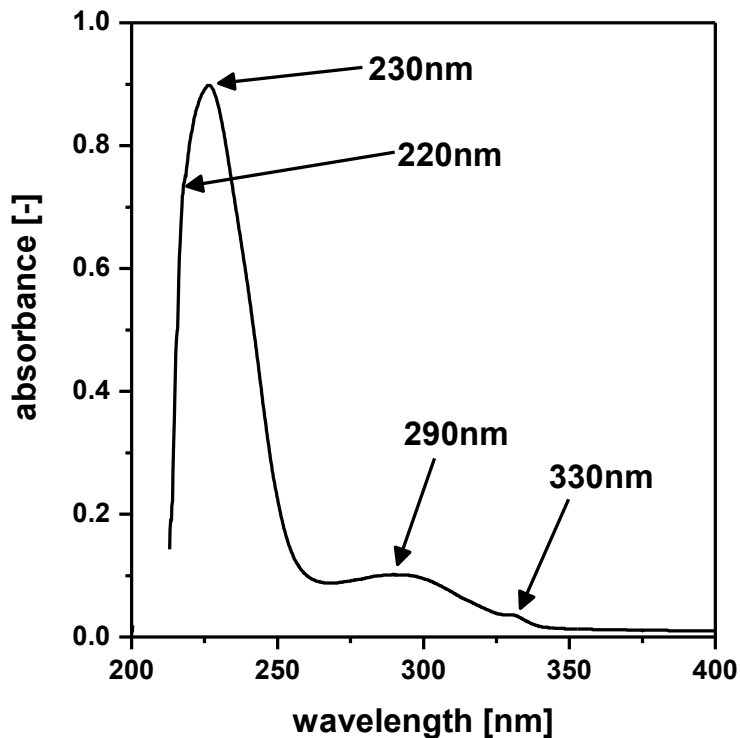


Figure 3.6: UV-Vis spectra of the NFS-MFS based superplasticiser with a concentration of 5.6 mg L^{-1} . The peaks for MFS are at 220 nm and for NFS at 230 nm, 290 nm and 330 nm.

3.2.2.6 High performance liquid chromatography mass spectrometry

In order to detect the superplasticiser in the eluates high performance liquid chromatography (HPLC-MS) was performed. Calibration was performed with Triisobutyl phosphate (CAS: 126 716) and different fragments of Polycarboxylate Ethers. 100 μl of each standard was dissolved in 5 ml MeOH and again diluted in the ratio 1:10 with MeOH. The solution was filtered through a 0.2 μm PTFE filter and used for calibration. The eluates were filtered through a 0.2 μm PTFE-membrane and analysed. Liquid chromatography was performed using a Rheos Allegro liquid chromatograph from FLUX Instruments (Switzerland) equipped with a mass spectrometer (MS) LTQ-Orbitrap XL from Thermo Scientific (Switzerland). As column a Luna 3u C8(2) 30 $\times$ 3.0mm (Phenomenex) was used. The aqueous mobile phase was HPLC-grade water, whereas the organic phase was HPLC-grade MeOH. The gradient elution can be seen in [Table 3.14](#). The flow rate was set to 700 $\mu\text{l min}^{-1}$ and an injection volume of 10 μl . The MS was operated in atmospheric pressure chemical ionisation (APCI) positive ion mode. Full scans were performed in the mass-to-charge-ratio (m/z) 100 to 2000. Following MS working parameters were used: a capillary voltage of 18 V, an APCI vaporise temperature of 400 $^{\circ}\text{C}$, sheath gas flow rate of 40 arb. unit and auxiliary gas flow rate of 5 arb. unit. The discharge current was set 5 μA . The capillary temperature was 275 $^{\circ}\text{C}$ with a capillary voltage of 18 V and the tube lens voltage was 60 V.

Table 3.14: Gradient elution of HPLC measurements.

[min]	water [vol.%]	MeOH [vol.%]
0.0	70	30
7.0	0	100
11.0	0	100
11.5	70	30
14.0	70	30

As a proof of principle the superplasticiser was analysed at a concentration of 100 $\mu\text{l mm}^{-1}$ dissolved in 5 ml MeOH (see [Figure 3.7](#)).

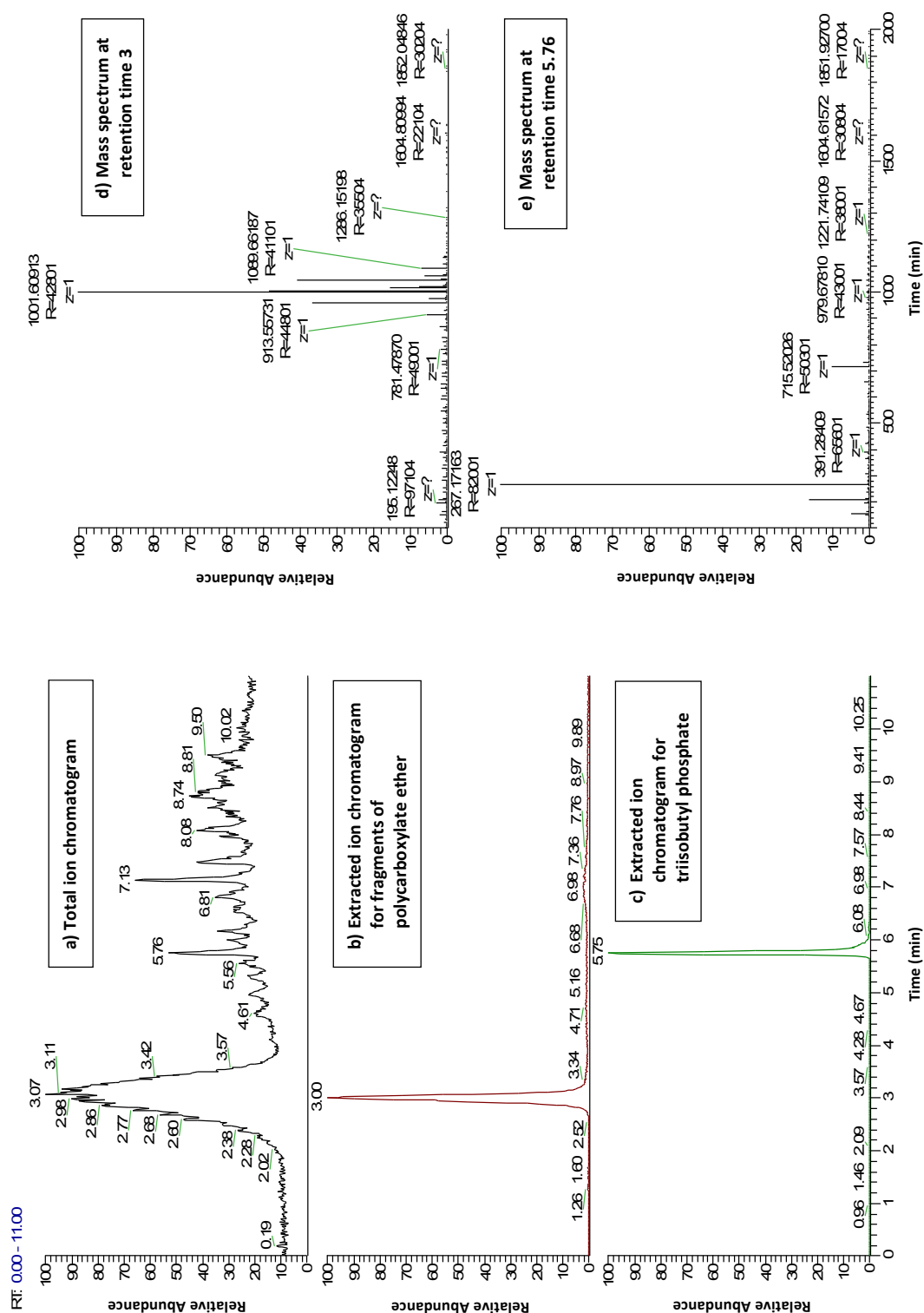


Figure 3.7: Analysis of the superplasticiser with LC-MS at a concentration of $100 \mu\text{l mm}^{-1}$ dissolved in 5 ml MeOH.

3.2.2.7 Liquid chromatography - organic carbon detection

Additional DOC determination was carried out via liquid chromatography-organic carbon detection (LC-OCD) by DOC-Labor Dr. Huber, Karlsruhe, Germany. The method is based on size exclusion chromatography (SEC) with continuous quantification of organic carbon fractions. Figure 3.8 schematically shows the working principle of the LC-OCD-system. The SEC-column (Toyopearl HW-50S, Alltech-Grom GmbH, Rottenburg-Hailfingen, Germany) and is further described in Table 3.15. The injected sample is separated in the SEC-column with a pressure of 4 bar. In addition the separated organic compounds are carried to the first UV detector (WellChrom K-200 from Knauer GmbH, Berlin, Germany) to measure UV absorbance. Subsequently the sample is acidified with ortho-phosphoric acid, in order to convert hydrogen carbonate (HCO_3^-) and carbonate ions (CO_3^{2-}) to dissolved organic carbon. The oxidation of the organic carbon compounds proceeds in the Grätzel thin film reactor where the inorganic carbon of the sample is stripped out using nitrogen as carrier gas. Similarly the aqueous sample is impinged with UV light to form radicals which promote oxidation of the dissolved organic compounds. The so formed CO_2 is stripped out with nitrogen and continuously measured using a nondispersive infrared sensor (Siemens Ultramate 6 from Siemens AG Munich, Germany). Subsequently an additional UV-oxidation at 185 nm is carried out in order to fully oxidise the nitrogen of the organic compounds to nitrate (NO_3^-). The formed nitrogen is measured by the secondary UV-detector (WellChrom K-2000 from Knauer GmbH, Berlin, Germany) at a wave length of 220 nm. The used eluent and acids are listed in Table 3.16. For analysis 1 ml of sample was used.

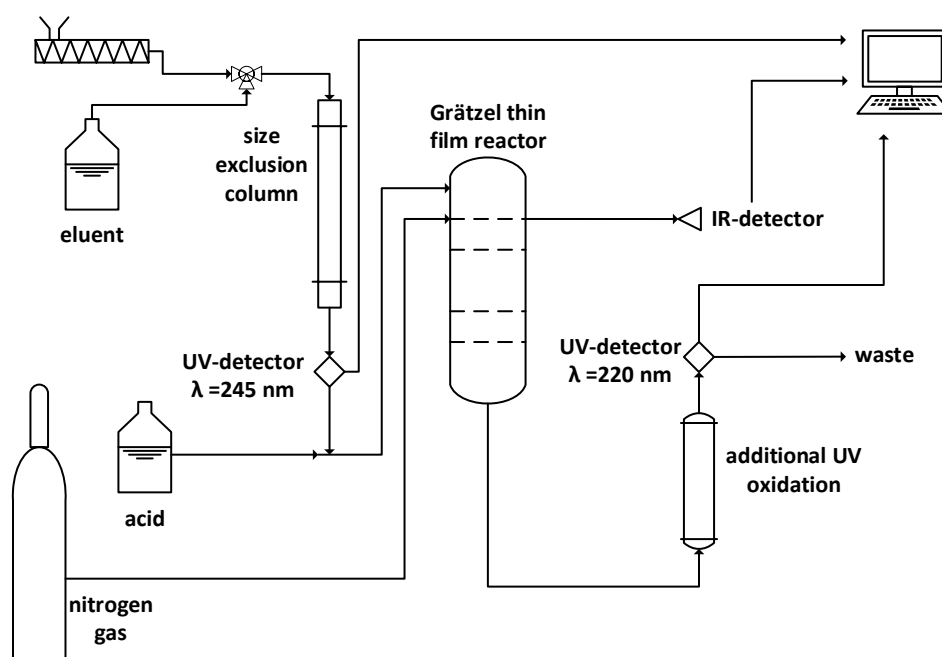


Figure 3.8: Flow-diagram of the LC-OCD-system with nitrogen detector [Huber et al., 2011].

Table 3.15: Properties of the size exclusion column.

parameter	condition
column	Toyopearl HW-50S, (250 mm x 20 mm)
particle size	20 μm to 40 μm
exclusion limit	1.8×10^4 Da ^a
pore size	12.5 nm
separation range for polyethylene glycols and oxides	500 to 18 000 Da
separation range for dextrans	500 to 20 000 Da
separation range for globular proteins	500 to 80 000 Da

^aDalton - standard unit of mass that quantifies mass on an atomic or molecular scale

Table 3.16: Eluent and acid solution used in LC-OCD system.

eluent	unit	
di-sodium hydrogen phosphate-dihydrate $\text{Na}_2\text{HPO}_4 \cdot 2\text{H}_2\text{O}$	mmol l^{-1}	8.4
potassium di-hydrogen phosphate KH_2PO_4	mmol l^{-1}	8.4
pH	-	6.6
flux	ml min^{-1}	1
acid	unit	
ortho-phosphoric acid	mmol l^{-1}	60
pH	-	1.8
flux	ml min^{-1}	0.5

3.2.3 Ecotoxicological measurements

3.2.3.1 Algal growth inhibition test with *Desmodesmus subspicatus*

This method is based on the standard [DIN EN ISO 8692, 2012] and is described briefly below. *Desmodesmus subspicatus* (formerly *Scenedesmus subspicatus*) were grown in medium BG 11 (which consists of a stock solution and a trace metal mix) with the composition provided in Table 3.17. Prior to the experiments the stock was autoclaved. The algae cultures were grown photoautotrophically at 20 °C in Erlenmeyer flasks under constant agitation. As inoculum, algae during the exponential phase of growth was used like described in [OECD, 2011] and [DIN 38412-33, 1991, DIN EN ISO 8692, 2012]. The bioassay was carried out in agitated 250 ml Erlenmeyer flasks at 20 °C with continuous illumination. The test solutions were 100 ml at dilution ratios of 1:4, 1:6, 1:8, 1:12, 1:14, 1:18 and 1:25 in the experiments. Incubation lasted 72 hours. Algal suspension density was determined by manual cell counting under a light microscope and by hemocytometer (Neubauer improved counting chamber). To calculate the specific growth rate μ of the sample the algae cell density at the beginning B_i and at the end B_j of the experiments, as well as the time at the beginning t_i and the end t_j (c.f. (3.6)) was used. An initial algal cell density of 2.0×10^4 cells ml^{-1} was used for all calculations [OECD, 2011].

$$\mu = \frac{\ln B_j - \ln B_i}{t_j - t_i} \quad (3.6)$$

Table 3.17: Algal growth medium.

	nutrition	mass [gram]
stock solution per 1 l distilled water	NaNO ₃	1.5
	K ₂ HPO ₄	0.04
	MgSO ₄ · 7 H ₂ O	0.075
	CaCl ₂ · 2 H ₂ O	0.036
	Ferric ammonium citrate	0.06
	EDTA	0.001
	Na ₂ CO ₃	0.02
	Trace metal mix	1 ml
Trace metal mix per 1 l distilled water	HBr	2.86
	MnCl ₂	1.81
	ZnSO ₄ · 7 H ₂ O	0.222
	CuSO ₄ · 5 H ₂ O	0.079
	Co(NO ₃) ₂ · 6 H ₂ O	0.049
	NaMoO ₄ · 2 H ₂ O	0.39

3.2.3.2 Mortality assay with *Enchytraeus albidus*

This terrestrial bio assay was chosen in order to investigate the influence of leachates on living organisms including the buffer function of soil. As *Enchytraeus albidus* live in the soil pore water the exposure proceeds via the water surrounding. As it is a decomposer the uptake by the food also needs to be considered. Furthermore enchytraeids have a short reproduction time at high reproduction rates, are easy to cultivate and the endpoint mortality is easy to determine [Didden and Römbke, 2001, Römbke and Moser, 2002]. The assay is based on [DIN EN ISO 16387, 2014, Römbke and Moser, 2002] and briefly described in the following. Tests were performed using a loamy sand standard soil material LUFA 2.3 from Landwirtschaftliche Untersuchungsanstalt in Speyer, Germany. In addition pure sand Schlingmeier S1-2T with a $d_{50}=1.6$ mm from Schlingmeier Quarzsand, Germany was used. Further details on the soil and the sand are listed in Table 3.18. The soil and the sand were defaunated by heating up to 80 °C for at least 16 hours [Scott-Fordsmand et al., 2008] prior to sample preparation and experiments. All tests were carried out under standardised climatic conditions at 20 °C. Tests were performed in light-dark-regime of 8-16 hours. *Enchytraeus albidus* was kept as permanent culture in soil at 10 °C to 15 °C and fed with damped oat flakes.

The mortality test was conducted in 50 ml glass containers sealed with cellulose plugs. Prior to the tests the soil or the sand was mixed with the eluate and adjusted to 60 % maximum water holding capacity (MWC). MWC was determined according to [DIN EN ISO 16387, 2014]. Eluate proportions of 100 % v/v and 50 % v/v were tested. 10 test animals were placed onto 20 g soil-eluate-mixture or sand-eluate-mixture for each test at five replicates. The dilution and control were prepared with artificial fresh water (294 mg CaCl₂ · H₂O, 123 mg MgSO₄ · 7 H₂O; 65 mg NaHCO₃ and 5.8 mg KCl in 1 l deionised water with a conductivity of less than 10 µS cm and pH 7.8) according to a procedure suggested by [Römbke and Knacker, 1989] and treated in the same way. The moisture content was adjusted daily using deionised water, as it was assumed that just the water evaporates from the eluates such that the content of substances leached from the PU was not affected. Mortality was examined after 7 d. Additional images of the test setup can be found in Appendix 2. Water tests were conducted by placing 10 animals in 5 ml eluate with the proportion 100 % v/v and 50 % v/v.

5 replicates were tested of each proportion. Mortality was checked after 24, 48, 72 h. Glass containers with screw-caps were used in order to prevent evaporation of water.

Table 3.18: Chemical composition of the soil and sand as determined by means of XRF. Data given in [wt.%].

	LUFA soil 2.3	sand Schlingmeier S1-2T
SiO ₂	80.14	>99.00
Al ₂ O ₃	5.33	0.50
Fe ₂ O ₃	1.29	0.08
CaO	0.31	0.04
MgO	0.24	< 0.02
K ₂ O	2.25	0.05
Na ₂ O	0.46	< 0.02
TiO ₂	0.38	0.02
L.O.I. ^a	9.33	< 0.30
MWC ^b	35.03	21.85

^a Loss on ignition.

^b Maximum water holding capacity determined according to [DIN EN ISO 16387, 2014].

3.2.3.3 Primary root growth test of cress (*Lepidium Sativum*) and white mustard (*Sinapis Alba*)

For the germination test, cress (*Lepidium Sativum*) and white mustard seeds (*Sinapis Alba*) were used. 25 seeds were placed on four layers of tissue (Carl Roth, Germany) in 9 cm petri dishes. The petri dishes were equipped with a lid to prevent evaporation of the eluate. Tissues were used as substrate to guarantee no influence of soil. The eluates were prepared in the concentration 100 % v/v, 50 % v/v, 25 % v/v and 12.5 % v/v, as diluter distilled water was used. To each petri dish 5 mL of each concentration was added. Distilled water was used as a control and each experiment was conducted with five replicates. The seeds were incubated at 25 °C with a light intensity of 4 lm m⁻². Additional images of the test setup can be found in [Appendix 3](#). After 4 d the primary root growth of the cress was measured. The percentage of relative seed growth (RSG) (3.7), the relative root growth (RRG) (3.8) and germination index (GI) (3.9) were calculated as follows:

$$\text{RSG [\%]} = \frac{\text{number of seeds germinated in eluate}}{\text{number of seeds germinated in control}} \times 100 \quad (3.7)$$

$$\text{RRG [\%]} = \frac{\text{mean root length in eluate}}{\text{mean root length in control}} \times 100 \quad (3.8)$$

$$\text{GI [\%]} = \frac{\text{RSG} \times \text{RRG}}{100} \quad (3.9)$$

3.2.3.4 Genotoxicity determination with umuC-assay

The UmuC-assay was chosen to get fast but reliable perceptions whether the leachates exhibit a genotoxic effect and are harmful to the environment. The assay was performed according to [Reifferscheid et al., 1991], with modifications described in [ISO 13829, 2000] as briefly described in the following. The assay was carried out with the UMU-ChromoTest kit from EBPI (Environmental bio-detection products inc., Canada) using *Salmonella typhimurium* TA1535 [pSK1002]. The bacteria were exposed to potentially genotoxic compounds/leachates. If genotoxic lesions are caused by the leachate or its ingredients, the umuC gene is induced as part of the bacterial SOS response. The plasmid pSK1002 contains the umuC gene fused to the lacZ reporter gene. The induction of lacZ is measured by conversion of colorless ONPG solution (o-Nitrophenol- β -D-galactopyranoside) to the yellowish product o-Nitrophenol by the lacZ encoded β -galactosidase. *Salmonella typhimurium* TA1535 [pSK1002] bacteria in the exponential growth phase are exposed for 120 min to 4 concentrations of the leachate, as well as to a positive control, a solvent control and a negative control. After 2 h the exposure cultures are diluted in fresh medium and allowed to grow for another 2 h. The induction and expression of the umuC-lacZ reporter gene is then assessed after lysis of the bacteria. Colorless ONPG is converted to yellowish product o-nitrophenol in the presence of induced β -galactosidase. The intensity of the colour correlates with the amount of β -galactosidase present and thus with the genotoxicity potency of the leachate. Adsorption (A) was measured at 420 nm and at 600 nm. The bacterial growth rate (G) was calculated according to equation (3.10). The relative enzyme activity of β -Galactosidase (U_S) in relative units was calculated with equation (3.11) and the induction ratio (I_R) with equation (3.12). A growth ratio less than 0.5 that expresses 50 % inhibition of biomass growth was considered to be indicative of water samples being cytotoxic. An induction ratio ≥ 1.5 was taken as the threshold at which the sample was considered as genotoxic.

$$G = \frac{\text{sample } A_{600} - \text{blank } A_{600}}{\text{control } A_{600} - \text{blank } A_{600}} \quad (3.10)$$

$$U_S = \frac{\text{sample } A_{420} - \text{blank } A_{420}}{\text{control } A_{420} - \text{blank } A_{420}} \quad (3.11)$$

$$I_R = \frac{1}{G} \times U_S \quad (3.12)$$

3.2.3.5 Mutagenicity determination with Ames-assay

The Ames fluctuation assay was performed according to OECD guidelines and [DIN 38415-4, 1999, ISO 16240, 2005]. The Muta-ChromoPlate Test kit and reagents were purchased from EBPI (Environmental bio-detection products inc., Canada) without S9 mix. As lyophilised bacteria strain, the *Salmonella Typhimurium* TA100 was chosen because for its sensitivity to detect test chemicals that cause base pair mutations [Mortelmans and Zeiger, 2000]. The assay is briefly described in the following. The used test strain of *Salmonella Typhimurium* is auxotrophic mutants in terms of histidine synthesis. This means the bacteria needs a medium with minimal amount of histidine for growth for example. If the bacteria is given to a minimum amount of histidine and allowed to grow for some time, it has the possibility to mutate back.

This prototrophic reverse mutation allows the bacteria to synthesise its own histidine now. A pH respectively colour change caused by metabolic processes of the reproducing bacteria, was used as indicator. The fluctuation assay is carried out in liquid culture. The bacteria were grown over night under constant agitation at 37 °C. The resulting TA100 culture was diluted and mixed with exposure medium. The exposure medium consisted of Davis-Mingioli salt (21.62 mL), D-glucose (4.75 mL), the pH indicator bromocresol purple (2.38 mL), D-biotin (1.19 mL) and L-histidine (0.06 mL). The exposure medium, leachate, distilled water and positive control were mixed as presented in Table 3.19. The mutagen standard was sodium azide and the negative control was DMSO. An aliquot of 200 µL was transferred into the 96 well plate, followed by incubation for 5 days at 37 °C. To prevent from evaporation, the well plates were kept in air tight plastic bags. For each experiment a negative and positive control was run. Negative wells showed a purple colour and yellow, yellowish and turbid wells were considered as positive. The experiments were conducted in triplicate. Counted positive wells per replicate were compared with counted spontaneous revertant wells in the negative control. The results were expressed as a mutagenicity ratio (MR) (3.13).

$$\text{MR [\%]} = \frac{\text{number of positive wells in eluate}}{\text{number of positive wells in negative control}} \times 100 \quad (3.13)$$

Table 3.19: Ames fluctuation assay set-up.

Procedure	Volume added [ml]				<i>S. Typhimurium</i> strain
	Mutagen standard	leachate	Exposure medium	Distilled water	
Blank	-	-	2.5	17.5	-
Background	-	-	2.5	17.5	0.005
Positive control	0.1	-	2.5	17.5	0.005
Test sample	-	0.005	2.5	17.5	0.005

3.2.3.6 Statistical analysis of the ecotoxicological assays

In order to evaluate ecotoxicological data statistical tests are necessary to exclude variations between the data and their overestimation. Experimental results were statistically analysed using one- or multi-way analysis of variance (ANOVA) which were performed for multiple comparisons or for analysing interactive effects between different factors in the phytotoxicity assays. In the Ames assay statistical significance was determined using the chi-square (χ^2) analysis as illustrated by [Gilbert, 1980]. The analysis was performed with GraphPad Prism version 7 for Windows, GraphPad Software, La Jolla, California, USA. Statistical significance is used to determine whether the null hypothesis should be rejected or retrained. The null hypothesis is the default assumption that nothing happened or changed. For the null hypothesis to be rejected, an observed result has to be statistically significant. To determine whether a result is statistically significant, one calculates the p-value, which is the probability of observing an effect given that the null hypothesis is true. The null hypothesis is rejected if the p-value is less than a predetermined level, α . α is called the significance level, and is the probability of rejecting the null hypothesis given that it is true (a type I error). It is usually set at or below 5 % [Devore, 2011].

A schematic overview of the statistic data analysis is depicted in [Figure 3.9](#).

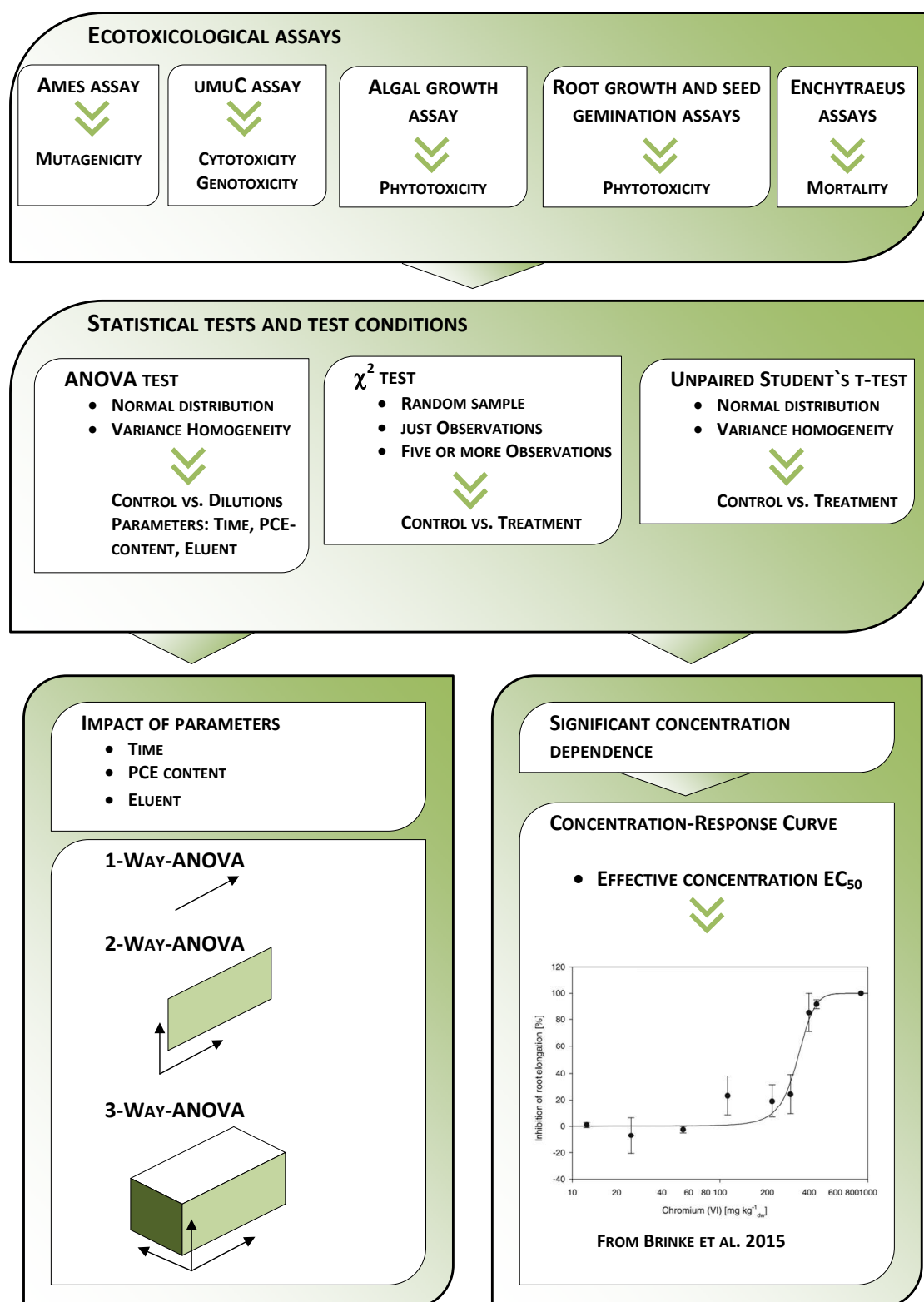


Figure 3.9: Schematic diagram of the statistical data analysis. Concentration-response curve from [\[Brinke et al., 2015\]](#).

Leaching of polyurethane systems for waterproofing purpose whilst curing¹¹

Leaching of polyurethane systems for waterproofing purposes of buildings was investigated in this study. As the curing step is the crucial point for potential impacts on the environment, leaching during this period was assessed by applying three different catalysts in different amounts as well as two eluents. A modified version of the European Horizontal dynamic surface leaching test was used. Complex assessment of all observed parameters was performed by using chemical as well as ecotoxicological tests. Inorganic and organic parameters were detected in a multi-method approach. The study was supplemented by an aquatic ecotoxicological assay on freshwater algae *Desmodesmus subspicatus* and a terrestrial assay with *Enchytraeus albidus*. While sum parameters like pH stayed constant over the test period, up to a maximum of $0.004 \text{ mmol l}^{-1}$ Zn could be leached from one of the systems. Leaching of organic compounds reached a maximum (612 mmol l^{-1}) during the first leaching steps and decreased rapidly to a minimum. Ecotoxicological tests confirm the first leaching steps to be crucial as well as the dosage of the catalyst. Soil tests with *E. albidus* showed realistic impact of the eluates on the environment.

4.1 Experimental

For detailed information on the chemical and mineralogical compositions as well as physical properties of the raw materials and the mix design of the matrix under investigation it is referred to 3.1.2. This also applies for in-depth considerations on the used analytical techniques (3.2.2).

The sample notation in this chapter refers to the following abbreviations: ZINC=zinc based catalyst, TEDA=triethylene diamine, DOTL=di-n-octyltin di-laurate, high/middle/low=dosage of catalyst.

¹¹An extended version of this chapter has been published as: Märkl, V. et al., *Water, Air & Soil Pollution* (2017) 228:280. <https://doi.org/10.1007/s11270-017-3451-0>

4.2 Results and discussion

4.2.1 Sum parameters and electrolytes

The pH value is in the range between 4 and 7 for all the samples (see Figure 4.1A and Figure 4.1B).

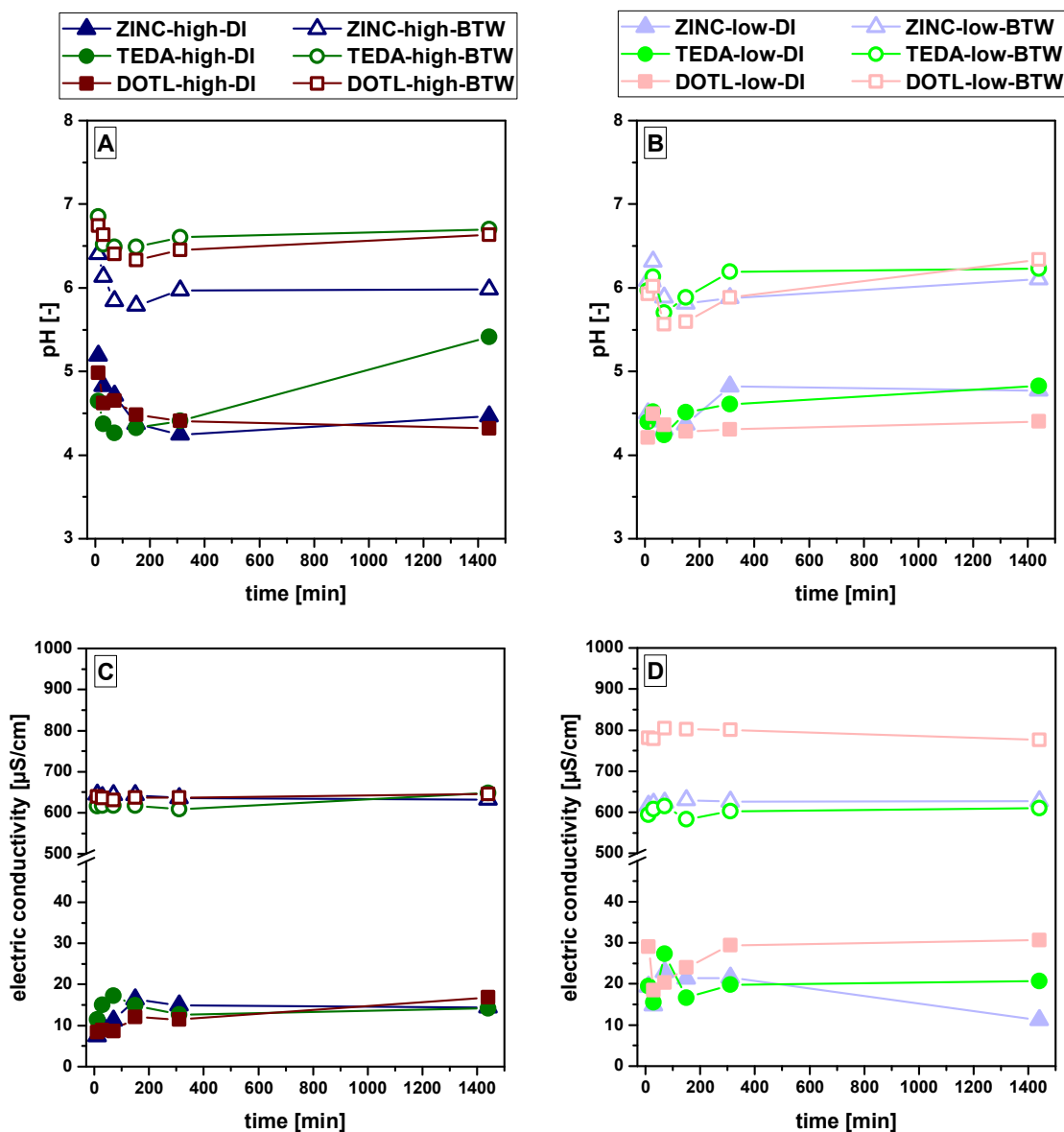
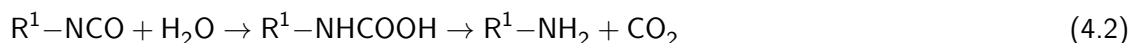


Figure 4.1: pH-value (A and B) and electric conductivity (C and D) of the eluates at the end of each leaching step .

The PUR leached with BTW shows a constant pH around 6 while the samples leached with DI have a constant pH around 4.5. This is due to the different ion concentration of the eluents and their different aggressiveness in leaching. The slight drop at the first leaching steps is due to the formation of CO_2 during the curing process (cf. equation (4.1) and (4.2)).





Here the isocyanate reacts with water under the formation of fast degrading carbamid acids to amines and carbon dioxide. Electric conductivity is nearly constant for each sample and is mainly depending on the eluent, which can be seen in Figure 4.1C and D. The samples leached with BTW show an electric conductivity around $650 \mu S cm^{-1}$ and the samples leached in DI around $20 \mu S cm^{-1}$. In every case the values of both parameters are below the threshold values given by German authorities [Deutsches Institut für Bautechnik, 2011].

A crucial parameter of the PUR systems can also be the leached amount of inorganic species. The values of Al^{3+} , Ca^{2+} , K^+ , Na^+ , Si^{4+} , Cl^- and SO_4^{2-} were in any case in the range of the eluent itself and were constant over the whole leaching period. This means that these ions are not influenced and no possible take up of ions from the PUR system takes place.

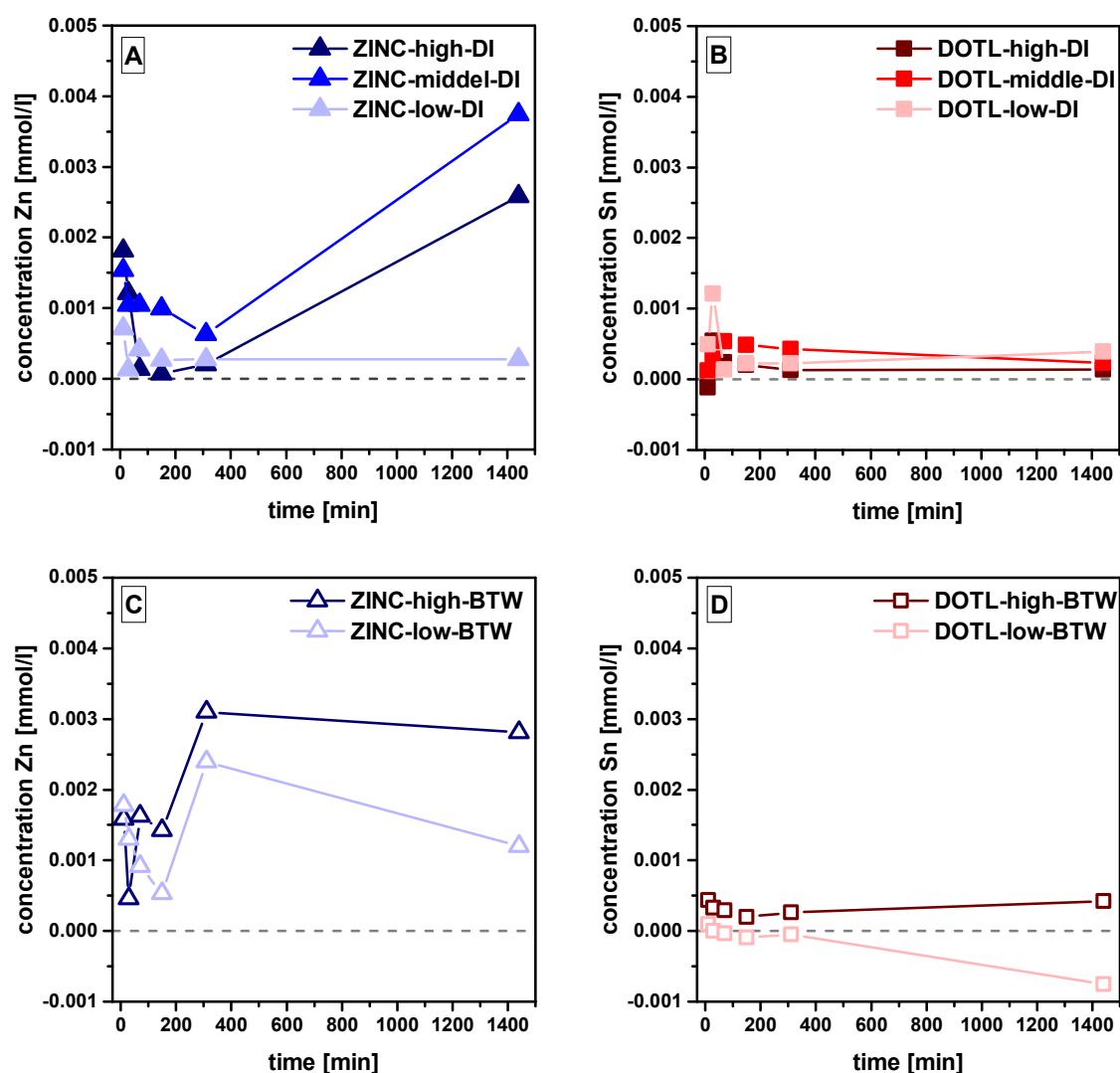


Figure 4.2: Leached Zn (A and C) respectively Sn (B and D) concentration of the catalysts at the end of each leaching step.

Therefore these ions are not further discussed here. The metal ions Zn and Sn of two of the catalysts which might have an impact on the environment are depicted for the catalysts ZINC and DOTL in [Figure 4.2A](#) and [B](#).

As the organic TEDA catalyst is of high purity, these samples were not analysed for Sn and Zn. The release of Zn decreases during the first leaching steps, while at extended leaching periods increased accumulation of Zn in the eluates is visible up to a maximum of $0.004 \text{ mmol l}^{-1}$ for ZINC-middle-DI. According to WHO standards a maximum of $0.0765 \text{ mmol l}^{-1}$ of zinc is allowed in drinking water [[World Health Organization, 2011](#)]. However organo-zinc-compounds might lead to environmental concerns even at low concentrations. In case of the DOTL catalyst Sn is leached in presence of both eluents in very low amounts, which are close to the detection limit. Furthermore DOTL is just slightly soluble according to REACH [[ECHA, 2017](#)]. Only the sample DOTL-low-DI shows a slight increase up to $0.0012 \text{ mmol l}^{-1}$ in the second leaching step. This is caused by the low amount of catalyst which causes a slow polyaddition reaction of the PUR such that more Sn can be released.

4.2.2 Organic parameters

Variations between TOC and DOC were found to be only slight. Therefore just DOC is depicted in [Figure 4.3](#). This also indicates that particles of high molecular weight are not present in the eluates. DOC is rapidly decreasing in all analysed systems. This behavior fulfills the demands of Deutsche Institut für Bautechnik [[Deutsches Institut für Bautechnik, 2011](#)]. Only in the last elution step a partially increased DOC is visible, which is related to accumulation effects due to extended leaching periods. In case of DI higher DOC values are detected throughout, caused by the higher aggressiveness of the eluent. The samples containing low amounts of catalysts show also higher DOC values, with a maximum in the first leaching step of 612 mmol l^{-1} for ZINC-low-DI. This results from low amounts of catalysts which cause a delayed polymerisation reaction leading to a longer period of starting materials not yet crosslinked. It has to be noted that the high amounts of leached organic load are due to leaching of pure PU while in other test set-ups according to [[DIN 19631, 2013](#)] the material is injected into quartz sand. In general the lowest amounts of DOC are detected in presence of DOTL as catalyst.

To obtain more specific information on the composition of the DOC the eluates were also investigated using liquid chromatography-organic carbon detection. In [Figure 4.4](#) a typical example of the chromatogram of the eluates is depicted. The detected signals correspond to Huber et al. [[Huber et al., 2011](#)] in the region of low molecular weight neutrals. Differentiation of the compounds is possible due to their retention time and the corresponding molecular weight. The UVD signals (signal A, B and C in [Figure 4.4](#)) refer to UV active substances as nitrogenous compounds and the detected peaks can be ascribed to amines. In case of TEDA as catalyst the humps are caused by the catalyst itself. In general the UVD signal is composed of a mixture of high and low weight nitrogenous molecules. The signals D and E in [Figure 4.4](#) refer to the detected OCD. Signal D can be ascribed to higher molecular weight carbonaceous molecules, which might be caused by first leached reaction products. Signal E can be traced back to the used polyols. The measured OCD and CDOC¹² values as presented in [Table 4.1](#) are in good agreement with the DOC measurements ([Figure 4.3](#)). Only the values of TEDA-low-DI deviate notably from each other, which might be due to the different measurement techniques and variations during sample preparation. However, the

¹²chromatographically detectable DOC

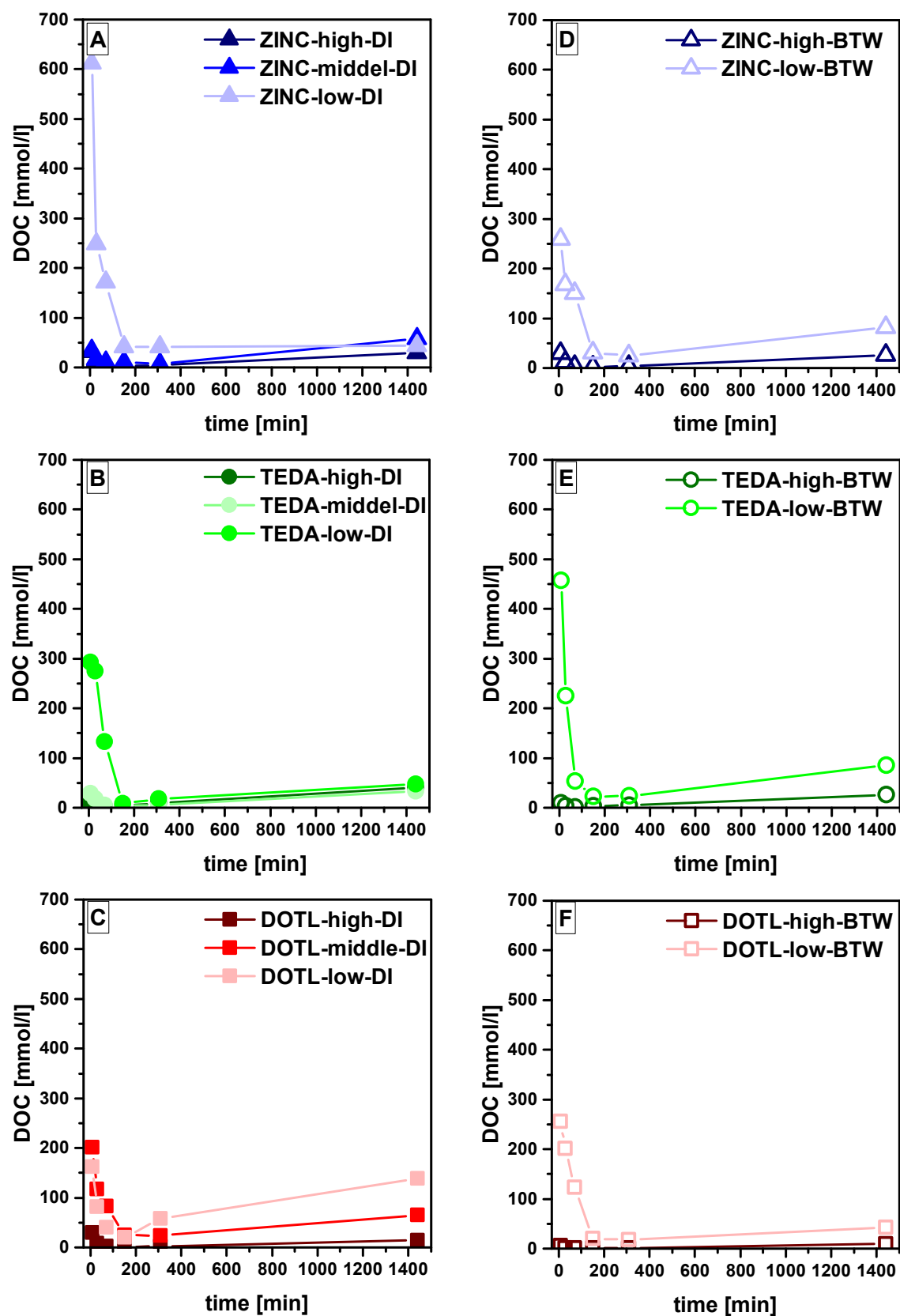


Figure 4.3: DOC of the eluates at the end of each leaching step leached with demineralised water (A, B and C) and Berlin tap water (D, E and F).

qualitative curve progression is similar for all investigated systems showing the reduction of leached organic compounds over time.

