Key mechanisms for the release of metal(loid)s from a construction material in hydraulic engineering

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Content

SUMMARY

Hydraulic engineering and thus construction materials are necessary to enable the navigability of water ways. Since, a variety of natural as well as artificial materials are used, this materials are world wide tested on a potential release of dangerous substances to prevent adverse effects on the environment. To determine the potential release, it is important to identify and to understand key mechanisms which are decisive for the release of hazardous substances. A limited correlation between the conditions used in regulatory tests and those found in environmental systems is given and hence, often the significance of results from standardised tests on construction materials is questioned, since they are not designed to mimic environmental conditions.

In Germany industrial by-products are used as armour stones in hydraulic engineering. Especially the by-product copper slag is used during the last 40 years for the construction of embankments, groynes and coastal protection. On the one hand, this material has a high density and natural resources (landscape) are protected. One the other hand, the material contains high quantities of metal(loid)s. Therefore the copper slag (product name: iron silicate stones) is very suitable as test material. Metal(loid)s examined were As, Sb and Mo as representatives for (hydr)oxide forming elements and Cd, Co, Cu, Fe, Ni, Pb and Zn were studied as representatives for elements forming cations during the release.

Questions addressed in this Thesis were: (i) can we transfer the results from batch experiments to construction scenarios under the prevalent environmental conditions, (ii) which long-term trends exist for the release of metal(loid)s from copper slags and (iii) how environmental conditions influence the leaching of metal(loid)s from water construction materials?

To answer the first question the surface depending release of the metal(loid)s from the construction materials was examined. Therefore, batch leaching experiments with different particle sizes and a constant liquid/solid ratio were performed. In a second step a comparison between different methods for the determination of the specific surface area of armour stones with a 3D laser scanning method as a reference were performed. In a last step it was possible to show that via a roughness factor the results of the specific surface area from small stones, measured with gas adsorption, can be connected with the results from armour stones, determined with an aluminium foil method. Based on calculations of the specific surface area, it was possible to significantly improve catchment scale calculation about the release of metal(loid)s and to evaluate a potential impact of construction materials in hydraulic engineering on the water chemistry of rivers and streams.

To answer the second question long-term leaching diffuse gradient in thin films supported experiments were performed for half a year. Diffuse gradients in thin films (DGT) is an *in situ* method to passive sample metal(loid)s in water, sediments and soils. They were used as a sink for metal(loid)s in the eluate to provide solution equilibriums. Thus the exchange of the eluent, which is performed normally in long-term experiments, was superfluous and long-term effects under undisturbed conditions were studied. The long-term leaching experiments with DGT have proven to be capable (i) to differentiate between the depletion of the material surface and the solution equilibriums and (ii) to study sorption processes with or without a further release of the analytes. This means for the practically relevant test material copper slag that: (i) the cations Cd, Co, Cu, Ni and Pb are confirmed to be released from the slag over the whole time period of six months, (ii) a surface depletion of Zn was detected, and (iii) that the (hydr)oxide forming elements As, Mo and Sb were released from the slag over the hole periods of six months but the release was masked by adsorption to Fe-oxide colloids, which were formed during the leaching experiments. It was confirmed, that sulphide minerals are the main source for long-term release of Cd, Cu, Ni, Pb and Mo.

To answer the third question short-term leaching experiments simulating environmental conditions in hydraulic engineering were performed. One factor is the salinity. The influence of this parameter was tested in batch experiments with sea salt solution (30 g/l), river Rhine water, ultra pure water and in addition with different NaCl concentration (5, 10, 20 and 30 g/l). In general, the ionic strength is an important factor for the metal(loid) release but the composition of the water (e.g. the HCO_3^- content) may superimpose this effect. Therefore, the concentrations of the metal(loid)s in the experiments with ultra-pure water spiked with sea salt or native river water and the ultra-pure water spiked with NaCl were significantly different. In a second experiment the influence of the environmental parameters and the interactions between the environmental parameters pH (4–10), sediment content (0 g–3.75 g), temperature (4 °C–36 °C) and ionic strength (0 g/l–30 g/l NaCl) on the release of metal(loid)s from the test material was examined. The statistical Design of Experiments (DoE) was used to study the influence of these factors as well as their interactions. All studied factors may impact the release of metal(loid)s from the test material to the eluent, whereas the release and the partitioning between sediment and eluate of metal(loid)s was impacted by interactions between the studied factors. The main processes were sorption, complexation, solubility, buffering and ion exchange. In addition, by separating the sediment from the slag after the experiments by magnetic separation, the enrichment of metal(loid)s in the sediment was visible. Thus, the sediment was the most important factor for the release of the metal(loid)s, via pH, temperature and ionic strength, because the sediment acted as a sink.