As LC-OCD analyses are mainly used to get deeper information on the mode of action of filtration processes in water treatment, more in-depth investigations are needed regarding the analysis of building materials leachates.

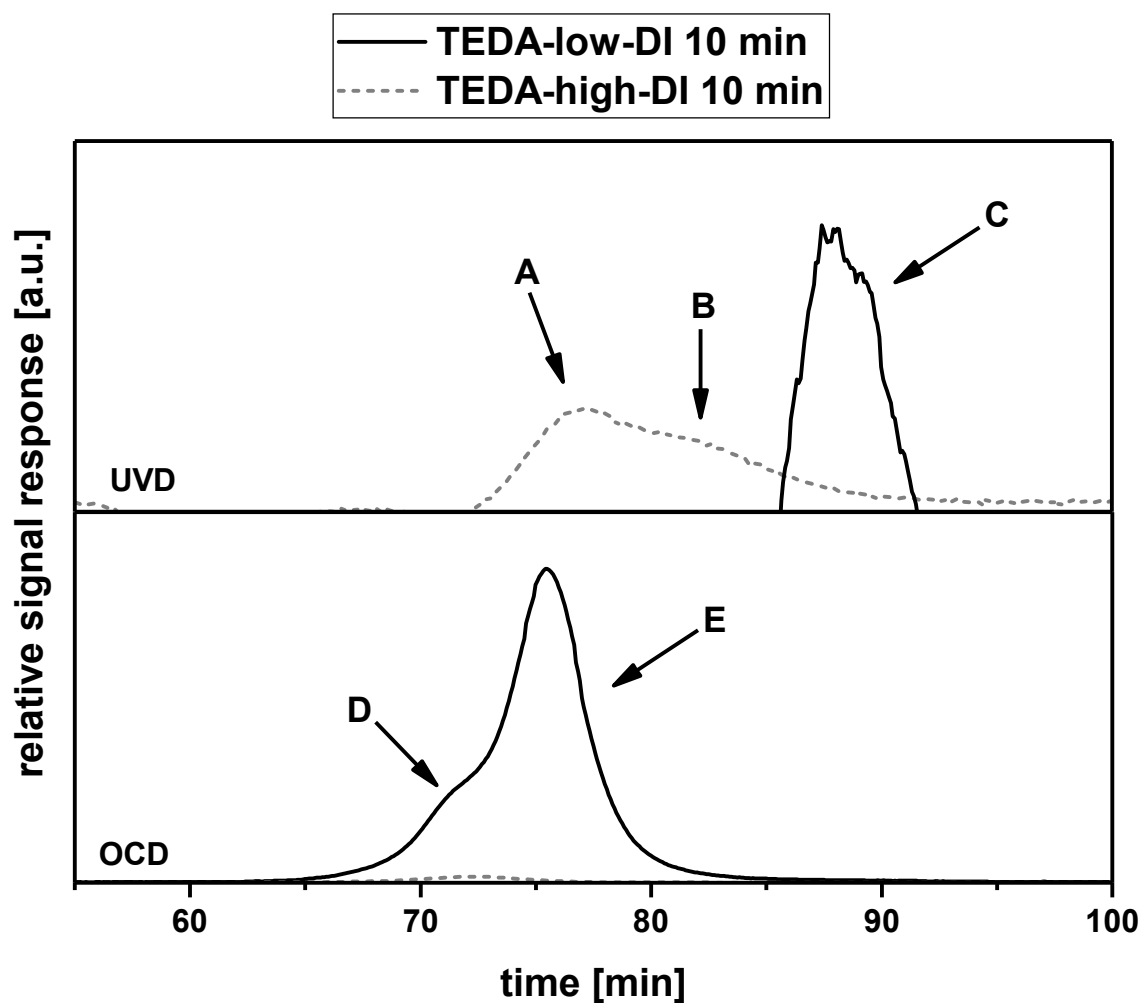


Figure 4.4: Typical LC-OCD chromatogram of the eluates. A - higher weight nitrogenous molecules; B and C - lower weight nitrogenous molecules; D - higher weight carbonaceous molecules; E - lower weight carbonaceous molecules.

Table 4.1: LC-OCD data.

time [min]	ZINC-high-DI		ZINC-low-DI		TEDA-high-DI		TEDA-low-DI	
	DOC	CDOC ^a	DOC	CDOC ^a	DOC	CDOC ^a	DOC	CDOC ^a
	[mmol l ⁻¹]							
10	20.23	18.15	717.18	790.94	10.82	16.65	891.52	782.62
30	9.32	7.74	222.63	256.02	4.58	5.49	363.83	324.70
70	4.58	3.50	55.87	62.44	2.66	3.66	75.35	68.27
150	3.75	2.83	64.94	58.28	2.75	3.00	55.95	49.12
310	3.50	2.66	70.60	74.10	6.24	7.91	70.10	63.28
1140	22.56	18.82	245.44	218.55	35.55	46.12	197.57	203.98

^a CDOC = chromatographically detectable DOC.

Sample notation: ZINC=zinc based catalyst, TEDA=triethylene diamine, DOTL=di-n-octyltin di-laurate, high/middle/low=dosage of catalyst.

4.2.3 Ecotoxicological aspects

4.2.4 Algal growth inhibition assays with *Desmodesmus subspicatus*

The impact of PUR leachates on the aquatic environment was simulated with *Desmodesmus subspicatus*. Results on the determined growth rates are depicted in Figure 4.5. Within each group significant effects (on a 5% acceptance level ¹³) on algal growth rates compared with their respective control could be detected. Algal growth rate was influenced variously, depending on the type of catalyst, the catalyst dosage and the contact time of the eluent with the PUR-system. In general the ZINC-catalyst promotes the growth rate less pronounced compared to its control at a 5% acceptance level. However, one exception can be made for early age leachates for the ZINC-low-DI system at low dilutions, where an increased algae growth rate could be observed. This is due to the organic carbon, which is leached to a higher extent in the early leaching steps. Only moderate effects on the growth rate can be seen for the released zinc catalyst samples. The organic TEDA catalyst promotes algae growth for low diluted samples in the TEDA-low-DI system in the early and late stage. Additionally the growth ratio is also promoted in the TEDA-high-DI system for late age leachates. In consistency with the results of the DOC and LC-OCD analysis more organic carbon is leached during the early age stage (10 and 30 min) which contributed to an increased algae growth rate. Although the contact time is short, enough organic carbon could be released from the PUR-system, which is in the process of forming a dense network. The last leaching step (1440 min) is longer in time, thus accumulation of organic carbon takes place, which again promotes algae growth.

In addition Cuellar-Bermudez et al. [Cuellar-Bermudez et al., 2016] report that some microalgae species can grow on organic compounds such as urea by changing their metabolism and therefore algae species show increased growth rates in such bio-assays. Furthermore it is reported that heavy metals can be removed by algae species from wastewater due to sorption and bio-accumulation effects [Cuellar-Bermudez et al., 2016].

¹³The acceptance level was set to 5%, which means that if the P value is less than 0.05, the null hypothesis is rejected; if P is greater than or equal to 0.05, the null hypothesis is not rejected.

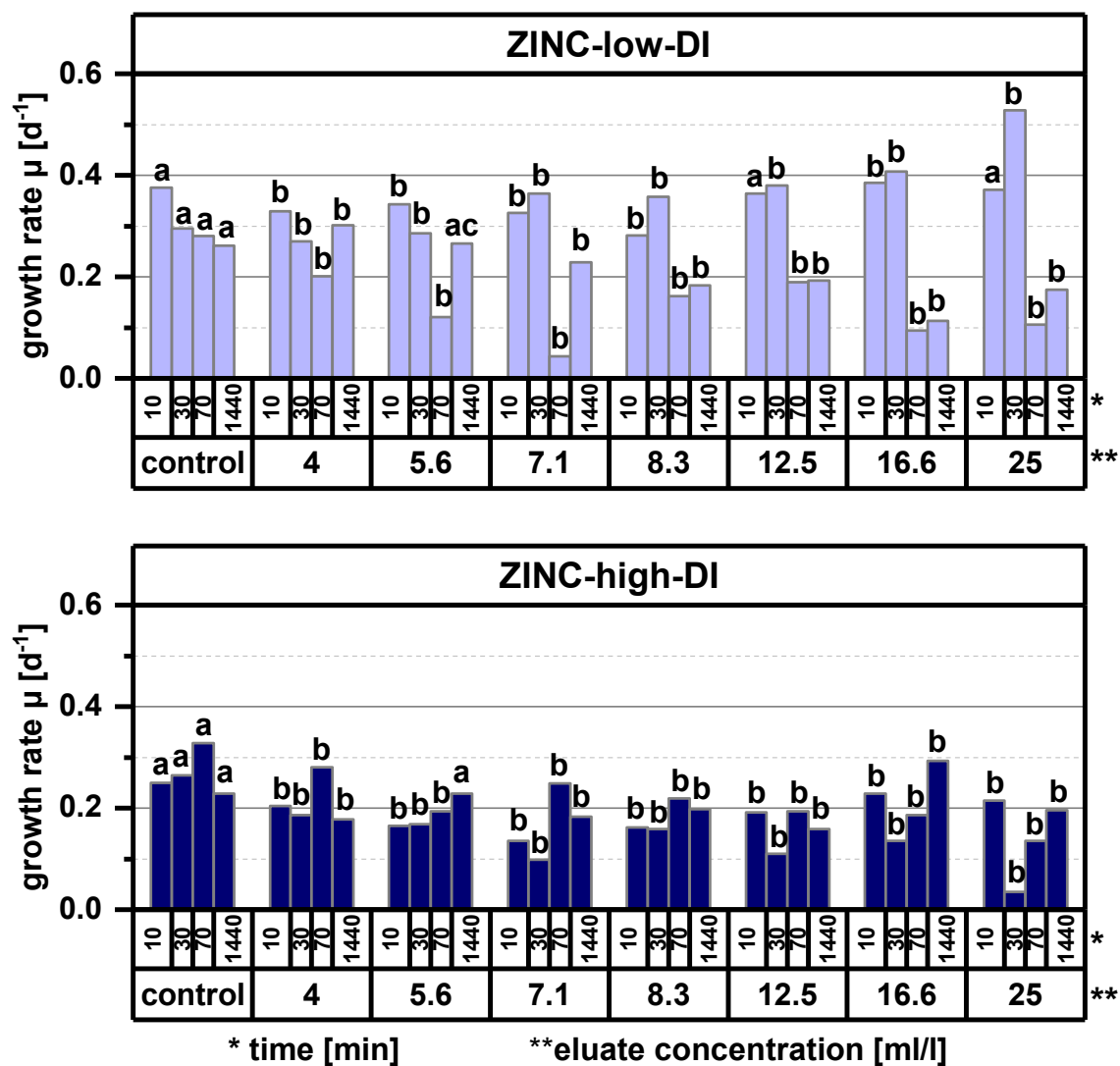


Figure 4.5: Growth rate of *Desmodesmus subspicatus* exposed to different concentrations of polyurethane eluates with different catalysts (ZINC and TEDA). Standard deviations were in any case not higher than $\pm 5\%$. Columns within each type of eluate, marked with the same letter are not significant different from its control (Dunnett test, $p > 0.05$).

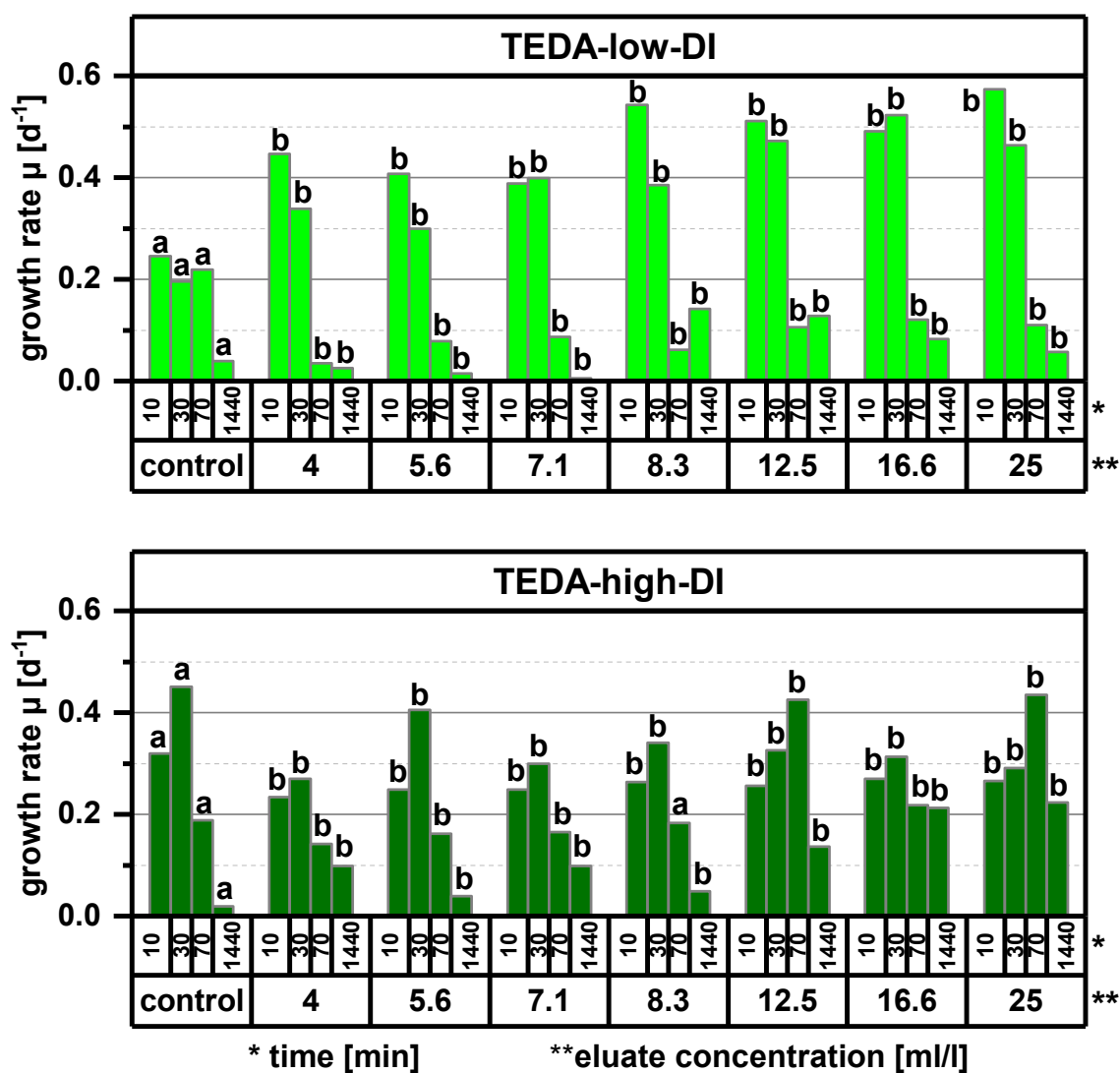


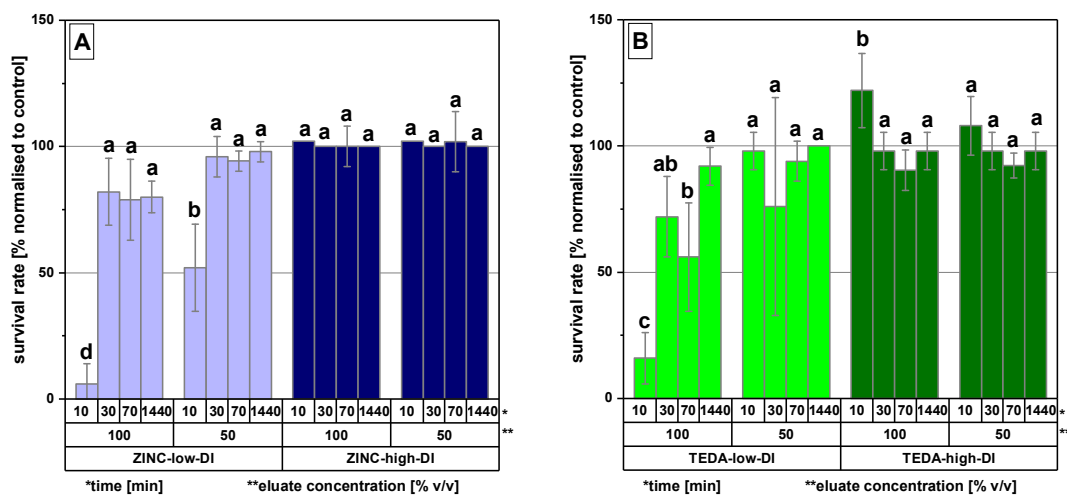
Figure 4.5 (Continued): Growth rate of *Desmodemus subspicatus* exposed to different concentrations of polyurethane eluates with different catalysts (ZINC and TEDA). Standard deviations were in any case not higher than $\pm 5\%$. Columns within each type of eluate, marked with the same letter are not significant different from its control (Dunnnett test, $p > 0.05$).

4.2.5 Mortality assays with *Enchytraeus albidus*

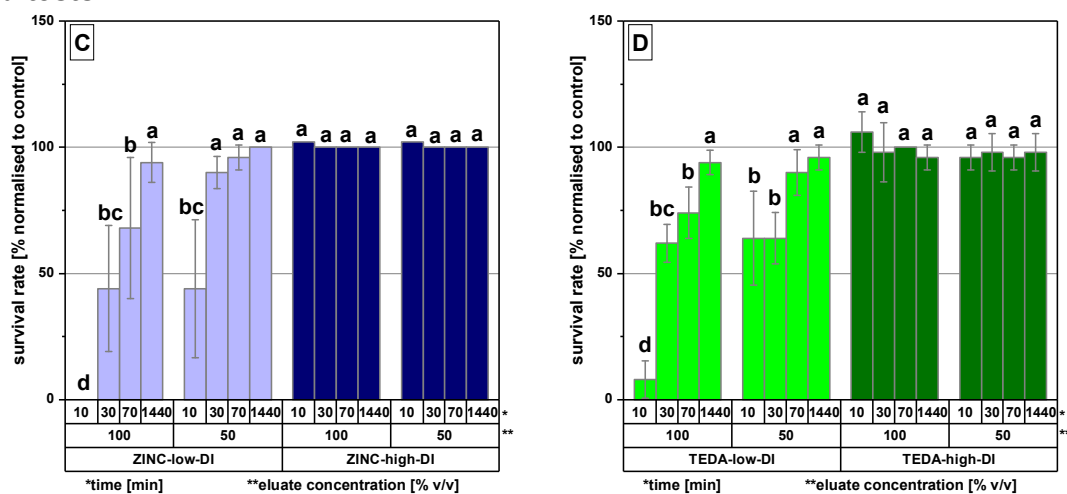
To determine the effect of the leachates on terrestrial organisms three different assays with *Enchytraeus albidus* have been performed (Figure 4.6). In all three tests the samples with high dosage of catalyst show no significant difference compared to the control. This results from an increasing degree of reaction with increasing catalyst content such that a faster formation of a dense PUR network occurs. As a result less inorganic and organic compounds can be leached from the PUR. Nonetheless, at low catalyst dosages toxic effects can be observed in all three assays. Especially the early age leachates are significantly different at a 5% acceptance level. If less catalyst is added to the PUR mixture, the reaction is promoted less, the network is formed slower and therefore more components can be leached. However, until 70 min the toxic effect is reduced significantly and these samples are not significantly different from the control or the 1440 min leachate. In the soil tests the ten minutes ZINC-low-DI leachates show significant toxic effects for both eluate concentrations. In this context it should also be noted that Lock and Janssen [Lock and Janssen, 2001] report that zinc toxicity to *E. albidus* is mainly depending on the pH and the cation exchange capacity of the soil. For TEDA-low-DI only the pure eluate shows toxic effects at 10, 30 and 70 min while no toxic effects can be observed for the diluted eluate. In the sand tests (Figure 4.6C and D) the buffering function of the soil is not given. This results in a reduced survival ratio of the 10, 30 and 70 min leachates of ZINC-low-DI and TEDA-low-DI compared to the soil tests. The toxic effect of the early age leachates can not only be attributed to the zinc ion in the catalyst but also to the high organic carbon load. The results of the water tests for ZINC-low-DI and TEDA-low-DI are depicted in Figure 4.6E and F. In general the results do not differ noteworthy from the ones discussed above. At high catalyst dosages only the 10 min leachate for TEDA-high-DI shows toxic effects with a survival ratio of 90% due to unknown reasons.

As the leachates show toxic effects only in the early stage it can be assumed that the high TOC in combination with the leached ions cause of the significantly reduced survival ratio of the annelids.

soil tests



sand tests



water tests

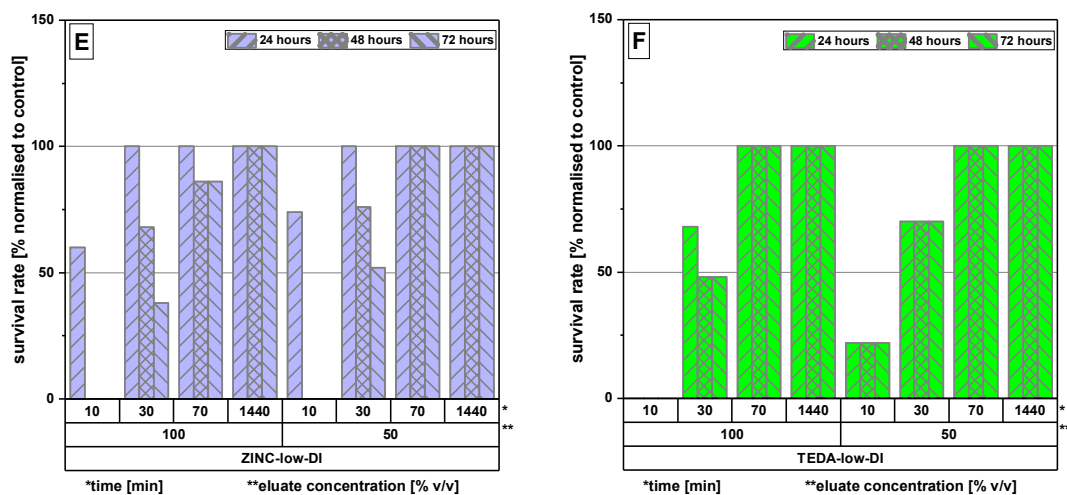


Figure 4.6: Survival ratio of *Enchytraeus albidus* during soil tests (A and B), sand tests (C and D) and water tests (E and F) with ZINC (left) and TEDA (right) eluates. Note that different concentrations of catalyst and different proportions of leachates were examined. Columns within each type of eluate, marked with the same letter are not significant different (Tukey test, $p > 0.05$).

4.3 Conclusions

In this study polyurethane materials for waterproofing purposes prepared with different catalysts at different dosages were tested for their environmental sustainability. The leachates were analysed from a chemical and an ecotoxicological point of view applying a multi-method approach.

- (i) A tank test was used to get information of leachable components of polyurethane materials. The test was customised to the material to get information whilst curing.
- (ii) Three dosages of catalyst were investigated during this study, while the low dosage was close to the reaction minimum and represents an improper composition. In this case the polymerisation reaction is very slow, a poor PU-network is formed thus leaching of inorganic and organic compounds is increased which results in significantly increased effects in the ecotoxicological assays. In contrast the middle and high dosages of the catalysts, representing correct compositions lead to fast polymerisation reactions with a dense PU-network. From these systems marginal amounts of inorganic and organic constituents can be leached and only marginal effects during the ecotoxicological assays are visible.
- (iii) pH and electrical value stayed constant over the whole leaching period depending on the aggressiveness of the eluent.
- (iv) Ionic species are leached only in very low amounts and within the limits of different regulations, however an intensified version of the tank leaching test was used. A maximum of zinc of $0.004 \text{ mmol l}^{-1}$ and a maximum of tin of $0.001 \text{ mmol l}^{-1}$ was observed. The maximum of DOC was 612 mmol l^{-1} during the first leaching step. DOC decreased rapidly to about 25 mmol l^{-1} in any case. LC-OCD measurements confirm these results and showed that the leached OCD was in the region of low molecular weight neutrals.
- (v) Aquatic and terrestrial ecotoxicological bioassays were performed on PUR leachates. The systems with low catalyst dosage showed a higher toxic ability, especially in the early age leachates. This effect might be caused by the catalyst but also by the organic carbon load. This should be investigated in further research.

The results of all performed tests showed that after a first wash-off period in combination with the ongoing network formation, from the leached compounds only slight hazard impact is to be expected. This effect can be minimized by selecting a suitable catalyst and by choosing the proper concentration. In accordance with other leaching studies on building materials for grouting purpose like cement in combination with superplasticisers, a wash-off of the organic compounds can be determined [Märkl and Stephan, 2016, Märkl et al., 2017]. Investigation of different types of bio-based polyols based on renewable resources would enable to gain better understanding of eco-friendly, low ecotoxicological impact polyurethane systems. Further in depth investigations of the ecotoxicological aspects using a bio test battery might also be rewarding.

Investigation of the leaching behaviour of a novel cement-polyurethane hybrid material for waterproofing purpose¹⁴

A novel cement-polyurethane hybrid material invented to stop massive water ingress during e.g. tunnel construction is presented in this study. A special emphasis is put on the leaching behaviour and the environmental impact of the material. For this purpose, a batch test as worst-case scenario and a tank leaching test were used to compare different material combinations. Besides sum parameters like pH value, major elements from cement and organic species were analysed in the leachates. Simulations about the release behaviour of ionic species as well as the total organic carbon were performed. Release was governed by surface wash-off effects for all species except for Al which was controlled by diffusion. Leaching of major elements correlated with the amount of ground granulated blast-furnace slag added to substitute ordinary Portland cement. Total organic carbon content was measured and the cumulative value was in the range of 83 mmol m⁻² to 49 mmol m⁻² after 64 d of leaching. All investigated parameters were below the threshold values governed by German authorities. In addition, ecotoxicological tests with earthworm species (*Enchytraeus albidus*) have been performed to explore the impact of the leachates on the environment. While in pure eluate tests the early age leachates showed toxic effects, in soil and sand tests the buffering function plays a key role to prevent possible hazardous effects.

5.1 Experimental

For detailed information on the chemical and mineralogical compositions as well as physical properties of the raw materials and the mix design of the matrix under investigation it is referred to 3.1.3 and 3.2.1.2. This also applies for in-depth considerations on the used analytical techniques.

The sample notation in this chapter refers to the following abbreviations: C1/C2/CIII=kind of cement, 0/10/20/30=substitution of cement with GGBFS.

¹⁴An extended version of this chapter has been accepted as: Märkl, V., Stenzel, J., Reichert, A. et al. *Water Air Soil Pollut* (2017) 228: 350. <https://doi.org/10.1007/s11270-017-3537-8>

5.2 Results and discussion

5.2.1 Batch test

During the batch test a reduced matrix was investigated, including all samples prepared with C1 and the sample with C III. In Table 5.1 the pH value and the electrical conductivity after the 24 hours batch leaching test is presented for all three parallel samples.

Table 5.1: Measured pH value and electric conductivity at the end of the 24 h batch test.

Sample	pH	electric conductivity [mS cm ⁻¹]
C1-0	12.5	9.86
C1-10	12.6	11.04
C1-20	12.5	9.04
C1-30	12.5	9.70
C III	12.4	8.16

Sample notation: C1/CIII=kind of cement,
0/10/20/30=substitution of cement with GGBFS.

The high pH value caused by the typical alkaline character of Portland cement-containing systems dominates both parameters. Electric conductivity and pH value correspond well with data from literature for leached fresh cast concrete or concrete at very early curing times [Meza et al., 2008, Engelsen et al., 2009, Butera et al., 2014]. The total fraction of leached ionic species after the batch test is presented in Figure 5.1. Amounts of leached Al³⁺ were close to the detection limit in any case and are not presented here. The leached ions (SO₄²⁻, K⁺, Cl⁻ and Si⁴⁺) depend on the amount of GGBFS in the used mixtures as indicated in Figure 5.1. Ca²⁺ and Na⁺ are leached in the same amounts, but the amounts of those leached ions are increased for C III. It is assumed that a solubility limit is reached for those ions, which could be circumvented by choosing a different w/s-ratio. The amount of leached SO₄²⁻ and Si₄⁺ decrease with increasing amount of GGBFS as sulfate originates mainly from the OPC (cf. Table 3.3), just mixture C III shows higher values. The amount of leached Cl⁻ and K⁺ increase with increasing GGBFS content for all C1 samples, however C III showed lower amounts. In any case the TOC and DOC after correction to the blank were -0.03 mmol l⁻¹ and 0.007 mmol l⁻¹ for C III. The TOC and DOC values were comparable throughout without any significant differences. Although a high amount of PUR is included in the samples the observed TOC values were not found to be increased. The values determined for C III show clear differences compared to the remaining matrix under investigation (Figure 5.1). C III contains commercially available CEM III with a GGBFS-content in the range of 36 wt.% to 65 wt.% in accordance to EN 196-1. The content of GGBFS cannot be determined exactly. This also applies for the composition of OPC and GGBFS used in this cement. Higher amounts of SO₄²⁻ and TOC might be caused by different type and/or amount of grinding aid (often lignosulfonate, triethanolamine, triisopropanolamine, etc.) and different cement or GGBFS-composition.

In general none of the ionic parameters investigated during the batch test as worst-case scenario exceeded the threshold values defined by the German Drinking Water Regulations [Bundesministerium der Justiz, 2001]. Only pH-value and electrical conductivity show increased

values. However, according to the [Deutsches Institut für Bautechnik, 2011] these two parameters are by no means an exclusion criteria as they reflect a typical behaviour for cementitious materials which has to be taken in consideration during the evaluation procedure.

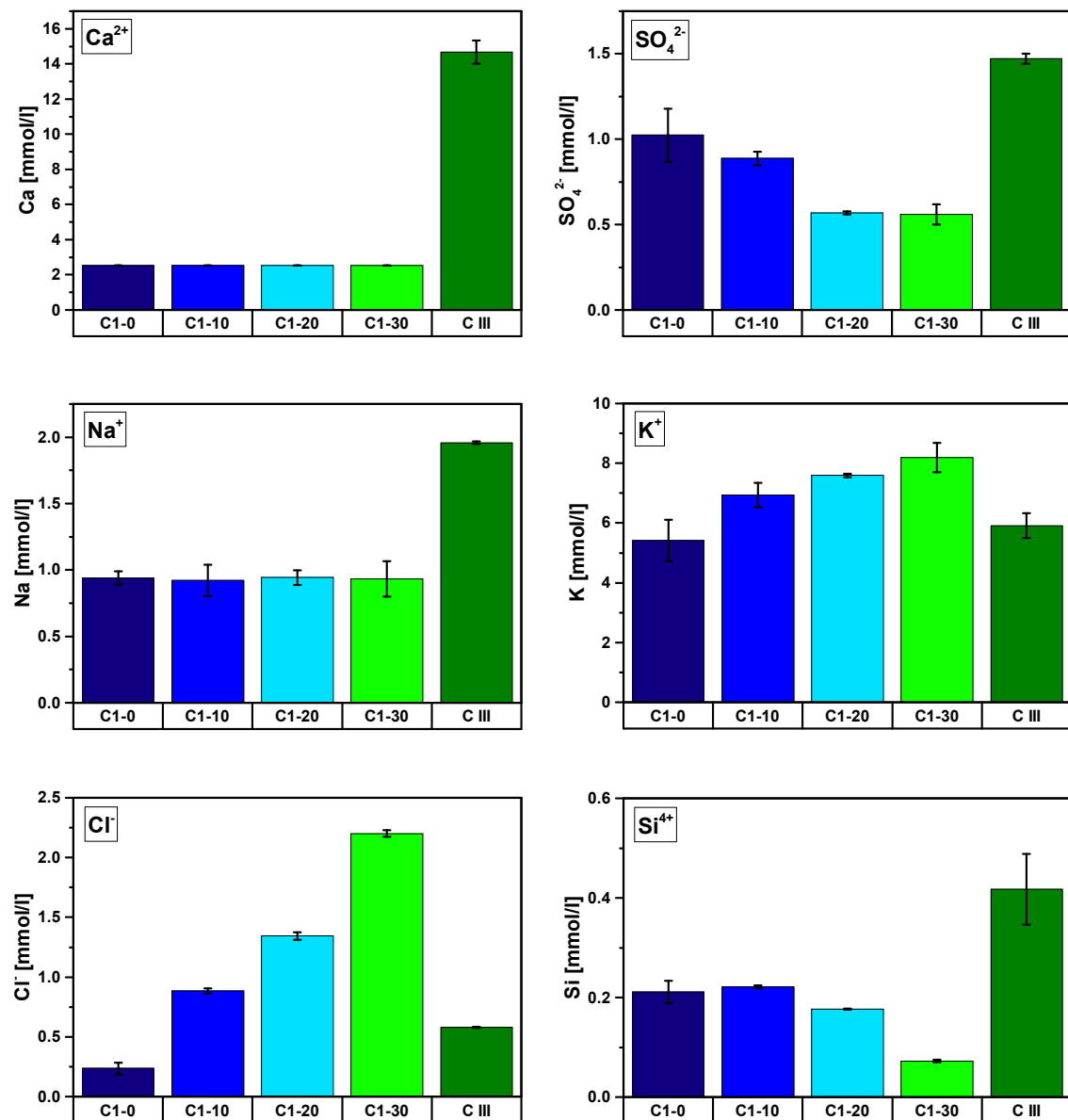


Figure 5.1: Amount of leached ions at the end of the batch test.

The results of the 24 hours batch test are summarised in [Table 5.2](#).

Table 5.2: Summarised results of the 24 h batch test.

sample	GGBFS content	pH	electric conductivity	Ca ²⁺	Na ⁺	Cl ⁻	SO ₄ ²⁻	K ⁺	Si ⁴⁺	TOC
C1-0	increase ↓	→	→	→	→	increase ↓	decrease ↓	increase ↓	decrease ↓	→
C1-10										
C1-20										
C1-30										
C III										

↓ = decreasing value.

↑ = increasing value.

→ = comparable values.

Sample notation: C1/C2/CIII=kind of cement, 0/10/20/30=substitution of cement with GGBFS.

5.2.2 Tank test

5.2.2.1 Sum parameters, inorganic and organic species

Pore solutions of cement based materials typically show a pH of ≥ 13 with a corresponding OH⁻ concentration between 110 mmol l⁻¹ and 140 mmol l⁻¹ [Deschner et al., 2012, Schöler et al., 2015, Lothenbach and Winnefeld, 2006, Leemann et al., 2011, Nebel and Spanka, 2013]. Whilst leaching the surrounding eluent has a different pH which is normally lower than the pH of the cement pore solution. This leads to a concentration gradient which is present where hydroxyl ions can diffuse from the pore solution towards the surrounding eluent. The built hydrate phases are more or less soluble and in consequence a concentration gradient also increases the possible dissolution of hydrates. The measured pH value and electric conductivity of the investigated cement-polyurethane hybrid material are given in [Figure 5.2](#). The pH is around 11.5 throughout the first four elution steps, whereas towards later eluate changes pH decreases. Electric conductivity, which is in any case lower than the threshold value stated by [Deutsches Institut für Bautechnik, 2011], increases during the first four elution steps until a maximum is reached while at extended leaching periods a decrease is observed. Constant or just slightly increasing pH values combined with increasing electric conductivity indicate a uniform release of ions.

The decreases of both parameters towards later leaching periods in combination with extended leaching steps indicate interaction processes between the sample and the eluent. As the material basically is of a cement suspension the behavior in terms of pH and electric conductivity is different comparing to concrete or mortar [Müllauer et al., 2012, Müllauer et al., 2015, Märkl and Stephan, 2016] which can be attributed to the included polyurethane. The overall tendency of decreasing pH and electric conductivity at increasing GGBFS-content might be caused by a decreasing porosity towards higher GGBFS additions [Kocaba, 2009]. However, as no porosity measurements were performed this phenomenon is not fully explored.

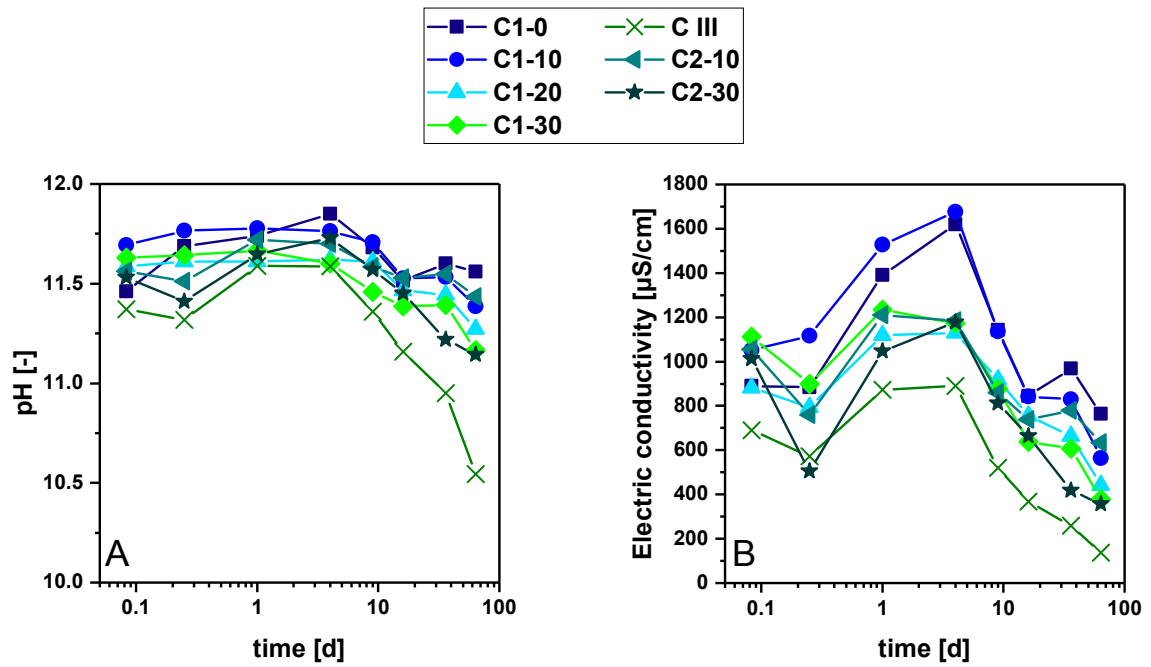


Figure 5.2: Measured pH-value (A) and electric conductivity (B) at the end of each elution step during the tank test.

According to Kamali et al. [Kamali et al., 2003] SCM play a key role in the improvement of the leaching behaviour. Porosity is decreased by the addition of SCM like fly ash or silica fume which increases the resistance to leaching. Furthermore, pozzolanic effects, especially in the presence of fly ash, reduce the portlandite content whereby a more stable and denser C-S-H is formed. This leads to decelerated diffusion of ions and dissolution of hydrates. In this study latent-hydraulic GGBFS is used. According to Çakır et al. [Çakır and Aköz, 2008] porosity decreases with increasing GGBFS addition which induces improved resistance against water ingress or aggressive solutions. Similar behaviour is also reported by Wang et al. [Wang et al., 2003] and De Belie et al. [De Belie et al., 2010]. Besides the main reaction of the polyol and the isocyanate to form polyurethane during the polyaddition reaction a side reaction which might play a key role in the leaching behaviour of this hybrid material proceeds. During this side reaction the isocyanate reacts with water provided by the cement suspension to form carbon dioxide. Additionally the formed carbon dioxide may cause an increased degree of porosity which leads to a higher degree of leached ionic species. This proceeds as schematically shown in equation (4.1) and (4.2) in Chapter 4.

In Figure 5.3 the leached amount of ionic species after each eluate change during the tank test is depicted. Weakly bound ions like sodium, potassium and chloride are preferably leached. Especially with increased amount of GGBFS, leaching of chloride and potassium also increased. These two ion species can also act as counter ion¹⁵ of the used additives. They dissolve in the mixing water, are weakly bound in the hardened paste and easily dissolve in the pore solution and the eluent. However, the amount of chloride leached for samples C III, C2-10 and C2-30 was negligible, which may be due to the formation of monochloroaluminates

¹⁵An ion accompanying the PCE in order to maintain its electric neutrality. When adding the PCE to the mixing water its active component adsorbs on the cement particle and the counter ion dissociates in the water [Plank et al., 2015].

of calcium [Malviya and Chaudhary, 2006b]. Sulphate is leached from sulphur-containing hydrates like ettringite or monosulphoaluminate [Batchelor, 1990]. However, most of the sulphate is leached during the first three leaching intervals. Calcium was leached at every leaching step from portlandite ($\text{Ca}(\text{OH})_2$) which is formed during the hydration of OPC but also from C-S-H phases and calcium metal compounds. According to [Malviya and Chaudhary, 2006b] portlandite can dissolve at relatively high pH (≥ 13) during leaching.

Aluminium is leached at increasing amounts towards the late leaching steps. Especially with increasing amounts of GGBFS more aluminium can be leached. With further reaction of the GGBFS or other Al-containing SCM like especially fly ash, Al increases in the pore solution towards later ages [Deschner et al., 2012, Schöler, 2016] which is a typical behaviour of such SCMs that act as additional Al-carrier. The Al concentration in the leachate exceeds the Al threshold value of the German regulations for drinking water [Bundesministerium der Justiz, 2001]. The above described amount of leached ionic species is in good accordance with findings of [Müllauer et al., 2015], who also stated that calcium, aluminium and sulphate leaching is caused by dissolution of AFt ($[\text{Ca}_3(\text{Al,Fe})(\text{OH})_6 \cdot 12 \text{H}_2\text{O}]_2 \cdot x_3 \cdot n\text{H}_2\text{O}$) and AFm ($[\text{Ca}_2(\text{Al,Fe})(\text{OH})_6] \cdot x \cdot n\text{H}_2\text{O}$) [Faucon et al., 1996, Faucon et al., 1997]. The above described findings also correspond with the cumulative release rate $E_{64,i}$ of the ionic species (Table 5.3). It needs to be mentioned that increasing GGBFS-content leads to a decreasing C/S-ratio [Schöler et al., 2015] such that Si is able to accumulate at the peripheral zone and can be leached [Han et al., 2014].

Table 5.3: Cumulative release rate $E_{64,i}$ of the ionic species at the end of the tank test. Data given in $[\text{mmol m}^{-2}]$.

	Al^{3+}	Ca^{2+}	Na^+	K^+	Si^{4+}	Cl^-	SO_4^{2-}
C1-0	5.7	1287.2	112.6	444.0	100.5	24.5	84.7
C1-10	8.1	1243.9	120.5	518.1	122.7	62.2	78.1
C1-20	9.1	948.9	115.0	544.9	113.4	80.2	43.9
C1-30	10.4	961.8	119.4	659.2	112.9	132.7	50.0
C III	22.7	726.6	119.2	403.6	145.1	36.6	23.3
C2-10	18.7	918.1	182.8	718.4	117.3	45.8	24.7
C2-30	21.1	942.2	154.4	560.3	136.9	66.0	28.9

Sample notation: C1/C2/CIII=kind of cement, 0/10/20/30=substitution of cement with GGBFS.

The determination of the dominant leaching mechanism of Ca^{2+} , K^+ and Al^{3+} for selected systems is presented in Figure 5.4 and Table 5.4. Each ion shows the same leaching mechanism independently from the amount of GGBFS added to the mixture. The leaching mechanism for the weakly bound potassium and the constantly leached calcium are controlled by surface wash-off effects while Al-leaching was controlled by diffusion. Furthermore [Malviya and Chaudhary, 2006a] and [Dutre and Vandecasteele, 1996] state that calcium shows low mobility, especially with increasing cement content. In contrast potassium showed medium to high mobility as the cement content decreased in the mixtures.

The amount of TOC as used as sum parameter to describe the amount of leached organic species is depicted in Figure 5.5. It can be seen that the amount of leached organic species is continuously decreasing and therefore fulfills the requirements of German regulations [Deutsches Institut für Bautechnik, 2011, Bundesministerium der Justiz, 2001]. The cumulative released amount of TOC after 64 d of leaching ranges from 83 mmol m^{-2} for C1-10 to 49 mmol m^{-2} for C1-20. Table 5.5 summarizes the dominating leaching mechanisms,

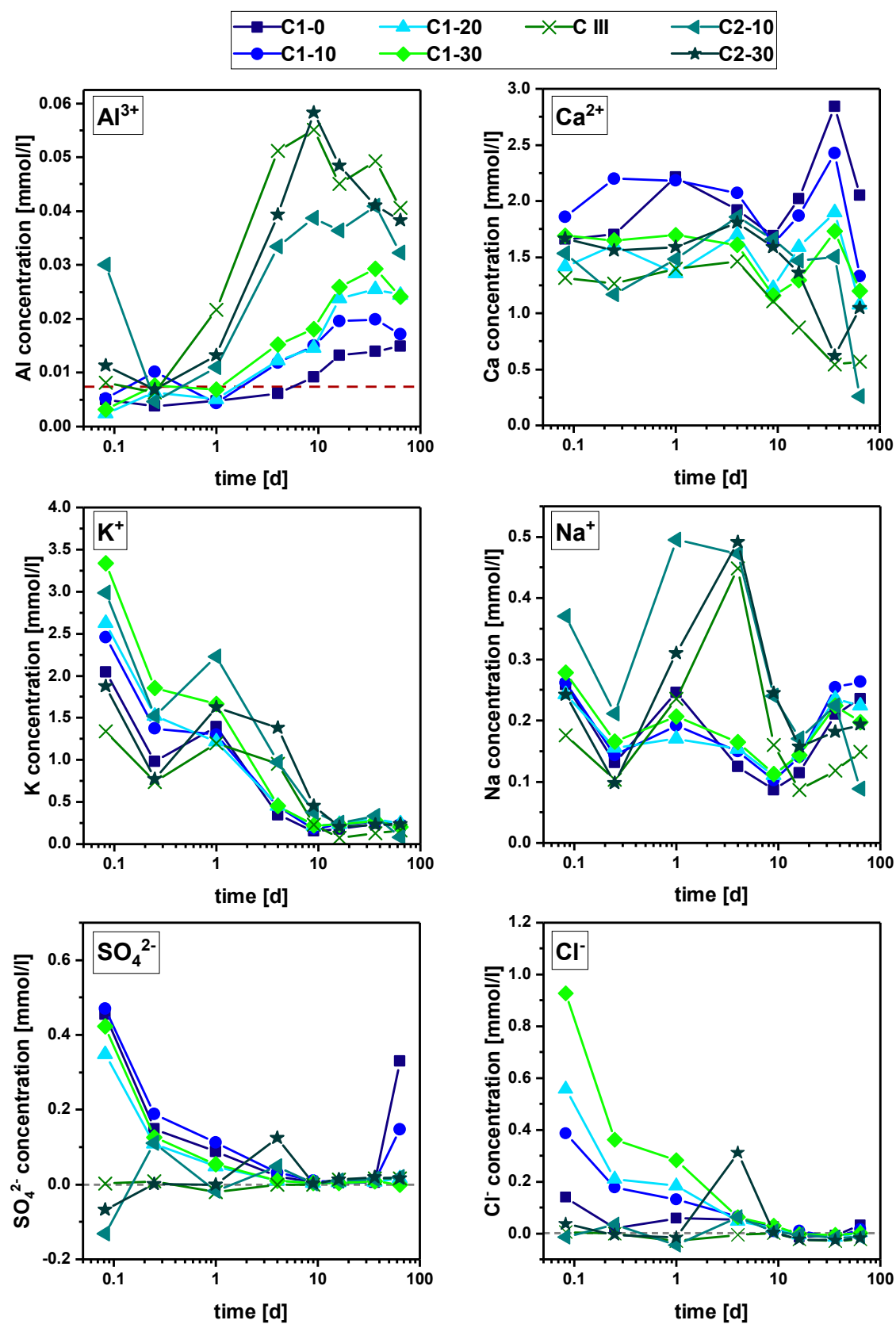


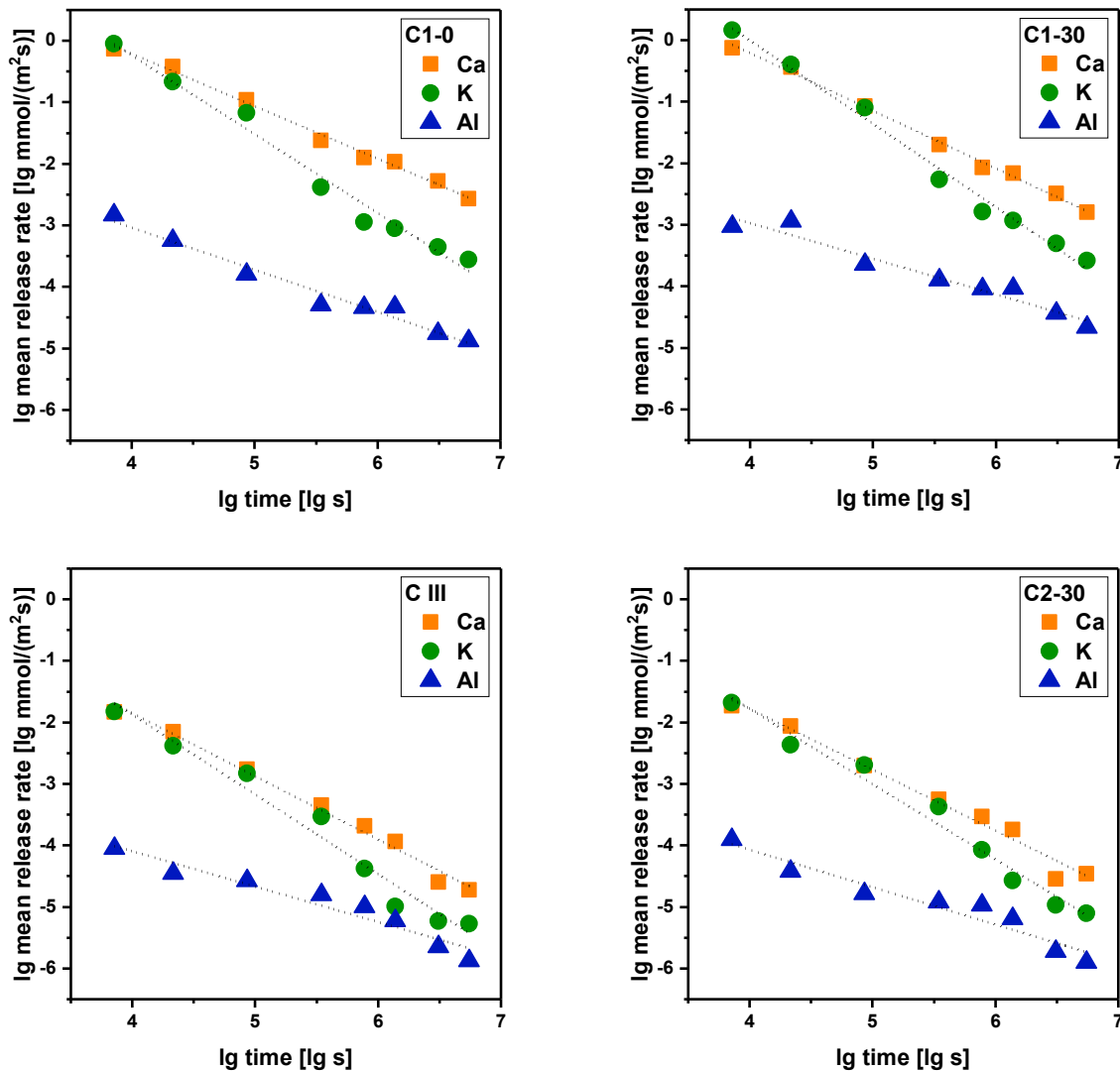
Figure 5.3: Measured ion release of Al^{3+} , Ca^{2+} , K^{+} , Na^{+} , SO_4^{2-} and Cl^{-} as determined after each eluate change during the tank leaching test. The dotted red line in the first split image indicates the threshold value according to [Bundesministerium der Justiz, 2001].

Table 5.4: Equation, coefficient of determination and leaching mechanism of selected ions and selected systems.

	Ca^{2+}			K^+			Al^{3+}		
	equation	R^2	LM ^a	equation	R^2	LM ^a	equation	R^2	LM ^a
C1-0	$-0.85x+3.10$	0.99	SW ^b	$-1.28x+4.88$	0.97	SW ^b	$-0.68x-0.29$	0.96	DF ^c
C1-30	$-0.93x+3.54$	0.99	SW ^b	$-1.35x+5.41$	0.98	SW ^b	$-0.58x-0.65$	0.94	DF ^c
C III	$-1.03x+2.26$	0.98	SW ^b	$-1.29x+3.30$	0.96	SW ^b	$-0.57x-1.79$	0.92	DF ^c
C2-30	$-0.99x+2.18$	0.97	SW ^b	$-1.22x+3.10$	0.97	SW ^b	$-0.60x-1.63$	0.92	DF ^c

^a Leaching mechanism.^b SW = Surface wash-off.^c DF = Diffusion.

Sample notation: C1/C2/CIII=kind of cement, 0/10/20/30=substitution of cement with GGBFS.

Figure 5.4: Graphical determination of Ca^{2+} , K^+ and Al^{3+} depicted for Systems A) C1-0 B) C1-30 C) C III and D) C2-30.s.

which are determined from the slope by plotting the mean release rate in function of time (Figure 5.5B). For all samples the slope is close to $m=-1$ which indicates a wash-off effect of the organic species. The observed data correspond well to the measurements of [Hohberg and Schiessl, 1996] and [Togerö, 2006], who state wash-off from the surface of the sample is a fast process compared to diffusion through the pore system. Basically the TOC can be ascribed to the amount of PUR and the additives (e.g. superplasticisers) in the cement suspension. However, a minor amount of organic content can also be ascribed to organic compounds used during the cement manufacturing process (e.g. grinding aids) [Katsioti et al., 2009, Sun et al., 2016, Zhang et al., 2016, Lupsea et al., 2014].

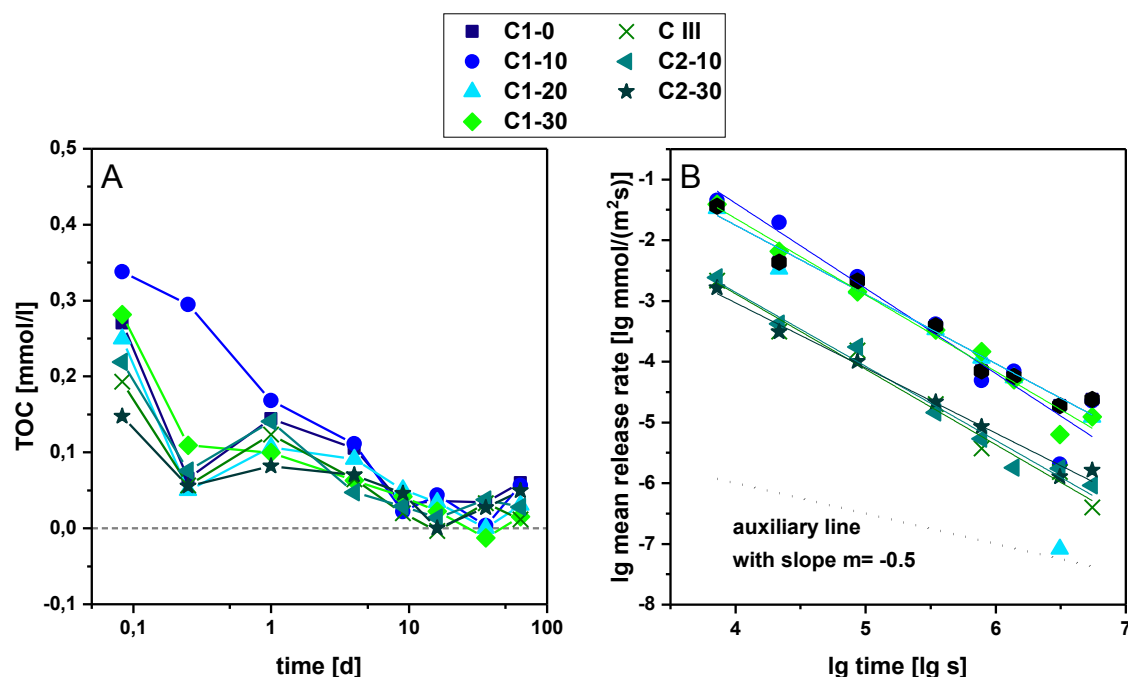


Figure 5.5: Concentration of leached amount of TOC after each elution step during the 64 d tank leaching test (A) and graphical determination of the leaching mechanism (B).

Table 5.5: Equations used to specify the dominant leaching mechanism of the TOC and coefficient of determination R^2 .

	equation	R^2
C1-0	$-1.13x+2.80$	0.97
C1-10	$-1.40x+4.21$	0.92
C1-20	$-1.13x+2.80$	0.97
C1-30	$-1.25x+3.39$	0.97
C III	$-1.24x+2.08$	0.97
C2-10	$-1.21x+2.02$	0.98
C2-30	$-1.07x+1.25$	0.98

Sample notation: C1/C2/CIII=kind of cement,
0/10/20/30=substitution of cement with GGBFS.

The results of the 64 d tank test are summarised in Table 5.6.

Table 5.6: Summarised results of the 64 d tank test.

sample	GGBFS content	pH	electric conductivity	Al ³⁺	Ca ²⁺	Na ⁺	Cl ⁻	SO ₄ ²⁻	K ⁺	Si ⁴⁺	TOC
C1-0											
C1-10	↑			↑	↑		↑		↑	↑	
C1-20	↑			↑	↑	↑	↑	↓	↑	↑	
C1-30	↑	→	→	↑	↑	↑	↑	↓	↑	↑	→
C III											
C2-10	↑			↑	↑	↓	↑		↓	↑	
C2-30	↑			↑	↑	↓	↑	↓	↓	↑	

→ = comparable values.

Sample notation: C1/C2/CIII=kind of cement, 0/10/20/30=substitution of cement with GGBFS.

5.2.2.2 Ecotoxicological Assay with *Enchytraeus Albidus*

Because too little knowledge has so far been gained with terrestrial ecotoxicological assays in the case of construction materials, the implementation of these test systems in the context of a regulatory assessment are postponed towards later times [Deutsches Institut für Bautechnik, 2011]. Hence it is necessary to get information about the interaction of leachates from building materials with the compartments soil and water which was shown by [Giese, 2007]. As threshold values have not yet been defined by European and international authorities, values considered meaningful for product assessment were chosen for the evaluation of the eluates with a suitable terrestrial ecotoxicological assay. This assay with *E. albidus* was chosen to show that it could be used and recommended as a reference assay for product assessment. It is important to note that with leachates in the concentrations 100% and 50% stringent test requirements are set compared to international standards as available for other ecotoxicological test (c.f. [Römbke and Knacker, 1989]). In Figure 5.6 the results of the survival rate of *E. albidus* during the water test are depicted.

While in general the results of mixes with CIII (Figure 5.6) are not significantly different from the control (at a 5% acceptance level), the survival rate of *E. albidus* exposed to leachates from C1-30 is significantly influenced. Especially for the early age leachates of C1-30 in the 100% concentration the survival of the test species is significantly reduced after 48 h and 72 h (0% survival rate of 0.083 and 0.25 d leachates). According to [Römbke and Knacker, 1989] *E. albidus* prefer surroundings with pH values between 6.7 and 7.5. The relatively high pH values in combination with increased values of K⁺, Cl⁻ and SO₄²⁻ in this system especially during the early age leachates affect the test species during the water test. However, these ions are also naturally available in soils, which is the living environment of *E. albidus* and a certain resistance of the animals against high dosed ions is given. Also the slightly increased TOC might contribute to the significantly decreased survival rate of *E. albidus* while exposed to the early age leachates of the C1-30 system. Similarly [Roithmeier and Pieper, 2009] report increased water extractable concentrations of ions like sodium and potassium and also higher DOC concentrations, due to the presence and the digestion of *E.*

albidus. In addition the trace elements of the cement systems and the heavy metals of the blast-furnace slag might contribute to the phenomenon, which has to be studied in future research.

water tests

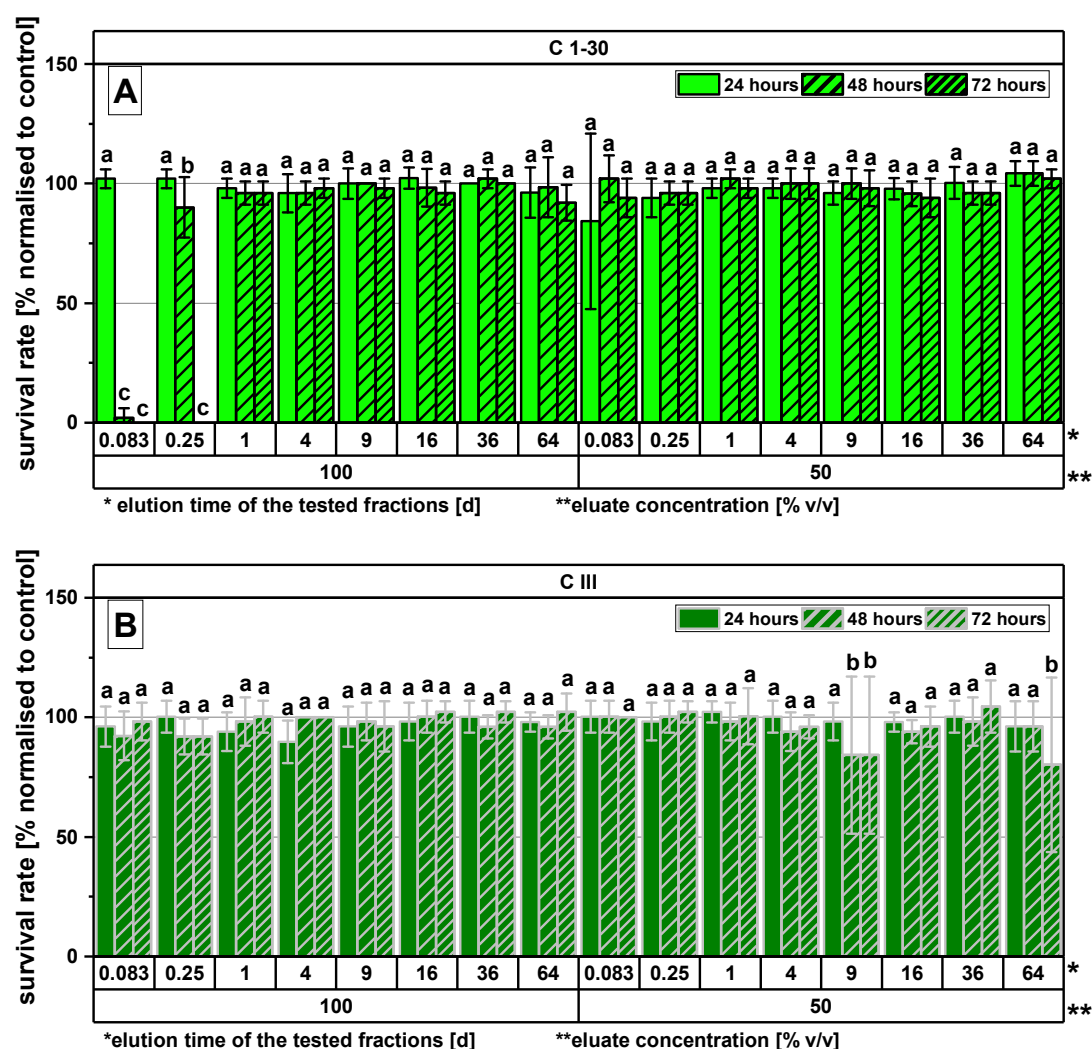


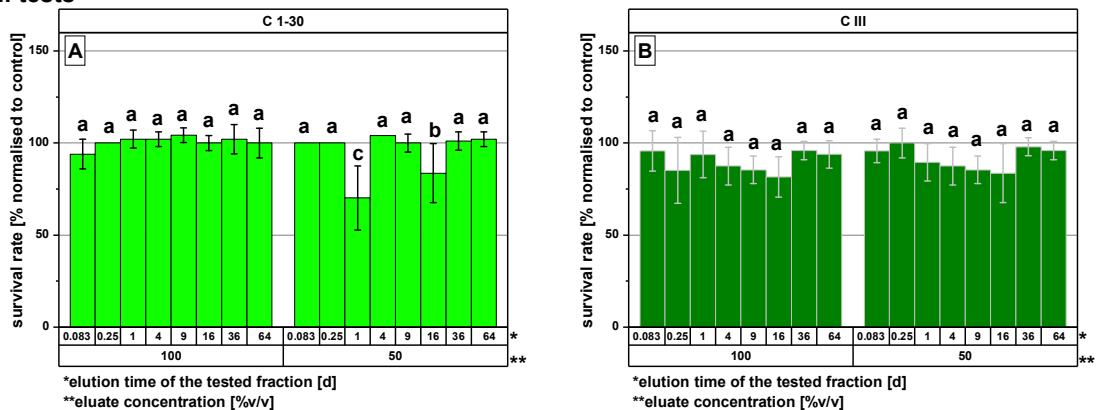
Figure 5.6: Water tests with *E. albidus*: Survival rate measured for A) C1-30 and B) C III gained during the tank leaching test. Note that the control was set to 100 % at any time step. Columns within each type of eluate, marked with the same letter are not significant different (Tukey test, $p > 0.05$).

In contrast to the water tests, the soil and sand tests depicted in [Figure 5.7](#) show no impact of the early age leachates on the survival rate of *E. albidus* during the extended test period. Just the 50 % diluted leachates of 1 d and 16 d show a significantly reduced survival rate (at a 5 % acceptance level) for the C1-30 system in the soil test. While in the sand tests for the 100 % concentrated eluate the 0.083 d and 9 d leachate of the system C1-30 show decreased survival rates, the 50 % concentrated eluate for 1 day shows increased survival. In contrary the system CIII shows no significant differences at all. As soon as soil, sand or a mixture of both is present, the buffering function due to the ion exchange capacity is noticeable, which

is why no significant difference can be stated (Figure 5.7). Furthermore it is reported that enchytraeids are able to control the mobilisation of nutrients in soils [Roithmeier and Pieper, 2009, Pieper and Weigmann, 2008].

Although three different bio-assays with *E. albidus* have been performed, just significant toxic effects can be visible in the water tests. Only few studies deal with this complex topic, this is why the drawn conclusions have to be scrutinised and in-depth investigations have to be performed by setting up a biological test battery.

soil tests



sand tests

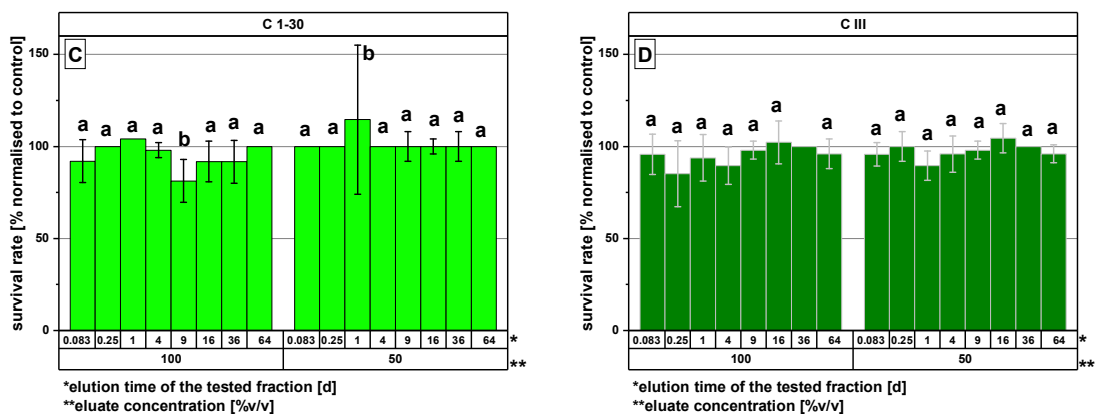


Figure 5.7: Soil and sand test with *E. albidus*: Survival rate for A) C1-30 in soil, B) C III in soil, C) C1-30 in sand and D) C III in sand as measured for each eluate gained during the tank leaching test. Note that the control was set to 100 % at any time step. Columns within each type of eluate, marked with the same letter are not significant different (Tukey test, $p > 0.05$).

5.2.3 Conclusions

The present study investigates the leaching behaviour of a novel hybrid material composed of a cement suspension and polyurethane especially designed to seal against massive water ingress during tunnel construction. The data gained in the multi method approach applying leaching tests and ecotoxicological tests lead to findings as summarised below:

- (i) Batch tests were performed as worst-case scenarios. None of the determined ionic species exceeded threshold values according to German drinking water regulations. The TOC values were marginal, although PUR was included in the samples.
- (ii) During the tank leaching test constant pH values were observed. Relatively high amounts of ions were leached, which might be caused by a high degree of porosity due to the formation of CO₂ from the isocyanate-water-reaction. The increased values of Al³⁺ seem to be a result of the incorporation of slag in the system. All other amounts of leached ions were below the threshold values given by Deutsches Institut für Bautechnik and German drinking water regulations.
- (iii) Dominant leaching mechanisms were determined for Ca²⁺, K⁺ and Al³⁺. Surface wash-off was specified for Ca²⁺ and K⁺, whereas leaching of Al³⁺ was controlled by diffusion.
- (iv) The cumulative maximum of organic leached species during tank leaching test was 83 mmol m⁻². Leaching of the organic species can be ascribed to wash-off effects and originate mainly from PUR and the contained superplasticiser.
- (v) High test requirements have been set to ecotoxicological assays with *Enchytraeus albidus*, which have been performed with undiluted (100%) and 1:1 diluted (50%) eluates. Just the early age leachates in the water tests have hazardous impacts on the test species. As soon as sand or soil is present, no hazardous impact on the test species can be detected. However, further in-depth investigations have to be performed to compare the used ecotoxicological assays with standard procedures as with algae (*Scenedesmus subspicatus*) or daphnia (*Daphnia magna*).
- (vi) Next development steps should include the definition of a biological test battery including assays with *E. albidus* and phytotoxicity assays.
- (vii) As undiluted leachates are used for assays with *Enchytraeus albidus* a worst-case scenario is illustrated in this study. As a real biological species in its natural environment is used the presented test scenario is close to reality, conclusive and verifiable for regulatory authorities.

Even though the results show that the application of this hybrid material is a promising new method to seal against massive water ingress during tunnel construction, further investigations need to be conducted in order to fully understand the leaching process and the ecotoxicological impacts. To gain realtime information about the ecotoxicological impact of the eluates, it could be recommended to test just the first fraction with the highest organic and inorganic load, which might have the highest impact to the environment in the vast majority of cases. However, it has to be considered that even eluates with low organic and inorganic load might have severe impact to the environment. Also investigations including other SCM instead or besides of GGBFS (e.g. fly ash or silica fume) should be taken into consideration. To

fully understand the behaviour of the material in terms of strength, porosity and hydration a detailed characterisation should be performed.

Release behaviour of major elements and superplasticiser from cement suspensions ¹⁶

In this chapter the effect of different w/c ratios, pre-storage times and eluents on the leaching behaviour of micro fine cement containing a superplasticiser based on MFS and NFS in various amounts is discussed. Investigations on the leaching behaviour of the inorganic species have been carried out with ion chromatography (IC) and inductively coupled plasma atomic emission spectroscopy (ICP-AES). Organic species have been attempted via total organic carbon analysis (TOC) and via ultraviolet-visible-spectroscopy (UV-Vis). Information was gained on samples up to 56 d pre-storage and additional leaching over 56 d. The German tank leaching test [DAfStb-Richtlinie, 2005] was used at 20 °C.

6.1 Experimental

The present study was carried out with materials described in 3.1. Detailed information on the German tank leaching test and analysis of the leachates are given in 3.2.

The sample notation in this chapter refers to the following abbreviations: P = paste, M = mortar, digit 1 = w/c, digit 2 = pre-storage time [d], digit 3 = superplasticiser content [wt.%].

6.2 Results and discussion

6.2.1 General parameters

General parameters like pH-value and electric conductivity measured at the end of each elution step are shown in Figure 6.1. The release of ions has an impact on pH and electrical conductivity which is governed by the length of the elution step and the concentration and release behaviour of the ions in the pore solution. Due to the short elution time interval between the first and the second elution step there is a slight drop of pH value and electrical conductivity. Afterwards pH and electrical conductivity are constantly rising or reach a plateau at a constant value which is connected to the longer leaching intervals and an elongated release of inorganic species. These findings are in good accordance with other studies using

¹⁶An extended version of this chapter has been published as: Märkl, V. and Stephan, D. A., *Water, Air & Soil Pollution* (2016) 227:30. <https://doi.org/10.1007/s11270-015-2730-x>

comparable leaching conditions [Kazuko et al., 2005, Müllauer et al., 2012, Müllauer et al., 2015]. Due to higher porosity and therefore increased inner surface, the samples with higher w/c-ratio are able to release more ions which is shown in Figure 6.1. Furthermore longer pre-storage times were found to lead to higher values [Gerven et al., 2007] due to the higher degree of hydration of the samples. The slight increase of pH and electric conductivity towards the last elution steps can be explained by the presence of remaining clinker which can be leached as well. Samples leached with BTW remigrate to neutral pH after three elution steps, electric conductivity is in any case lower than leaching with demineralised water. One possible explanation is the higher overall ion content of the BTW and therefore it is less 'aggressive' compared to demineralised water.

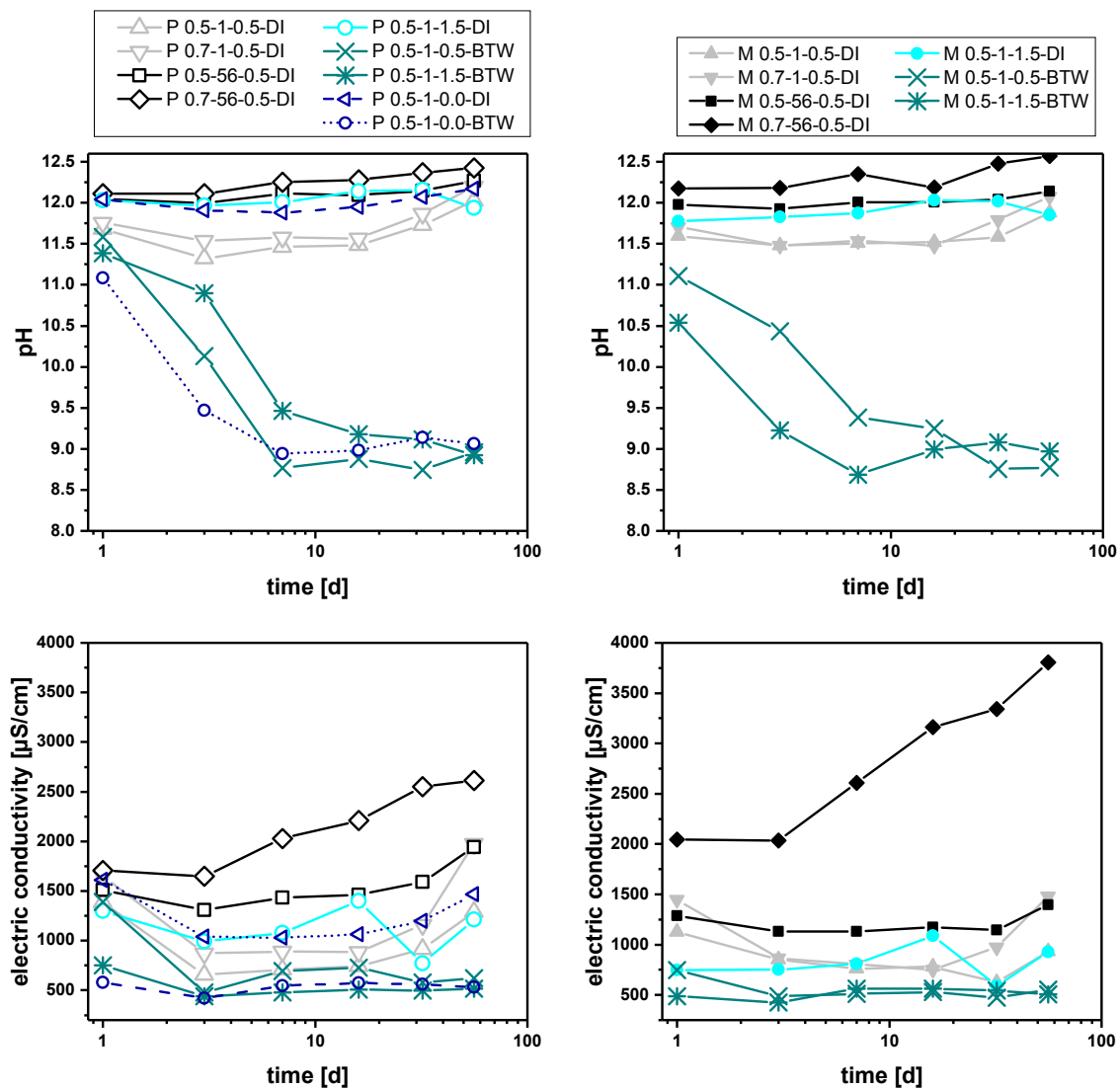


Figure 6.1: pH-value (top) and electric conductivity (bottom) of the eluates during the tank leach test.

According to [Kamali et al., 2008] the presence of ions in the leaching water strongly modifies the leaching kinetics. For example calcium ions decrease the leaching kinetics and carbonate ions in combination with Portlandite and C–S–H may form a less soluble outer

layer of CaCO_3 . This means that the precipitation of CaCO_3 at the surface of the sample and at the inner porosity results in a decrease of diffusivity. These findings are in good accordance with the leached amounts of inorganic species.

6.2.2 Inorganic species

As leaching is an interaction of the ongoing hydration and consumption of ions in the hydration products on the one hand and a chemical attack of the eluent from outside on the other hand, concentrations of major elements are of special interest (Figure 6.2 and Figure 6.3).

The amount of leachable ions of the major elements is strongly related to the availability of ions (originating from the pore solution and from the solid sample) and to the duration of each elution step. Most of the samples show a lower concentration at the second elution step, which can be a result of a slower release rate or of sorption effects. With longer elution steps towards later ages, the concentrations incline to increase because a steady leaching state can be reached and release rates close to equilibrium are present. This is caused by the increasingly higher degree of hydration towards later ages, i.e. most of the clinker phases have already reacted. First the hydration products can be leached followed by the remaining clinker, which further contributes to the amount of released ions. Assuming a diffusion controlled release of ions as shown by [Hohberg, 2002], the cumulative release $E_{56,i}$ over the test period can be calculated as presented by equation (2.5) and (2.6).

In Table 6.1 the cumulative release of the electrolytes at the end of the tank leaching test is listed.

Table 6.1: Cumulative release $E_{56,i}$ of major electrolytes during the tank leaching test. Data in $[\text{mmol m}^{-2}]$.

	Al^{3+}	Ca^{2+}	Cl^-	K^+	Na^+	Si^{4+}	SO_4^{2-}
P 0.5-1-0.0-DI	14.9	610.3	12.6	530.1	281.8	186.0	3.8
P 0.5-1-0.5-DI	0.2	525.1	5.5	516.0	363.1	226.9	1.8
P 0.7-1-0.5-DI	0.1	878.0	5.6	503.5	374.7	288.9	0.3
P 0.5-56-0.5-DI	11.0	1554.1	13.3	610.1	412.9	191.4	3.7
P 0.7-56-0.5-DI	9.6	2037.9	11.2	386.5	282.9	49.1	2.1
P 0.5-1-1.5-DI	14.2	1079.5	13.8	572.9	476.5	372.1	6.1
P 0.5-1-0.0-BTW	0.3	-334.3	-27.6	455.5	253.9	73.5	-27.3
P 0.5-1-0.5-BTW	0.1	-92.1	-51.6	416.3	254.9	2.3	-43.1
P 0.5-1-1.5-BTW	-0.5	-540.1	255.8	566.7	463.4	156.8	188.1
M 0.5-1-0.5-DI	5.7	615.6	0.6	310.5	215.1	276.0	3.7
M 0.7-1-0.5-DI	4.3	719.5	2.7	349.2	258.2	272.3	0.3
M 0.5-56-0.5-DI	11.4	1381.2	5.6	397.2	256.9	113.4	7.2
M 0.7-56-0.5-DI	8.3	2854.2	5.0	509.6	367.3	53.9	2.8
M 0.5-1-1.5-DI	14.9	933.3	13.4	376.7	309.7	322.6	6.2
M 0.5-1-0.5-BTW	0.3	-353.1	-77.4	258.3	137.5	89.6	-68.2
M 0.5-1-1.5-BTW	2.7	-259.5	304.0	347.8	292.1	127.5	215.6

Sample notation: P=paste, M=mortar, digit 1=w/c , digit 2=pre-storage time [d] , digit 3=superplasticiser content [wt.%].

Leaching of inorganic species from hardened cement paste starts when an eluent is in contact with the cementitious sample. This can be at the outer but also at the inner surface e.g. the pore system. Due to different chemical composition of the eluent compared to the pore solution, prevailing concentration gradients are the driving forces in the leaching process.

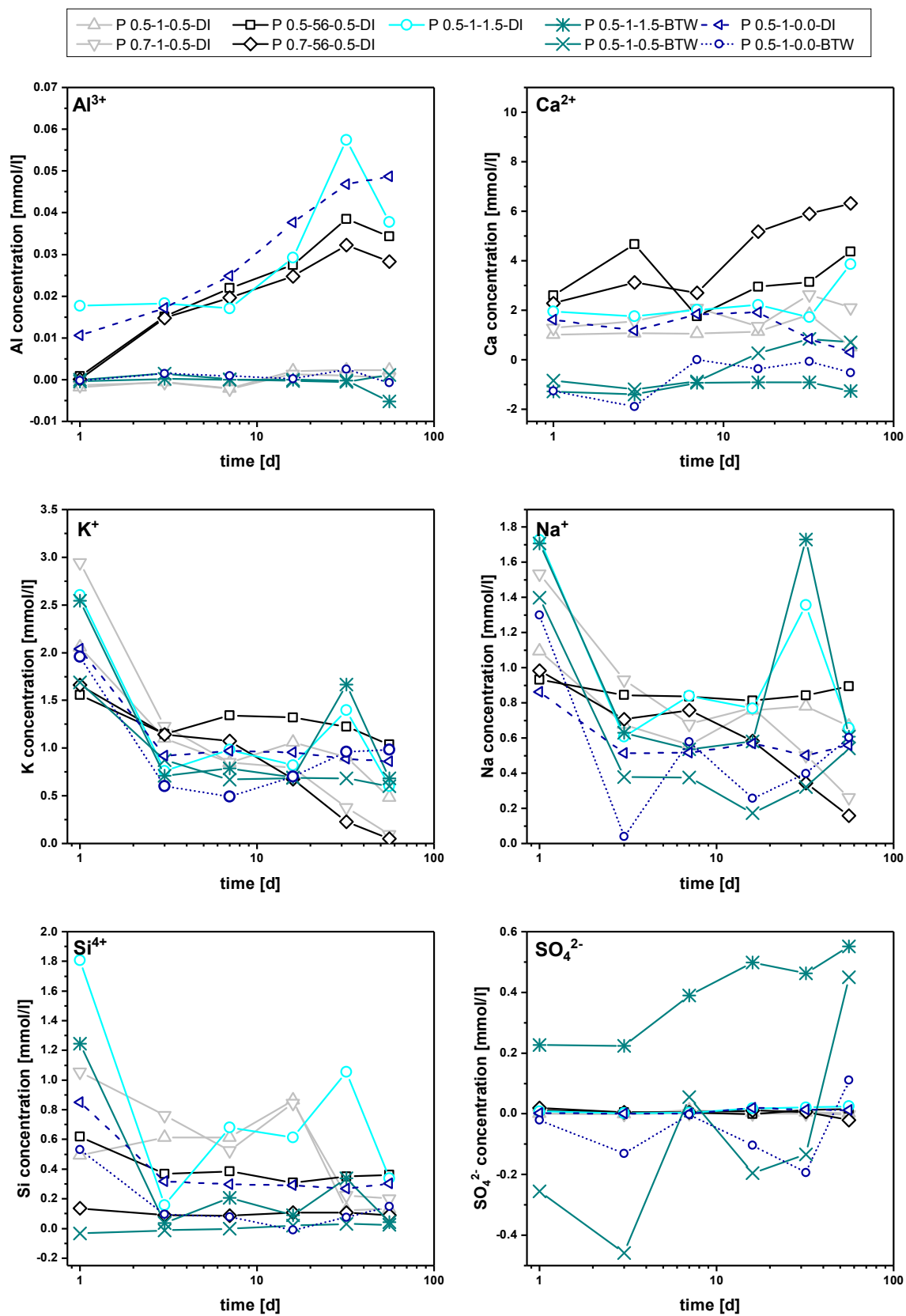


Figure 6.2: Paste samples: Concentration of the major elements at the end of each leaching step during the tank leach test. Data corrected to the blank value.

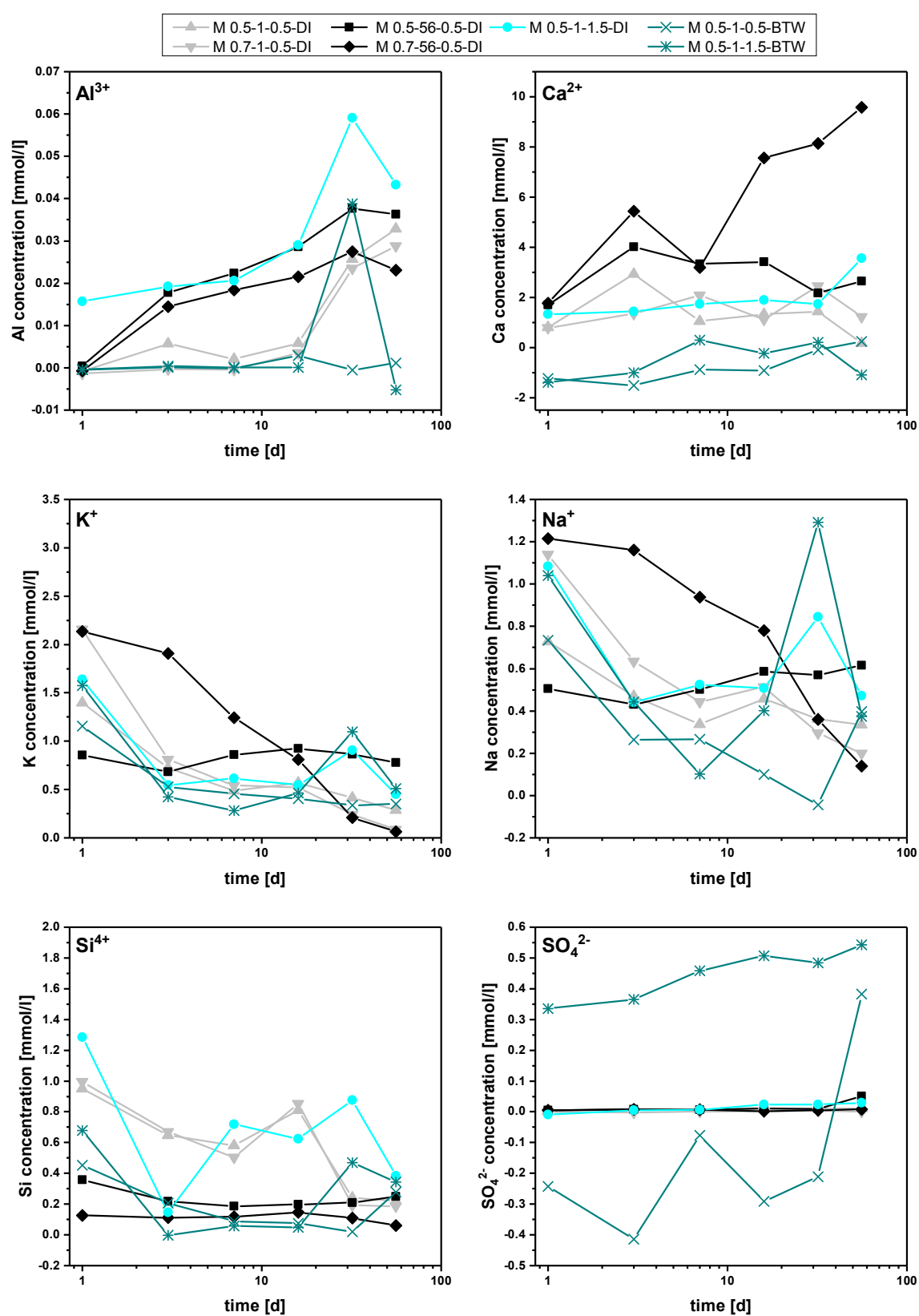


Figure 6.3: Mortar samples: Concentration of the major elements at the end of each leaching step during the tank leach test. Data corrected to the blank value.

First the surface of the sample is leached which is described as a wash-off effect [Hohberg, 2002]. This is followed by a diffusion controlled process, where the leached constituents are transported from the sample into the eluent. The remaining degraded-zone is impoverished in readily soluble hydration products or ionic species. Thus the chemical equilibrium of the sample is changed, which results in an active dissolution and/or precipitation of inorganic species and hydrates [Faucon et al., 1998a]. In addition the degraded zone proceeds to the inner of the sample, where dissolution and precipitation starts again. Furthermore leaching is accompanied with a decrease in physicochemical and mechanical performances and an increase in porosity as has been shown by [Kazuko et al., 2005]. The 56 d pre-stored samples inhibit a higher release rate but for Si^{4+} compared with the 1 d pre-stored samples. The support of the formation of reaction products like C-S-H-phases or Ettringite formation which both consume water during hydration might explain this phenomenon. Furthermore Portlandite (Ca(OH)_2) is soluble in water which causes the increased pH of the 56 d pre-stored systems and a higher overall release. Once Portlandite is dissolved in the eluent the chemical equilibrium is influenced and local increases of certain species like SO_4^{2-} are generated in the sample. These alterations in combination with leaching of Portlandite lead to local precipitation of secondary monosulfoaluminate (AFm) and ettringite (AFt) (for further explanation see [Faucon et al., 1997, Matschei et al., 2007]). According to [Kamali et al., 2008] also C-S-H can be decalcified during the leaching process. It is also likely that a wash-off effect of not consumed ions or hydration products on the surface of the samples occurs. In general low level concentrations of Al are characteristic for OPC-systems. The hydration of OPC, especially of its most reactive phase tricalciumaluminate (C_3A), is controlled by calcium sulphate as set regulator. This leads to a significant deceleration of the reaction rate in the first minutes while the reaction rate increases again after some hours. Depending on the amount of dissolved SO_4^{2-} available for the reaction, the dissolved aluminum reacts with calcium, sulfate and water to form ettringite. The formation of such Al containing phases e.g. ettringite, inserts early in the hydration process but can be significantly leached respectively measured after a longer pre-storage time. According to [Müllauer et al., 2015] the release of Al^{3+} and S respectively SO_4^{2-} is mainly controlled by surface dissolution due to dissolution of AFt and AFm. The measured cumulative release for the samples leached in demineralised water is generally higher than for BTW, which is in good agreement with the findings of the pH measurements. Since demineralised water is more aggressive compared to water inhibiting minerals [Kamali et al., 2008], the differences of the eluents in terms of their different release can be explained. Samples leached in BTW exhibit even a negative release rate which means ions of the tap water can be absorbed by the sample. According to the measured carbonate hardness, which can react with the released calcium ions derived from Portlandite and decalcified C-S-H. Carbonates, e.g. CaCO_3 , can be formed which inhibit a low solubility. These carbonates form a layer right at the surface of the sample or respectively the pore space and therefore decrease the release. This layer controls the diffusion process and the leaching kinetics as described in [Kamali et al., 2008]. Even high sodium contents in the eluent can influence the leachability of the built hydrates. As K^+ and Na^+ act as counterions of the active component of the superplasticiser, they can easily be dissolved in water and hence be leached. In aqueous medium the alkali ions are not just leached from the cement but also from the superplasticizer. Thus a higher superplasticizer content leads to a higher release of K^+ and Na^+ . The alkali release from the sample surface is mainly controlled by wash-off. Comparing the release of the samples with different w/c-ratios it can be observed that the higher the w/c, the higher the porosity and therefore the higher the release of inorganic species. According to [Kazuko et al., 2005] the pore volume becomes

larger with longer leaching periods, weakening the mechanical properties. However, the samples inhibiting a higher w/c-ratio and a longer pre-storage time show the contrary in terms of ionic release but for Ca^{2+} . Ca^{2+} and OH^- are leached (cf. Figure 6.1) and therefore decrease in the interstitial solution. To compensate for this and to build up a local equilibrium the other ions have to increase like SO_4^{2-} . This means also a backward diffusion is possible [Faucon et al., 1997]. For example Ca^{2+} and OH^- ions can be released from AFm phases, other ions like SO_4^{2-} or CO_3^{2-} increase locally and can therefore diffuse back to the inner of the sample. Subsequently re-precipitation of AFm occurs. In addition the release of Ca^{2+} from Portlandite can again lead to precipitation of AFm. These ions (Ca^{2+} , Al^{3+} and SO_4^{2-}) are mainly released by dissolution of Portlandite, AFm and Aft rather than diffusion.

6.2.3 Organic species

In Figure 6.4 the release of organic substances expressed in the sum parameters TOC and DOC are presented. In all systems the TOC and DOC decrease rapidly during the first three leaching steps caused by surface wash-off effects.

The following leaching steps show a steady behaviour which can be explained by diffusion controlled leaching processes. A clear difference of the release of organic species can be noticed between the low and high dosage of the superplasticiser. The higher the superplasticiser dosage, the more could be released, especially during the first leaching steps. The samples leached in BTW show a lower release, probably due to the formation of the above discussed carbonate layer acting as a leaching boundary. An uptake of organic substances is possible as indicated by the negative release of the samples leached in BTW. The leaching behaviour is clearly affected by the w/c-ratio. At a higher w/c-ratio more water is in the system, the tendency towards a higher degree of porosity and increased leaching rates of the organic species can be observed. Worth mentioning is the higher TOC and DOC of the 56 d pre-stored samples. This may indicate adsorption of the active component of the superplasticiser during the early lifetime of the paste and mortar. In other words the active component is not or just partly embedded in the hydration products and can therefore be leached. Another possibility is that the superplasticiser absorbs just partly on the hydration products and can therefore be washed-off.

Assuming that the release of organic species is also driven by diffusion, equation (2.5) and (2.6) can be used to calculate the mean release rate J_i .

The graphical determination of the leaching behaviour is shown in the lgJ-lgt-diagram in Figure 6.5.