ZUSAMMENFASSUNG

Wasserbau und die dabei benötigten Wasserbaumaterialien sind essenziell um die Schiffbarkeit von Wasserstraßen zu erhalten. Da eine Vielzahl von natürlichen und künstlichen Materialien zum Einsatz kommt, werden diese weltweit auf die potenzielle Freisetzung von Schadstoffen untersucht. Dies geschieht um negative Effekte für die Umwelt zu vermeiden. Um die potenzielle Freisetzung abschätzen zu können, ist es wichtig, die Schlüsselmechanismen zu verstehen, welche für die Freisetzung von Schadstoffen entscheidend sind. Die potenzielle Freisetzung von Schadstoffen wird mit genormten Verfahren untersucht. Jedoch ist die Übereinstimmung zwischen den Bedingungen in genormten Versuchen und denen in der Umwelt meist sehr beschränkt, was die Aussagekraft unter Einsatzbedingungen betrifft, da genormte Versuche nicht die Aufgabe haben Umweltbedingungen abzubilden.

In Deutschland werden industrielle Nebenprodukte als Wasserbausteine eingesetzt. Speziell das Nebenprodukt Kupferschlacke wurde in den letzten 40 Jahren zum Bau von Ufersicherungen, Buhnen und zum Küstenschutz genutzt. Dieses Material ist einerseits für den Wasserbau gut geeignet, da es eine hohe Dichte besitzt und zusätzlich natürliche Ressourcen (Landschaftsschutz) geschont werden. Andererseits enthält dieses Material einen hohen Anteil an Metallen und Metalloiden (Metall(oid)en). Aufgrund dieser Merkmale wurde Kupferschlacke (Eisensilikatgestein) als Testmaterial ausgewählt. Als relevante Metall(oid)e wurden für die Studien As, Sb und Mo als Vertreter für die Hydr(oxid) bildenden Elemente gewählt und Cd, Co, Cu, Fe, Ni, Pb und Zn als Vertreter für die Elemente die Kationen bei der Freisetzung bilden.

Die Fragen welche im Zusammenhang mit der Freisetzung von gefährlichen Stoffen beantwortet werden sollen sind: (i) können Ergebnisse aus Laborexperimenten auf Einbaubedingungen übertragen werden, (ii) welche Entwicklungen sind für die Freisetzung

der Metall(oid)e über lange Zeiträume zu erwarten und (iii) wie beeinflussen die am Einsatzort herrschenden Umweltbedingungen die Freisetzung der Metall(oid)e aus dem Material?

Zur Beantwortung der ersten Frage wurde die oberflächenabhängige Freisetzung der Metall(oid)e untersucht. Hierfür wurden Auslaugexperimente mit verschiedenen Korngrößen und einem konstanten Wasser/Feststoff-Verhältnis durchgeführt. Im nächsten Schritt wurden verschiedenen Methoden zur Bestimmung der spezifischen Oberfläche für Wasserbausteine mit dem 3D Laser Scan als Referenzmethode verglichen. Im letzten Schritt war es möglich die Ergebnisse der Oberflächenmessung von Proben welche für Laborversuche geeignet sind (Korngröße 0–5 mm), gemessen mittels Gasabsorption, mit den Ergebnissen für Wasserbausteine, gemessen mittels Aluminiumfolie-Methode, über einen Rauhigkeitsfaktor zu verbinden. Auf Grundlage dieser Berechnungen zur spezifischen Oberfläche war es möglich die Berechnungen für die Freisetzung von Metall(oid)en unter Einbaubedingungen deutlich zu verbessern.

Zur Beantwortung der zweiten Frage wurden Langzeitexperimente mit Diffuse Gradient in Thin films (DGT) über einen Zeitraum von sechs Monaten durchgeführt. DGT ist eine *in situ* Passivsammlermethode für Metall(oid)e in Wasser, Sedimenten und Böden. In diesen Fall wurde DGT als Senke für Metall(oid)e im Eluat eingesetzt um Lösungsgleichgewichte zu unterbinden. Da diese Passivsammler einen Austausch des Eluenten, zur Störung des Lösungsgleichgewichtes, überflüssig machen, können Langzeiteffekte unter ungestörten Bedingungen betrachtet werden. Die Langzeitexperimente mit DGT ermöglichten somit (i) die Unterscheidung zwischen Verarmung der Materialoberfläche und Lösungsgleichgewichten und (ii) die Untersuchung von Sorptionsprozessen mit oder ohne weitere Freisetzung der Analyten. Für das Testmaterial bedeutete dies (i) die Kationen Cd, Co, Cu, Ni and Pb wurden über den gesamten Zeitraum von 6 Monaten aus der Kupferschlacke freigesetzt (hauptsächlich durch Sulfidverwitterung), (ii) eine Verarmung der Oberfläche konnte für Zn nachgewiesen werden und (iii) die Hydr(oxid) bildenden Elemente As, Mo und Sb wurden ebenfalls über den kompletten Zeitraum freigesetzt, wobei die Freisetzung durch die Sorption an Eisenoxidkolloiden, die während der Auslaugversuche gebildet wurden, maskiert wurde. Es konnte bestätigt werden, dass Sulfide die Hauptquelle für die Freisetzung von Cd, Cu, Ni, Pb und Mo über lange Zeiträume darstellen.