The slopes of the fitted curves are in the range between -0.96 to -1.0 for the samples P 0.5-56-0.5-DI, P 0.5-1-1.5-DI, M 0.5-56-0.5-DI and M 0.5-1-1.5-DI. These slopes are clearly settled around the straight line for wash-off effects. During the first leaching steps samples P 0.5-1-0.5-DI and M 0.5-1-0.5-DI also show wash-off effects. Towards latter leaching times for P 0.5-1-0.5-DI respectively M 0.5-1-0.5-DI, the slope is between -0.14 and -0.24 . Taking into account the uncertainty of measurement ($\pm 5\%$) one can assume that the values are right in the middle of diffusion and dissolution. The samples leached in BTW show a comparable release rate to M 0.5-1-0.5-DI and P 0.5-1-0.5-DI. Note that some points cannot be shown due to their negative release/adsorption behaviour such that they cannot be expressed in the lg-lg-diagram.

In Table 6.2 the cumulative release of the superplasticiser is presented.

Generally, the mortar samples show a smaller amount of released organic species, which is possibly due to the lower amount of superplasticiser that originates from the inclusion of

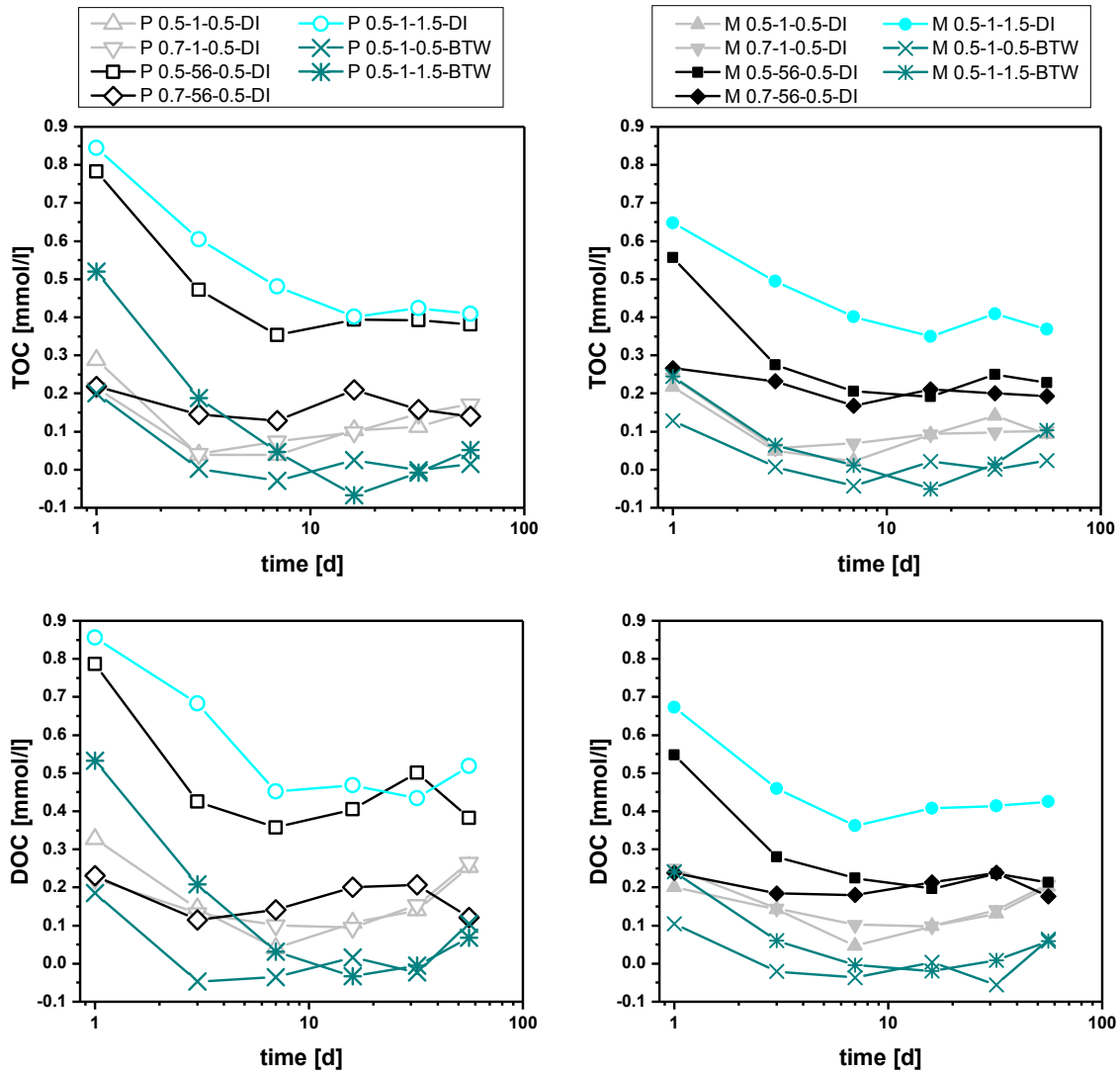


Figure 6.4: TOC and DOC of the eluates originating from paste and mortar samples.

Table 6.2: Cumulative release $E_{56, \text{TOC}}$ of organic species measured as sum parameter TOC. Data given in $[\text{mmol m}^{-2}]$ corrected to the blank value.

mixture	TOC	mixture	TOC
P 0.5-1-0.5-DI	58.7	M 0.5-1-0.5-DI	49.1
P 0.7-1-0.5-DI	59.8	M 0.7-1-0.5-DI	53.0
P 0.5-56-0.5-DI	222.1	M 0.5-56-0.5-DI	136.6
P 0.7-56-0.5-DI	79.9	M 0.7-56-0.5-DI	101.5
P 0.5-1-1.5-DI	253.0	M 0.5-1-1.5-DI	213.6
P 0.5-1-0.5-BTW	16.9	M 0.5-1-0.5-BTW	11.0
P 0.5-1-1.5-BTW	58.3	M 0.5-1-1.5-BTW	31.0

Sample notation: P=paste, M=mortar, digit 1=w/c , digit 2=pre-storage time [d] , digit 3=superplasticiser content [wt.%].

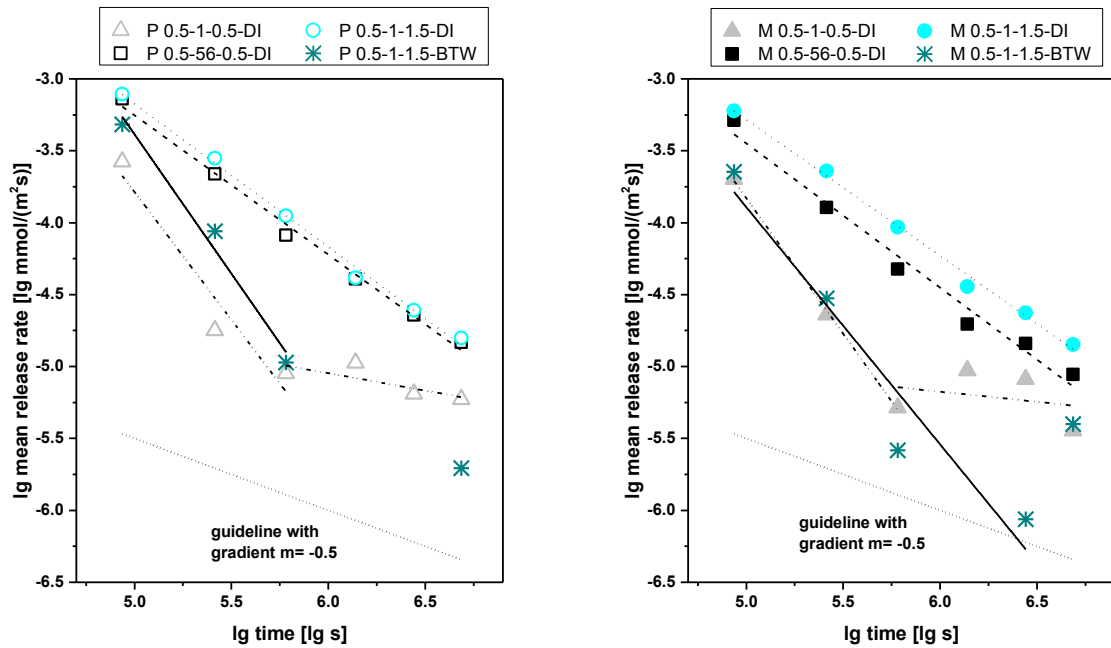


Figure 6.5: Mean release rate of organic carbon of selected systems.

aggregates. Significant differences are present between the samples leached in demineralised water and BTW. As BTW is a less aggressive eluent, the cumulative release is lower. Another finding is that with longer pre-storage time the cumulative release of organic species is higher. It is possible that the superplasticiser is first adsorbed on the hydration products, but after longer times of hydration adsorption effects mitigate and superplasticiser can be leached.

Figure 6.6 depicts the total leached concentrations of the superplasticiser measured via UV-Vis.

In general the leaching behaviour can be described as follows. The first three leaching steps inhibit a close elution time interval where a decrease of the superplasticiser concentration can be determined. This is mainly due to wash-off-effects (see Figure 6.5). Also a blockage of the pore system and a hindered release of the superplasticiser by water adsorption of the organic species can contribute to the low release. As described before, the surface layer formed by carbonates can contribute to this effect. The last three leaching steps inhibit longer leaching intervals and therefore elongated release time which results in close to equilibrium conditions. The samples leached in BTW release less superplasticiser, but follow the trend described above.

The total added and leached amount of superplasticiser after 56 d is given in Table 6.3.

There is a clear difference between added and leached amount of superplasticiser within the test period. Consequently the traced concentration of leached superplasticiser is low. These findings can also be observed by the normalised data given in Figure 6.7.

After 56 d up to the maximum of 2% of active total component of the superplasticiser could be found in the leachate, which means in contrary that most of the active component of the superplasticiser is adsorbed on or still bound in the cement matrix. In contrast to the paste samples, the active component is leached to a higher extent from the mortar samples. As the superplasticiser is a mixture of naphthalene and melamine sulfonate condensate the release behaviour of the single components is also of interest. According to the Lambert-Beer

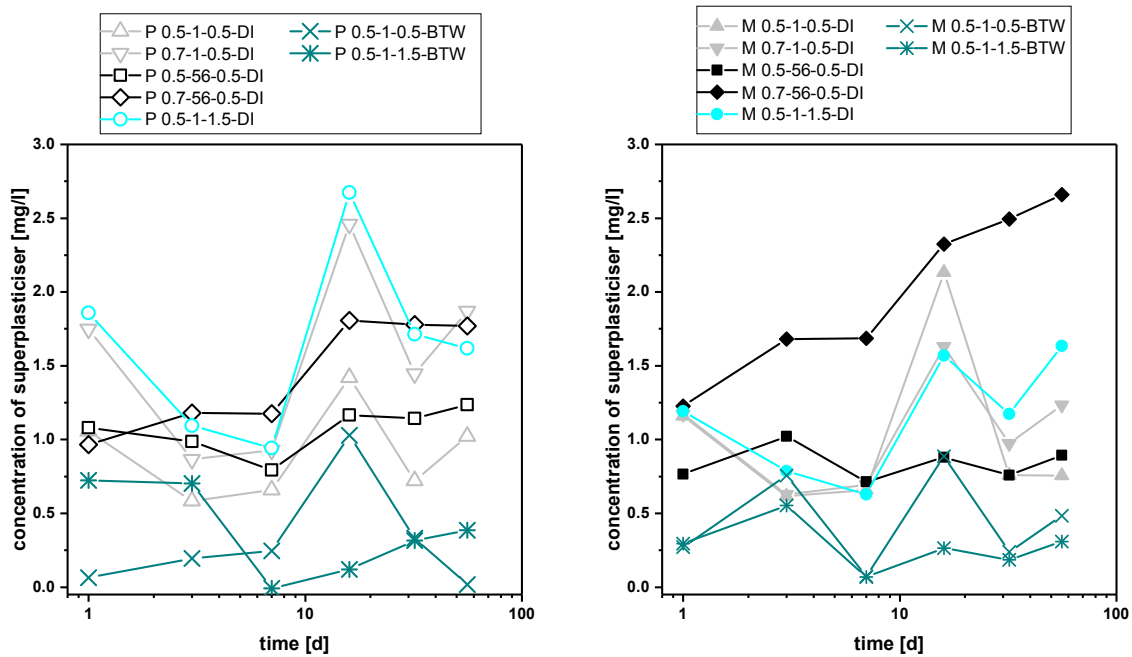


Figure 6.6: Concentration of leached total superplasticiser measured via UV-Vis.

Table 6.3: Amount of total active component added and leached within 56 d.

mixture	conc.-added ^a		mixture	conc.-added ^a	
	[g l ⁻¹]	conc. _{56 d} ^b [mg l ⁻¹]		[g l ⁻¹]	conc. _{56 d} ^b [mg l ⁻¹]
P 0.5-1-0.5-DI	5639	5.46	M 0.5-1-0.5-DI	4392	6.08
P 0.7-1-0.5-DI	4889	9.31	M 0.7-1-0.5-DI	3923	6.32
P 0.5-56-0.5-DI	5639	6.41	M 0.5-56-0.5-DI	4392	5.03
P 0.7-56-0.5-DI	4889	8.67	M 0.7-56-0.5-DI	3923	12.07
P 0.5-1-1.5-DI	18 230	9.90	M 0.5-1-1.5-DI	13 961	6.98
P 0.5-1-0.5-BTW	5639	1.88	M 0.5-1-0.5-BTW	4392	2.71
P 0.5-1-1.5-BTW	18 230	2.24	M 0.5-1-1.5-BTW	13 961	1.67

^a Amount of total active component added.^b Amount of total active component leached within 56 d.

Sample notation: P=paste, M=mortar, digit 1=w/c, digit 2=pre-storage time [d], digit 3=superplasticiser content [wt.%].

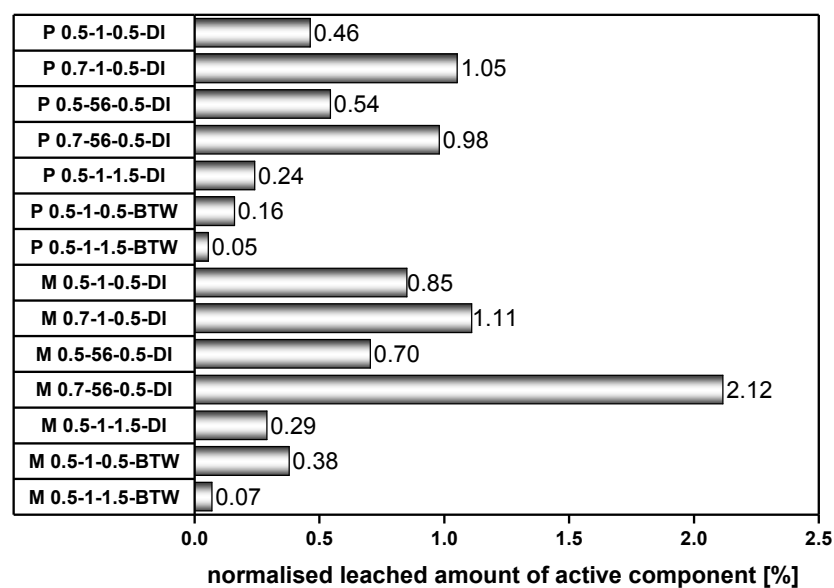


Figure 6.7: Normalised leached amount of active component. Data given in [%].

law (equation (3.5)) it is possible to calculate the single components, MFS and NFS, from the sum of the signal obtained from the superplasticiser.

The molar attenuation coefficients of the two components, ε_{MFS} and ε_{NFS} were calculated with the help of a serial dilution. The equation system was solved by applying Cramer's rule. The single components showed a similar leaching behaviour like the total superplasticiser (see Figure 6.8). However MFS shows a more constant leaching rate during the first measurements, followed by a slight increase towards the end of the test period. The samples leached with BTW show a negative release respectively an adsorption of MFS, which might be caused by the favoured leaching of NFS during the first three leaching periods. During the latter elution steps a reverse leaching behaviour can be noticed.

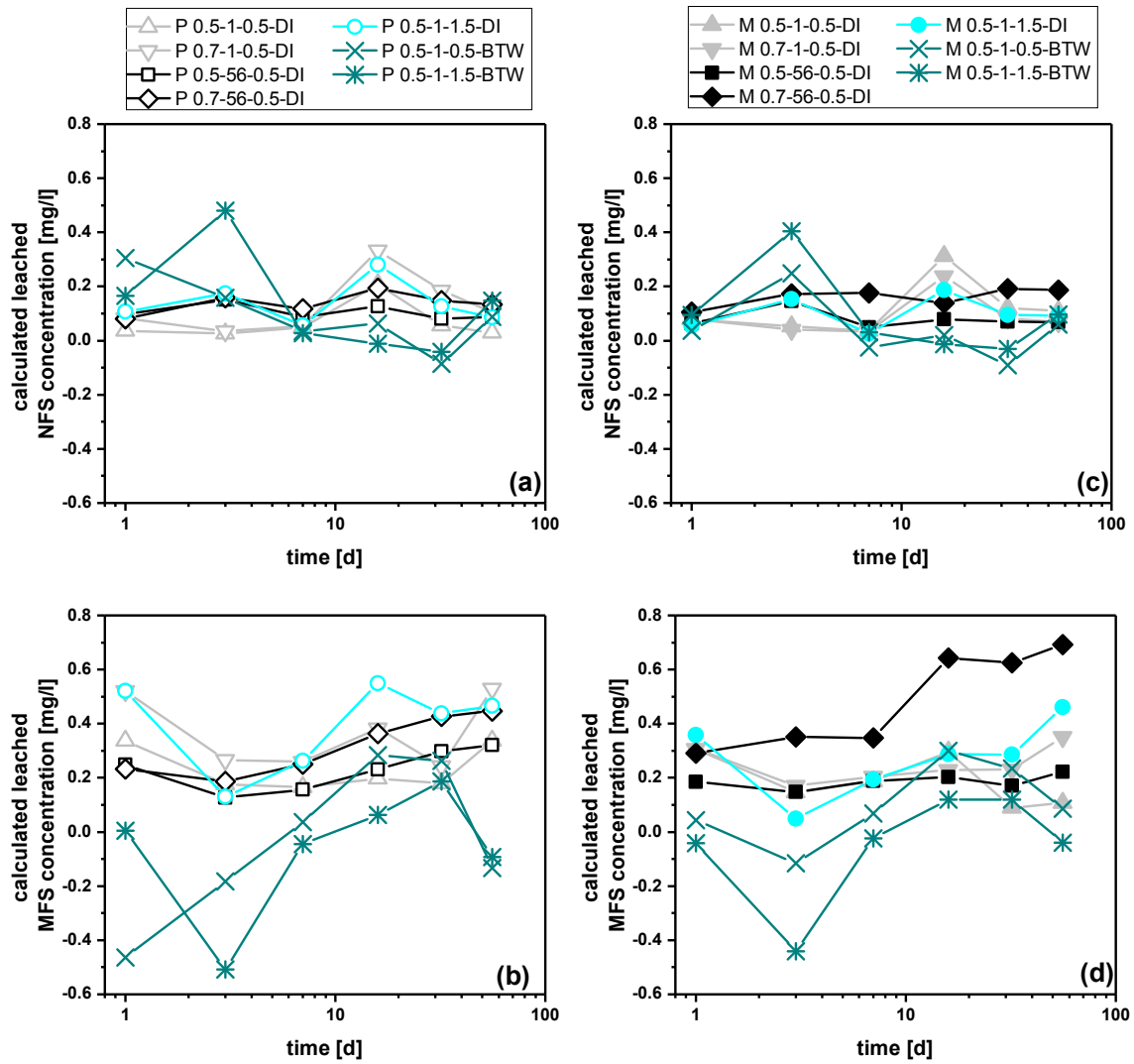


Figure 6.8: Calculated leached concentration from UV-Vis measurements: (a) NFS in paste samples (b) MFS in paste samples (c) NFS in mortar samples (d) MFS in mortar samples.

6.3 Conclusions

In this study cement suspensions and mortars with different amounts of superplasticiser, w/c-ratio and pre-storage times were leached. The influence of demineralised and Berlin tab water was investigated.

- (i) The trend of the general parameters like pH value and electrical conductivity is governed by the length of the elution step. Samples leached with demineralised water generally inhibit higher values, whereas higher w/c-ratios and longer pre-storage times lead to a further increase in pH and electrical conductivity. Samples leached with BTW show lower pH and electrical conductivity and remigrate to neutral pH after a few elution steps.
- (ii) The cumulative release after 56 d of leaching is generally higher for samples leached in demineralised water as it is more aggressive than BTW. Even negative release rates are possible for BTW, which are caused by adsorption or take-up of ions. Generally a high solubility of alkali ions results in diffusion controlled release into the eluate whereas the release of multivalent ions is controlled by the dissolution of Portlandite, AFt and AFm. Longer pre-storage times and higher w/c-ratios generally lead to higher release rates of ions. Thereby ion charges are compensated such that also a backward diffusion to the inner of the sample is possible.
- (iii) It was possible to obtain sum and single parameters for the leached organic species. In addition mean release rates are presented (see [Figure 6.5](#)) which cause wash-off and diffusion effects for the released organic species. BTW was found to exert a lower effect on leaching of the superplasticiser than demineralised water. Leaching of the total superplasticiser as well as the single components follow a two stage leaching process which is shown by UV-Vis spectra. After 56 d up to a maximum of 2% total active component of the total superplasticiser can be found in the leachate. MFS and NFS alternate their released amount during the test period.

The results reveal that only low amounts of superplasticiser could be leached under the given conditions. Nevertheless, further investigations taking into account ecological and ecotoxicological aspects are inevitable to clearly evaluate the environmental threat endangerment of superplasticisers.

Leaching of PCE-based superplasticiser from micro fine cement: A chemical and ecotoxicological point of view¹⁷

The construction materials industry faces major challenges since 2013 when the European Construction Products Regulation was implemented, especially in the sector of environmentally friendly construction products. This study determined concentrations of leachable inorganic and organic compounds from micro fine cement paste with and without superplasticiser addition. Furthermore the leached superplasticiser amounts were detected via LC-MS. The multi-method approach was supplemented by ecotoxicological assays. Phytotoxicity was tested with white mustard (*Sinapis alba*) and cress (*Lepidium sativum*). The mutagenic and genotoxic potential of the leachates was tested with the Ames fluctuation assay and the umuC assay. As leaching protocol the European Horizontal dynamic surface leaching test was used. The cement paste samples with superplasticiser followed the wash-off effect with a total organic carbon release up to 43 mmol m^{-2} , whereas the release of samples without superplasticiser was driven by diffusion. The ecotoxicological assays showed a clear time depending behaviour. No cytotoxicity and mutagenicity could be observed; anyhow some leachates show minor genotoxic potential. In all tests a clear difference between the samples with and without superplasticiser could be detected. This study clearly demonstrates the importance of further studies in the field of leaching of construction products.

7.1 Experimental

For detailed information on the chemical and mineralogical compositions as well as physical properties of the raw materials and the mix design of the matrix under investigation it is referred to 3.1.4 and 3.2.1.3. This also applies for in-depth considerations on the used analytical techniques.

The sample notation in this chapter refers to the following abbreviations: REF=without superplasticiser, PCE=with 0.5 wt.% superplasticiser.

¹⁷An extended version of this chapter has been published as: Märkl, V. et al., *Water, Air & Soil Pollution* (2017) 228:217. <https://doi.org/10.1007/s11270-017-3373-x>

7.2 Results and discussion

7.2.1 General parameters and inorganic species

During leaching the cement sample interacts with the surrounding medium, the eluent. Thus the released ionic species exert influence on the measured pH and electric conductivity as depicted in Figure 7.1. Extenuating pH values and electric conductivity followed by constant levels, of samples leached with BTW point to interaction processes. On the contrary a relatively constant pH value can be observed for samples leached with DI water, indicating a uniform release of ions. The amounts of released ions depend on the solubility of the ions and the composition of the eluent, which can be seen in Figure 7.2.

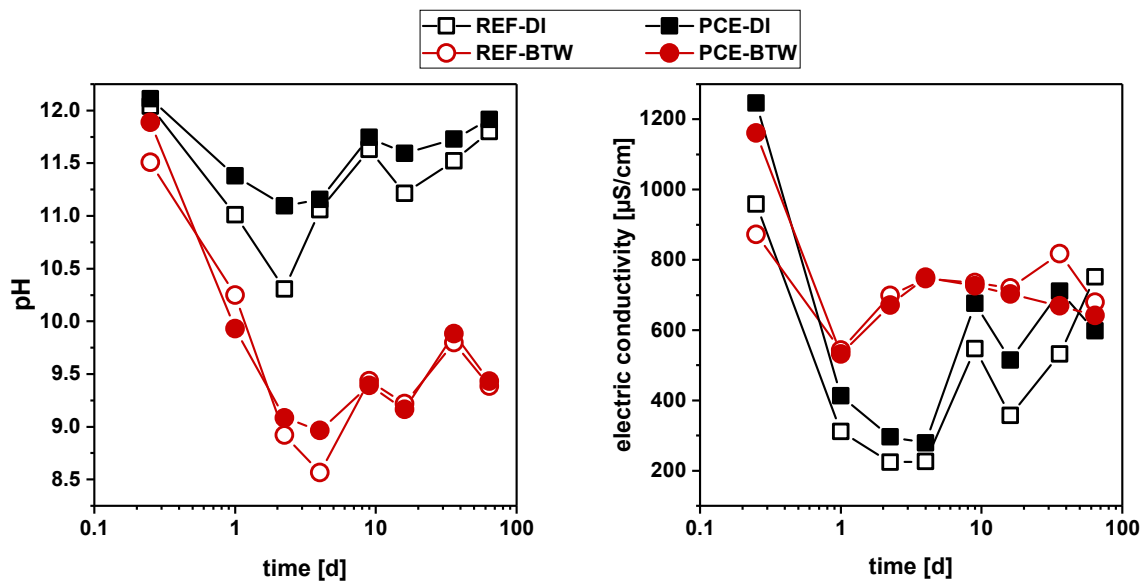


Figure 7.1: pH-value (left) and electric conductivity (right) of the eluates.

Clear differences can be observed between the samples leached in DI and BTW. According to [Kamali et al., 2008] ions on the surface of the sample (especially Ca^{2+} -ions provided by portlandite and C-S-H) interact with the eluent and its included ions by forming a boundary layer consisting of calcite (CaCO_3) which hinders further release of ionic species. This can be clearly seen for Ca^{2+} and SO_4^{2-} , which are trapped inside or on the surface of the sample and just small amounts can be released into the eluate. K^+ may interact as counter ion of the PCE based superplasticiser, which can be seen by the higher leachable amount of the PCE-containing samples during the early leaching steps. Further in-depth considerations in the interacting and complex processes during leaching can be found in [Faucon et al., 1996, Kamali et al., 2003, Kamali et al., 2008, Barbir et al., 2012, Märkl and Stephan, 2016]. The cumulative release rate $E_{64,i}$ of the ionic species is presented in Table 7.1. A clear difference in aggressiveness can be seen between the two eluents. Hence higher amounts of ions can be leached by DI.

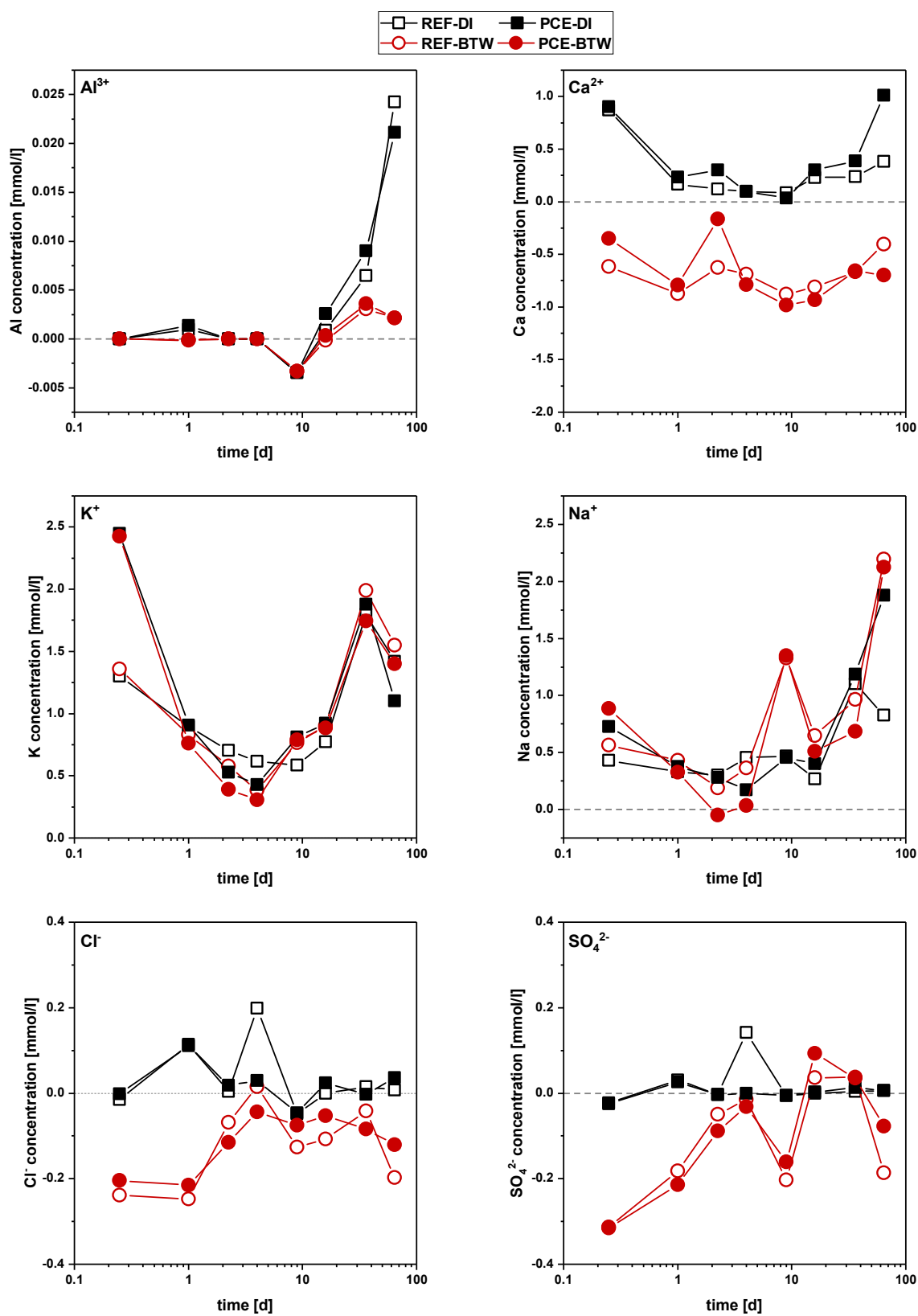


Figure 7.2: Concentration of ionic species at the end of each elution step. Data corrected to the blank value. Note the different scales on the ordinate.

Table 7.1: Cumulative release rate $E_{64,i}$ after 64 d of leaching of the ionic species. Data presented in $[\text{mmol m}^{-2}]$.

	Al^{3+}	Ca^{2+}	K^{+}	Na^{+}	Si^{4+}	Cl^{-}	SO_4^{2-}
REF-DI	2.3	175.4	646.9	334.0	250.0	−22.1	12.1
PCE-DI	0.9	260.7	721.8	437.5	217.5	13.4	1.0
REF-BTW	0.1	−264.8	668.3	534.5	48.8	−80.9	−70.0
PCE-BTW	0.2	−268.5	695.7	468.7	41.9	−72.9	−60.8

Sample notation: REF=without superplasticiser, PCE=with 0.5 wt.% superplasticiser.

7.2.2 Organic species

Figure 7.3 presents the organic sum parameters TOC and DOC. It is clearly visible that during the first leaching steps the PCE-containing samples release higher amounts of organic content compared to the samples without superplasticiser. Even the reference samples contain a certain amount of organic content which can be ascribed to organic compounds such as grinding aids that are used during the manufacturing process of the cement. The cumulative released amount of TOC after 64 d is 43 mmol m^{-2} for PCE-DI and 15 mmol m^{-2} for PCE-BTW. The higher amount of leached organic content in case of PCE-DI is ascribed to the high aggressiveness of DI compared to BTW due to the higher purity of this eluent.

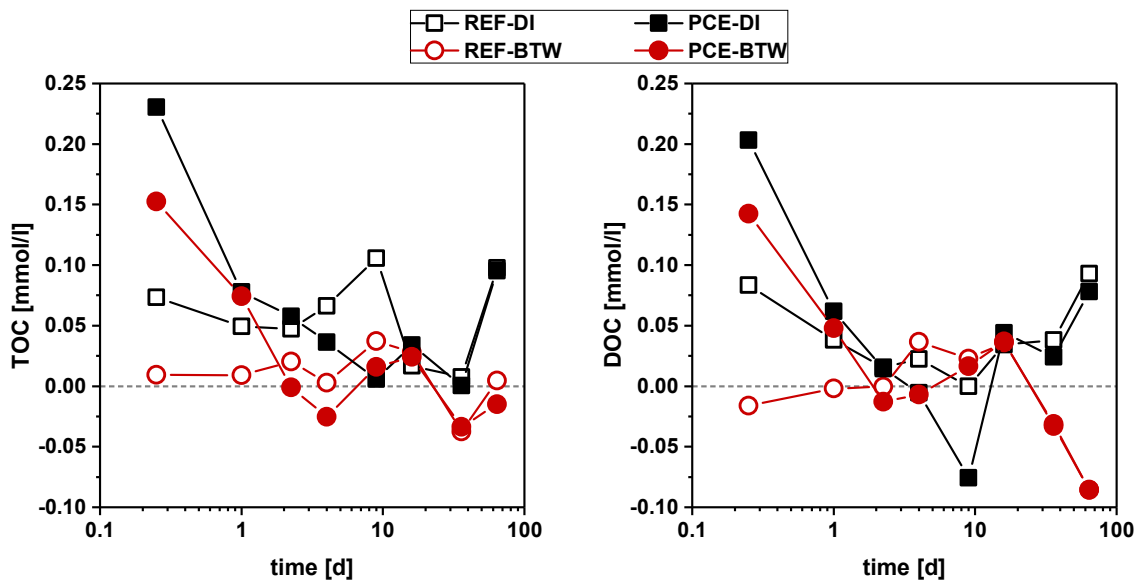


Figure 7.3: TOC (left) and DOC (right) of the eluates. Data corrected to the blank value.

The controlling leaching mechanism of the organic species was evaluated and is presented in Figure 7.4. Outliers were excluded from the analysis (shown in light blue at the 1.5 acceptance level). In addition the slopes and R^2 values based on the diffusion model are presented. The slope values were -1.3289 for PCE-BTW and -1.02367 for PCE-DI. The samples containing superplasticiser indicate that wash-off was the dominating leaching mechanism. According to [Hohberg and Schiessl, 1996] and [Togerö, 2006] wash-off from the surface of the sample proceeds faster than diffusion through the pore space. Hence the reference samples without

further addition of superplasticiser show that diffusion is the controlling leaching mechanism, as the slopes values are between -0.47413 and -0.85453 .

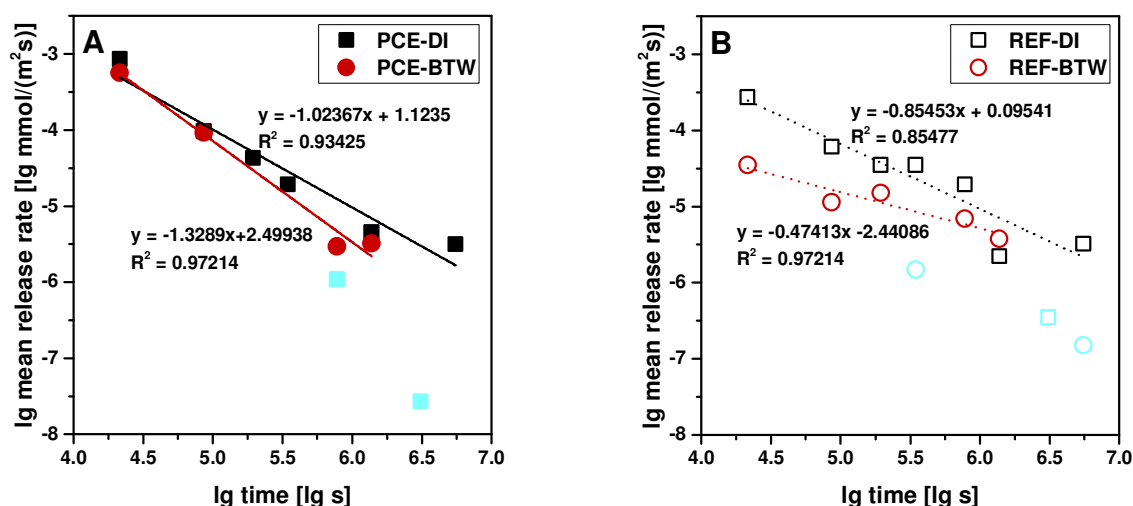


Figure 7.4: Release rate of total organic carbon (TOC). Outliers in light blue are excluded from the linear fit.

In order to identify the organic species HPLC-MS experiments were performed. As the measurement down to trace amounts and to the limit of detection is extraordinary difficult, it is performed to proof-the-principle. This means that only qualitative detection was carried out. The chromatograms shown in Figure 7.5 indicate that till 0.25 d of leaching traces of superplasticiser are detectable in the leachate. No leached traces of superplasticiser could be detected in further leachates. Triisobutyl phosphate was detected at a retention time of 5.73 min and an m/z of 267.2 only for PCE-DI after data were corrected to the blank value. Triisobutyl phosphate was used for its good isolation and detection during the measurement. Hence it may also be used as anti-foaming agent in superplasticisers and could be a component of commercially available superplasticisers. Fragments of polycarboxylate ethers were detected at a retention time of 3 min only for the samples PCE-DI and PCE-BTW after 0.25 d of leaching. These findings are in good accordance with the TOC measurements and underline that the wash-off effect controls leaching for the samples containing superplasticiser.

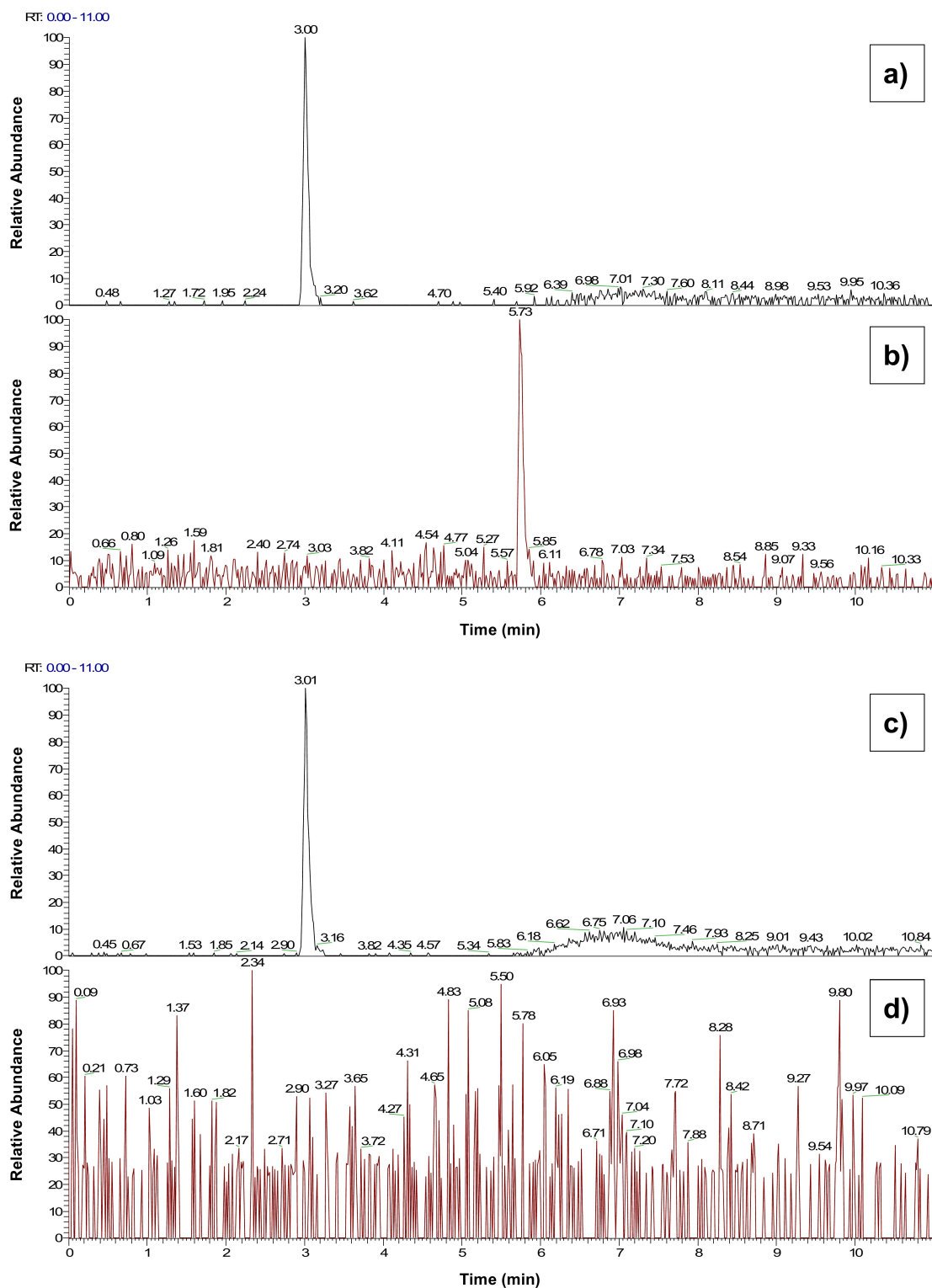


Figure 7.5: HPLC-MS chromatogram of the different eluates: A) PCE-DI after 0.25 days for fragments of polycarboxylate ether as tracer ions, B) PCE-DI after 0.25 days for Triisobutyl phosphate as tracer ion, C) PCE-BTW after 0.25 days for fragments of polycarboxylate ether as tracer ions and D) PCE-BTW after 0.25 days for Triisobutyl phosphate as tracer ion.

7.2.3 Phytotoxicity assays

To get a first and rapid impression of the obtained data gained during the phytotoxicity tests with *S. alba* and *L. sativum* regression analysis were performed (Figure 7.6). Outliers (shown in turquoise at the 1.5 acceptance level) were not included in the analysis.¹⁸ Figure 7.6A and B display the relative root growth for white mustard (*S. alba*) and cress (*L. sativum*). For *S. alba* in general the toxic effect seems to be higher, while the eluates show just slight toxic effects for *L. sativum*. For samples containing superplasticiser the RRG is increasing over time which means their eluates act like a fertiliser. This may be an effect of the released ionic species from the cement and the superplasticiser (mainly the soluble counter ion potassium). In contrast the reference samples prepared without superplasticiser tend to lose their positive effect on root growth over time for both test species. A possible explanation could be the different release of ionic species, the different pH value and electric conductivity over time. Also it seems to be possible that the superplasticiser covers the cement particle such that the components with negative effects on root growth are prevented from release. However the exact mechanisms underlying this process remain undetermined. In-depth investigations on the composition of the eluates and the corresponding effects on relevant parameters like RRG need to be carried out to get better insight to this behaviour. The eluates for both species seem to exert only little effect on the seed germination (Figure 7.6C and D) as the observed RSG is close to the control in any case. Consequently germination is not hindered or influenced by high pH-values or high amounts of ionic species. However, the eluates show slight toxic effects compared to the control, e.g. RSG for *S. alba* 83 % for REF-DI at 16 d for and *L. sativum* is 84 % for PCE-DI at 1 d. The germination index as the product of RRG and RSG is presented in Figure 7.6E and F. Concluding it can be stated that seed germination and root growth are positively influenced by the cement samples. In fact Ca^{2+} , Si^{4+} (and Fe^{3+}) as main constituents of Portland cement act as essential nutrients for plant growth [Mengel et al., 1984].

To clarify whether construction products have an impact on plant development and which parameters are important, different statistical analysis have been performed. The effect of time, eluent and PCE content as well as the combined effect of these variables on root growth (RRG), seed germination (RSG) and germination index (GI) were evaluated using a three-way ANOVA (Table 7.2). It is shown that root growth, seed germination and the germination index depend on the variable time ($p < 0.05$) for both tested plant species. Seed germination and the germination index of *S. alba* are influenced by the PCE content, whereas *L. sativum* shows no response. The combined effect of time and eluent only has an impact on the root growth of *S. alba*, while the combination of time and PCE content influences the seed germination of *S. alba* and the root growth and the germination index of *L. sativum*. The interaction of all three parameters (time, eluent and PCE content) affects the seed germination of *S. alba* and the root growth and the germination index of *L. sativum*. In contrast the factor eluent and its combination with time is not significant at all ($p < 0.05$) and therefore a two-way ANOVA was performed (Table 7.3). The PCE content influences the seed germination of *S. alba*, whereas time affects its root growth. The germination index depends on time and PCE content for samples eluted with BTW. The interaction of both parameters is significant for the seed germination of *S. alba*. On the one hand, *L. sativum* is not influenced by the PCE content ($p < 0.05$), while on the other hand its root growth and germination index depend on time and the interaction of both parameters ($p < 0.05$).

¹⁸Value was indicated as outlier when it fell either below the lower quartile minus 1.5 times the inter quartile range or when it was above the upper quartile plus 1.5 times the inter quartile range.

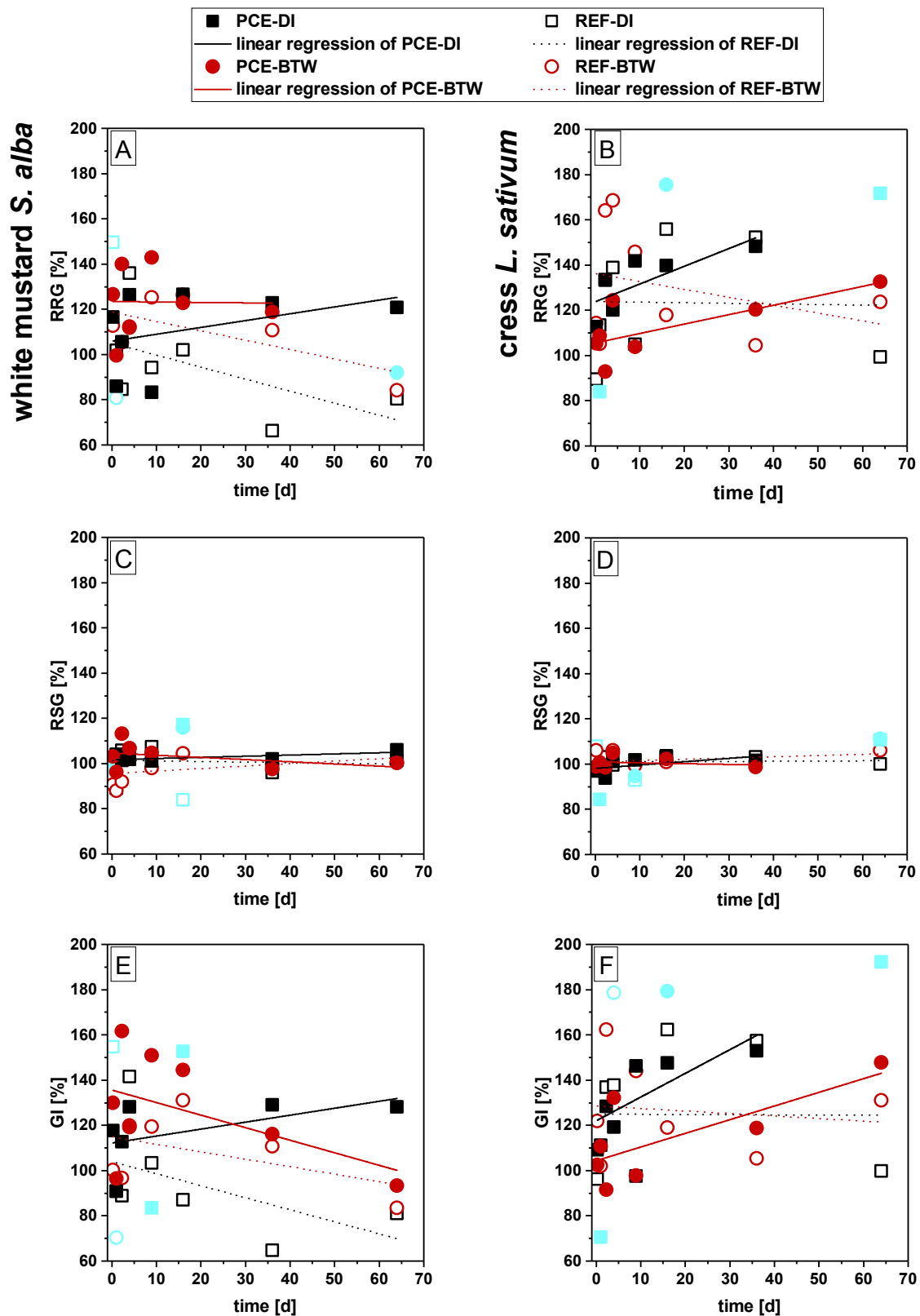


Figure 7.6: *S. alba* and *L. sativum* growth test: Comparison and linear regression of RRG, RSG and GI of *S. alba* and *L. sativum*. Outliers in light blue are excluded from the linear fit.

Only the seed germination of *L. sativum* eluted with BTW is affected by time. In conclusion this analysis shows that the development of the seedlings is influenced by the cementitious samples and its released constituents. However, the influence is strongly time dependent, which is in good correlation with the wash-off-effect presented in [Figure 7.4](#).

Table 7.2: Results of three-way ANOVA with Tukey post hoc test of *S. alba* and *L. sativum*.

effect ^a	df ^b	RSG		RRG		GI	
		F	p-value	F	p-value	F	p-value
<i>S. alba</i>							
time	7	2.2	0.001 **	4.4	0.0002***	4.6	0.0001***
eluent	1	0.04	0.29	0.1	0.69	0.04	0.83
PCE content	1	12.2	0.38	0.04	0.83	0.03	0.86
time x eluent	7	0.8	0.55	1.3	0.25	1.4	0.17
time x PCE content	7	2.5	0.12	3.1	0.004 **	3.2	0.003 **
eluent x PCE content	1	0.3	0.76	3.1	0.07	2.4	0.11
time x eluent x PCE	7	2.4	0.25	3.6	0.001 **	3.2	0.003 **
<i>L. sativum</i>							
time	7	3.5	0.03 *	2.7	0.01 *	2.7	0.01 *
eluent	1	1.1	0.83	1.6	0.20	0.7	0.39
PCE content	1	0.7	0.0006***	3.8	0.05	8.9	0.003 **
time x eluent	7	0.8	0.51	2.2	0.03 *	1.6	0.12
time x PCE content	7	1.6	0.01 *	1.0	0.38	1.1	0.30
eluent x PCE content	1	0.09	0.55	0.07	0.78	0.2	0.63
time x eluent x PCE	7	1.3	0.02 *	1.3	0.24	1.8	0.09

^a time (0.25 d to 64 d), eluent (DI and BTW) and PCE content (0 and 0.5) are the factors considered in the analyses.

^b degree of freedom.

* significant.

** very significant.

*** extremely significant.

Sample notation: REF=without superplasticiser, PCE=with 0.5 wt.% superplasticiser.

Table 7.3: Results of two-way ANOVA with Sidak post hoc test attached to previous three-way ANOVA of *S. alba* and *L. sativum*.

effect ^a	eluent	df ^b	RSG		RRG		GI		
			F	p-value	F	p-value	F	p-value	
<i>S. alba</i>									
interaction	DI	7	4.1	0.06	2.7	0.01 *	2.8	0.01 *	
time	DI	7	0.6	0.06	3.4	0.003 **	3.4	0.003 **	
PCE content	DI	1	4.8	0.45	1.2	0.27	0.8	0.34	
interaction	BTW	7	1.1	0.72	4.0	0.001 **	3.6	0.002 **	
time	BTW	7	2.2	0.03 *	2.2	0.03 *	2.6	0.01 *	
PCE content	BTW	1	7.5	0.64	1.9	0.16	1.7	0.19	
<i>L. sativum</i>									
interaction	DI	7	2	0.0007***	1.9	0.08	2.0	0.06	
time	DI	7	2	0.68	2.4	0.02 *	1.7	0.11	
PCE content	DI	1	0.5	0.03 *	1.3	0.25	2.7	0.10	
interaction	BTW	7	0.6	0.36	0.3	0.92	0.7	0.62	
time	BTW	7	2.3	0.03 *	2.5	0.02 *	2.8	0.01 *	
PCE content	BTW	1	0.2	0.007 **	2.7	0.10	7.0	0.01 *	

^a time (0.25 d to 64 d) and PCE content (0 and 0.5) are the factors in the analyses.

^b degree of freedom.

* significant.

** very significant.

*** extremely significant.

Sample notation: REF=without superplasticiser, PCE=with 0.5 wt.% superplasticiser.

7.2.4 Genotoxicity and mutagenicity

To get a simplified and reliable ecotoxicological test battery for European and international standardisation the Ames assay and umuC-assay were performed (detailed information see [Appendix 4](#)). Most of the samples tested in the Ames assay showed no toxicity and therefore no mutagenic potential. Only few of them are suspected to be mutagenic at a significance level of $p < 0.05$ and therefore no clear dose-response relation can be observed. However, within the different dilutions of the Ames assays no trend or pattern is visible. This leads to the conclusion that generally no mutagenicity prevails in the eluates such that neither an inorganic compound nor an organic compound in the cement matrix or in the superplasticiser exhibits mutagenic potential. The umuC-assay allows to detect cytotoxicity as well as genotoxicity. Specifically it responds to compounds that cause DNA damages. As the growth factor (G) is below 0.5 no cytotoxicity is indicated throughout. An $I_R \geq 1.5$ is considered genotoxic, hence only the samples showing increased I_R are plotted in [Figure 7.7](#). An increased induction ratio seems to occur without a general trend or pattern within the dilution ratio, thus it was not possible to calculate effect concentrations $EC_{IR 1.5}$ for significant samples. However, the samples without superplasticiser (REF-DI and REF-BTW) especially in the first two leaching steps show significant genotoxic effects. This corresponds to the findings of the phytotoxicity assays with *S. alba* and *L. sativum*. It would be interesting in future testing

to compare different ordinary Portland cements from different manufacturers. Furthermore Portland cements blended with for example fly ash or ground granulated blast-furnace slag should be included in the test scheme. Also the testing of different superplasticisers or other additives (e.g. retarders) is of significant interest.

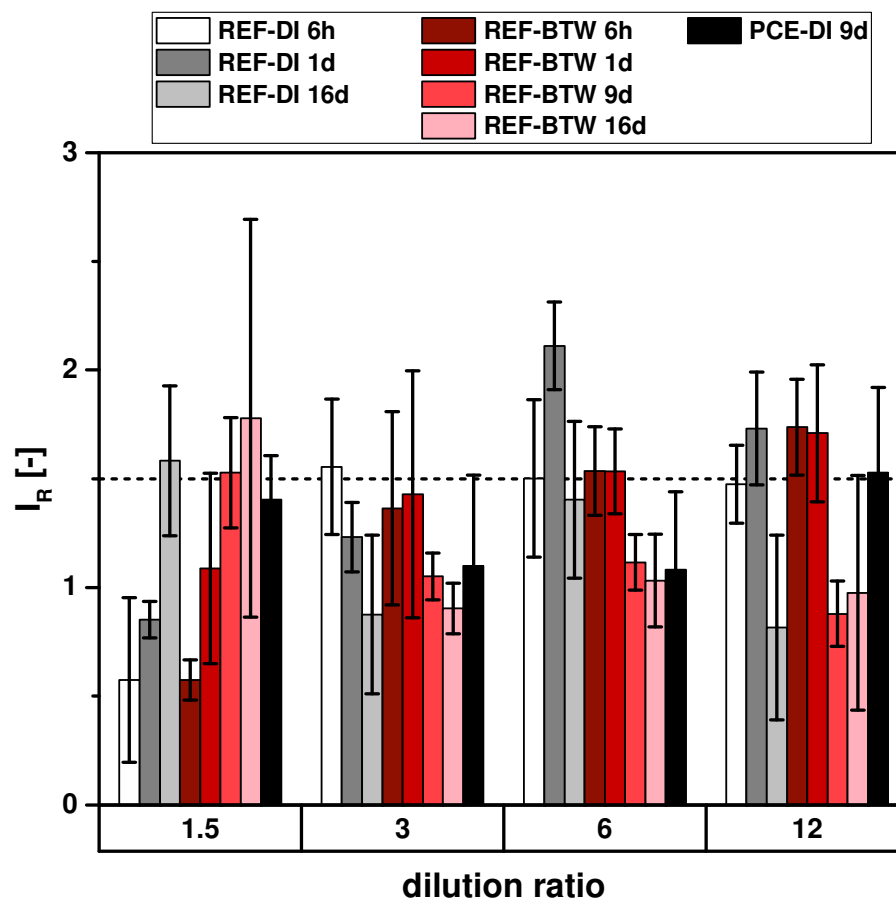


Figure 7.7: Induction ratio (I_R) of relevant samples. Mean and standard deviation of 3 replicates are presented.

7.3 Conclusions

In the present study, cement pastes from micro fine cement with and without addition of polycarboxylate ether as superplasticiser was leached with demineralised water or Berlin tap water. The leachates were investigated in a multi method approach. The results of the conducted experiments lead to the following conclusions:

- (i) As the cement sample interacts with the eluent during leaching, clear differences are visible between samples leached in demineralised water and Berlin tap water by means of released inorganic species. This is a result of the different aggressiveness of the eluates due to their purity. In general this is ascribed to the formation of a boundary layer mainly of calcite, hindering the release of ionic species when leaching with BTW. Potassium is found to be the counter ion of the used superplasticiser.
- (ii) The released organic species were determined as sum parameter TOC. Superplasticiser release is dominated by the wash-off effect for both eluents, whereas the organic species in samples without superplasticiser is released by diffusion.
- (iii) The detection of polycarboxylate ether in the eluates was also performed with LC-MS. It was possible to detect the superplasticiser up to 6 hours of leaching time in both eluents (PCE-DI and PCE-BTW). This finding supports the release of the superplasticiser by the wash-off effect.
- (iv) Phytotoxicity assays have been performed with white mustard (*S. alba*) and cress (*L. sativum*). Relative root growth and seed germination show only slight toxic effects, but mostly positive influences (e.g. enhanced root growth) due to essential nutrients released by the cement such as Ca^{2+} , Si^{4+} and Fe^{3+} . There is a significant difference between samples with and without superplasticiser, as samples without superplasticiser lose their positive effects over time. The seed germination is not significantly influenced by the eluates despite their high pH-values and/or high ionic load.
- (v) The results of the Ames assay do not indicate mutagenic potential of the compounds included in the cement matrix and the superplasticiser.
- (vi) In contrast to the Ames assay the results of the umuC-assay show that for some samples, especially for the ones without superplasticiser, no cytotoxic but some genotoxic potential might be present.
- (vii) In general the first eluates (0.25 d and 1 d) especially without superplasticiser show a strong influence on relative root growth, the germination index and the umuC-assay. This means the effects are strongly time dependent.

Further and in-depth investigations are needed especially in terms of the higher toxic potential of the cement samples without superplasticiser. This means different ordinary Portland cements and cements blended with e.g. fly ash should be tested. Furthermore different superplasticisers or other organic additives should be included in the test scheme. As this study covers only one Portland cement, cements from different batches and producers need to be investigated to get a broader understanding of the influence of cement composition on the leaching and possible toxicity. Also it has to be taken into account that most cement compositions used nowadays are blended systems including so-called supplementary cementitious materials (SCM) such as fly ash and blast-furnace slag. Such cements need to be

included in future test schemes in order to clarify the role of SCM-presence. Also different superplasticisers or other chemical admixtures, e.g. retarders, need to be considered in future studies. Although only low amounts of superplasticiser could be leached from the investigated samples, it has to be taken into consideration that concrete is a mass product and is used in huge quantities such that important environmental effects might occur.

Effect of leached cement paste samples with different superplasticiser content on germination and initial root growth of cress (*Lepidium Sativum*) and white mustard (*Sinapis Alba*)¹⁹

With an annual production of about 10 Gt concrete is by far the most used solid man-made material. In order to adjust the workability of fresh concrete most often so-called superplasticisers, essentially water-soluble organic polymers, are utilised. As concrete is commonly in direct contact with soil or water, the leaching of organic and inorganic compounds and their environmental impact needs to be assessed. The present study contributes to this purpose by investigating leachates from hardened cement pastes gained using the horizontal dynamic surface leaching test. Pastes were prepared with and without superplasticiser. The root growths as well as the germination behaviour of cress (*Lepidium sativum*) and white mustard (*Sinapis alba*) were examined with respect to phytotoxicity. Different proportions (100 %, 50 %, 25 % and 12.5 %) of the leachates were considered in the test scheme. The results indicate a positive effect of most of the leachates on seed germination and root growth, although statistical significance was only found in some cases. Both test species showed no or only slight harmful effects as relative root growth exceeded always 66 % for white *S. alba* and 74 % for *L. sativum*. Seed germination was not negatively influenced by the leachates. Slight beneficial effects on both test species could be observed for leachates containing superplasticiser compared to samples in absence of superplasticiser.

8.1 Experimental

For detailed information on the chemical and mineralogical compositions as well as physical properties of the raw materials and the mix design of the matrix under investigation it is referred to 3.1.4 and 3.2.1.3. This also applies for in-depth considerations on the used

¹⁹An extended version of this chapter has been published as: Märkl, V. et al., *Water, Air & Soil Pollution* (2017) 228: 111. <https://doi.org/10.1007/s11270-017-3271-2>

analytical techniques (3.2.2).

The sample notation in this chapter refers to the following abbreviations: REF=without superplasticiser, PCE=with 0.5 wt.% superplasticiser.

8.2 Results and discussion

8.2.1 Relative root growth

As simple bioassays provide a method to test stabilised solidified waste and sludge leachates with regard to phytotoxicity [Walter et al., 2006], they were included in the test scheme. In Figure 8.1 the root elongation is depicted for *S. alba* and *L. sativum* after the incubation time. It can be seen that in general *S. alba* shows a diminished root length compared to *L. sativum*. However, both test species exhibit a suitable root length after the chosen test period. Anyhow *S. alba* shows a higher distribution of root elongation.



Figure 8.1: Observed root growth of *S. alba* (top) and *L. sativum* (bottom) after exposure time of 4 days.

According to other studies [Grieve and Grattan, 1999, Hu and Schmidhalter, 2005] saline conditions with extreme ionic ratios, cause reduced plant growth due to ion toxicities and ionic imbalances influencing biophysical and/or metabolic components of plants. Due to the high pH-values and high amounts of leached ionic species [Märkl and Stephan, 2016] in cement leachates reduced root growth was expected to be observed. However, hardly any of the leachates lead to significantly reduced growth rates for both test species (Figure 8.2). Only

for 1 d leachates REF-BTW tested with *S. alba* and PCE-DI tested with *L. sativum* showed significantly reduced root elongation at a 5 % level. It has been reported on a beneficial effect of Ca^{2+} on the root growth while also alleviation of the adverse effect of salt stress on germination and vegetative growth might happen [Awada et al., 1995, Hu and Schmidhalter, 2005]. This could be an explanation of the promoted RRG during the bioassays as Ca^{2+} is constantly leached from the cement paste samples (for further explanation see Appendix 5). In fact for most of the leachates beneficial effects on the root growth could be observed although in most cases without statistical significance ($p < 0.05$). *S. alba* shows reduced RRG towards late age leachates, which means that the leached organic matter of the first eluates promotes the root elongation of *S. alba* beneficially. In addition the counter ion (Potassium) of the superplasticiser is also leached which has to be taken into account as another potential source influencing RRG. However, a possible release of inorganic species from hardened cement paste (e.g. Aluminium and Chromium) towards late age leachates may influence *S. alba* in a more toxic way [Mengel et al., 1984] although no significant difference at a 5 % level compared to the control can be found. The root growth of *L. sativum* tended to show a RRG comparable to the control for the early age leachates (0.25 and 1 d) whereas towards late age leachates the RRG is often significantly promoted (16 and 64 d). This might be caused by *L. sativum* being very sensitive to the leached organic superplasticiser and thus showing RRG around 100 % as the superplasticiser is washed from the sample during the first few eluate exchanges. In fact some of the chemical elements contained in cement such as Calcium, Silicon and Iron are essential for plants. The possible counter ions of superplasticisers typically Sodium and Potassium act in the same way as macro- and micronutrients that have to be available for healthy plant growth [Mengel et al., 1984, Hu and Schmidhalter, 2005]. However, cement also contains heavy metals such as nickel, zinc (which is a micronutrient) and lead. These elements may be harmful to plants [Arambasic et al., 1995]. In general it was not possible to calculate effect-concentration values e.g. EC_{50} out of the obtained data from the different dilutions. Down to a dilution of 12.5 % the RRG was promoted, which lead to even higher values compared to the control. Either effect-concentration values could only be calculated at higher dilution factors or at higher concentrated leachates. The latter could be achieved through choosing a lower liquid-to-solid-ratio in the leaching test.

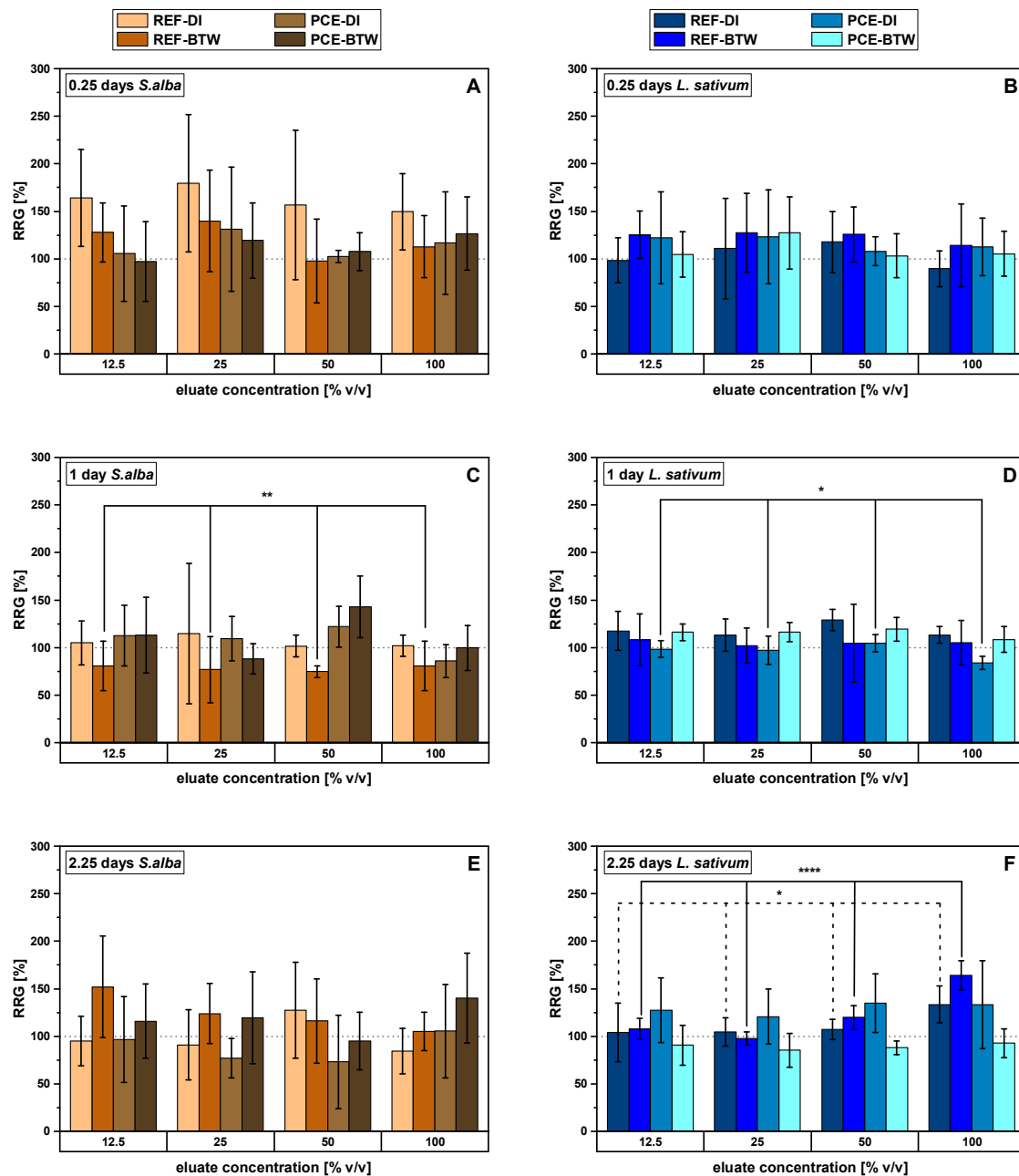


Figure 8.2: Mean RRG of *S. alba* and *L. sativum* in water eluates depicted for all four concentrations after 0.25 d (A and B), 1 d (C and D) and 2.25 d (E and F). Distilled water was used as control for which the RRG was 100 % throughout. Asterisks indicate significant differences from the control (Bonferroni-Test, *= $p < 0.05$; **= $p < 0.01$; ***= $p < 0.001$; ****= $p < 0.0001$).

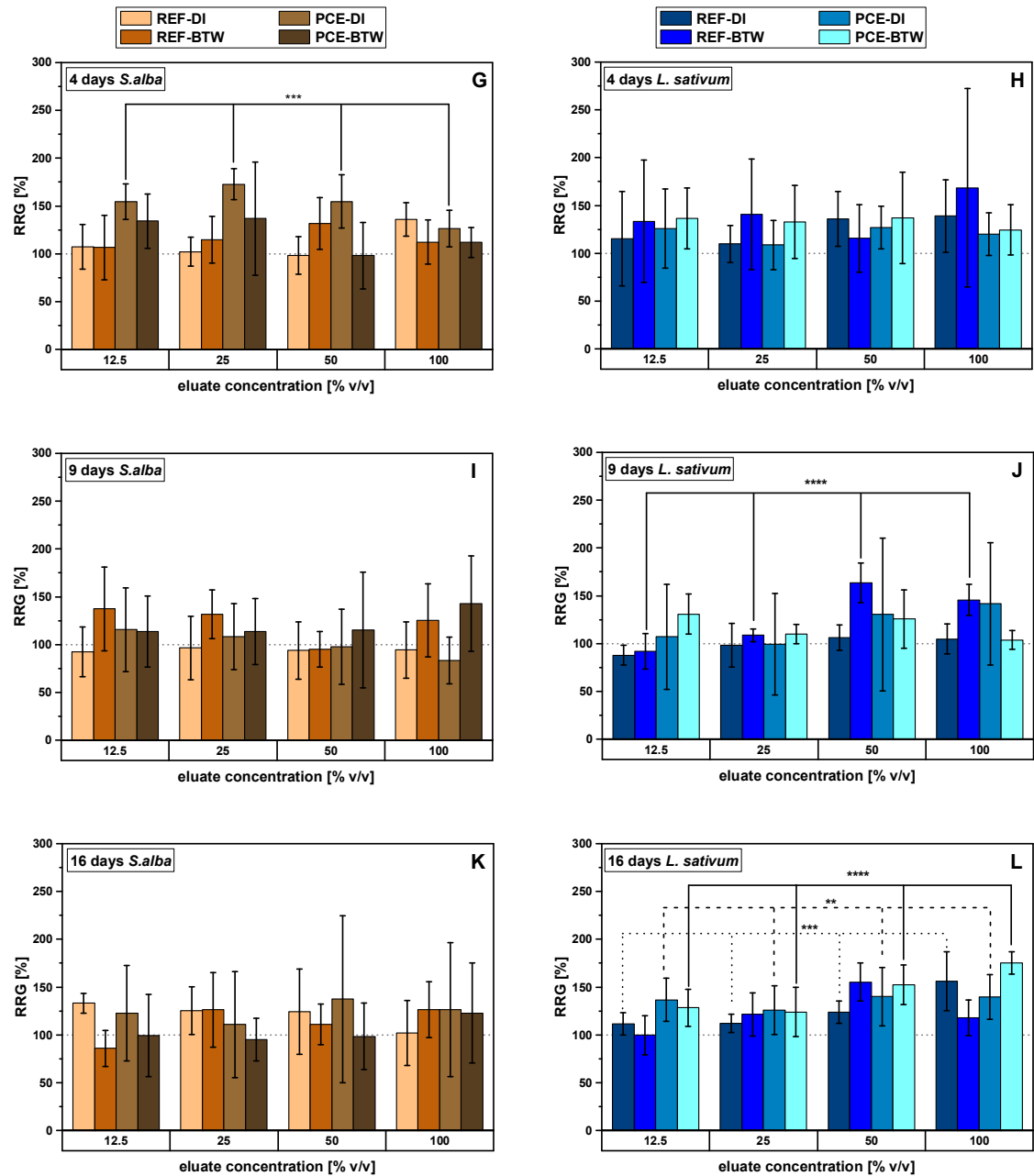


Figure 8.2 (Continued): Mean RRG of *S. alba* and *L. sativum* in water eluates depicted for all four concentrations after 4 d (G and H), 9 d (I and J) and 16 d (K and L). Distilled water was used as control for which the RRG was 100 % throughout. Asterisks indicate significant differences from the control (Bonferroni-Test, $*=p<0.05$; $**=p<0.01$; $***=p<0.001$; $****=p<0.0001$).

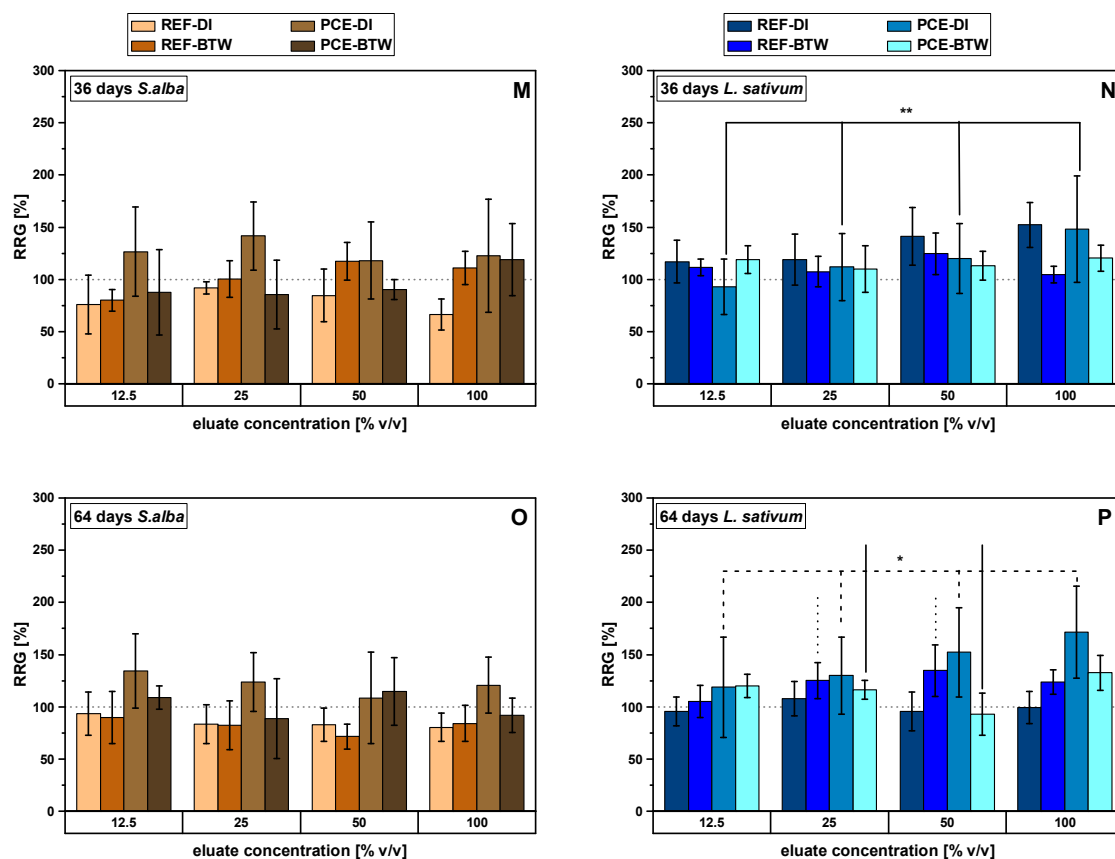


Figure 8.2 (Continued): Mean RRG of *S. alba* and *L. sativum* in water eluates depicted for all four concentrations after 36 d (M and N) and 64 d (O and P). Distilled water was used as control for which the RRG was 100 % throughout. Asterisks indicate significant differences from the control (Bonferroni-Test, $*=p<0.05$; $**=p<0.01$; $***=p<0.001$; $****=p<0.0001$).

8.2.2 Relative seed germination and germination index

An ANOVA followed by a Bonferroni post-hoc test evidenced that there are no significant differences ($p < 0.05$) between dilution steps of the samples and the control when they are evaluated with *S. alba* and *L. sativum* seeds in the germination bioassay (RSG). However, the GI, which is the mathematical product of RRG and RSG, shows beneficial effects on both test species often with significant differences at a 5 % level compared to the control (Table 8.1).

The order in means of *S. alba* seeds exposed to the 0.25 d eluates was PCE-BTW < REF-BTW < PCE-DI < REF-DI and for *L. sativum* seeds was REF-DI < PCE-BTW < PCE-DI < REF-BTW. All of them promoted the GI, which may be explained by the leached organic matter and the leached ions from the cement at the beginning of the leaching experiment. The order in means of *S. alba* seeds exposed to the 64 d eluates was REF-BTW < REF-DI < PCE-BTW < PCE-DI and for *L. sativum* was REF-DI < PCE-BTW < REF-BTW < PCE-DI. This indicates that the samples without superplasticiser exhibit slight toxic effects, with a significance at a 5 % level for *S. alba*, which can be related to the different discharge of organic and inorganic species, the pH-value and the electric conductivity of the samples. Also a nearly full coverage of the cement particles with superplasticiser can give rise to a protective layer which in turn prevents the release of components from the cement matrix, e.g. heavy metal ions, which may negatively influence the germination. However, the exact mechanisms underlying this process remain undetermined. In-depth investigations on the composition of the eluates and the corresponding effects on relevant parameters like seed germination need to be carried out to get better insight to this behaviour.

Other studies [Fuentes et al., 2004, Alvarenga et al., 2007] investigated different sewage sludge concentrations in soils and water extracts thereof in phytotoxicity tests with species like *L. sativum* and barley. It was found that *L. sativum* is more sensitive to toxic effects. In contrast both species as used in this study were equal in sensitivity and confirmed that the tested cement leachates show only minor phytotoxicity. While [Kapustka and Reporter, 2009] stated that seed germination is a critical stage in the plant life cycle and could therefore be representative, [Dorn et al., 1998] expound that seed germination is limited in estimating the toxicity of substances due to two reasons. First, various chemicals may not penetrate into the seed and second the germinating seed receives its nutritional requirements from the internal seed storage materials. In general more research needs to be carried out using different methods including statistical correlation methods to get better insight on the effects of cement paste eluates and the included superplasticisers on the environment.

Table 8.1: RSG and GI of *S. alba* seeds and *L. sativum* seeds as affected by leachates of cement samples in four different concentrations after 0.25 d and 64 d. Entries marked with the same superscript letter within each type of sample are not significantly different ($p>0.05$).

sample	RSG					GI				
	concentration [vol.%]				mean	concentration [vol.%]				mean
	12.5	25	50	100		12.5	25	50	100	
<i>S. alba</i> seeds - age 0.25 d										
REF-DI	101.8 ^a	103.7 ^a	99.4 ^a	102.4 ^a	101.8	166.3 ^b	189.9 ^b	160.7 ^b	154.6 ^b	167.8
PCE-DI	102.9 ^a	104.6 ^a	88.2 ^a	98.1 ^a	98.4	106.6 ^a	135.9 ^b	90.9 ^a	117.5 ^a	112.7
REF-BTW	97.4 ^a	96.7 ^a	93.0 ^a	90.6 ^a	94.4	124.9 ^b	134.0 ^b	91.2 ^a	100.2 ^a	112.5
PCE-BTW	94.6 ^a	94.4 ^a	100.1 ^a	103.0 ^a	98.0	93.2 ^a	115.7 ^a	110.2 ^a	129.8 ^a	112.2
<i>S. alba</i> seeds - age 64 d										
REF-DI	107.3 ^a	108.1 ^a	94.6 ^a	101.2 ^a	102.8	100.3 ^a	89.2 ^a	77.8 ^b	80.9 ^b	87.0
PCE-DI	106.9 ^a	108.2 ^a	103.3 ^a	106.0 ^a	106.1	144.6 ^b	134.1 ^b	113.4 ^a	128.0 ^a	130.0
REF-BTW	104.9 ^a	94.2 ^a	100.9 ^a	100.3 ^a	100.0	95.3 ^a	78.0 ^b	72.3 ^b	83.4 ^b	82.2
PCE-BTW	112.5 ^a	117.0 ^a	101.9 ^a	100.1 ^a	107.8	122.6 ^a	105.5 ^a	120.6 ^a	93.2 ^a	110.4
<i>L. sativum</i> seeds - age 0.25 d										
REF-DI	90.6 ^a	104.1 ^a	102.6 ^a	107.7 ^a	101.2	87.5 ^a	117.7 ^a	120.0 ^a	96.2 ^a	105.3
PCE-DI	96.7 ^a	95.9 ^a	93.9 ^a	96.9 ^a	95.8	117.2 ^a	117.5 ^a	100.7 ^a	109.1 ^a	111.1
REF-BTW	102.1 ^a	106.9 ^a	105.6 ^a	106.0 ^a	105.1	127.1 ^a	142.3 ^b	135.4 ^b	121.7 ^a	131.6
PCE-BTW	98.2 ^a	104.9 ^a	94.6 ^a	98.7 ^a	99.1	103.8 ^a	135.8 ^b	99.6 ^a	102.5 ^a	110.4
<i>L. sativum</i> seeds - age 64 d										
REF-DI	93.3 ^a	97.5 ^a	96.5 ^a	100.0 ^a	96.8	90.4 ^a	105.6 ^a	92.4 ^a	99.6 ^a	97.0
PCE-DI	97.3 ^a	99.0 ^a	110.3 ^a	110.6 ^a	104.3	117.1 ^a	208.9 ^c	167.4 ^d	192.1 ^c	171.3
REF-BTW	112.6 ^a	111.3 ^a	107.8 ^a	106.0 ^a	109.4	117.5 ^a	139.2 ^b	145.8 ^a	131.0 ^b	133.3
PCE-BTW	107.5 ^a	110.3 ^a	94.4 ^a	111.1 ^a	105.8	129.5 ^a	128.1 ^a	88.5 ^b	147.7 ^c	123.4

Sample notation: REF=without superplasticiser, PCE=with 0.5 wt.% superplasticiser.

8.3 Conclusions

The present study shows the effect of cement leachates with and without superplasticiser on white mustard *S. alba* and cress *L. sativum*.

In general, it can be concluded that cement leachates promote RRG, RSG and GI of both test species although the promoting effect is only significant in few cases. The cement leachates exert different influences in both test species. The root growth of *S. alba* is promoted by leachates from the early stage (0.25 and 1 d) while for *L. sativum* a promotion is observed towards later ages of the leachates (16 and 64 d). The RSG was not significantly influenced throughout. From the RRG, RSG and GI data it was not possible to calculate effect-concentration-values as all the diluted eluates (from pure eluate 100 % down to 12.5 %) influence the plant growth in a positive way. As a consequence no or only slight harmful effects could be observed during this study. In case of samples containing superplasticiser a promotion of the GI is indicated. However, this effect can not be explained from the data obtained during this study.

Further research needs to be done including correlation analysis and multivariate statistics. This applies also concerning the leaching of inorganic and organic constituents and their impact on phytotoxicity which is beyond the scope of this study. To gain better insight towards this aspect the buffer function of soil needs to be investigated in detail.

General summary and conclusions

Ever since the new construction products regulations came into force in 2013, well established building materials need to be scrutinised just as new and innovative ones. The environmental impact during the whole life-cycle of a construction product is the main focus of this regulation. The aim of the present thesis is to contribute to this purpose by in-depths investigations on the leaching behaviour and the environmental impact of these leachates using different relevant waterproofing materials. Distinct aspects related to waterproofing building materials and their leaching behaviour were examined in a multi-method approach. Three different waterproofing materials, namely polyurethane, a Portland cement-based cement-polyurethane hybrid material and Portland cement pastes were investigated. Three key aspects were evaluated in this thesis, namely (i) leaching of inorganic ions, (ii) detection of the organic compounds as sum parameter, simulation of the leaching behaviour and whenever possible single compound detection and (iii) effects of the leachates on the environment. In summary, leached amounts of inorganic ions were in the typical range for the corresponding materials and did not exceed threshold values defined by national and international authorities. The leached TOC was in any case very low and decreased within the first few leaching steps. However, the early age leachates show increased toxic effects for all investigated systems and groups of materials, which means that the first contact period of the waterproofing materials with the environment and especially in presence of water is a crucial phase.

9.1 Leaching of inorganic ions from waterproofing materials

A first step to understand leaching of building materials is to gain knowledge about the leached inorganic constituents. To this purpose the leaching behaviour of selected waterproofing materials and the underlying mechanisms need to be described and understood in detail. Hereby information on the leaching mechanisms as prevailing in inorganic cement-based materials serve as guide values to describe the mechanisms of hybrid materials containing significant fractions of organic additives (e.g. PCE-based superplasticisers). On this basis inorganic constituents in the leachates were investigated with pH-value, electric conductivity, ion chromatography and inductively coupled plasma atomic emission spectroscopy.

Waterproofing polyurethane materials

Leachates gained from polyurethane materials showed pH ~4.5 for demineralised water and ~6 for Berlin tap water as eluent. A slight drop of pH during the first few leaching steps was due

to the formation of CO_2 . Electric conductivity stayed also constant at values of $650 \mu\text{S cm}^{-1}$ for Berlin tap water and $20 \mu\text{S cm}^{-1}$ for demineralised water. The detected ions (Al^{3+} , Ca^{2+} , K^+ , Na^+ , Si^{4+} , Cl^- and SO_4^{2-}) were found to be in the range of the neat eluents themselves, which means that none of these ions were uptaken in the PU systems. The metal ions of the catalysts, Zn and Sn, were also analysed in the eluates. For ZINC-middle-DI (0.083 g catalyst per 100 g PU mixture) maximums of up to $0.004 \text{ mmol l}^{-1}$ were measured, which is way below the maximum of $0.0765 \text{ mmol l}^{-1}$ which is set for drinking water by the WHO. As the Sn containing catalyst (DOTL) is only slightly soluble in water the measured values for Sn are $\sim 0.0012 \text{ mmol l}^{-1}$ for DOTL-low-DI (0.0036 g catalyst per 100 g PU mixture).

Waterproofing cement-polyurethane hybrid materials

Results showed typical pH-values for Portland cement based systems (pH 12.5) in the 24-hours batch test. Electrical conductivity was $\sim 9 \mu\text{S cm}^{-1}$ resulting from ultra pure water (high aggressiveness) which was used as eluent. Depending on the replacement of cement by GGBFS (overall composition of the inorganic binder) inorganic ions are leached in different amounts. Values of SO_4^{2-} and Si^{4+} decrease with increasing amount of GGBFS. Al^{3+} was in any case close to the detection limit. Leached amounts of Ca^{2+} ($\sim 2.5 \text{ mmol l}^{-1}$) and Na^+ ($\sim 0.9 \text{ mmol l}^{-1}$) are approximately the same for the different systems. Results of the batch test as worst case scenario did not exceed values of $0.007 \text{ mmol l}^{-1}$ (Al^{3+}), 8.7 mmol l^{-1} (Na^+), 2.6 mmol l^{-1} (SO_4^{2-}) and therefore fulfil the requirements of international and national standards on drinking water. Although the hybrid material consists of binder and polyurethane, the leached pH and electric conductivity is dominated by the included cement and GGBFS in the tank tests. Alternating pH (~ 11.5) during the first four elution steps (and decrease later on) and electric conductivity might be a result of interaction processes along with decreasing porosity due to the formation of hydrate phases. With increased amounts of GGBFS leaching of Cl^- , K^+ and Al^{3+} increased. However, for the latter threshold values according to German drinking water regulations are exceeded. This might be a result of the polyurethane incorporated in the composite material, which reacts with water by forming CO_2 leading to increased porosity. For selected systems (e.g. C1-30) the dominant leaching mechanism of Ca^{2+} , K^+ and Al^{3+} was determined. Leaching of K^+ and Ca^{2+} was found to be controlled by surface wash-off while Al^{3+} leaching was controlled by diffusion. These leaching behaviours of the particular ions were independent from the composition of the inorganic binder.

Waterproofing cement pastes

Samples leached with demineralised water showed constant pH-values (~ 11.5) and electrical conductivity ($\sim 500 \mu\text{S cm}^{-1}$). In contrary both values decreased during the first leaching steps for samples leached with Berlin tap water while constant values were observed at later leaching steps (pH ~ 9 and el. conduct. $\sim 600 \mu\text{S cm}^{-1}$). Depending on the solubility of the ion and the aggressiveness of the eluent the ionic species are leached from hardened cement paste and mortar samples. Amounts of leached K^+ and Na^+ decrease rapidly, which indicates that these ions possibly act as counter ion of the superplasticisers. Leaching of Al^{3+} in detectable amounts (lower detection limit $0.002 \text{ mmol l}^{-1}$) is observed after a longer pre-storage time (56 d) or in the late leaching steps (36 to 64 d). Leached Ca^{2+} is provided by portlandite (Ca(OH)_2) and C–S–H. However, Ca^{2+} can interact with CO_2 provided by the eluent, forming a dense boundary layer consisting of calcite (CaCO_3) which hinders further release of ions like SO_4^{2-} and might exert influence on the leaching kinetics. In addition changes

in chemical equilibrium lead to local increased or decreased concentrations of ionic species, which results in local equilibria. In case of portlandite ($\text{Ca}(\text{OH})_2$) leaching, ions like SO_4^{2-} or CO_3^{2-} increase locally and can diffuse back into the inner of the sample to compensate for this. Cumulative leached amounts of ions were found to depend on the aggressiveness of the eluent, the w/c-ratio and the pre-storage time.

9.2 Leaching of organic species from waterproofing materials

Waterproofing materials often contain significant fractions of organic additions or are hybrids of inorganic and organic binders (e.g. polyurethane and chemical admixtures). In consequence not only the leaching behaviour and mechanisms of inorganic compounds but also of organic compounds is a crucial point to be considered. The organic fraction of the leachates was analysed as sum parameters TOC and/or DOC and the leaching behaviour was determined along with the leaching mechanism. In addition it is also aimed at gaining better information on the structure of the single leached organic compounds which is an analytical challenge. Yet, the structure of these compounds needs to be resolved in order to fully understand the environmental impact and to determine the origin of toxic effects. Wherever possible, further analysis of the organic constituents was performed. Therefore liquid chromatography and UV-Vis spectrometry measurements have been applied.

Waterproofing polyurethane materials

Both organic sum parameters showed identical values of 21.6 mmol l^{-1} (TOC) and 20.2 mmol l^{-1} (DOC) for ZINC-high-DI at 10 min. This means that particles of higher molecular weight are not present in the leachates. For all leachates the amount of detected organic carbon is rapidly decreasing over time. The maxima of leached organic carbon are higher with demineralised water indicating a higher aggressiveness of this eluent and are highest for ZINC-low-DI at 612 mmol l^{-1} . To gain further information on the leached organic compounds and the composition of the leachates LC-OCD was performed. The signals as received using different detectors (UVD and OCD) showed compounds in the low molecular weight region. The UVD signals correspond to nitrogenous compounds which can be ascribed to amines while the OCD signals correspond to carbonaceous molecules in amounts that correspond well to the DOC measurements.

Waterproofing cement-polyurethane hybrid materials

The measured TOC after the 24-h batch test was marginal for all samples ($0.007 \text{ mmol l}^{-1}$ for commercially available CEM III containing samples), although polyurethane was included (cement slurry:polyurethane = 10:1) in the samples. During the tank leaching tests the TOC is continuously decreasing for all the samples, which points to wash-off effects. Additionally the cumulative release of organic carbon as calculated after 64 d of leaching was in the range from 83 mmol m^{-2} for sample C1-10 (containing 90 wt.% CEM I and 10 wt.% GGBFS in the neat cement slurry) to 49 mmol m^{-2} for sample C1-20 (containing 80 wt.% CEM I and 20 wt.% GGBFS in the neat cement slurry). The differences in cumulative release of organic carbon can be ascribed to the GGBFS substitution and the resulting filler-effect. For all samples the dominating leaching mechanism showed a slope of $m=-1$ which indicates wash-off effects of the organic species. This results from loosely bound organic species on the sample surface, which are able to quickly dissolve in the eluent. However, after the first

three elution steps (up to 1 d) the surface is impoverished in organic species and leaching thereof is marginal. The leached TOC can be ascribed to the polyurethane and the chemical admixtures in the cement suspension.

Waterproofing cement pastes

Cement pastes were prepared with two different chemical admixtures (PCE and a mixture of NFS and MFS). Different pre-storage times (1 and 56 d) as well as different eluents (DI and BTW) were evaluated. The detected values of TOC as well as of DOC decreased rapidly during the first three leaching steps up to 7 d for all investigated systems independently of the superplasticiser type contained. Increased cumulative release is observed at higher superplasticiser content, with longer pre-storage time and a more aggressive eluent. Under similar conditions comparable organic fractions are leached from the samples (up to 58 mmol l^{-1} for DI), independent from the type of contained superplasticiser. The leaching mechanism was allocated to wash-off effects with slopes around $m=-1$. HPLC-MS was applied to identify the used PCE in the leachates. Fragments of the superplasticiser were detected at retention times of 3 min only in the first eluate (6 h) independently of the eluent. As was the case by the determination of the prevailing leaching mechanism, these results also indicate that wash-off effects are the dominating mechanism. The leachates gained from hardened cement paste samples containing a mixture of NFS and MFS were additionally analysed with UV-Vis spectrometry. The results show that up to 2 wt.% of total active component of the superplasticiser mixture can be leached from the samples in a test period of 56 d.

9.3 Ecotoxicological effects of waterproofing materials

An important aspect towards leaching of building materials is to understand the effects of leachates on the environment. In this regard eluates have to be tested concerning their environmental harmfulness and toxicity. This also includes the possible time dependence of the environmental impact such that different stages may be defined during the life cycle of constructions. Numerous parameters have to be incorporated and evaluated, accordingly investigations on the environmental impact of construction materials leachates are a complex topic which is perceived more and more in the construction sector. In-depth considerations and investigations on this topic are inevitable, especially as national and international regulations are becoming noticeable more stringent in recent years. Several ecotoxicological assays have been included in the test scheme in order to cover aquatic and terrestrial compartments. The algal growth inhibition test with *Desmodesmus subspicatus*, as well as genotoxicity and mutagenicity tests with Ames and UmuC-assays cover the aquatic compartment. Phytotoxicity tests with white mustard *Sinapis alba* and cress *Lepidium sativum* as well as three mortality tests (in pure eluate, with sand and with soil) with *Enchytraeus albidus* were included to cover the terrestrial compartment.

Waterproofing polyurethane materials

Depending on the type of catalyst, its dosage and the contact time of the eluent with the polyurethane system the algal growth rate was affected variously. The ZINC-catalyst promotes algal growth rates less pronounced compared to its control at a 5 % acceptance level. However, low dilutions (1:8) of ZINC-catalyst at low dosages (0.0053 g catalyst per 100 g PU mixture) show increased algae growth rates, which might be a result of the increased organic carbon

load at early leaching steps. In all three mortality assays with *E.albidus* the high dosages of catalyst did not show significant difference from the control ($p=0.05$) throughout. In contrary significant toxic effects can be observed for the low catalyst dosages. Especially for the early age leachates, e.g. ZINC-low-DI 10 min, up to 100 % mortality was observed in the sand tests and in the water tests after 48 and 72 h. However, the leachates gained at 70 min are not significantly different compared to the control as no toxic effects can be observed at these later ages. In all three assays, the pure eluate test gives the fastest and most definite results. As soon as sand or soil is incorporated in the test scheme a buffer function is present which leads to reduced toxic effects.

Waterproofing cement-polyurethane hybrid materials

To evaluate the toxicity of the cement-polyurethane hybrid materials the three different assays (as described above) with *E. albidus* have been performed. For all samples included in the test scheme no significant difference comparing with the control ($p=0.05$) can be observed in the sand and soil tests. In these tests the buffering function of soil and sand is present which is related to a certain ion exchange capacity. Only in the pure eluate tests toxic effects on *E. albidus* can be observed. Especially when GGBFS is present in the mixture (30 wt.%), the early age leachates show significant toxic effects. For example after 48 and 72 h the survival ratio of *E. albidus* is at 0 % for the 0.083 and 0.25 h leachates which corresponds to a significant reduction compared to the control at an acceptance level of 5 %. However, the commercially available blast-furnace slag cements (CEM III according to EN 196-1) with higher amounts of GGBFS (36 wt.% to 65 wt.%) showed no toxic effects. Significantly reduced survival ratios seem to be an effect of the increased K^+ , Cl^- and SO_4^{2-} values in these leachates where also slightly increased TOC values were detected.

Waterproofing cement pastes

In the phytotoxicity assays the observed vegetative growth was attributed to leached ions like Ca^{2+} , Si^{4+} and Fe^{3+} which act as essential nutrients for plants. The leached counter ion (K^+) is a macronutrition which is necessary for healthy plant growth. The RRG of *S. alba* is promoted by leachates from the early stage (0.25 and 1 d) while for *L. sativum* a promotion is observed towards later ages of leachates (16 and 64 d). The GI often showed significant differences at a 5 % level compared to the control. The means of the GIs were sorted for the 0.25 d and 64 d leachates (e.g. for *S. alba* at 64 d: REF-BTW<REF-DI<PCE-BTW<PCE-DI) and indicated that the samples without superplasticiser exhibit slight toxic effects. These effects can be related to the organic and inorganic species, the pH-value and the electric conductivity. ANOVA analysis of the results showed that the eluent has no statistical significant impact. The two test species revealed equal sensitivity and confirmed that the tested cement leachates show only minor phytotoxicity. Only a few of the leachates were suspected to be mutagenic at a significance level $p<0.05$. These samples did not confirm to a clear pattern. Most of the samples showed no toxicity and therefore no mutagenic potential. In the UmuC-assay no cytotoxicity was detected while the early age leachates (6 h and 1 d) for samples without superplasticiser are considered to be genotoxic. However, no unequivocal trend or pattern emerges in terms of genotoxicity which is in good accordance with the results from the phytotoxicity tests.

Outlook and suggestions for future work

The work presented in this thesis covers aspects of the fundamental effects of leaching of different construction products for waterproofing purposes. The adaption of standardised leaching methods to the needs of the surveillance of the materials curing process is investigated. Analysis of leachates is performed for chemical as well as ecotoxicological parameters that might be possible parameters to categorise the investigated materials as hazardous for the environment. New insights in complex systems like advanced cement-polyurethane composites are provided on which basis advanced eco-friendly waterproofing construction materials can be further developed. However, despite the contribution provided in this work waterproofing construction products need to be studied in more detail and it is indispensable to gain deeper knowledge on the actual leaching reactions/mechanisms and the influence of the chemical and mineralogical composition of the raw materials. In addition the environmental impact of leachates obtained from construction materials requires a better understanding. To this purpose, comprehensive studies on the physical, chemical and ecotoxicological characteristics of construction materials and leachates thereof need to be conducted. Based on these considerations a number of aspects can be listed that might serve as subjects for further research:

- As in this thesis just the standardised tank leaching tests and the batch test were performed other leaching tests like the percolation test [DIN 19631, 2013] are worth considering, as this test is close to reality. Also an up-scaling to lysimeters and field tests would be helpful, as has been shown by [Togerö, 2004] who found higher leached amounts in the latter comparing to lab scale test. In this regard it is highly recommended to develop methods that would allow conversion of results obtained from different test scenarios for the purpose of direct comparability.
- While the type of catalyst and its contained fraction was found to be a key parameter of the leaching of polyurethane systems the leaching test itself and its parameters could be adjusted further. Extension of the test period up to several days is recommended such that the early strong reaction of the material directly after application is fully covered. To gain deeper information of the chemical composition of the leachates more sophisticated liquid chromatography techniques such as HPLC-MS and SEC are promising methods. As some chemical substances used for polyurethanes are highly volatile the application of gas chromatography in combination with different detectors could also be a method of choice.

- The cement-polyurethane hybrid injection material investigated in this work is a promising new material. However, it should be considered that this system is highly depending on the used cement which is subject to wide variations from a composition point of view. Better understanding has to be gained in terms of real cement-systems achieved by the usage of supplementary cementitious materials like fly ash. Here in-depth considerations on the physical, mineralogical and chemical material properties would be helpful. With regard to the higher porosity of this material caused by the polyurethane reaction long term leaching studies should be performed. Due to increasing inner surface an increased interface exists and thus leaching can be intensified.
- As cement is a complex material investigations on its leaching behaviour are challenging. A combination of analytical methods (like XRD, pore solution analysis in combination with leaching etc.) could be used to get better insight and understand the leaching mechanisms. In this regard special designed experimental set-ups could be used to detect the leaching boundary/ frontier or explore certain leaching mechanisms especially of the organic components like superplasticisers.
- In this study only the leaching behaviour of specific organic additives was investigated. A much broader set including a greater range of different organic additives such as rheology and air-entraining agents is necessary to get better understanding of the chemical and ecotoxicological impact on the environment. In this regard also the consumption of cement and concrete has to be taken into account. These mass products are manufactured in tremendous amounts such that the incorporation of a few percent of admixtures with respect to the mass of cement in concrete mixtures needs to be extrapolated. In this way the worldwide consumption of organic admixtures can at least be estimated as reliable data on the global consumption are not available. Accordingly the ecotoxicological impact of leachates needs to be reviewed with respect to the global admixture consumption.
- With respect to an official registration of (waterproofing) construction materials it is necessary to perform ecotoxicological assays. As such tests are complex, time consuming and often expensive, it is recommended to set up a meaningful and dynamic biological test battery. Accordingly test set-ups should be highly application-oriented by always considering two ecological compartments, consequently including terrestrial ecotoxicological assays. Test scenarios need to be as close to reality as possible to gain realistic insight into the complex correlations. Furthermore the impact of leachates on the enzymology or the DNA of the test organisms is also a crucial point to be investigated where long term effects and late age leachates should be implied likewise.

References

- [Adenot, 1992] Adenot, F. (1992). *Durabilité du béton: caractérisation et modélisation des processus physiques et chimiques de dégradation du ciment*. PhD thesis, Université d'Orleans.
- [Afolabi et al., 2012] Afolabi, A., Francis, F. A., and Adejomo, F. (2012). Assessment of health and environmental challenges of cement factory on ewekoro community residents, ogun state, nigeria. *American Journal of Human Ecology*, 1(2):51–57.
- [Ahmed et al., 2015] Ahmed, M., Ibrahim, A., et al. (2015). Strengthening of the permeability of sandy soil by different grouting materials for seepage reduction. *Global Journal of Research In Engineering*, 15(3).
- [Aïtcin and Flatt, 2015] Aïtcin, P.-C. and Flatt, R. J., editors (2015). *Science and Technology of Concrete Admixtures*. Elsevier LTD, Oxford.
- [Allport et al., 2003] Allport, D. C., Gilbert, D. S., and Outterside, S. M., editors (2003). *MDI and Tdi: Safety, Health and the Environment: A Source Book and Practical Guide*. John Wiley & Sons.
- [Alvarenga et al., 2007] Alvarenga, P., Palma, P., Gonçalves, A., Fernandes, R., Cunha-Queda, A., Duarte, E., and Vallini, G. (2007). Evaluation of chemical and ecotoxicological characteristics of biodegradable organic residues for application to agricultural land. *Environment International*, 33(4):505–513.
- [Amarantos et al., 1985] Amarantos, S., Papadokostaki, K., and Petropoulos, J. (1985). Comparison of leaching tests and study of leaching mechanisms. Technical report, National Research Centre for the Physical Sciences Democritos.
- [Anagnostopoulos, 2014] Anagnostopoulos, C. A. (2014). Effect of different superplasticisers on the physical and mechanical properties of cement grouts. *Construction and Building Materials*, 50(0):162 – 168.
- [Anagnostopoulos et al., 2016] Anagnostopoulos, C. A., Sapidis, G., and Papastergiadis, E. (2016). Fundamental properties of epoxy resin-modified cement grouts. *Construction and Building Materials*, 125:184–195.
- [Andac and Glasser, 1999] Andac, M. and Glasser, F. P. (1999). Long-term leaching mechanisms of portland cement-stabilized municipal solid waste fly ash in carbonated water. *Cement and Concrete Research*, 29(2):179 – 186.
- [Andersen et al., 1986] Andersen, P., Kumar, A., Roy, D., and Wolfe-Confer, D. (1986). The effect of calcium sulphate concentration on the adsorption of a superplasticizer on a cement: Methods, zeta potential and adsorption studies. *Cement and Concrete Research*, 16(2):255 – 259.
- [Andersen et al., 1987] Andersen, P., Roy, D., Gaidis, J., and Grace, W. (1987). The effects of adsorption of superplasticizers on the surface of cement. *Cement and Concrete Research*, 17(5):805 – 813.
- [Andersson and Stromvall, 2001] Andersson, A. C. and Stromvall, A.-M. (2001). Leaching of concrete admixtures containing thiocyanate and resin acids. *Environmental Science and Technology*, 35:788–793.
- [Arambasic et al., 1995] Arambasic, M. B., Bjelic, S., and Subakov, G. (1995). Acute toxicity of heavy metals (copper, lead, zinc), phenol and sodium on allium cepa l., lepidium sativum l. and daphnia magna st.: Comparative investigations and the practical applications. *Water Research*, 29(2):497 – 503.
- [Arendt et al., 2012] Arendt, F., Annokkée, G., Bosman, R., and van den Brink, W. (2012). *Contaminated Soil '93: Fourth International KfK/TNO Conference on Contaminated Soil 3–7 May 1993, Berlin, Germany*, volume 2. Springer Science & Business Media.
- [Arnold et al., 2010] Arnold, W. R., Cotsifas, J. S., Ogle, R. S., DePalma, S. G. S., and

- Smith, D. S. (2010). A comparison of the copper sensitivity of six invertebrate species in ambient salt water of varying dissolved organic matter concentrations. *Environmental Toxicology and Chemistry*, 29(2):311–319.
- [Austin and Hicks, 2016] Austin, A. and Hicks, D. (2016). A review of the global pu industry of 2015 and outlook for 2016. *PU Magazine*, 13(1):22–34.
- [Awada et al., 1995] Awada, S., Campbell, W. F., Dudley, L. M., Jurinak, J. J., and Khan, M. A. (1995). Interactive effects of sodium chloride, sodium sulfate, calcium sulfate, and calcium chloride on snapbean growth, photosynthesis, and ion uptake. *Journal of Plant Nutrition*, 18(5):889–900.
- [Azizian et al., 2003] Azizian, M. F., Nelson, P. O., Thayumanavan, P., and Williamson, K. J. (2003). Environmental impact of highway construction and repair materials on surface and ground waters: Case study: crumb rubber asphalt concrete. *Waste Management*, 23(8):719 – 728.
- [Baker and Bishop, 1997] Baker, P. G. and Bishop, P. L. (1997). Prediction of metal leaching rates from solidified/stabilized wastes using the shrinking unreacted core leaching procedure. *Journal of Hazardous Materials*, 52(2-3):311–333.
- [Baldisserotto et al., 2004a] Baldisserotto, B., Kamunde, C., Matsuo, A., and Wood, C. (2004a). Acute waterborne cadmium uptake in rainbow trout is reduced by dietary calcium carbonate. *Comparative Biochemistry and Physiology Part C: Toxicology & Pharmacology*, 137(4):363 – 372.
- [Baldisserotto et al., 2004b] Baldisserotto, B., Kamunde, C., Matsuo, A., and Wood, C. (2004b). A protective effect of dietary calcium against acute waterborne cadmium uptake in rainbow trout. *Aquatic Toxicology*, 67(1):57 – 73.
- [Barbir et al., 2012] Barbir, D., Dabic, P., and Krolo, P. (2012). Evaluation of leaching behavior and immobilization of zinc in cement-based solidified products. *Journal of Hemijska industrija*, 66:781–786.
- [Barbosa et al., 2013] Barbosa, R., Lapa, N., Dias, D., and Mendes, B. (2013). Concretes containing biomass ashes: Mechanical, chemical, and ecotoxic performances. *Construction and Building Materials*, 48(0):457 – 463.
- [Barna et al., 1994] Barna, R., Moszkowicz, P., Veron, J., and Tirnoveanu, M. (1994). Solubility model for the pore solution of leached concrete containing solidified waste. *Journal of Hazardous Materials*, 37(1):33–39.
- [Barna et al., 1997] Barna, R., Sanchez, F., Moszkowicz, P., and Méhu, J. (1997). Leaching behavior of pollutants in stabilized/solidified wastes. *Journal of Hazardous Materials*, 52(2-3):287–310.
- [Batchelor, 1990] Batchelor, B. (1990). Leach models: Theory and application. *Journal of Hazardous Materials*, 24(2-3):255–266.
- [Bäverman, 1997] Bäverman, C. (1997). *Long-term leaching mechanisms of ashes and slags; Combining laboratory experiments with computer simulations*. PhD thesis, Royal Institute of Technology Stockholm.
- [BBT-Brenner Basistunnel, 2017] BBT-Brenner Basistunnel (2017). <https://www.bbt-se.com/>.
- [Becker et al., 1993] Becker, G., Braun, D., and Oertel, G. (1993). *Kunststoff-handbuch*, band 7: Polyurethane.
- [Beddoe, 2016] Beddoe, R. E. (2016). Modelling acid attack on concrete: Part II. a computer model. *Cement and Concrete Research*, 88:20–35.
- [Beddoe and Dorner, 2005] Beddoe, R. E. and Dorner, H. W. (2005). Modelling acid attack on concrete: Part I. the essential mechanisms. *Cement and Concrete Research*, 35(12):2333–2339.
- [Benedix, 2008] Benedix, R. (2008). *Bauchemie*. Vieweg+Teubner.
- [Berger et al., 2013] Berger, S., Aouad, G., Coumes, C. C. D., Bescop, P. L., and Damiot, D. (2013). Leaching of calcium sulfoaluminate cement pastes by water at regulated ph and temperature: Experimental investigation and modeling. *Cement and Concrete Research*, 53(0):211 – 220.
- [Bérigny, 1832] Bérigny, C. (1832). Mémoire sur un procédé d'injection propre à prévenir ou arrêter les filtrations sous les fondations des ouvrages hydrauliques. *Carilian-Goury*.

- [Blachnik, 2001] Blachnik, B. (2001). *Zusatzmittel in Putzmörteln: Wirksamkeit, Dauerhaftigkeit und Auslaugung*. PhD thesis, Universität-Gesamthochschule Siegen.
- [Blankenhorn, 1994] Blankenhorn, I. (1994). *Derzeitige Anwendung und Entwicklungen von Elutionsverfahren*. Landesanstalt für Umweltschutz, Baden-Württemberg.
- [Bodi et al., 2012] Bodi, J., Bodi, Z., Scucka, J., and Martinec, P. (2012). Polyurethane grouting technologies. In *Polyurethane*. InTech.
- [Böhm et al., 2012] Böhm, M., Salem, M. Z., and Srba, J. (2012). Formaldehyde emission monitoring from a variety of solid wood, plywood, blockboard and flooring products manufactured for building and furnishing materials. *Journal of Hazardous Materials*, 221-222:68–79.
- [Borka, 1980] Borka, G. (1980). The effect of cement dust pollution on growth and metabolism of *helianthus annuus*. *Environmental Pollution Series A, Ecological and Biological*, 22(1):75 – 79.
- [Brameshuber and Vollpracht, 2004] Brameshuber, W. and Vollpracht, A. (2004). *Konzept zur Bewertung des Auslaugverhaltens mineralischer Baustoffe/-körper durch Sicker- und Kontaktgrundwasserprognose - Teil 2: Bestimmung der Quellstärke für Boden und Grundwasser in Kontakt mit Betonfundamenten und Bodeninjektionen*. ibac RWTH Aachen.
- [Breitenbücher et al., 1992] Breitenbücher, R., Springenschmid, R., and Dorner, H. W. (1992). Verringerung der Auslaugbarkeit von Spritzbeton im Tunnelbau durch besondere Auswahl von Zementen und Betonzusätzen. *Beton-Informationen*, 1:10.
- [Bringmann and Kühn, 1980] Bringmann, G. and Kühn, R. (1980). Comparison of the toxicity thresholds of water pollutants to bacteria, algae, and protozoa in the cell multiplication inhibition test. *Water Research*, 14(3):231 – 241.
- [Brinke et al., 2015] Brinke, A., Buchinger, S., Reifferscheid, G., Klein, R., and Feiler, U. (2015). Development of a sediment-contact test with rice for the assessment of sediment-bound pollutants. *Environmental Science and Pollution Research*, 22(16):12664–12675.
- [Bundesministerium der Justiz, 2001] Bundesministerium der Justiz (2001). *Verordnung über die Qualität von Wasser für den menschlichen Gebrauch (Trinkwasserverordnung-TrinkwV)* Fassung vom 21. Mai 2001.
- [Burkhardt et al., 2009] Burkhardt, M., Jung-hans, M., Zuleeg, S., Boller, M., Schoknecht, U., Lamani, X., Bester, K., Vonbank, R., and Simmler, H. (2009). Biocides in building façades - Ecotoxicological effects, leaching and environmental risk assessment for surface waters [Biozide in Gebäudefassaden - Ökotoxikologische Effekte, Auswaschung und Belastungsabschätzung für Gewässer]. *Umweltwissenschaften und Schadstoff-Forschung*, 21(1):36–47.
- [Burkhardt et al., 2007] Burkhardt, M., Kupper, T., Hean, S., Haag, S., Schmid, P., Kohler, M., and Boiler, M. (2007). Biocides used in building materials and their leaching behavior to sewer systems. *Water Science and Technology*, 56:63–67.
- [Burkhardt et al., 2011] Burkhardt, M., Zuleeg, S., Vonbank, R., Schmid, P., Hean, S., Lamani, X., Bester, K., and Boller, M. (2011). Leaching of additives from construction materials to urban storm water runoff. *Water Science and Technology*, 63:1974–1982.
- [Butera et al., 2014] Butera, S., Christensen, T., and Astrup, T. (2014). Composition and leaching of construction and demolition waste: Inorganic elements and organic compounds. *Journal of Hazardous Materials*, 276:302 – 311.
- [Butscher, 2012] Butscher, C. (2012). Steady-state groundwater inflow into a circular tunnel. *Tunnelling and Underground Space Technology*, 32:158–167.
- [Cairns et al., 1982] Cairns, M. A., Garton, R. R., and Tubb, R. A. (1982). Use of fish ventilation frequency to estimate chronically safe toxicant concentrations. *Transactions of the American Fisheries Society*, 111(1):70–77.
- [Çakır and Aköz, 2008] Çakır, O. and Aköz, F. (2008). Effect of curing conditions on the mortars with and without GGBFS. *Construction and Building Materials*, 22(3):308–314.
- [Clemitson, 2008] Clemitson, I. (2008). *Castable Polyurethane Elastomers*. Informa UK Limited.

- [Côté et al., 1987] Côté, P. L., Constable, T. W., and Moreira, A. (1987). An evaluation of cement-based waste forms using the results of approximately two years of dynamic leaching. *Nuclear and Chemical Waste Management*, 7(2):129–139.
- [Crank, 1975] Crank, J. (1975). *The Mathematics of Diffusion: 2d Ed.* Clarendon Press.
- [CRC press, 1993] CRC press, editor (1993). *Grouting in rock and concrete: proceedings of the International Conference on Grouting in Rock and Concrete, Salzburg, Austria, 11-12 October 1993.* Balkema.
- [Croce et al., 2014] Croce, P., Flora, A., and Modoni, G. (2014). *Jet grouting: technology, design and control.* CRC Press.
- [Cuellar-Bermudez et al., 2016] Cuellar-Bermudez, S. P., Aleman-Nava, G. S., Chandra, R., Garcia-Perez, J. S., Contreras-Angulo, J. R., Markou, G., Muylaert, K., Rittmann, B. E., and Parra-Saldivar, R. (2016). Nutrients utilization and contaminants removal. a review of two approaches of algae and cyanobacteria in wastewater. *Algal Research*, pages 438–449.
- [Curtis and Ward, 1981] Curtis, M. and Ward, C. (1981). Water for survival aquatic toxicity of forty industrial chemicals: Testing in support of hazardous substance spill prevention regulation. *Journal of Hydrology*, 51(1):359 – 367.
- [Czaja, 1960] Czaja, A. T. (1960). Die Wirkung von verstäubtem Kalk und Zement auf Pflanzen. *Qualitas Plantarum et Materiae Vegetabiles*, 7(2):184–212.
- [DAfStb-Richtlinie, 2005] DAfStb-Richtlinie (2005). *DAfStb-Richtlinie - Bestimmung der Freisetzung anorganischer Stoffe durch Auslaugung aus zementgebundenen Baustoffen.* Deutscher Ausschuss für Stahlbeton.
- [Damtoft et al., 2008] Damtoft, J., Lukasik, J., Herfort, D., Sorrentino, D., and Gartner, E. (2008). Sustainable development and climate change initiatives original research article. *Cement and Concrete Research*, 38:115–127.
- [Davies et al., 2003] Davies, N. A., Hodson, M. E., and Black, S. (2003). Is the OECD acute worm toxicity test environmentally relevant? The effect of mineral form on calculated lead toxicity. *Environmental Pollution*, 121(1):49 – 54.
- [De Belie et al., 2010] De Belie, N., Kratky, J., and Van Vlierberghe, S. (2010). Influence of pozzolans and slag on the microstructure of partially carbonated cement paste by means of water vapour and nitrogen sorption experiments and bet calculations. *Cement and Concrete Research*, 40:1723–1733.
- [de Groot et al., 1999] de Groot, G., Hohberg, I., Lamers, F., van der Veen, A., Wassing, W., Quevauvillier, P., et al. (1999). Development of a leaching method for the determination of the environmental quality of concrete. *European Commission, BCR information EUR*, 17869.
- [Deschner et al., 2012] Deschner, F., Winnefeld, F., Lothenbach, B., Seufert, S., Schwesig, P., Dittrich, S., Goetz-Neunhoeffler, F., and Neubauer, J. (2012). Hydration of portland cement with high replacement by siliceous fly ash. *Cement and Concrete Research*, 42(10):1389–1400.
- [Deutsche Bahn-Bahnprojekt Stuttgart-Ulm, 2017] Deutsche Bahn-Bahnprojekt Stuttgart-Ulm (2017). <http://www.bahnprojekt-stuttgart-ulm.de/aktuell/>.
- [Deutsche Bauchemie e.V., 2016] Deutsche Bauchemie e.V. (2016). Jahresbericht 2015/ 2016.
- [Deutsches Institut für Bautechnik, 2009] Deutsches Institut für Bautechnik (2009). Grundsätze zur Bewertung der Auswirkungen von Bauprodukten auf Boden und Grundwasser. *DIBt Mitteilungen*, 40(5):169–179.
- [Deutsches Institut für Bautechnik, 2011] Deutsches Institut für Bautechnik (2011). Grundsätze zur Bewertung der Auswirkungen von Bauprodukten auf Boden und Grundwasser-Teil II. *DIBt Mitteilungen*, 42(6):196–212.
- [Devore, 2011] Devore, J. (2011). *Probability and Statistics for Engineering and the Sciences.* DUXBURY.
- [Dhir and Henderson, 1999] Dhir, R. K. and Henderson, N. A. (1999). *Specialist techniques and materials for concrete construction: proceedings of the international conference held at the University of Dundee, Scotland, UK on 8-10 September 1999.* Thomas Telford.
- [Didden and Römbke, 2001] Didden, W. and Römbke, J. (2001). Enchytraeids as indicator organisms for chemical stress in terrestrial ecosystems. *Ecotoxicology and Environmental Safety*, 50(1):25 – 43.

- [DIN 12715, 2000] DIN 12715 (2000). Ausführung von besonderen geotechnischen Arbeiten (Spezialtiefbau) Injektionen.
- [DIN 19528, 2009] DIN 19528 (2009). Elution von Feststoffen-Perkulationsverfahren zur gemeinsamen Untersuchung des Elutionsverhaltens von anorganischen und organischen Stoffen.
- [DIN 19631, 2013] DIN 19631 (2013). Elution von Baustoffen - Perkulationsverfahren zur Untersuchung des Elutionsverhaltens von Injektionsmitteln.
- [DIN 38412-33, 1991] DIN 38412-33 (1991). Deutsche Einheitsverfahren zur Wasser-, Abwasser- und Schlammuntersuchung - Testverfahren mit Wasserorganismen (Gruppe L) - Bestimmung der nicht giftigen Wirkung von Abwasser gegenüber Grünalgen (Scenedesmus-Chlorophyll-Fluoreszenztest) über Verdünnungsstufen.
- [DIN 38414-4, 1984] DIN 38414-4 (1984). Deutsche Einheitsverfahren zur Wasser-, Abwasser- und Schlammuntersuchung - Schlamm und Sedimente (Gruppe S) - Bestimmung der Eluierbarkeit mit Wasser (S4).
- [DIN 38415-4, 1999] DIN 38415-4 (1999). Deutsche Einheitsverfahren zur Wasser-, Abwasser- und Schlammuntersuchung Suborganismische Testverfahren Teil 4: Bestimmung des erbgutverändernden Potential mit dem Almonella-Mikrosomen-Test (Ames-Test).
- [DIN CEN/TS 16637-2, 2014] DIN CEN/TS 16637-2 (2014). Bauprodukte - Bewertung der Freisetzung von gefährlichen Stoffen - Teil 2: Horizontale dynamische Oberflächenauslaugprüfung.
- [DIN EN 12457-4, 2003] DIN EN 12457-4 (2003). Charakterisierung von Abfällen - Auslaugung - Übereinstimmungsuntersuchungen für die Auslaugung von körnigen Abfällen und Schlämmen - Teil 4: Einstufiges Schüttelverfahren mit einem Flüssigkeits-Feststoffverhältnis von 10 l/kg für Materialien mit einer Korngröße unter 10 mm (ohne oder mit Korngrößenreduzierung).
- [DIN EN 16105, 2011] DIN EN 16105 (2011). Beschichtungsstoffe - Laborverfahren zur Bestimmung der Freisetzung von Substanzen aus Beschichtungen in intermittierendem Kontakt mit Wasser.
- [DIN EN 196-1, 2005] DIN EN 196-1 (2005). Prüfverfahren für Zement - Teil 1: Bestimmung der Festigkeit.
- [DIN EN 206, 2017] DIN EN 206 (2017). Beton-Festlegung, Eigenschaften, Herstellung und Konformität.
- [DIN EN ISO 16387, 2014] DIN EN ISO 16387 (2014). Bodenbeschaffenheit - Wirkungen von Verunreinigungen auf Enchytraeidae (Enchytraeus sp.) - Bestimmung der Wirkungen auf die Reproduktion.
- [DIN EN ISO 8692, 2012] DIN EN ISO 8692 (2012). Wasserbeschaffenheit - Süßwasseralgen-Wachstumshemmtest mit einzelligen Grünalgen.
- [Dinnel et al., 1989] Dinnel, P. A., Link, J. M., Stober, Q. J., Letourneau, M. W., and Roberts, W. E. (1989). Comparative sensitivity of sea urchin sperm bioassays to metals and pesticides. *Archives of Environmental Contamination and Toxicology*, 18(5):748–755.
- [Donel and Feder, 1981] Donel, M. and Feder, G. (1981). *Sanierung eines wasserführenden Niederbruchkamines mit 300 m² Querschnittsfläche im Salzbergbau Altaussee*, pages 215–236. Springer Vienna, Vienna.
- [Dorn et al., 1998] Dorn, P. B., Vipond, T. E., Salanitro, J. P., and Wisniewski, H. L. (1998). Assessment of the acute toxicity of crude oils in soils using earthworms, microtox®, and plants. *Chemosphere*, 37(5):845 – 860.
- [Duan et al., 2012] Duan, H., Jiang, Z., Zhu, S., Yao, P., and Sun, Q. (2012). New composite grouting materials: Modified urea-formaldehyde resin with cement. *International Journal of Mining Science and Technology*, 22(2):195–200.
- [Duong et al., 2013] Duong, V., Sahamitmongkol, R., and Tangtermsirikul, S. (2013). Effect of leaching on carbonation resistance and steel corrosion of cement-based materials. *Construction and Building Materials*, 40:1066–1075.
- [Dutre and Vandecasteele, 1996] Dutre, V. and Vandecasteele, C. (1996). An evaluation of the solidification/stabilisation of industrial arsenic containing waste using extraction and semi-dynamic leach tests. *Waste Management*, 16(7):625 – 631.

- [E DIN EN 197-1, 2014] E DIN EN 197-1 (2014). Zement - Teil 1: Zusammensetzung, Anforderungen und Konformitätskriterien von Normalzement.
- [ECHA, 2017] ECHA (2017). European chemicals agency.
- [El-Hawary and Abdul-Jaleel, 2010] El-Hawary, M. M. and Abdul-Jaleel, A. (2010). Durability assessment of epoxy modified concrete. *Construction and Building Materials*, 24(8):1523–1528.
- [Engelsen et al., 2009] Engelsen, C., van der Sloot, H., Wibetoe, G., Petkovic, G., Stoltenberg-Hansson, E., and Lund, W. (2009). Release of major elements from recycled concrete aggregates and geochemical modelling. *Cement and Concrete Research*, 39:446 – 459.
- [Engelsen et al., 2017] Engelsen, C. J., van der Sloot, H. A., and Petkovic, G. (2017). Long-term leaching from recycled concrete aggregates applied as sub-base material in road construction. *Science of The Total Environment*, 587-588:94–101.
- [Engelsen et al., 2012] Engelsen, C. J., Wibetoe, G., van der Sloot, H. A., Lund, W., and Petkovic, G. (2012). Field site leaching from recycled concrete aggregates applied as sub-base material in road construction. *Science of The Total Environment*, 427-428:86–97.
- [Engert, 1915] Engert, E. (1915). *Die geschichtliche Entwicklung und der heutige Stand des Zementierverfahrens*. Cementfabrik Thuringia.
- [EU Parlament und Rat, 2006] EU Parlament und Rat (2006). Verordnung (EG) Nr. 1907/2006 des Europäischen Parlaments und des Rates.
- [Exley et al., 1996] Exley, C., Wicks, A. J., Hubert, R. B., and Birchall, D. J. (1996). Kinetic constraints in acute aluminium toxicity in the rainbow trout (*Oncorhynchus mykiss*). *Journal of Theoretical Biology*, 179(1):25 – 31.
- [Faramarzi et al., 2016] Faramarzi, L., Rasti, A., and Abtahi, S. M. (2016). An experimental study of the effect of cement and chemical grouting on the improvement of the mechanical and hydraulic properties of alluvial formations. *Construction and Building Materials*, 126:32–43.
- [Faucon et al., 1998a] Faucon, P., Adenot, F., Jacquinet, J., Petit, J., Cabrillac, R., and Jorda, M. (1998a). Long-term behaviour of cement pastes used for nuclear waste disposal: review of physico-chemical mechanisms of water degradation. *Cement and Concrete Research*, 28(6):847 – 857.
- [Faucon et al., 1997] Faucon, P., Adenot, F., Jorda, M., and Cabrillac, R. (1997). Behaviour of crystallised phases of portland cement upon water attack. *Materials and Structures*, 30(202):480–485.
- [Faucon et al., 1996] Faucon, P., Bescop, P. L., Adenot, F., Bonville, P., Jacquinet, J., Pineau, F., and Felix, B. (1996). Leaching of cement: Study of the surface layer. *Cement and Concrete Research*, 26(11):1707 – 1715.
- [Faucon et al., 1998b] Faucon, P., Gerard, B., Jacquinet, J., and Marchand, J. (1998b). Water attack of a cement paste: towards an improved accelerated test? *Advances in Cement Research*, 10(2):67–73.
- [Ferrari et al., 2010] Ferrari, L., Kaufmann, J., Winnefeld, F., and Plank, J. (2010). Interaction of cement model systems with superplasticizers investigated by atomic force microscopy, zeta potential, and adsorption measurements. *Journal of Colloid and Interface Science*, 347(1):15 – 24.
- [Ferrari et al., 2011] Ferrari, L., Kaufmann, J., Winnefeld, F., and Plank, J. (2011). Multi-method approach to study influence of superplasticizers on cement suspensions. *Cement and Concrete Research*, 41(10):1058 – 1066.
- [Font-Capó et al., 2011] Font-Capó, J., Vázquez-Suñé, E., Carrera, J., Martí, D., Carbonell, R., and Pérez-Estaún, A. (2011). Groundwater inflow prediction in urban tunneling with a tunnel boring machine (TBM). *Engineering Geology*, 121(1-2):46–54.
- [FSK, 2017] FSK (2017). Fachverband Schaumkunststoffe und Polyurethane e.V. <http://www.fsk-vsv.de/>.
- [Fuentes et al., 2004] Fuentes, A., Llorens, M., Saez, J., Aguilar, M. I., Ortuno, J. F., and Meseguer, V. F. (2004). Phytotoxicity and heavy metals speciation of stabilised sewage sludges. *Journal of Hazardous Materials*, 108(3):161 – 169.

- [Galardi et al., 2007] Galardi, F., Corrales, I., Mengoni, A., Pucci, S., Barletti, L., Barzanti, R., Arnetoli, M., Gabbrielli, R., and Gonnelli, C. (2007). Intra-specific differences in nickel tolerance and accumulation in the ni-hyperaccumulator *alysium bertolonii*. *Environmental and Experimental Botany*, 60(3):377 – 384.
- [Gallagher et al., 2013] Gallagher, P. M., Spataro, S., and Cucura, J. (2013). Hybrid life cycle assessment comparison of colloidal silica and cement grouted soil barrier remediation technologies. *Journal of Hazardous Materials*, 250-251:421–430.
- [Gälli et al., 1998] Gälli, R., Ochs, M., and Mäder, U. (1998). Assessment of the environmental compatibility of concrete admixture. In *Proceedings CIB World Building Congress*.
- [Gérard and Tang, 1998] Gérard, B. and Tang, L. (1998). Some preliminary models for discussion concerning chloride diffusion coupled to calcium leaching in saturated concretes. In *Proceeding Material Science and Concrete Properties first Int. Meeting. Toulouse, France*, pages 215–22.
- [Gerven et al., 2007] Gerven, T. V., Cornelis, G., Vandoren, E., and Vandecasteele, C. (2007). Effects of carbonation and leaching on porosity in cement-bound waste. *Waste Management*, 27(7):977 – 985.
- [Gerven et al., 2004] Gerven, T. V., Moors, J., Dutré, V., and Vandecasteele, C. (2004). Effect of CO₂ on leaching from a cement-stabilized MSWI fly ash. *Cement and Concrete Research*, 34(7):1103 – 1109.
- [Gestel et al., 1991] Gestel, C. A. M., Dis, W. A., Dirven-van Breemen, E. M., Sparenburg, P. M., and Baerselman, R. (1991). Influence of cadmium, copper, and pentachlorophenol on growth and sexual development of *eisenia andrei* (oligochaeta; annelida). *Biology and Fertility of Soils*, 12(2):117–121.
- [Giese, 2007] Giese, E. (2007). *Evaluierung ausgewählter biologischer Testverfahren zur vorsorgeorientierten Beurteilung ökotoxikologischer Wirkungen von Bauprodukten auf Böden*. PhD thesis, Freie Universität Berlin.
- [Gilbert, 1980] Gilbert, R. (1980). The analysis of fluctuation tests. *Mutation Research/Environmental Mutagenesis and Related Subjects*, 74(4):283 – 289.
- [Gilliam and Wiles, 1996] Gilliam, T. M. and Wiles, C. C. (1996). *Stabilization and solidification of hazardous, radioactive, and mixed wastes*. ASTM International.
- [Giri and Boyd, 2000] Giri, B. J. and Boyd, C. E. (2000). Effects of frequent, small doses of calcium carbonate on water quality and phytoplankton in channel catfish ponds. *North American Journal of Aquaculture*, 62(3):225–228.
- [Girmscheid, 2012] Girmscheid, G. (2012). *Baubetrieb und Bauverfahren im Tunnelbau*. John Wiley & Sons.
- [Godbee et al., 1980] Godbee, H., Compere, E., Joy, D., Kibbey, A., Moore, J., Nestor, C., Anders, O., and Neilson, R. (1980). Application of mass transport theory to the leaching of radionuclides from waste solids. *Nuclear and Chemical Waste Management*, 1(1):29 – 35.
- [Godbee et al., 1978] Godbee, H., Kibbey, A., and Joy, D. (1978). Assessment of the loss of radioactive isotopes from solidified wastes. Technical report, Oak Ridge National Lab., Tenn.(USA).
- [Godbee and Joy, 1974] Godbee, H. W. and Joy, D. (1974). Assessment of the loss of radioactive isotopes from waste solids to the environment. part i. background and theory. Technical report, Oak Ridge National Lab., Tenn.(USA).
- [Gollmann et al., 2007] Gollmann, A. M., Walesko, A., Fisch, A., Stedile, F. C., Da Silva, M. M., Dos Santos, J. H. Z., and Lattuada, R. M. (2007). Evaluation of lead desorption from cement matrices. *Journal of Environmental Science and Health, Part A*, 42(8):1183–1189.
- [Gonzalez, 1991] Gonzalez, S. P. (1991). Upper critical level of copper to alfalfa, in ten chilean soils. *Water, Air, and Soil Pollution*, 57(1):201–208.
- [Gopalapillai et al., 2013] Gopalapillai, Y., Hale, B., and Vigneault, B. (2013). Effect of major cations (Ca²⁺, Mg²⁺, Na⁺, K⁺) and anions (SO₄²⁻, Cl⁻, NO₃⁻) on Ni accumulation and toxicity in aquatic plant (*Lemna minor* L.): Implications For Ni risk assessment. *Environmental Toxicology and Chemistry*, 32(4):810–821.
- [Grieve and Grattan, 1999] Grieve, C. and Grattan, S. (1999). *Mineral Nutrient Acquisition and Response by Plants Grown in Saline Environments*, pages 203–229. CRC Press.

- [Guan et al., 2012] Guan, X., peng Yang, Z., and jing Zhang, C. (2012). Bonding mechanism between waterglass/polyurethane adhesive and coal. *The Journal of Adhesion*, 88(9):802–811.
- [Guerandel et al., 2011] Guerandel, C., Vernex-Loiset, L., Krier, G., De Lanève, M., Guillot, X., Pierre, C., and Muller, J. (2011). A new method to analyze copolymer based superplasticizer traces in cement leachates. *Talanta*, 84:133–140.
- [Guo, 1997] Guo, Q. (1997). Increases of lead and chromium in drinking water from using cement-mortar-lined pipes: Initial modeling and assessment. *Journal of Hazardous Materials*, 56(1-2):181–213.
- [Haegermann, 1970] Haegermann, G. (1970). Dokumente zur Entstehungsgeschichte des Portland-Cements.
- [Han et al., 2014] Han, F., Liu, R., and Yan, P. (2014). Effect of fresh water leaching on the microstructure of hardened composite binder pastes. *Construction and Building Materials*, 68:630–636.
- [He et al., 2016] He, Z., Li, Q., Wang, J., Yin, N., Jiang, S., and Kang, M. (2016). Effect of silane treatment on the mechanical properties of polyurethane/water glass grouting materials. *Construction and Building Materials*, 116:110–120.
- [Heitmuller et al., 1981] Heitmuller, P. T., Holister, T. A., and Parrish, P. R. (1981). Acute toxicity of 54 industrial chemicals to sheepshead minnows (*cyprinodon variegatus*). *Bulletin of Environmental Contamination and Toxicology*, 27(1):596–604.
- [Hemphill, 2012] Hemphill, G. B. (2012). *Practical tunnel construction*. John Wiley & Sons.
- [Henn, 1996] Henn, R. W. (1996). *Practical guide to grouting of underground structures*. Thomas Telford.
- [Henn et al., 2003] Henn, R. W., American Underground Construction Association, et al. (2003). *American Underground Construction Association guidelines for backfilling and contact grouting of tunnels and shafts*. American Society of Civil Engineers (ASCE).
- [Henn and Soule, 2010] Henn, R. W. and Soule, N. C. (2010). *Ultrafine cement in pressure grouting*. American Society of Civil Engineers (ASCE).
- [Hernández et al., 1997] Hernández, M., Guerrero, A., Goñi, S., and Lorenzo, M. (1997). Effect of the temperature on the leaching performance of the cement-based immobilization systems: Sulfate and chloride behavior. *Cement and Concrete Research*, 27(4):515–524.
- [Hinsenveld, 1992] Hinsenveld, M. (1992). *A shrinking core model as a fundamental representation of leaching mechanisms in cement stabilized waste*. PhD thesis, University of Cincinnati Cincinnati, OH, USA.
- [Hinsenveld and Bishop, 1996] Hinsenveld, M. and Bishop, P. L. (1996). Use of the shrinking core/exposure model to describe the leachability from cement stabilized wastes. In *Stabilization and Solidification of Hazardous, Radioactive, and Mixed Wastes: 3rd Volume*. ASTM International.
- [Hohberg, 2002] Hohberg, I. (2002). *Charakterisierung, Modellierung und Bewertung des Auslaugverhaltens umweltrelevanter, anorganischer Stoffe aus Beton*. PhD thesis, Rheinisch-Westfälische Technische Hochschule Aachen.
- [Hohberg and Schiessl, 1996] Hohberg, I. and Schiessl, P. (1996). Einfluss betontechnischer Parameter auf das Auslaugverhalten von Mörteln und Betonen. In *4. Internationale Kolloquium Werkstoffwissenschaften und Bauinstandsetzen*, pages 1505–1519.
- [Höll and Dahlke, 2003] Höll, W. and Dahlke, T. (2003). *Entwicklung der Anwendung magnetischer Mikrosorbentien zur Elimination gesundheitsbedenklicher anorganischer Schadstoffe aus natürlichen Wässern*. Forschungszentrum Karlsruhe, Inst. für Technische Chemie, Bereich WGT.
- [Homma et al., 2005] Homma, S., Ogata, S., Koga, J., and Matsumoto, S. (2005). Gas-solid reaction model for a shrinking spherical particle with unreacted shrinking core. *Chemical Engineering Science*, 60(18):4971–4980.
- [Hong et al., 2015] Hong, X., Dong, W., Yang, S., Mu, B., and Liang, B. (2015). Study on structure and performance of reactive silicate reinforced polyurethane composite. *Polymer Engineering & Science*, 55(10):2322–2327.
- [HSE, 2017] HSE (2017). Health and Safety Executive, Great Britain.
- [Hu and Schmidhalter, 2005] Hu, Y. and Schmidhalter, U. (2005). Drought and salinity:

- A comparison of their effects on mineral nutrition of plants. *Journal of Plant Nutrition and Soil Science*, 168(4):541–549.
- [Huber et al., 2011] Huber, S. A., Balz, A., Abert, M., and Pronk, W. (2011). Characterisation of aquatic humic and non-humic matter with size-exclusion chromatography – organic carbon detection – organic nitrogen detection (LC-OCD-OND). *Water Research*, 45(2):879 – 885.
- [Hussain et al., 2014] Hussain, H. K., Liu, G. W., and Yong, Y. W. (2014). Experimental study to investigate mechanical properties of new material polyurethane-cement composite (puc). *Construction and Building Materials*, 50:200–208.
- [Hussain et al., 2013] Hussain, H. K., Zhang, L. Z., and Liu, G. W. (2013). An experimental study on strengthening reinforced concrete t-beams using new material poly-urethane-cement (PUC). *Construction and Building Materials*, 40:104–117.
- [Huth, 1996] Huth, W. (1996). Betongerechter Einsatz von Feinstzementsuspensionen in der Bauwerksabdichtung. In *4. Internationales Kolloquium Werkstoffwissenschaften und Bauinstandsetzen*.
- [IAL consultants, 2017] IAL consultants (2017). <http://www.ialconsultants.com/industry-sectors/polyurethane-market-research-reports-data>.
- [ISO 13829, 2000] ISO 13829 (2000). Water quality - determination of the genotoxicity of water and waste water using the umu-test.
- [ISO 16240, 2005] ISO 16240 (2005). Water quality - Determination of the genotoxicity of water and waste water - Salmonella/microsome test (Ames test).
- [Issa and Debs, 2007] Issa, C. A. and Debs, P. (2007). Experimental study of epoxy repairing of cracks in concrete. *Construction and Building Materials*, 21(1):157–163.
- [Jackson, 2005] Jackson, K. A. (2005). *Kinetic Processes*. Wiley-Blackwell.
- [Jiacai et al., 1982] Jiacai, L., Baochang, W., Wengguang, C., Yuhua, G., and Hesheng, C. (1982). Polyurethane grouting in hydraulic engineering. In *Grouting in Geotechnical Engineering*, pages 403–417. ASCE.
- [Joosten, 1953] Joosten, H. (1953). *Das Joosten-Verfahren zur chemischen Bodenverfestigung und Abdichtung in seiner Entwicklung und Anwendung von 1925 bis heute*. Joosten-Verlag.
- [Joyce, 1992] Joyce, J. T. (1992). Polyurethane grouts. *Concrete construction*.
- [Kamali et al., 2003] Kamali, S., Gérard, B., and Moranville, M. (2003). Modelling the leaching kinetics of cement-based materials—influence of materials and environment. *Cement and Concrete Composites*, 25(4-5):451–458.
- [Kamali et al., 2008] Kamali, S., Moranville, M., and Leclercq, S. (2008). Material and environmental parameter effects on the leaching of cement pastes: Experiments and modelling. *Cement and Concrete Research*, 38:575 – 585.
- [Kapustka and Reporter, 2009] Kapustka, L. A. and Reporter, M. (2009). *Terrestrial Primary Producers*, pages 278–298. Blackwell Publishing Ltd.
- [Karol, 2003] Karol, R. H. (2003). *Chemical grouting and soil stabilization, revised and expanded*, volume 12. CRC Press.
- [Katsioti et al., 2009] Katsioti, M., Tsakiridis, P., Giannatos, P., Tsi bouki, Z., and Marinos, J. (2009). Characterization of various cement grinding aids and their impact on grindability and cement performance. *Construction and Building Materials*, 23(5):1954–1959.
- [Kazuko et al., 2005] Kazuko, H., Shunkichi, S., Michihiko, H., Satoru, T., and Shinya, N. (2005). Effects of porosity on leaching of Ca from hardened ordinary Portland cement paste. *Cement and Concrete Research*, 35:1764 – 1775.
- [Keivani et al., 2014] Keivani, M., Bagheri, R., Kouchakzadeh, M. A., and Abadyan, M. (2014). Synergistic toughening in ternary silica/hollow glass spheres/epoxy nanocomposites. *Polymer-Plastics Technology and Engineering*, 54(6):581–593.
- [Khatib, 2016] Khatib, J. (2016). *Sustainability of construction materials*. Woodhead Publishing.
- [Kocaba, 2009] Kocaba, V. (2009). *Development and evaluation of methods to follow microstructural development of cementitious systems including slags*. PhD thesis, École polytechnique fédérale de Lausanne.

- [Koenig, 1951] Koenig, H. (1951). Neuzeitliche einpreßtechnik. *Die Wasserwirtschaft*, 42:120–132.
- [Korthals et al., 1996] Korthals, G. W., Bongers, T., Kammenga, J. E., Alexiev, A. D., and Lexmond, T. M. (1996). Long-term effects of copper and ph on the nematode community in an agroecosystem. *Environmental Toxicology and Chemistry*, 15(6):979–985.
- [Kosmatka et al., 2011] Kosmatka, S. H., Kerkhoff, B., and Panarese, W. C. (2011). *Design and control of concrete mixtures*. Portland Cement Association.
- [Kosmatka et al., 2002] Kosmatka, S. H., Panarese, W. C., and Kerkhoff, B. (2002). *Design and control of concrete mixtures*, volume 5420. Portland Cement Association.
- [Koß, 1997] Koß, V. (1997). *Umweltchemie*. Springer-Verlag Berlin Heidelberg.
- [Kulacki et al., 2012] Kulacki, K. J., Cardinale, B. J., Keller, A. A., Bier, R., and Dickson, H. (2012). How do stream organisms respond to, and influence, the concentration of titanium dioxide nanoparticles? a mesocosm study with algae and herbivores. *Environmental Toxicology and Chemistry*, 31(10):2414–2422.
- [Kutzner, 1985] Kutzner, C. (1985). Considerations on rock permeability and grouting criteria. In *Proceedings of the 15th international congress on large dams (ICOLD), Lausanne, Switzerland*, volume 3.
- [Kutzner, 1991] Kutzner, C. (1991). *Injektionen im Baugrund*. Enke.
- [Lalonde et al., 2011] Lalonde, B., Ernst, W., Julien, G., Jackman, P., Doe, K., and Schaefer, R. (2011). A comparative toxicity assessment of materials used in aquatic construction. *Archives of Environmental Contamination and Toxicology*, 61(3):368–375.
- [Leemann et al., 2011] Leemann, A., Lothenbach, B., and Thalmann, C. (2011). Influence of superplasticizers on pore solution composition and on expansion of concrete due to alkali-silica reaction. *Construction and Building Materials*, 25(1):344 – 350.
- [Lei and Plank, 2012] Lei, L. and Plank, J. (2012). Synthesis, working mechanism and effectiveness of a novel cycloaliphatic superplasticizer for concrete. *Cement and Concrete Research*, 42(1):118–123.
- [Leppkes, 1996] Leppkes, R. (1996). *Polyurethane: Werkstoff mit vielen Gesichtern*. Verlag Moderne Industrie.
- [Levin, 1989] Levin, H. (1989). Building materials and indoor air quality. *Occupational medicine (Philadelphia, Pa.)*, 4:667–693.
- [Lilius et al., 1995] Lilius, H., Hästbacka, T., and Isomaa, B. (1995). Short communication: A comparison of the toxicity of 30 reference chemicals to daphnia magna and daphnia pulex. *Environmental Toxicology and Chemistry*, 14(12):2085–2088.
- [Littlejohn, 2003] Littlejohn, S. (2003). The development of practice in permeation and compensation grouting: A historical review (1802–2002): Part 1 permeation grouting. In *Grouting and Ground Treatment*. American Society of Civil Engineers (ASCE).
- [Lock and Janssen, 2001] Lock, K. and Janssen, C. R. (2001). Modeling zinc toxicity for terrestrial invertebrates. *Environmental Toxicology and Chemistry*, 20(9):1901–1908.
- [Lothenbach et al., 2011] Lothenbach, B., Scrivener, K., and Hooton, R. (2011). Supplementary cementitious materials. *Cement and Concrete Research*, 41(12):1244–1256.
- [Lothenbach and Winnefeld, 2006] Lothenbach, B. and Winnefeld, F. (2006). Thermodynamic modelling of the hydration of portland cement. *Cement and Concrete Research*, 36:209–226.
- [Lou et al., 2013] Lou, H., Lai, H., Wang, M., Pang, Y., Yang, D., Qiu, X., Wang, B., and Zhang, H. (2013). Preparation of lignin-based superplasticizer by graft sulfonation and investigation of the dispersive performance and mechanism in a cementitious system. *Industrial & Engineering Chemistry Research*, 52(46):16101–16109.
- [Lupsea et al., 2014] Lupsea, M., Tiruta-Barna, L., and Schiopu, N. (2014). Leaching of hazardous substances from a composite construction product: An experimental and modelling approach for fibre-cement sheets. *Journal of Hazardous Materials*, 264(0):236 – 245.
- [Mäder et al., 2004] Mäder, U., Gälli, R., and Ochs, M. (2004). The impact of concrete admixtures on the environment. Technical report, Sika Technologies.

- [Malviya and Chaudhary, 2006a] Malviya, R. and Chaudhary, R. (2006a). Evaluation of leaching characteristics and environmental compatibility of solidified/stabilized industrial waste. *Journal of Material Cycles and Waste Management*, 8(1):78–87.
- [Malviya and Chaudhary, 2006b] Malviya, R. and Chaudhary, R. (2006b). Leaching behavior and immobilization of heavy metals in solidified/stabilized products. *Journal of Hazardous Materials*, 137:207 – 217.
- [Märkl et al., 2017] Märkl, V., Pflugmacher, S., and Stephan, D. A. (2017). Leaching of PCE-based Superplasticiser from Microfine Cement: a Chemical and Ecotoxicological Point of View. *Water, Air, & Soil Pollution*, 228:217(6).
- [Märkl and Stephan, 2016] Märkl, V. and Stephan, D. A. (2016). Release behaviour of major elements and superplasticiser from cement suspensions. *Water, Air, & Soil Pollution*, 227:30(1).
- [Martens, 1998] Martens, J. (1998). *Untersuchungen zur Grundwasserkontamination-swirkung verschiedener Injektionsmittel auf Acrylatbasis bei der Abdichtung im Lockergesteinsbaugrund*. PhD thesis, Technische Universität Darmstadt.
- [Mastella et al., 2014] Mastella, M. A., Gislon, E. S., Pelisser, F., Ricken, C., da Silva, L., Angioletto, E., and Montedo, O. R. K. (2014). Mechanical and toxicological evaluation of concrete artifacts containing waste foundry sand. *Waste Management*, 34(8):1495 – 1500.
- [Matschei et al., 2007] Matschei, T., Lothenbach, B., and Glasser, F. (2007). Thermodynamic properties of Portland cement hydrates in the system $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2\text{-CaSO}_4\text{-CaCO}_3\text{-H}_2\text{O}$. *Cement and Concrete Research*, 37:1379–1410.
- [McShane, 2013] McShane, H. (2013). *Metal oxide nanoparticle chemistry and toxicity in soils*. PhD thesis, McGill University, Montreal.
- [McShane et al., 2012] McShane, H., Sarrazin, M., Whalen, J. K., Hendershot, W. H., and Sunahara, G. I. (2012). Reproductive and behavioral responses of earthworms exposed to nano-sized titanium dioxide in soil. *Environmental Toxicology and Chemistry*, 31(1):184–193.
- [Meier-Westhues, 2007] Meier-Westhues, U. (2007). *Polyurethanes*. Vincentz Network GmbH & Co.
- [Mengel et al., 1984] Mengel, K., Kirkby, E. A., Kosegarten, H., and Appel, T. (1984). Principles of plant nutrition. *Soil Science*, 138(1):88–89.
- [Meza et al., 2008] Meza, S. L., Garrabrants, A. C., van der Sloot, H., and Kosso, D. S. (2008). Comparison of the release of constituents from granular materials under batch and column testing. *Waste Management*, 28(10):1853–1867.
- [Mikutta, 2006] Mikutta, C. (2006). *Controls of the phosphate sorption and desorption kinetics of organic matter-goethite associations*. PhD thesis, TU Berlin.
- [Mishra and Siddiqui, 2014] Mishra, S. and Siddiqui, N. A. (2014). A review on environmental and health impacts of cement manufacturing emissions. *International Journal of Geology, agriculture and environmental sciences*, 2(3):26–31.
- [Mittal and Pizzi, 2009] Mittal, K. L. and Pizzi, A. (2009). *Handbook of sealant technology*. CRC Press.
- [Mollamahmutoglu and Avci, 2015] Mollamahmutoglu, M. and Avci, E. (2015). Effectiveness of microfine portland cement grouting on the strength and permeability of medium to fine sands. *Periodica Polytechnica Civil Engineering*, 59(3):319–326.
- [Mortelmans and Zeiger, 2000] Mortelmans, K. and Zeiger, E. (2000). The Ames salmonella/microsome mutagenicity assay. *Mutation Research/Fundamental and Molecular Mechanisms of Mutagenesis*, 455:29 – 60.
- [Moszkowicz, 1998] Moszkowicz, P. (1998). Pollutants leaching behaviour from solidified wastes: a selection of adapted various models. *Talanta*, 46(3):375–383.
- [Moszkowicz et al., 1997] Moszkowicz, P., Barna, R., Sanchez, F., Bae, H. R., and Mehu, J. (1997). Models for leaching of porous materials. In *Studies in Environmental Science*, pages 491–500. Elsevier BV.
- [Mount, 1968] Mount, D. I. (1968). Chronic toxicity of copper to fathead minnows (pimephales promelas, rafinesque). *Water Research*, 2(3):215 – 223.

- [Müllauer et al., 2012] Müllauer, W., Beddoe, R. E., and Heinz, D. (2012). Effect of carbonation, chloride and external sulphates on the leaching behaviour of major and trace elements from concrete. *Cement and Concrete Composites*, 34(5):618 – 626.
- [Müllauer et al., 2015] Müllauer, W., Beddoe, R. E., and Heinz, D. (2015). Leaching behaviour of major and trace elements from concrete: Effect of fly ash and GGBS. *Cement and Concrete Composites*, 58(0):129–139.
- [Nebel and Spanka, 2013] Nebel, H. and Spanka, G. (2013). Harmonisation of test methods for the execution of the european construction products directive (cpd). validation of a european leaching test for construction products. *Waste and Biomass Valorization*, 4(4):759–767.
- [Nebel et al., 2012] Nebel, H., Vollpracht, A., and Brameshuber, W. (2012). Auslaugverhalten von Putzen und Mörteln. *Mauerwerk*, 16:2–9.
- [NEN 7341, 1995] NEN 7341 (1995). Leaching characteristics of solid earthy and stony building and waste materials. Leaching tests. Determination of the availability of inorganic components for leaching.
- [Neumann, 1972] Neumann, H. (1972). Die entwicklung der injektionstechnik. *Erzmetall*, 25:16–25.
- [Newman and Choo, 2003] Newman, J. and Choo, B. S. (2003). *Advanced concrete technology 3: processes*. Butterworth-Heinemann.
- [NIOSH, 2017] NIOSH (2017). *Pocket guide to chemical hazards*. The national Institute for occupational safety and health.
- [OECD, 2011] OECD (2011). Test No. 201: Freshwater Alga and Cyanobacteria, Growth Inhibition Test.
- [Oertel and Abele, 1983] Oertel, G. and Abele, L. (1983). *Polyurethane*. Hanser Verlag, München [u.a.].
- [Osebold, 2008] Osebold, R. (2008). Entwicklung und Erprobung mineralischer Injektionssuspensionen zur Sanierung von Grundleitungsnetzen. Technical report, RWTH Aachen und Ministerium für Umwelt und Nturschutz.
- [Pacheco-Torgal, 2016] Pacheco-Torgal, F. (2016). *Biopolymers and Biotech Admixtures for Eco-Efficient Construction Materials*. Elsevier Science & Technology.
- [Page et al., 1981] Page, C., Short, N., and Taras, A. E. (1981). Diffusion of chloride ions in hardened cement pastes. *Cement and Concrete Research*, 11(3):395–406.
- [Pantazopoulos et al., 2012] Pantazopoulos, I. A., Markou, I. N., Christodoulou, D. N., Droudakis, A. I., Atmatzidis, D. K., Antiohos, S. K., and Chaniotakis, E. (2012). Development of microfine cement grouts by pulverizing ordinary cements. *Cement & Concrete Composites*, 34:593–603.
- [Paracelsus, 2009] Paracelsus (2009). *Gesammelte Schriften*. Schwabe Verlag Basel.
- [Pei et al., 2016] Pei, J., Cai, J., Zou, D., Zhang, J., Li, R., Chen, X., and Jin, L. (2016). Design and performance validation of high-performance cement paste as a grouting material for semi-flexible pavement. *Construction and Building Materials*, 126:206–217.
- [Perfilov et al., 2016] Perfilov, V., Oreshkin, D., and Semenov, V. (2016). Environmentally safe mortar and grouting solutions with hollow glass microspheres. *Procedia Engineering*, 150:1479–1484.
- [Perret et al., 2000] Perret, S., Palardy, D., and Ballivy, G. (2000). Rheological behavior and setting time of microfine cement-based grouts. *Materials Journal*, 97(4):472–478.
- [Pickering and Gast, 1972] Pickering, Q. H. and Gast, M. H. (1972). Acute and chronic toxicity of cadmium to the fathead minnow (pimephales promelas). *Journal of the Fisheries Research Board of Canada*, 29(8):1099–1106.
- [Pieper and Weigmann, 2008] Pieper, S. and Weigmann, G. (2008). Interactions between isopods and collembolans modulate the mobilization and transport of nutrients from urban soils. *Applied Soil Ecology*, 39(2):109 – 126.
- [Pinto et al., 2015a] Pinto, D., Bernardo, L., Amaro, A., and Lopes, S. (2015a). Mechanical properties of epoxy nanocomposites using alumina as reinforcement - a review. *Journal of Nano Research*, 30:9–38.
- [Pinto et al., 2015b] Pinto, D., Bernardo, L., Amaro, A., and Lopes, S. (2015b). Mechanical properties of epoxy nanocomposites using

- titanium dioxide as reinforcement – a review. *Construction and Building Materials*, 95:506–524.
- [Plank, 2005] Plank, J. (2005). *Applications of Biopolymers in Construction Engineering*. Wiley-VCH Verlag GmbH & Co. KGaA.
- [Plank et al., 2008] Plank, J., Pöllmann, K., Zouaoui, N., Andres, P., and Schaefer, C. (2008). Synthesis and performance of methacrylic ester based polycarboxylate superplasticizers possessing hydroxy terminated poly(ethylene glycol) side chains. *Cement and Concrete Research*, 38(10):1210 – 1216.
- [Plank et al., 2015] Plank, J., Sakai, E., Miao, C., Yu, C., and Hong, J. (2015). Chemical admixtures - chemistry, applications and their impact on concrete microstructure and durability. *Cement and Concrete Research*, 78, Part A:81 – 99. Keynote papers from 14th International Congress on the Chemistry of Cement (ICCC 2015).
- [Puertas et al., 2005] Puertas, F., Santos, H., Palacios, M., and Martinez-Ramirez, S. (2005). Polycarboxylate superplasticiser admixtures: effect on hydration, microstructure and rheological behaviour in cement pastes. *Advances in Cement Research*, 17(2):77–89.
- [Pusch, 1993] Pusch, R. (1993). Longevity of bentonite and cement grouts. In *Grouting in rock and concrete: proceedings of the International Conference on Grouting in Rock and Concrete, Salzburg, Austria, 11-12 October 1993*, pages 81–85.
- [Radix et al., 1999] Radix, P., Leonard, M., Papanтониou, C., Roman, G., Saouter, E., Gallotti-Schmitt, S., Thiebaud, H., and Vasseur, P. (1999). Comparison of brachionus calyciflorus 2-d and microtox chronic 22-h tests with daphnia magna 21-d test for the chronic toxicity assessment of chemicals. *Environmental Toxicology and Chemistry*, 18(10):2178–2185.
- [Ramachandran, 1997] Ramachandran, V. S. (1997). *Concrete Admixtures Handbook: Properties, Science and Technology*. William Andrew.
- [Raymond and Nathan, 2010] Raymond, W. and Nathan, C. (2010). *Ultrafine cement in pressure grouting*. ASCE Publications.
- [Reifferscheid et al., 1991] Reifferscheid, G., Heil, J., Oda, Y., and Zahn, R. (1991). A microplate version of the sos/umu-test for rapid detection of genotoxins and genotoxic potentials of environmental samples. *Mutation Research/Environmental Mutagenesis and Related Subjects*, 253(3):215 – 222.
- [Reuben et al., 2003] Reuben, H. et al. (2003). *Chemical grouting and soil stabilization*. Marcel Dekker Inc.
- [Riedlich, 2010] Riedlich, C. (2010). Risk of isocyanate exposure in the construction industry. Technical report, CPWR - The Center for Construction Research and Training.
- [RILEM TC 73-SBC, 1988] RILEM TC 73-SBC (1988). Final report siliceous by-products for use in concrete. *Materials and Structures*, 21(1):69–80.
- [Roithmeier and Pieper, 2009] Roithmeier, O. and Pieper, S. (2009). Influence of enchytraeidae (enchytraeus albidus) and compaction on nutrient mobilization in an urban soil. *Pedobiologia*, 53(1):29 – 40.
- [Römbke and Knacker, 1989] Römbke, J. and Knacker, T. (1989). Aquatic toxicity test for enchytraeids. *Hydrobiologia*, 180(1):235–242.
- [Römbke and Moser, 2002] Römbke, J. and Moser, T. (2002). Validating the enchytraeid reproduction test: organisation and results of an international ringtest. *Chemosphere*, 46(7):1117 – 1140.
- [Ruckstuhl, 2001] Ruckstuhl, S. (2001). *Environmental Exposure Assessment of Sulfonated Naphthalene Formaldehyde Condensates and Sulfonated Naphthalenes Applied as Concrete Superplasticizers*. PhD thesis, Eidgenössische Technische Hochschule Zürich.
- [Saclier, 1908] Saclier, R. (1908). *Sur le creusement des puits du siège Édouard-Agache par cimentation des assises aquifères*, volume 13, pages 347–378. Bibliothèque patrimoniale numérique de l'École nationale supérieure des mines de Paris (Mines ParisTech).
- [Safari et al., 2009] Safari, V., Arzpeyma, G., Rashchi, F., and Mostoufi, N. (2009). A shrinking particle—shrinking core model for leaching of a zinc ore containing silica. *International Journal of Mineral Processing*, 93(1):79–83.

- [Sajwani et al., 1996] Sajwani, K. S., Ornes, W. H., Youngblood, T. V., and Alva, A. K. (1996). Uptake of soil applied cadmium, nickel and selenium by bush beans. *Water, Air, and Soil Pollution*, 91(3):209–217.
- [Sanchez et al., 2003] Sanchez, F., Massry, I., Eighmy, T., and Kosson, D. (2003). Multi-regime transport model for leaching behavior of heterogeneous porous materials. *Waste Management*, 23(3):219–224.
- [Savric, 2001] Savric, I. (2001). *Einfluss auf die Bindung und Mobilität organischer und anorganischer Stoffe in kontaminierten Rieselfeldböden*. PhD thesis, TU Berlin.
- [Scherer, 2012] Scherer, C. (2012). *Umwelteigenschaften mineralischer Werkmörtel*. PhD thesis, Universität Stuttgart.
- [Schneider et al., 2011] Schneider, M., Romer, M., Tschudin, M., and Bolio, H. (2011). Sustainable cement production - present and future. *Cement and Concrete Research*, 41:642–650.
- [Schöler, 2016] Schöler, A. (2016). *Hydration of multi-component cements containing clinker, slag, type-V fly ash and limestone*. PhD thesis, Bauhaus-Universität Weimar.
- [Schöler et al., 2017] Schöler, A., Lothenbach, B., Winnefeld, F., Haha, M. B., Zajac, M., and Ludwig, H.-M. (2017). Early hydration of SCM-blended portland cements: A pore solution and isothermal calorimetry study. *Cement and Concrete Research*, 93:71–82.
- [Schöler et al., 2015] Schöler, A., Lothenbach, B., Winnefeld, F., and Zajac, M. (2015). Hydration of quaternary portland cement blends containing blast-furnace slag, siliceous fly ash and limestone powder. *Cement and Concrete Composites*, 55:374–382.
- [Schubauer-Berigan et al., 1993] Schubauer-Berigan, M. K., Dierkes, J. R., Monson, P. D., and Ankley, G. T. (1993). pH-dependent toxicity of cd, cu, ni, pb and zn to ceriodaphnia dubia, pimephales promelas, hyalella azteca and lumbriculus variegatus. *Environmental Toxicology and Chemistry*, 12(7):1261–1266.
- [Schulze, 2002a] Schulze, B. (2002a). Merkblatt für Einpreßarbeiten mit Feinstbindemitteln in Lockergestein - Teil 1. *Bautechnik*, 79:499–508.
- [Schulze, 2002b] Schulze, B. (2002b). Merkblatt für Einpreßarbeiten mit Feinstbindemitteln in Lockergestein - Teil 2. *Bautechnik*, 79:589–597.
- [Schwerd, 2011] Schwerd, R. (2011). *Verweilverhalten biozider Wirkstoffe in Außenbeschichtungen im mehrjährigen Freilandversuch*. PhD thesis, Universität Stuttgart.
- [Scott-Fordsmand et al., 2008] Scott-Fordsmand, J. J., Maraldo, K., and van den Brink, P. J. (2008). The toxicity of copper contaminated soil using a gnotobiotic soil multi-species test system (sms). *Environment International*, 34(4):524 – 530.
- [Segura et al., 2013] Segura, I., Molero, M., Aparicio, S., Anaya, J., and Moragues, A. (2013). Decalcification of cement mortars: Characterisation and modelling. *Cement and Concrete Composites*, 35(1):136–150.
- [Shamsuddoha et al., 2013] Shamsuddoha, M., Islam, M. M., Aravinthan, T., Manalo, A., and tak Lau, K. (2013). Characterisation of mechanical and thermal properties of epoxy grouts for composite repair of steel pipelines. *Materials & Design*, 52:315–327.
- [Shan and Liu, 2011] Shan, C.-b. and Liu, Y.-x. (2011). Performance of polyurethane grouting material modified by sodium silicate. *Building Science*, 9:13.
- [Sheppard et al., 1993] Sheppard, S. C., Evenden, W. G., Abboud, S. A., and Stephenson, M. (1993). A plant life-cycle bioassay for contaminated soil, with comparison to other bioassays: Mercury and zinc. *Archives of Environmental Contamination and Toxicology*, 25(1):27–35.
- [Shukla et al., 1990] Shukla, J., Pandey, V., Singh, S., Yunus, M., Singh, N., and Ahmad, K. (1990). Effect of cement dust on the growth and yield of brassica campestris l. *Environmental Pollution*, 66(1):81 – 88.
- [Singh and Rao, 1981] Singh, S. and Rao, D. (1981). Certain responses of wheat plants to cement dust pollution. *Environmental Pollution Series A, Ecological and Biological*, 24(1):75 – 81.
- [Smit and Gestel, 1997] Smit, C. and Gestel, C. V. (1997). Influence of temperature on the regulation and toxicity of zinc infolsomia candida(collembola). *Ecotoxicology and Environmental Safety*, 37(3):213 – 222.

- [Smolczyk, 2003] Smolczyk, U. (2003). *Geotechnical Engineering Handbook, Procedures*, volume 2. John Wiley & Sons.
- [Spanka and Thielen, 1995] Spanka, G. and Thielen, G. (1995). Investigation into the detection of plasticizing concrete admixtures and into their sorption and elution behaviour. *beton*, 45:320–327.
- [Staples et al., 2000] Staples, C., Murphy, S., McLaughlin, J., Leung, H.-W., Cascieri, T., and Farr, C. (2000). Determination of selected fate and aquatic toxicity characteristics of acrylic acid and a series of acrylic esters. *Chemosphere*, 40(1):29 – 38.
- [Starovoitova et al., 2009] Starovoitova, I., Khozin, V., Abdrakhmanova, L., Rodionova, O., and Pomerantsev, A. (2009). Application of nonlinear PCR for optimization of hybrid binder used in construction materials. *Chemo-metrics and Intelligent Laboratory Systems*, 97(1):46–51.
- [Stein et al., 1992] Stein, D., Lühr, H. P., Grunder, T., and Gersum, F. (1992). Entwicklung und Erprobung umweltfreundlicher Injektionsmittel und -verfahren zur Behebung örtlich begrenzter Schäden und Undichtigkeiten in Kanalisationen unter Berücksichtigung des Gewässerschutzes. Technical report, Umweltbundesamt.
- [Stein, 2004] Stein, V. (2004). *Untersuchungen zur Optimierung und Bewertung des Auslaugverhaltens versinterungsrelevanter Stoffe aus Spritzbetonen als Beitrag zur Verbesserung der Umweltverträglichkeit*. PhD thesis, Ruhr-Universität Bochum.
- [Sun et al., 2003] Sun, H., Tateda, M., Ike, M., and Fujita, M. (2003). Short- and long-term sorption/desorption of polycyclic aromatic hydrocarbons onto artificial solids: effects of particle and pore sizes and organic matters. *Water Research*, 37(12):2960 – 2968.
- [Sun et al., 2016] Sun, Z., Yang, H., Shui, L., Liu, Y., Yang, X., Ji, Y., Hu, K., and Luo, Q. (2016). Preparation of polycarboxylate-based grinding aid and its influence on cement properties under laboratory condition. *Construction and Building Materials*, 127:363–368.
- [Sverdrup et al., 2001] Sverdrup, L. e., Källqvist, T., Kelley, A., Fürst, C., and Hagen, S. (2001). Comparative toxicity of acrylic acid to marine and freshwater microalgae and the significance for environmental effects assessments. *Chemosphere*, 45(4-5):653–658.
- [Szycher, 2012] Szycher, M. (2012). *Szycher's handbook of polyurethanes*. CRC press.
- [Tiruta-Barna et al., 2006] Tiruta-Barna, L., Fantozzi-Merle, C., de Brauer, C., and Barna, R. (2006). Leaching behaviour of low level organic pollutants contained in cement-based materials: Experimental methodology and modelling approach. *Journal of hazardous materials*, 138:331–342.
- [Togerö, 2004] Togerö, A. (2004). *Leaching of hazardous substances from concrete constituents and painted wood*. PhD thesis, Chalmers University of Technology, Göteborg.
- [Togerö, 2006] Togerö, A. (2006). Leaching of hazardous substances from additives and admixtures of concrete. *Environmental Engineering Science*, 23:102–117.
- [US EPA, 2017] US EPA (2017). United states environmental protection agency.
- [USGS, 2017] USGS (2017). United States Geological Survey.
- [van der Sloot and Dijkstra, 2004] van der Sloot, H. and Dijkstra, J. (2004). Development of horizontally standardized leaching tests for construction materials: a material based or release based approach? Identical leaching mechanisms for different materials. Technical report, Energy Research Centre (ECN).
- [van der Sloot et al., 2016] van der Sloot, H., Kosson, D., and van Zomeren, A. (2016). Leaching, geochemical modelling and field verification of a municipal solid waste and a predominantly non-degradable waste landfill. *Waste Management*, 63:74–95.
- [Van Gestel and Hensbergen, 1997] Van Gestel, C. A. M. and Hensbergen, P. J. (1997). Interaction of Cd and Zn toxicity for *Folsomia candida* (Collembola: Isotomidae) in relation to bioavailability in soil. *Environmental Toxicology and Chemistry*, 16(6):1177–1186.
- [Velzeboer et al., 2008] Velzeboer, I., Hendriks, A. J., Ragas, A. M. J., and van de Meent, D. (2008). Nanomaterials in the environment aquatic ecotoxicity tests of some nanomaterials. *Environmental Toxicology and Chemistry*, 27(9):1942–1947.

- [Venugopal et al., 1997] Venugopal, K. N. B. R., Ramesh, D. T. V. D., Reddy, S. D., and Reddy, N. S. L. (1997). Effect of cadmium on antioxidant enzyme activities and lipid peroxidation in a freshwater field crab, *Barthelphusa guerini*. *Bulletin of Environmental Contamination and Toxicology*, 59(1):132–138.
- [Vollpracht and Brameshuber, 2010] Vollpracht, A. and Brameshuber, W. (2010). Investigations on the leaching behaviour of irrigated construction elements. *Environmental Science and Pollution Research*, 17:1177–1182.
- [Vollpracht and Brameshuber, 2016] Vollpracht, A. and Brameshuber, W. (2016). Binding and leaching of trace elements in portland cement pastes. *Cement and Concrete Research*, 79:76–92.
- [Wagner, 2011] Wagner, R. (2011). *Inverser Säulenversuch zur Beurteilung der Auswirkungen von Bodeninjektionsmitteln auf Boden und Grundwasser - Laborvergleichsuntersuchung und ökotoxikologische Bewertung am Beispiel von Polyacrylaten/Acrylatgelenjektionen*. PhD thesis, Freie Universität Berlin.
- [Wagner and Dumm, 2010] Wagner, R. and Dumm, M. (2010). *Laborvergleichstest zur Normierung der inversen Säulenelution nach Schössner und Validierung der Parameter und Kriterien für die ökotoxikologische Bewertung von Bauprodukten mittels Ammoniumoxidaions- und Bodenatmungstest als Bestandteil einer ökotoxikologischen Testbatterie zur Bewertung der Wirkung von Bauprodukten auf Böden (Bewertung der ökotoxikologischen Auswirkung von Bauprodukten auf Böden Tl. 3)*. Fraunhofer IRB Verlag.
- [Walter et al., 2006] Walter, I., Martinez, F., and Cala, V. (2006). Heavy metal speciation and phytotoxic effects of three representative sewage sludges for agricultural uses. *Environmental Pollution*, 139(3):507 – 514.
- [Wang et al., 2003] Wang, K.-S., Lin, K.-L., and Tzeng, B.-Y. (2003). Latent hydraulic reactivity of blended cement incorporating slag made from municipal solid waste incinerator fly ash. *Journal of the Air & Waste Management Association*, 53(11):1340–1346.
- [Wangler et al., 2012] Wangler, T., Zuleeg, S., Vonbank, R., Bester, K., Boller, M., Carmeliet, J., and Burkhardt, M. (2012). Laboratory scale studies of biocide leaching from façade coatings. *Building and Environment*, 54:168 – 173.
- [Warner, 2004] Warner, J. (2004). *Practical handbook of grouting: soil, rock, and structures*. John Wiley & Sons.
- [Wehrer and Totsche, 2008] Wehrer, M. and Totsche, K. (2008). Effective rates of heavy metal release from alkaline wastes - quantified by column outflow experiments and inverse simulations. *Journal of Contaminant Hydrology*, 101:53 – 66.
- [Widmann, 1996] Widmann, R. (1996). International society for rock mechanics commission on rock grouting. *International Journal of Rock Mechanics and Mining Sciences & Geomechanics Abstracts*, 33(8):803–847.
- [Wiench et al., 2009] Wiench, K., Wohlleben, W., Hisgen, V., Radke, K., Salinas, E., Zok, S., and Landsiedel, R. (2009). Acute and chronic effects of nano- and non-nano-scale tio₂ and zno particles on mobility and reproduction of the freshwater invertebrate daphnia magna. *Chemosphere*, 76(10):1356 – 1365.
- [Winnefeld et al., 2007] Winnefeld, F., Becker, S., Pakusch, J., and Götz, T. (2007). Effects of the molecular architecture of comb-shaped superplasticizers on their performance in cementitious systems. *Cement and Concrete Composites*, 29:251–262.
- [World Health Organization, 2011] World Health Organization (2011). *Guidelines for Drinking-Water Quality*. World Health Organisation.
- [Xiang et al., 2006] Xiang, X. J., Qian, J. W., Yang, W. Y., Fang, M. H., and Qian, X. Q. (2006). Synthesis and properties of nanosilica-reinforced polyurethane for grouting. *Journal of Applied Polymer Science*, 100(6):4333–4337.
- [Xu et al., 2009] Xu, J., Ke, X., Krogh, P. H., Wang, Y., Luo, Y.-M., and Song, J. (2009). Evaluation of growth and reproduction as indicators of soil metal toxicity to the collembolan, *sinella curviseta*. *Insect Science*, 16(1):57–63.
- [Yang et al., 2017] Yang, Z., Zhang, X., Liu, X., Guan, X., Zhang, C., and Niu, Y. (2017). Flexible and stretchable polyurethane/waterglass grouting material. *Construction and Building Materials*, 138:240–246.
- [Yu and Crump, 1998] Yu, C. and Crump, D. (1998). A review of the emission of VOCs from polymeric materials used in buildings. *Building and Environment*, 33(6):357–374.

-
- [Zhang et al., 2016] Zhang, Y., Fei, A., and Li, D. (2016). Utilization of waste glycerin, industry lignin and cane molasses as grinding aids in blended cement. *Construction and Building Materials*, 123:785–791.
- [Zingg, 2008] Zingg, A. (2008). *Cement-superplasticizer interaction: link between macroscopic phenomena and microstructural data of the early cement hydration*. PhD thesis, ETH Zürich.

List of Figures

1.1	Schematic picture of injection of waterproofing materials.	2
1.2	Structure of the thesis.	5
2.1	Application of soil injection materials [Wagner, 2011, Stein et al., 1992, Osebold, 2008, Martens, 1998].	9
2.2	Global cement production [Khatib, 2016, Schneider et al., 2011, USGS, 2017] and the amount of used chemical admixtures extrapolated from German data and from standard concrete recipes.	10
2.3	CaO–Al ₂ O ₃ –SiO ₂ ternary diagram of cementitious materials. Reproduced from [Lothenbach et al., 2011].	12
2.4	Chemical structure of melamine sulfonate formaldehyde condensate (left) and naphthalene sulfonate formaldehyde condensate (right).	12
2.5	Chemical structure of comb-shaped PCE [Aïtcin and Flatt, 2015].	14
2.6	Adsorption phenomena of PCEs on particle surfaces. Reproduced from [Benedix, 2008].	14
2.7	Comparison between polycondensate and polycarboxylate superplasticisers [Benedix, 2008, Ferrari et al., 2011, Ferrari et al., 2010].	15
2.8	Global PU market segments 2015 (A) and global annual PU production with average annual growth rate indicated with arrows (B) [Austin and Hicks, 2016, IAL consultants, 2017, FSK, 2017]	15
2.9	Consecutive reactions of urethane chemistry [Clemitson, 2008, Becker et al., 1993, Leppkes, 1996].	17
2.10	Oligomerisation reactions of isocyanates [Clemitson, 2008, Becker et al., 1993, Leppkes, 1996].	17
2.11	Influence of pH on bound and available fractions of a component with amphoteric character [van der Sloot and Dijkstra, 2004, de Groot et al., 1999].	19
2.12	Determination of the dominating leaching mechanism (m = slope of the straight line).	20
2.13	Principles of the shrinking unreacted core model according to [Baker and Bishop, 1997, Gilliam and Wiles, 1996, Hinsenveld and Bishop, 1996, Arendt et al., 2012].	23
2.14	Different shrinking core models according to [Safari et al., 2009].	23
2.15	Factors influencing the leaching process [van der Sloot and Dijkstra, 2004].	25
2.16	Dissolution fronts present in a cementitious material leached by pure water [Adenot, 1992, Faucon et al., 1996].	27

3.1	Ion concentrations of the eluents measured over a period of six month. . . .	35
3.2	Pneumatic 2-K cartridge dispenser COX CCA 380. 1) compressed air pistol 2) compressed air supply 3) safety system of the air pistol 4) compressed air control 5) co-axial cartridge 380 in the ratio 5:1 6) inner and outer cartridge lids 7) static mixing element.	38
3.3	Concluding overview of the used materials and the mix design.	41
3.4	Schematic overview of the used leaching tests.	42
3.5	Calibration curves of NFS-MFS in water.	48
3.6	UV-Vis spectra of the NFS-MFS based superplasticiser with a concentration of 5.6 mg L ⁻¹ . The peaks for MFS are at 220 nm and for NFS at 230 nm, 290 nm and 330 nm.	48
3.7	Analysis of the superplasticiser with LC-MS at a concentration of 100 µl mm ⁻¹ dissolved in 5 ml MeOH.	50
3.8	Flow-diagram of the LC-OCD-system with nitrogen detector [Huber et al., 2011].	51
3.9	Schematic diagram of the statistical data analysis. Concentration-response curve from [Brinke et al., 2015].	57
4.1	pH-value (A and B) and electric conductivity (C and D) of the eluates at the end of each leaching step	60
4.2	Leached Zn (A and C) respectively Sn (B and D) concentration of the catalysts at the end of each leaching step.	61
4.3	DOC of the eluates at the end of each leaching step leached with demineralised water (A, B and C) and Berlin tap water (D, E and F).	63
4.4	Typical LC-OCD chromatogram of the eluates. A - higher weight nitrogenous molecules; B and C - lower weight nitrogenous molecules; D - higher weight carbonaceous molecules; E - lower weight carbonaceous molecules.	64
4.5	Growth rate of <i>Desmodesmus subspicatus</i> exposed to different concentrations of polyurethane eluates with different catalysts (ZINC and TEDA). Standard deviations were in any case not higher than ±5%. Columns within each type of eluate, marked with the same letter are not significant different from its control (Dunnett test, p>0.05).	66
4.5	Growth rate of <i>Desmodesmus subspicatus</i> exposed to different concentrations of polyurethane eluates with different catalysts (ZINC and TEDA). Standard deviations were in any case not higher than ±5%. Columns within each type of eluate, marked with the same letter are not significant different from its control (Dunnett test, p>0.05).	67
4.6	Survival ratio of <i>Enchytraeus albidus</i> during soil tests (A and B), sand tests (C and D) and water tests (E and F) with ZINC (left) and TEDA (right) eluates. Note that different concentrations of catalyst and different proportions of leachates were examined. Columns within each type of eluate, marked with the same letter are not significant different (Tukey test, p>0.05).	69
5.1	Amount of leached ions at the end of the batch test.	73
5.2	Measured pH-value (A) and electric conductivity (B) at the end of each elution step during the tank test.	75

5.3	Measured ion release of Al^{3+} , Ca^{2+} , K^{+} , Na^{+} , SO_4^{2-} and Cl^{-} as determined after each eluate change during the tank leaching test. The dotted red line in the first split image indicates the threshold value according to [Bundesministerium der Justiz, 2001].	77
5.4	Graphical determination of Ca^{2+} , K^{+} and Al^{3+} depicted for Systems A) C1-0 B) C1-30 C) C III and D) C2-30.s.	78
5.5	Concentration of leached amount of TOC after each elution step during the 64 d tank leaching test (A) and graphical determination of the leaching mechanism (B).	79
5.6	Water tests with <i>E. albidus</i> : Survival rate measured for A) C1-30 and B) C III gained during the tank leaching test. Note that the control was set to 100 % at any time step. Columns within each type of eluate, marked with the same letter are not significant different (Tukey test, $p > 0.05$).	81
5.7	Soil and sand test with <i>E. albidus</i> : Survival rate for A) C1-30 in soil, B) C III in soil, C) C1-30 in sand and D) C III in sand as measured for each eluate gained during the tank leaching test. Note that the control was set to 100 % at any time step. Columns within each type of eluate, marked with the same letter are not significant different (Tukey test, $p > 0.05$).	82
6.1	pH-value (top) and electric conductivity (bottom) of the eluates during the tank leach test.	86
6.2	Paste samples: Concentration of the major elements at the end of each leaching step during the tank leach test. Data corrected to the blank value.	88
6.3	Mortar samples: Concentration of the major elements at the end of each leaching step during the tank leach test. Data corrected to the blank value.	89
6.4	TOC and DOC of the eluates originating from paste and mortar samples.	92
6.5	Mean release rate of organic carbon of selected systems.	93
6.6	Concentration of leached total superplasticiser measured via UV-Vis.	94
6.7	Normalised leached amount of active component. Data given in [%].	95
6.8	Calculated leached concentration from UV-Vis measurements: (a) NFS in paste samples (b) MFS in paste samples (c) NFS in mortar samples (d) MFS in mortar samples.	96
7.1	pH-value (left) and electric conductivity (right) of the eluates.	100
7.2	Concentration of ionic species at the end of each elution step. Data corrected to the blank value. Note the different scales on the ordinate.	101
7.3	TOC (left) and DOC (right) of the eluates. Data corrected to the blank value.	102
7.4	Release rate of total organic carbon (TOC). Outliers in light blue are excluded from the linear fit.	103
7.5	HPLC-MS chromatogram of the different eluates: A) PCE-DI after 0.25 days for fragments of polycarboxylate ether as tracer ions, B) PCE-DI after 0.25 days for Triisobutyl phosphate as tracer ion, C) PCE-BTW after 0.25 days for fragments of polycarboxylate ether as tracer ions and D) PCE-BTW after 0.25 days for Triisobutyl phosphate as tracer ion.	104
7.6	<i>S. alba</i> and <i>L. sativum</i> growth test: Comparison and linear regression of RRG, RSG and GI of <i>S. alba</i> and <i>L. sativum</i> . Outliers in light blue are excluded from the linear fit.	106

7.7	Induction ratio (I_R) of relevant samples. Mean and standard deviation of 3 replicates are presented.	109
8.1	Observed root growth of <i>S. alba</i> (top) and <i>L. sativum</i> (bottom) after exposure time of 4 days.	114
8.2	Mean RRG of <i>S. alba</i> and <i>L. sativum</i> in water eluates depicted for all four concentrations after 0.25 d (A and B), 1 d (C and D) and 2.25 d (E and F). Distilled water was used as control for which the RRG was 100 % throughout. Asterisks indicate significant differences from the control (Bonferroni-Test, $\ast=p<0.05$; $\ast\ast=p<0.01$; $\ast\ast\ast=p<0.001$; $\ast\ast\ast\ast=p<0.0001$).	116
8.2	Mean RRG of <i>S. alba</i> and <i>L. sativum</i> in water eluates depicted for all four concentrations after 4 d (G and H), 9 d (I and J) and 16 d (K and L). Distilled water was used as control for which the RRG was 100 % throughout. Asterisks indicate significant differences from the control (Bonferroni-Test, $\ast=p<0.05$; $\ast\ast=p<0.01$; $\ast\ast\ast=p<0.001$; $\ast\ast\ast\ast=p<0.0001$).	117
8.2	Mean RRG of <i>S. alba</i> and <i>L. sativum</i> in water eluates depicted for all four concentrations after 36 d (M and N) and 64 d (O and P). Distilled water was used as control for which the RRG was 100 % throughout. Asterisks indicate significant differences from the control (Bonferroni-Test, $\ast=p<0.05$; $\ast\ast=p<0.01$; $\ast\ast\ast=p<0.001$; $\ast\ast\ast\ast=p<0.0001$).	118
10.1	Test set-up of soil and sand tests with <i>Enchytraeus Albidus</i>	A 14
10.2	Test set-up at very end of <i>Enchytraeus Albidus</i> mortality tests. Note <i>Enchytraeus Albidus</i> are forced to float upwards due to a surplus of water.	A 14
10.3	Test set-up of primary root growth tests at test beginning.	A 15
10.4	Test set-up of primary root growth tests at test end.	A 15
10.5	Ca^{2+} concentration at the end of each elution step. Note the two breaks of the x-axis.	A 19

List of Tables

2.1	Concrete admixtures by classification. Partially reproduced from [Aïtcin and Flatt, 2015].	13
2.2	Material combinations for composite grouting materials.	18
2.3	Bond types and bond energies during sorption processes.	26
2.4	Summarised factors influencing leaching [van der Sloot and Dijkstra, 2004, Togerö, 2004, Hohberg, 2002].	29
3.1	Formulation of the waterproofing polyurethane.	36
3.2	Mixtures under investigation. Data given in [wt.%].	37
3.3	Chemical composition and physical properties of the used raw materials. n.d. = not detected.	37
3.4	Matrix under investigation. DI = demineralised water, BTW = Berlin tap water.	39
3.5	Chemical and mineralogical composition of the used raw materials.	39
3.6	Information on the used materials. n.d. = not detected/ not relevant.	40
3.7	Mixtures used for cement leaching experiments presented in Chapter 7 and Chapter 8.	40
3.8	Schedule of the tank leaching test for polyurethane material.	42
3.9	Schedule of the HIS tank leaching test. Note that the test procedure is very similar to the European Standardised Tank Leaching Test for construction materials [DIN CEN/TS 16637-2, 2014].	43
3.10	Schedule of the tank leaching test for the cement study according to the German Committee for Reinforced Concrete [DAfStb-Richtlinie, 2005].	44
3.11	Schedule of the tank leaching test for the cement study according to the European Standardised Tank Leaching Test for construction materials [DIN CEN/TS 16637-2, 2014].	44
3.12	Operation conditions for IC.	45
3.13	Operational parameters for determination of cations by ICP-AES. Atomic (I) and ionic (II) emission lines.	46
3.14	Gradient elution of HPLC measurements.	49
3.15	Properties of the size exclusion column.	52
3.16	Eluent and acid solution used in LC-OCD system.	52
3.17	Algal growth medium.	53
3.18	Chemical composition of the soil and sand as determined by means of XRF. Data given in [wt.%].	54
3.19	Ames fluctuation assay set-up.	56

4.1	LC-OCD data.	65
5.1	Measured pH value and electric conductivity at the end of the 24 h batch test.	72
5.2	Summarised results of the 24 h batch test.	74
5.3	Cumulative release rate $E_{64,i}$ of the ionic species at the end of the tank test. Data given in $[\text{mmol m}^{-2}]$	76
5.4	Equation, coefficient of determination and leaching mechanism of selected ions and selected systems.	78
5.5	Equations used to specify the dominant leaching mechanism of the TOC and coefficient of determination R^2	79
5.6	Summarised results of the 64 d tank test.	80
6.1	Cumulative release $E_{56,i}$ of major electrolytes during the tank leaching test. Data in $[\text{mmol m}^{-2}]$	87
6.2	Cumulative release $E_{56,\text{TOC}}$ of organic species measured as sum parameter TOC. Data given in $[\text{mmol m}^{-2}]$ corrected to the blank value.	92
6.3	Amount of total active component added and leached within 56 d.	94
7.1	Cumulative release rate $E_{64,i}$ after 64 d of leaching of the ionic species. Data presented in $[\text{mmol m}^{-2}]$	102
7.2	Results of three-way ANOVA with Tukey post hoc test of <i>S. alba</i> and <i>L. sativum</i>	107
7.3	Results of two-way ANOVA with Sidak post hoc test attached to previous three-way ANOVA of <i>S. alba</i> and <i>L. sativum</i>	108
8.1	RSG and GI of <i>S. alba</i> seeds and <i>L. sativum</i> seeds as affected by leachates of cement samples in four different concentrations after 0.25 d and 64 d. Entries marked with the same superscript letter within each type of sample are not significantly different ($p > 0.05$).	120
10.1	Ecotoxicological data on aquatic and terrestrial organisms for substances present in cementitious waterproofing materials.	A 3
10.2	Ecotoxicological data on aquatic and terrestrial organisms for substances present polyurethane based waterproofing materials.	A 12
10.3	Mutagenicity detected with Ames strain TA100 without metabolic activation displayed as mutagenicity ration (MR) and slope (m). Mutant ratios in bold italic indicate significant differences vs. control ($p < 0.05$). UmuC-assay: Growth rate (G) and induction ratio (I_R) compared to negative control. Growth rates below 0.5 and induction ratios above 1.5 indicate cytotoxicity (highlighted and bold).	A 17

Glossary

Cement notation

$\bar{C}$	carbon dioxide - CO_2
$\bar{S}$	sulfur trioxide - SO_3
C_3A	tricalciumaluminate
CH	portlandite
A	aluminium oxide/alumina - Al_2O_3
AFm	monosulfoaluminate
AFt	ettringite
C	calcium oxide/lime - CaO
C-S-H	calcium silicate hydrate
H	water - H_2O
K	potassium oxide - K_2O
N	sodium oxide - Na_2O
S	silicon dioxide/silica - SiO_2

Mathematical symbols

$\frac{\partial c}{\partial x}$	concentration gradient
λ	wave length
B_i	algae cell density at the beginning
B_j	algae cell density at the end
$c_{0,mo}$	mobilised concentration of substance i in sample at time $t=0$
c_0	blank; concentration of substance i in eluent
C_0	initial concentration in the solid sample
c_e	c_{mo} at time $0 = f \cdot c_T = c_{mo}$
c_{im}	immobilised concentration of substance
c_{mo}	mobilised concentration of substance
c_n	concentration of substance i in leachate per interval
C_{sat}	concentration in the pores when saturated
c_T	$(c_{mo} + c_{im})$
D_e^1	effective diffusion coefficient
D_0	pre-exponential factor

D_e	effective diffusion constant
d_{95}	the diameter at which 95 % of the sample's mass is comprised of particles with a diameter less than this value
E_D	activation energy of diffusion
I_R	induction ratio
J_i	leaching rate per interval
k_1	empirical constant
k_2	empirical constant
k_3	empirical constant
k_4	empirical constant
K_d	partition coefficient
K_F	sorption constant
K_L	sorption constant
$q_{\max}$	maximum load at mono-molecular layer
t_i	time at the beginning
U_S	relative enzyme activity of β -Galactosidase
$val.E_i$	valid release rate
V_E	volume of the eluent
c_i	concentration of the ion after each elution step
$E_{64,i}$	cumulative release rate after 64 days
S	surface area at the beginning of the leaching test
V	volume of the eluent
μ	specific growth rate
$\Sigma E(t)$	cumulative leached substance
ε	extinction coefficient
I_0	intensity of incident light
$J(t)$	leaching rate
k	reaction rate constant
t_j	time at the end
A	absorbance
A	sample surface
a	pre-exponential factor
c	concentration of the substance
c	speed of light
D	diffusion coefficient
d	optical path length
DMT	de minimis threshold
E	energy
f	mobilised fraction
G	bacterial growth rate
GI	germination index
h	Planck constant
I	intensity of transmitted light
J	diffusion flux
MR	mutagenicity ratio
N	amount of intervals
n	Freundlich-exponent
q	absorbed amount of substance per mass unit

R	ideal gas constant
RRG	relative root growth
RSG	relative seed growth
T	temperatur
t	contact time
X	position of the dissolution front

General abbreviations

APCI	atmospheric pressure chemical ionisation
arb. unit	arbitrary unit
BTW	Berlin tap water
Da	Dalton
DAfStb-Richtlinie	guideline of the German Committee for Reinforced Concrete
DI	distilled water
DOC	dissolved organic carbon
DOTL	di-n-octyltin di-laurate
GGBFS	ground granulated blast furnace slag
HPLC-MS	high performance liquid chromatography coupled to mass spectrometry
ICP-AES	inductively coupled plasma atomic emission spectroscopy
l.d.l.	lower detection limit
L/S-ratio	liquid-to-solid-ratio
LAWA	German Working Group of the Federal States on Water Issues
LC-OCD	liquid chromatography-organic carbon detection
M	mortar
MAK	maximum workplace concentration
MDI	methylene diphenyl diisocyanate
MFS	melamine sulfonate formaldehyde condensate
MS	mass spectrometer
MWC	maximum water holding capacity
n.d.	not determined
NDIR	non-dispersive infrared
NFS	naphthalene sulfonate formaldehyde condensate
OPC	ordinary Portland cement
P	cement paste
PCE	Polycarboxylate ether
PU	polyurethane
RH	relative humidity
SCC	self-compacting concrete
SCM	supplementary cementitious materials
SEC	size exclusion chromatography
TEDA	triethylene diamine
TLV	threshold limit value
TOC	total organic carbon
u.d.l.	upper detection limit
UHPC	ultra high performance concrete

UPW	Ultrapure Water
UV-Vis	ultraviolet-visible spectrophotometry
w/c-ratio	water-to-cement-ratio
XRF	X-ray fluorescence
ZINC	zinc based catalyst for PU system

Appendices

Contents

Appendix 1 - Ecotoxicological data for substances present in building materials . . .	A 2
Appendix 2 - <i>Enchytraus Albidus</i>	A 14
Appendix 3 - Primary root growth test	A 15
Appendix 4 - Results of Ames assay and UmuC-assay on cement leachates	A 16
Appendix 5 - Second cement study - additional data	A 19

Appendix 1 - Ecotoxicological data for substances present in building materials

A1.1 Ecotoxicological data on aquatic and terrestrial organisms for substances present in cementitious waterproofing materials

Table 10.1: Ecotoxicological data on aquatic and terrestrial organisms for substances present in cementitious waterproofing materials.

substance (CAS number)	organism	age [d]	effect or LC ₅₀ ^b	literature
component: cement				
Barium (7 440 393)	Cyprinodon variegatus	1 to 4	LC ₅₀ > 500 mg l ⁻¹	[US EPA, 2017] [Heitmüller et al., 1981]
	Lemna minor	10	EC ₅₀ = 59 nmol ml ⁻¹	[ECHA, 2017]
Aluminum (7 429 905)	Lemna minor	7	EC ₅₀ = 15 966 µg l ⁻¹ LOEC = 5313.8 µg l ⁻¹	[ECHA, 2017]
	Pimephales promelas	7	EC ₅₀ = 0.151 mg l ⁻¹	[ECHA, 2017]
	Pseudokirchnerella subcapitata	3	NOEC > 4 µg l ⁻¹	[ECHA, 2017]
Aluminium oxide (1 344 281)	Daphnia magna	2	NOEC > 0.071 mg l ⁻¹	[ECHA, 2017]
	Lemna minor	7	EC ₅₀ = 15 966 µg l ⁻¹	[ECHA, 2017]
	Oncorhynchus mykiss	2	pH 6.5 and 11 µmol l ⁻¹ → acute toxicity	[ECHA, 2017] [Exley et al., 1996]
	Pimephales promelas	4	EC ₅₀ = 1.16 mg l ⁻¹ at 25 mg l ⁻¹ EC ₅₀ = 44.8 mg l ⁻¹ at 200 mg l ⁻¹	[ECHA, 2017]
	Pseudokirchnerella subcapitata	3	EC ₅₀ = 229.8 µg l ⁻¹ at pH = 7.7 EC ₅₀ = 515.0 µg l ⁻¹ at pH = 8.0	[ECHA, 2017]
Cadmium (7 440 439)	Barytelphusa guerini	4	LC ₅₀ = 1820 µg l ⁻¹	[ECHA, 2017] [Venugopal et al., 1997]
	Eisenia fetida	84	NOEC = 18 mg kg ⁻¹ (soil dw)	[ECHA, 2017] [Gestel et al., 1991] [Van Gestel and Hensbergen, 1997]
Continued on next page				

Table 10.1 – continued from previous page

substance (CAS number)	organism	age [d]	effect or LC ₅₀ ^b	literature
Cadmium (7 440 439)	Folsomia candida	42	NOEC = 22 mg kg ⁻¹ (soil dw)	[ECHA, 2017, Sajwani et al., 1996]
			NOEC ^g = 50 µg g ⁻¹ (dw) ^d	
			LOEC ^g = 200 µg g ⁻¹ (dw)	
			EC ₅₀ = 51 µg g ⁻¹ (dw; reproduction)	
Phaseolus vulgaris	Pimephales promelas	30	NOEC = 6.7 mg kg ⁻¹ (soil dw)	[ECHA, 2017]
		4	LC ₅₀ = 1500 µg l ⁻¹	[ECHA, 2017]
		60	NOEC = 14 µg l ⁻¹	[ECHA, 2017] [Pickering and Gast, 1972]
Scenedesmus quadricauda	7	NOEC = 31 µg l ⁻¹	[ECHA, 2017] [Bringmann and Kühn, 1980]	
Calcium (7 440 702)	Daphnia magna	2	EC ₅₀ = 49.1 mg l ⁻¹ (mobility) NOEC = 33.3 mg l ⁻¹	[ECHA, 2017]
	Dicotyledonae	21	EC ₅₀ = 5.14 g kg ⁻¹ (soil dw)	[ECHA, 2017]
	Monocotyledonae	21	EC ₅₀ = 5.64 g kg ⁻¹ (soil dw)	[ECHA, 2017]
	Oncorhynchus mykiss	2	LOEC = 0.04 mol l ⁻¹	[US EPA, 2017]
Chloride (7 647 010)	Crassostrea virginica	2	EC ₅₀ = 11.2 µg l ⁻¹ to 40.7 µg l ⁻¹	[ECHA, 2017, Arnold et al., 2010]
	Daphnia magna	2	LC ₅₀ = 20 µg l ⁻¹ to 52 µg l ⁻¹ e,f	[ECHA, 2017]
	Dentaster excentricus	2	EC ₅₀ = 18.9 µg l ⁻¹ to 46.2 µg l ⁻¹	[ECHA, 2017, Arnold et al., 2010]
	Medicago sativa	364	NOEC = 816 mg kg ⁻¹	[ECHA, 2017, Gonzalez, 1991]
	Mytilus galloprovincialis	2	EC ₅₀ = 6.48 µg l ⁻¹ to 37.2 µg l ⁻¹	[ECHA, 2017, Arnold et al., 2010]
	Nematoda		EC ₁₀ = 108.6 mg kg ⁻¹	[ECHA, 2017, Korthals et al., 1996]
	Pimephales promelas	4	LC ₅₀ = 172.8 µg l ⁻¹	[ECHA, 2017]
				Continued on next page

Table 10.1 – continued from previous page

substance (CAS number)	organism	age [d]	effect or LC ₅₀ ^b	literature
Copper (7 440 508)	Pimephales promelas	330	NOEC = 33 µg l ⁻¹ (growth)	[ECHA, 2017, Mount, 1968]
			NOEC = 33 µg l ⁻¹ (mortality)	
			NOEC = 14.5 µg l ⁻¹ (reproduction)	
	Pseudokirchnerella subcapitata	3	NOEC = 37.6 µg l ⁻¹ to 170.8 µg l ⁻¹ EC ₅₀ = 26.9 µg l ⁻¹ to 506.8 µg l ⁻¹	[ECHA, 2017]
	Solanum tuberosum	n.d.	EC ₁₀ = 108.6 mg kg ⁻¹	[ECHA, 2017, Korthals et al., 1996]
Iron (7 439 896)	Strongylocentrotus purpuratus	2	EC ₅₀ = 14.8 µg l ⁻¹ to 46.4 µg l ⁻¹	[ECHA, 2017, Arnold et al., 2010]
	Zea mays	n.d.	EC ₁₀ = 108.6 mg kg ⁻¹	[ECHA, 2017, Korthals et al., 1996]
	Cyprinus carpio	4	LC ₅₀ = 0.56 mg l ⁻¹	[ECHA, 2017]
	Daphnia pulex	1	LC ₅₀ = 38.86 mg l ⁻¹	[Lilius et al., 1995]
	Eisenia fetida	28	EC ₅₀ = 993 mg l ⁻¹ (reproduction) EC ₅₀ = 1242 mg l ⁻¹ (growth) LC ₅₀ = 5292 mg l ⁻¹ (mortality)	[ECHA, 2017] [Davies et al., 2003]
Lead (7 439 921)	Lactuca sativa	30	soil a: EC ₁₀ = 1400 / 3533 / - / 4413 mg kg ⁻¹ soil b: EC ₁₀ = 374 / 338 / 309 / 433 mg kg ⁻¹ soil c: EC ₁₀ = 1792 / 1676 / - / 1173 mg kg ⁻¹ soil d: EC ₁₀ = 1116 / - / - / 468 mg kg ⁻¹ soil e: EC ₁₀ = 63 / - / 95 / 85 mg kg ⁻¹ (values correspond to t = 0 d/112 d/252 d/588 d)	[ECHA, 2017]
Lymnaea stagnalis	Oncorhynchus mykiss	60	EC ₁₀ = 18.4 µg l ⁻¹ NOEC = 241.5 µg l ⁻¹	[ECHA, 2017] [ECHA, 2017] [ECHA, 2017] [ECHA, 2017]
Pimephales promelas	Scenedesmus quadricauda	15	LC ₅₀ = 174 µg l ⁻¹ NOEC = 1000 µg l ⁻¹	[ECHA, 2017] [ECHA, 2017]

Continued on next page

Table 10.1 – continued from previous page

substance (CAS number)	organism	age [d]	effect or LC ₅₀ ^b	literature
Lead (7 439 921)	<i>sinella curviseta</i>	28	EC ₁₀ = 1221 mg kg ⁻¹ (soil dw reproduction)	[ECHA, 2017] [Xu et al., 2009]
	<i>Strongylocentrotus droebachiensis</i>	5	EC ₅₀ < 9700 µg l ⁻¹	[ECHA, 2017] [Dinnel et al., 1989]
Nickel (7 440 020)	<i>Alona affinis</i>	21	NOEC = 25.0 µg l ⁻¹ (mortality)	[ECHA, 2017]
	<i>Alyssum bertolonii</i>	n.d.		[Galardi et al., 2007]
	<i>Ceriodaphnia pulchella</i>	21	NOEC = 9.9 µg l ⁻¹ and 28.2 µg l ⁻¹ (reproduction)	[ECHA, 2017]
	<i>Ceriodaphnia quadrangular</i>	21	NOEC = 2.0 µg l ⁻¹ and 34.9 µg l ⁻¹ (mortality)	[ECHA, 2017]
	<i>Daphnia longispina</i>	21	NOEC = 26.6 µg l ⁻¹ and 118.0 µg l ⁻¹ (mortality)	[ECHA, 2017]
	<i>Lemna minor</i>	7	IC ₅₀ = 6.11 µg l ⁻¹	[ECHA, 2017] [Gopalapillai et al., 2013]
	<i>Peracantha truncata</i>	21	NOEC = 2.5 µg l ⁻¹ and 25.8 µg l ⁻¹ (reproduction)	[ECHA, 2017]
Titanium oxide (13 463 677)	<i>Simocephalus vetulus</i>	21	NOEC = 9.2 µg l ⁻¹ and 28.9 µg l ⁻¹ (reproduction)	[ECHA, 2017]
	<i>Scenedesmus quadricauda</i>	7	toxicity threshold	[ECHA, 2017] [Bringmann and Kühn, 1980]
	<i>Chydorus sphaericus</i>	2	LC ₅₀ > 100 mg l ⁻¹	[ECHA, 2017] [Velzeboer et al., 2008]
	<i>Cyprinodon variegatus</i>	4	LC ₅₀ > 10 000 mg l ⁻¹	[ECHA, 2017]
	<i>Daphnia magna</i>	21	up to 3 mg l ⁻¹ did not affect reproduction up to 30 mg l ⁻¹ did not affect mortality	[ECHA, 2017], [Wiench et al., 2009]
	<i>Eisenia fetida</i>	28	up to nominal concentrations of 10 g kg ⁻¹ did not affect survival, juvenile growth and reproduction	[ECHA, 2017], [McShane et al., 2012], [McShane, 2013]
	<i>Scenedesmus quadricauda</i>	32	NOEC > 1 mg l ⁻¹	[ECHA, 2017], [Kulacki et al., 2012]
				Continued on next page

Table 10.1 – continued from previous page

substance (CAS number)	organism	age [d]	effect or LC ₅₀ ^b	literature
Titanium oxide (13463677)	Stigeoclonium tenue	32	NOEC > 1 mg l ⁻¹	[ECHA, 2017], [Kulacki et al., 2012]
	Synedra ulna	32	NOEC > 1 mg l ⁻¹	[ECHA, 2017], [Kulacki et al., 2012]
Zinc (7440666)	Brassica rapa	n.d.	NOEC = 300 mg kg ⁻¹ (soil dw)	[ECHA, 2017] [Sheppard et al., 1993]
	Daphnia magna	2	EC ₅₀ = 330 µg l ⁻¹ (mobility)	[ECHA, 2017]
	Dunaliella euchlora	12	NOEC = 4800 µg l ⁻¹ (growth rate)	[ECHA, 2017]
	Eisenia fetida	21	14-day LC ₅₀ = 1340 mg kg ⁻¹	[ECHA, 2017] [Lock and Janssen, 2001]
	Folsomia candida	28	23-day EC ₁₀ = 224 mg kg ⁻¹ (reproduction at 24 °C)	[ECHA, 2017]
			28-day EC ₁₀ = 113 mg kg ⁻¹ (reproduction at 19 °C)	[Smit and Gestel, 1997]
			35-day EC ₁₀ = 136 mg kg ⁻¹ (reproduction at 16 °C)	
	Oncorhynchus mykiss	72	NOEC = 440 µg l ⁻¹	[ECHA, 2017] [Cairns et al., 1982]
	Pimephales promelas	4	LC ₅₀ = 780 µg l ⁻¹ (mortality)	[ECHA, 2017] [Schubauer-Berigan et al., 1993]
component: ground granulated blast furnace slag (GGBFS)				
(65996692)	Daphnia magna	2	NOEC > 50 g l ⁻¹	[ECHA, 2017]
		21	NOEC ≥ 5000 mg l ⁻¹	[ECHA, 2017]
	Desmodesmus subspicatus	3	NOEC > 50 g l ⁻¹	[ECHA, 2017]
	Eisenia fetida	14	LC ₅₀ = 770 g kg ⁻¹	[ECHA, 2017]
	Leuciscus idus	4	LC ₅₀ > 100 g l ⁻¹	[ECHA, 2017]
Continued on next page				

Table 10.1 – continued from previous page

substance (CAS number)	organism	age [d]	effect or LC ₅₀ ^b	literature
component: fly ash				
(93 924 197)	Daphnia magna	2	EC ₅₀ = 0.8 mg l ⁻¹	
	Eisenia fetida	14	LC ₅₀ = 29.2 mg kg ⁻¹ (soil)	[ECHA, 2017]
	Poecilia reticulata	4	LC ₅₀ = 137 mg l ⁻¹	[ECHA, 2017]
	Pseudokirchnerella subcapitata	3	EC ₅₀ > 100 mg l ⁻¹	[ECHA, 2017]
component: limestone				
(471 341)	Daphnia magna	2	EC ₅₀ = 0.65 mg l ⁻¹	[ECHA, 2017]
	Desmodesmus subspicatus		NOEC = 0.0625 mg l ⁻¹ (based on growth rate)	
		3	NOEC = 0.0625 mg l ⁻¹ (based on yield)	[ECHA, 2017]
			LOEC = 0.125 mg l ⁻¹ (based on growth rate)	
			LOEC = 0.125 mg l ⁻¹ (based on yield)	
	Eisenia fetida	14	LC ₅₀ > 1000 mg kg ⁻¹ (soil dw) NOEC = 1000 mg kg ⁻¹ (soil dw)	[ECHA, 2017]
	Ictalurus punctatus	103	NOEC = 8 kg ha ⁻¹	[US EPA, 2017] [Giri and Boyd, 2000]
	Oncorhynchus mykiss	4	LC ₅₀ > 100 % v/v saturated solution	[ECHA, 2017] [Baldissarro et al., 2004a] [Baldissarro et al., 2004b]
component: silica fume				
(69 012 642)	Danio rerio	4	LC ₅₀ > 100 mg l ⁻¹ (mortality)	[ECHA, 2017]
	Daphnia magna	1	EC ₅₀ > 1003 mg l ⁻¹ (mobility)	
	Pseudokirchnerella subcapitata	3	EC ₅₀ = 250 mg l ⁻¹ (growth rate)	[ECHA, 2017]
Continued on next page				

Table 10.1 – continued from previous page

substance (CAS number)	organism	age [d]	effect or LC ₅₀ ^b	literature
component: bottom ash				
	Daphnia magna	2	EC ₅₀ = 57.1 mg l ⁻¹	[ECHA, 2017]
	Daphnia magna	21	LOEC = 5.6 mg l ⁻¹ NOEC = 3.2 mg l ⁻¹	[ECHA, 2017]
	Dicotyledonae	3	reduced root elongation = 73±15 %	[ECHA, 2017]
	Eisenia fetida	14	LC ₅₀ = 29.2 mg kg ⁻¹ (soil)	[ECHA, 2017]
	Leuciscus idus	2	NOEC = 0.7 g l ⁻¹ to 2 g l ⁻¹	[ECHA, 2017]
	Monocotyledonae	3	reduced root elongation = 73±15 %	[ECHA, 2017]
	Pseudokirchnerella subcapitata	3	EC ₅₀ = 21.2 mg l ⁻¹	[ECHA, 2017]
component: plasticiser				
melamine sulphionate	Danio rerio	n.d.	EC ₅₀ = 560 mg l ⁻¹ to 200 mg l ⁻¹	[Galli et al., 1998] [Mäder et al., 2004]
	Daphnia magna	n.d.	EC ₅₀ < 100 mg l ⁻¹	[Galli et al., 1998] [Mäder et al., 2004]
naphthalene sulphionate (36 290 047)	Ames test	n.d.	negative	[Galli et al., 1998] [Mäder et al., 2004]
	Danio rerio	n.d.	EC ₅₀ = 100 mg l ⁻¹ to 2000 mg l ⁻¹	[Galli et al., 1998] [Mäder et al., 2004]
	Daphnia magna	n.d.	EC ₅₀ < 220 mg l ⁻¹	[Galli et al., 1998] [Mäder et al., 2004]
component: superplasticiser (PCE)				
Acrylic acid (79 107)	Daphnia magna	21	EC ₅₀ > 8.1 mg l ⁻¹ NOEC < 0.05 mg l ⁻¹	[ECHA, 2017] [Staples et al., 2000] [Radix et al., 1999]
Continued on next page				

Table 10.1 – continued from previous page

substance (CAS number)	organism	age [d]	effect or LC ₅₀ ^b	literature
Acrylic acid (79 107)	Eisenia fetida	14	LC ₅₀ > 1000 mg kg ⁻¹ (soil dw)	[ECHA, 2017]
	Scophthalmus maximus	4	LC ₅₀ > 1000 mg l ⁻¹	[ECHA, 2017] [Sverdrup et al., 2001]
Maleic anhydride (108 316)	Daphnia magna	21	NOEC = 10 mg l ⁻¹ (reproduction rate) EC ₅₀ = 77 mg l ⁻¹ (reproduction rate)	
	Leuciscus idus melanotus	2	LC ₅₀ = 115 mg l ⁻¹	[ECHA, 2017]
3-Methacryloxy- propyltrimethoxy- silane (2 530 850)	Danio rerio	4	LC ₅₀ > 100 mg l ⁻¹ NOEC = 100 mg l ⁻¹	[ECHA, 2017]
	Daphnia magna	2	EC ₅₀ > 876 mg l ⁻¹	[ECHA, 2017]
	Desmodesmus	3	EC ₅₀ > 100 mg l ⁻¹ (growth rate)	
	subspicatus		EC ₅₀ > 100 mg l ⁻¹ (biomass)	
Poly (oxy-1,2-ethanediyl), α-hydro-ω-hydroxy- Ethane-1,2-diol (25 322 683)	Daphnia magna	2	NOEC = 712.984 mg l ⁻¹	[ECHA, 2017]
	Poecilia reticulata	4	LC ₅₀ > 100 mg l ⁻¹	[ECHA, 2017]

^a n.d. = not detected / not given^b LC₅₀ = lethal concentration for 50% of the population exposed to the substance^c EC₅₀ = effect concentration for 50% of the population exposed to the substance^c NOEC = no observed effect concentration^c LOEC = lowest observed effect concentration^d not most sensitive endpoint^e fed animal^f unfed animal^g fresh weight

A1.2 Ecotoxicological data on aquatic and terrestrial organisms for substances present in polyurethane based waterproofing materials

Table 10.2: Ecotoxicological data on aquatic and terrestrial organisms for substances present polyurethane based waterproofing materials.

substance (CAS number)	organism	age [d]	effect or LC ₅₀ ^a	literature
component: component A polyol				
Glycerol, propoxylated (25 791 962)	Daphnia magna	0.875	NOEC = 10 mg l ⁻¹ , LOEC = > 10 mg l ⁻¹	[ECHA, 2017]
	Daphnia magna	2	EC ₅₀ > 100 mg l ⁻¹	[ECHA, 2017]
	Desmodesmus subspicatus	3	no toxic effect at the limit dose of 100 mg l ⁻¹	
Propane-1,2-diol, propoxylated (25 322 694)	Leuciscus idus	4	LC ₅₀ > 1000 mg l ⁻¹	[ECHA, 2017]
	Danio rerio	4	LC ₅₀ > 100 mg l ⁻¹	[ECHA, 2017]
	Daphnia magna	0.875	NOEC = 10 mg l ⁻¹ LOEC > 10 mg l ⁻¹	[ECHA, 2017]
	Daphnia magna	2	EC ₅₀ > 105.8 mg l ⁻¹	[ECHA, 2017]
	Desmodesmus subspicatus	3	EC ₅₀ > 100 mg kg ⁻¹	[ECHA, 2017]
component: component B isocyanate				
Diphenylmethan-2,2'- diisocyanat (MDI) (101 688)	Avena sativa	14	EC ₅₀ > 1000 mg kg ⁻¹ soil dw	
	Danio rerio	1	> 500 mg l ⁻¹	[ECHA, 2017]
	Daphnia magna	1	EC ₅₀ > 129.7 mg l ⁻¹	[ECHA, 2017]
		3		
	Eisenia fetida	14	LC ₅₀ > 1000 mg kg ⁻¹ soil dw	
Diphenylmethan-2,4'- diisocyanat (MDI) (5 873 541)	Lactuca sativa	14	EC ₅₀ > 1000 mg kg ⁻¹ soil dw	
	Daphnia magna	1	EC ₅₀ > 1000 mg l ⁻¹	[ECHA, 2017]
	Eisenia fetida	14	LC ₅₀ > 1000 mg kg ⁻¹ soil dw	
	Oryzias latipes	4	LC ₀ > 3000 mg l ⁻¹	[ECHA, 2017]
Continued on next page				

Table 10.2 – continued from previous page

substance (CAS number)	organism	age [d]	effect or LC ₅₀ ^a	literature
Diphenylmethan-4,4'- diisocyanat (MDI) (2 536 052)	Danio rerio	4	LC ₅₀ > 1000 mg l ⁻¹	[ECHA, 2017]
	Daphnia magna	1	EC ₅₀ 129.7 mg l ⁻¹	[ECHA, 2017]
	Eisenia fetida	14	LC ₅₀ > 1000 mg kg ⁻¹ soil dw	
1,6-Hexamethylen- diisocyanat (HDI) (822 060)	Danio rerio	4	LC ₀ > 82.8 mg l ⁻¹	[ECHA, 2017]
	Desmodesmus subspicatus	3	EC ₅₀ > 77.4 mg l ⁻¹	[ECHA, 2017]
	Avena sativa	14	EC ₅₀ > 1000 mg kg ⁻¹ soil dw	
Toluol-2,4- diisocyanat (TDI) (584 849)	Daphnia magna	2	12.5 mg l ⁻¹	[ECHA, 2017]
	Eisenia fetida	14	No observable effects (behaviour and appearance of worms) at 1000 mg kg ⁻¹ soil dw	[ECHA, 2017]
	Pimephales promelas	4	164 mg l ⁻¹	[ECHA, 2017]
component: catalyst				
Di-n-octyltin dilaurate (DOTL) (3 648 188)	Danio rerio	4	LC ₅₀ > limit of solubility	[ECHA, 2017]
	Daphnia magna	1	EC ₅₀ > water solubility	[ECHA, 2017]
	Desmodesmus subspicatus	3	EC ₅₀ > water solubility	[ECHA, 2017]
Triethylenediamine (TEDA) (280 579)	Daphnia magna	2	EC ₅₀ > 100 mg l ⁻¹	[ECHA, 2017]
	Leuciscus idus	4	LC ₅₀ 681 mg l ⁻¹	
	Pseudokirchnerella subcapitata		EC ₅₀ 110 mg l ⁻¹	[ECHA, 2017]

^a LC₅₀ = lethal concentration for 50% of the population exposed to the substance

Appendix 2 - *Enchytraeus Albidus*



Figure 10.1: Test set-up of soil and sand tests with *Enchytraeus Albidus*.



Figure 10.2: Test set-up at very end of *Enchytraeus Albidus* mortality tests. Note *Enchytraeus Albidus* are forced to float upwards due to a surplus of water.

Appendix 3 - Primary root growth test

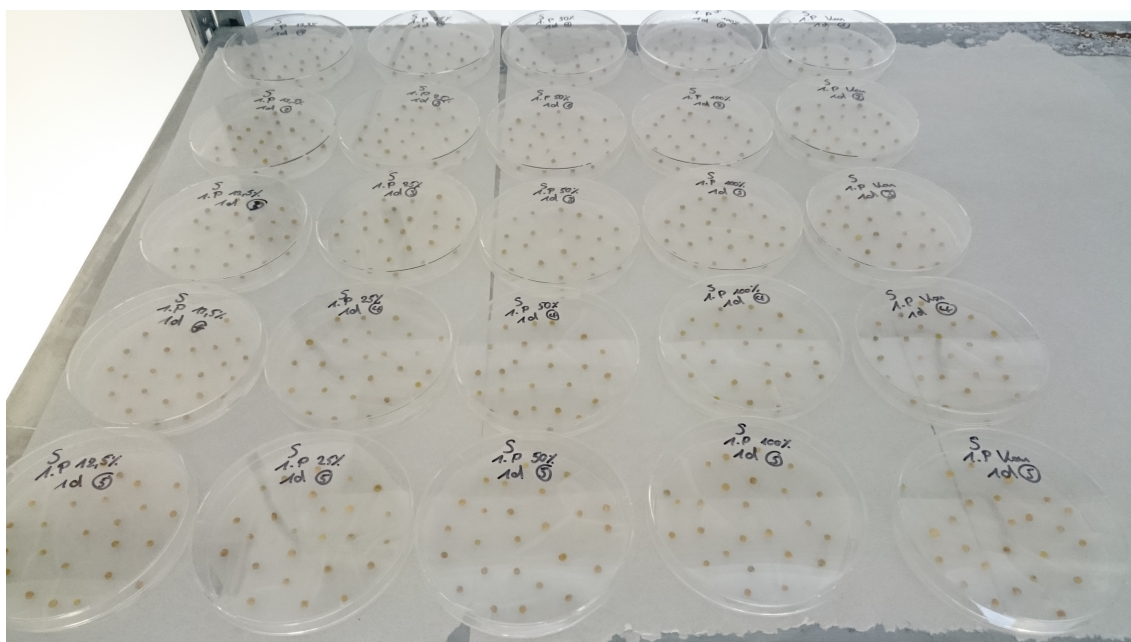


Figure 10.3: Test set-up of primary root growth tests at test beginning.

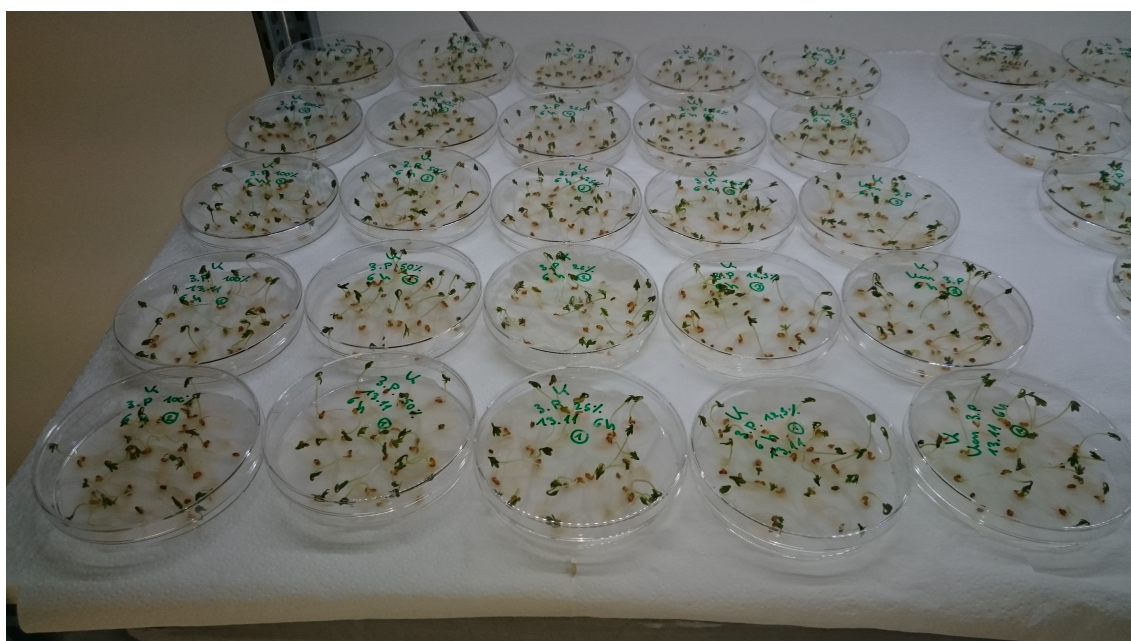


Figure 10.4: Test set-up of primary root growth tests at test end.

Appendix 4 - Results of Ames assay and UmuC-assay on cement leachates

Table 10.3: Mutagenicity detected with Ames strain TA100 without metabolic activation displayed as mutagenicity ratio (MR) and slope (m). Mutant ratios in bold italic indicate significant differences vs. control ($p < 0.05$). UmuC-assay: Growth rate (G) and induction ratio (I_R) compared to negative control. Growth rates below 0.5 and induction ratios above 1.5 indicate cytotoxicity (highlighted and bold).

sample	age [d]	Ames assay					umuC-assay				
		18.75 ng ml ⁻¹	12.5 ng ml ⁻¹	6.25 ng ml ⁻¹	slope	mutagenicity ratio (MR)	G	I_R	G	I_R	G
REF-DI	0.25	1.50	1.70	2.00	-0.04	0.93	0.93	0.61	1.08	1.56	1.12
REF-DI	1	0.53	0.84	1.00	-0.04	0.93	0.93	0.85	1.07	1.24	1.14
REF-DI	2.25	1.07	1.43	1.57	-0.04	0.99	0.99	0.83	0.90	0.52	1.00
REF-DI	4	2.50	2.00	2.33	0.01	0.96	0.96	0.80	0.94	0.73	1.01
REF-DI	9	0.95	0.68	0.79	0.01	0.93	0.93	1.34	1.13	0.88	1.06
REF-DI	16	1.64	1.18	1.36	0.02	0.96	0.96	1.62	1.08	0.86	1.04
REF-DI	36	0.42	0.67	0.92	-0.04	0.89	0.89	0.54	0.89	0.77	0.86
REF-DI	64	0.52	0.07	0.28	0.02	0.87	0.87	0.71	0.86	1.18	0.91
REF-BTW	0.25	1.80	1.00	1.20	0.05	0.92	0.92	0.58	1.13	1.36	1.09
REF-BTW	1	0.42	0.68	0.90	-0.04	0.87	0.87	1.05	0.96	1.46	1.14
REF-BTW	2.25	0.50	1.07	0.86	-0.03	1.00	1.00	0.96	0.95	0.78	1.03
REF-BTW	4	0.50	0.33	2.00	-0.12	0.96	0.96	0.81	0.92	0.75	1.02
REF-BTW	9	0.63	0.90	0.95	-0.03	1.00	1.00	1.57	1.16	1.05	1.04
REF-BTW	16	0.55	2.00	2.09	-0.12	0.95	0.95	1.90	1.04	0.91	1.01
REF-BTW	36	1.42	0.83	0.17	0.10	0.80	0.80	1.02	0.85	1.18	0.80
REF-BTW	64	0.45	0.59	0.79	-0.03	0.83	0.83	0.82	0.90	1.04	0.91

Continued on next page

Table 10.3 – continued from previous page

sample	age [d]	Ames assay				UmuC-assay											
		mutagenicity ratio (MR)				slope			1:1.5			1:3.0			1:6.0		
		18.75 ng ml ⁻¹	12.5 ng ml ⁻¹	6.25 ng ml ⁻¹	6.25 ng ml ⁻¹				G	I _R	G	I _R	G	I _R	G	I _R	G
PCE-DI	0.25	0.70	1.10	1.40	1.40	-0.06	-0.06	-0.06	0.80	-0.26	0.87	1.02	0.80	0.83	1.08	0.88	0.88
PCE-DI	1	0.63	0.90	1.11	1.11	-0.04	-0.04	-0.04	0.89	0.94	1.00	1.35	0.95	1.34	1.04	1.46	1.46
PCE-DI	2.25	0.64	1.29	1.14	1.14	-0.04	-0.04	-0.04	0.96	0.95	0.92	0.60	0.99	0.95	1.10	0.83	0.83
PCE-DI	4	0.00	0.33	2.33	2.33	-0.19	-0.19	-0.19	0.99	0.61	0.91	0.39	1.00	0.94	1.13	0.74	0.74
PCE-DI	9	1.21	0.90	0.79	0.79	0.03	0.03	0.03	0.86	1.42	0.97	1.07	0.98	1.11	1.06	1.57	1.57
PCE-DI	16	0.73	1.73	1.91	1.91	-0.09	-0.09	-0.09	0.97	1.44	0.97	1.42	0.99	1.07	1.10	0.57	0.57
PCE-DI	36	0.17	0.25	0.58	0.58	-0.03	-0.03	-0.03	0.71	0.33	0.60	0.62	0.55	0.69	0.71	0.92	0.92
PCE-DI	64	0.00	0.07	0.24	0.24	-0.02	-0.02	-0.02	0.83	0.63	0.85	1.08	0.86	0.77	0.94	1.19	1.19
PCE-BTW	0.25	2.42	2.08	2.33	2.33	0.01	0.01	0.01	0.72	0.59	1.01	0.89	1.22	0.79	1.14	1.19	1.19
PCE-BTW	1	0.90	0.30	0.20	0.20	0.06	0.06	0.06	0.89	1.12	1.25	0.77	1.52	0.57	1.35	0.71	0.71
PCE-BTW	2.25	0.00	0.00	0.20	0.20	-0.02	-0.02	-0.02	0.87	0.74	1.15	0.33	1.66	0.28	1.39	0.69	0.69
PCE-BTW	4	0.00	0.00	0.10	0.10	-0.01	-0.01	-0.01	0.92	0.70	1.40	0.78	1.65	0.91	1.45	0.54	0.54
PCE-BTW	9	0.35	0.55	1.10	1.10	-0.06	-0.06	-0.06	0.90	0.52	1.39	0.75	1.68	0.33	1.39	1.01	1.01
PCE-BTW	16	0.80	0.60	0.90	0.90	-0.01	-0.01	-0.01	0.94	1.26	1.29	0.64	1.65	0.71	1.42	1.43	1.43
PCE-BTW	36	1.67	2.08	2.17	2.17	-0.04	-0.04	-0.04	0.72	0.97	1.21	0.58	1.24	0.53	1.18	1.38	1.38
PCE-BTW	64	0.70	0.90	0.90	0.90	-0.02	-0.02	-0.02	0.92	0.94	1.19	0.84	1.57	0.70	1.28	1.20	1.20

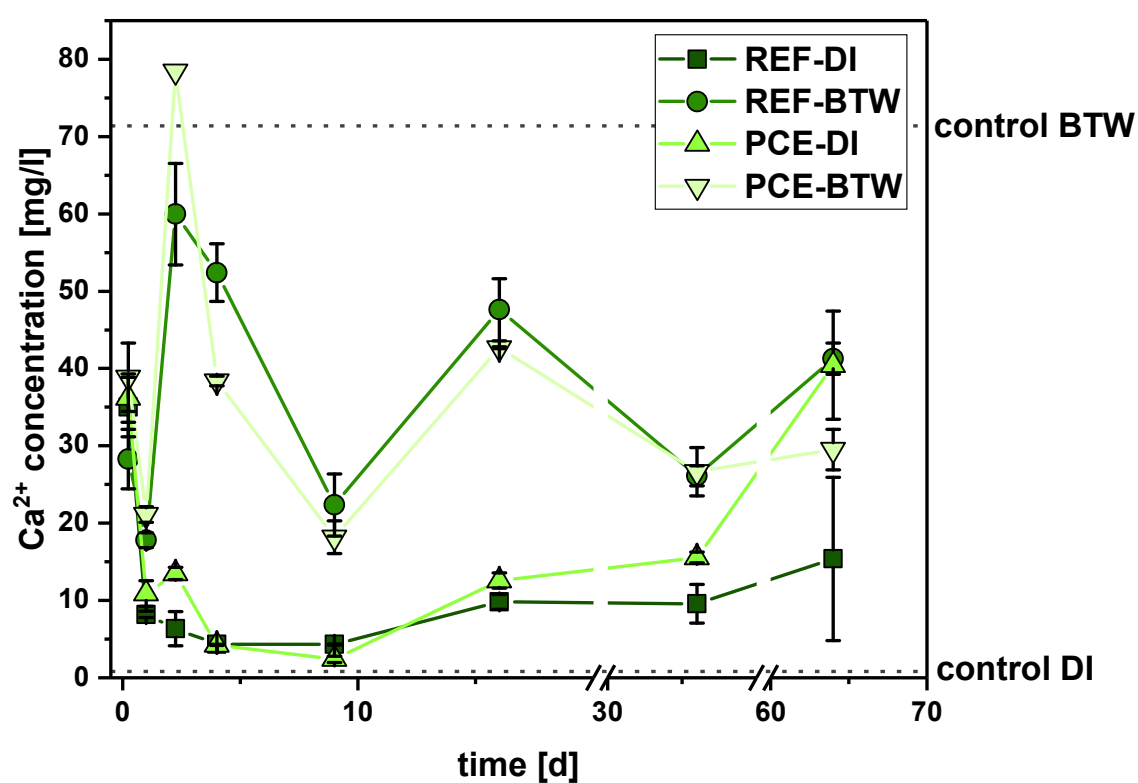
Appendix 5 - Second cement study - additional data

Figure 10.5: Ca^{2+} concentration at the end of each elution step. Note the two breaks of the x-axis.

Curriculum Vitae

Name: Veronika Märkl
Nationality: German

ACADEMIC EDUCATION

since 2012	Research Assistant at Group of Building Materials and Construction Chemistry at Technische Universität Berlin, Germany. Working areas: Impact of building materials on the environment, leaching of environmentally relevant substances of building materials
2012	Diploma thesis in the field of ceramics at Loughborough University, England: Processing of alumina ceramics with oriented microstructures
2010	Engineering training at the Laboratory for High Performance Ceramics at the Eidgenössische Materialprüfungsanstalt (Empa), Dübendorf, Switzerland: Microshaping of functional ceramic nanocomposites from nano dispersions in UV curable resins
2006–2012	Degree course <i>Keramik, Glas- und Baustofftechnik</i> , Technische Universität Bergakademie Freiberg, Germany, Graduation: Diplomingenieur (Dipl.-Ing.)
2003–2006	Vocational training as ceramist, Staatliche Berufsfachschule für Keramik Landshut, Germany

PARTICULAR KNOWLEDGE

EDP	MS Office, Origin, LaTeX, GraphPad Prism
Language skills	German - native language English - fluent in spoken and written French - basic knowledge

PUBLICATIONS

Journals	Märkl, V., Stenzel, J., Reichert, A. et al. Water Air Soil Pollut (2017) 228: 350. https://doi.org/10.1007/s11270-017-3537-8 Märkl, V., Pflugmacher, S., Reichert, A. et al. Water Air Soil Pollut (2017) 228: 280. https://doi.org/10.1007/s11270-017-3451-0 Märkl, V., Pflugmacher, S. & Stephan, D.A. Water Air Soil Pollut (2017) 228: 217. https://doi.org/10.1007/s11270-017-3373-x Märkl, V., Pflugmacher, S. & Stephan, D.A. Water Air Soil Pollut (2017) 228: 111. https://doi.org/10.1007/s11270-017-3271-2 Werner, I., Aldrich, A., Becker, B., Becker, D., Brinkmann, M., Burkhardt, M., Caspers, N., Campiche, S., Chèvre, N., Düring, R.A., Escher, B.I., Fischer, F., Giebner, S., Heye, K., Hollert, H., Junghans, M., Kienle, C., Knauer, K., Korkaric, M., Märkl, V., Muncke, J., Oehlmann, J., Reifferscheid, G., Rensch, D., Schäffer, A., Schiwy, S., Schwarz, S., Segner, H., Simon, E., Triebkorn, R., Vermeirssen, E., Wintgens, T., Zennegg, M., The 2015 Annual Meeting of SETAC German Language Branch in Zurich (7–10 September, 2015): Ecotoxicology and environmental chemistry—from research to application, Environmental Sciences Europe (2016) 28:20 Märkl, V., & Stephan, D.A. Water Air Soil Pollut (2016) 227: 30. https://doi.org/10.1007/s11270-015-2730-x De Hazan, Y., Märkl, V., Heinecke, J., Aneziris, C., Graule, T., Functional ceramic and nanocomposite fibers, cellular articles and microspheres via radiation curable colloidal dispersions, Journal of the European Ceramic Society 31 (2011) 2601-2611.
Conferences	V. Märkl, S. Pflugmacher, D. Stephan, Influence of Cement Paste Eluates on Primary Root Growth of Cress (<i>Lepidium Sativum</i>) and White Mustard (<i>Sinapis Alba</i>), 2nd International Conference on the Chemistry of Construction Materials 10.-12. October 2016, Munich V. Märkl, D. Stephan, Freisetzungsverhalten von organischen und anorganischen Bestandteilen aus Feinstzementsuspensionen für Nachverpressungen, 19. IBAUSIL 16. - 18. September 2015, Weimar, Germany, Band 2, 149-156

V. Märkl, S. Reddy, D. Stephan, S. Pflugmacher, A. Reichert, E. Meisel, Freisetzungsverhalten von organischen und anorganischen Bestandteilen aus Feinstzementsuspensionen für Nachverpressungen, in 20. Jahrestagung SETAC GLB 7.- 10. September 2015, Zürich

V. Märkl, D. Stephan, Auswirkungen von wasserabdichtenden Polyurethansystemen auf die Umwelt, in GDCh-Wissenschaftsforum Chemie 30. August - 2. September 2015, Dresden

V. Märkl, D. Stephan, Leaching of acrylate-based hydro-structural resins and analysis of organic carbon as sum parameter, in Tagung Bauchemie der GDCh-Fachgruppe Bauchemie 6. - 8. Oktober 2014, Kassel, GDCh-Monographie Bd. 48

Hazan, Y., Wozniak, M., Heinecke, J., Müller, G., Märkl, V., Graule, T., Shaping radiation curable colloidal dispersions - from polymer/ceramic fibers and microspheres to gradient porosity ceramic bulk materials, Advanced Processing and Manufacturing Technologies for Structural and Multifunctional Materials IV - 34th International Conference on Advanced Ceramics and Composites; Daytona Beach, FL; United States; 24 January 2010 through 29 January 2010; Code 84030