Zur Beantwortung der dritten Frage wurden Kurzzeitversuche unter für den Wasserbau relevanten Umweltbedingungen durchgeführt. Ein wichtiger Faktor speziell für den Wasserbau ist die Salinität. Somit wurde der Einfluss dieses Parameters in Auslaugexperimenten mit Meersalzlösung (30 g/l), Rheinwasser, Reinstwasser und zusätzlich mit verschiedenen NaCl-Konzentration (5, 10, 20 and 30 g/l) untersucht. Im Allgemeinen ist die Ionenstärke ein starker Einflussfaktor aber die Zusammensetzung des Wassers (z.B. HCO_3^- Gehalt) kann diesen Effekt überlagern. Demnach unterscheiden sich die Konzentrationen der Metall(oid)e in den Experimenten mit Meersalzlösung und Rheinwasser von denen mit verschiednen NaCl-Konzentrationen. Deswegen wurde in einem zweiten Experiment der Einfluss verschiedener Umweltparameter und ihr Zusammenspiel (pH (4–10), Sedimentgehalt (0 g–3.75 g), Temperatur (4 °C–36 °C) sowie Ionenstärke (0 g/l–30 g/l NaCl)) auf die Freisetzung der Metall(oid)e aus Wasserbaumaterialien untersucht. Dabei wurde die statistische Versuchsplanung (Design of Experiments, DoE) genutzt um den Einfluss der Faktoren und ihrer Interaktionen zu testen. Alle Faktoren zeigten einen mehr oder weniger starken Einfluss auf die Freisetzung der Metall(loid)e im Eluenten, wobei die Freisetzung und die Verteilung zwischen Eluat und Sediment von den Interaktionen zwischen den untersuchten Faktoren beeinflusst werden. Die Hauptprozesse sind Sorption, Komplexbildung, Löslichkeit, Pufferkapazität und Ionenaustauschprozesse. Zusätzlich wurden die Sedimente nach der Auslaugung mittels Magnetauftrennung von der Kupferschlacke getrennt und aufgeschlossen, um die Anreicherung der Metall(oid)e im Sediment zu bestimmen. Berücksichtigt man die Anreicherung im Sediment, so war das Sediment, im

Vergleich zu pH-Wert, Ionenstärke und Temperatur, der Faktor mit dem stärksten Einfluss auf die Freisetzung der Metall(oid)e. Wobei die Freisetzung der Metall(oid)e aus dem Testmaterial durch das Vorhandensein des Sedimentes, welches als Senke fungierte, deutlich erhöht wurde.

1. GENERAL INTRODUCTION

1.1 CONSTRUCTION MATERIALS IN HYDRAULIC ENGINEERING

Since the Middle Ages hydraulic engineering of rivers and coastal areas is practiced in Germany [1]. Related to an increase ship transport in the 16th century the construction measures increased to avoid accidents, to enable the passage of larger ships and to protect the embankments from an increasing hydraulic impact. Today the waterways in Germany comprise about 7 350 km of inland waterways and 18 000 km² of coastal waterways underlining the necessity for hydraulic engineering to enable the navigability of waterways [2]. Before the 19th century as construction materials wood, natural stones, clay and sand were used. After the 19th century the metal industry boomed, which leads to new construction materials. Therefore, slags (industrial by-product of metal industry) were applied in hydraulic engineering [1, 3]**.** The materials which are most commonly used today for constructions in hydraulic engineering are concrete, steal, geosynthetics, armour stones, joggle joint mortars and wood. In recent years construction materials in hydraulic engineering (as a simplification, in this thesis are also named as water construction materials) came stronger into academic and administrative focus. On the one hand, the European Water Framework Directive requires that all ground water and surface water should be of a good chemical and biological status [4]. On the other hand, natural resources (e.g., landscape) should be protected [5]. Therefore, industrial by-products which are used as aggregates for concretes or as armour stones should be studied in detail to avoid negative effects on the aquatic environment [6-9]. In the period from 1970 to 2000, approximately 12 mio. t of copper slags have been applied for hydraulic and coastal engineering purpose [10]. From 2000 until today, the application increased to approximately 20 mio. t in Germany [11]. The copper slags were used because of their high density and the high stability. The industrial by-products contain high amounts of metal(loid)s which might be released into the aquatic environment [10, 12].

1.2 COPPER SLAG

Copper slag is a by-product of copper production and world-wide more than 20 million tonnes per year were generated [13]. Hence, different options of management exist, e.g., recycling, recovery of metals, production of construction materials.

The chemical composition of copper slags varies with the types of furnace or process of treatment [14]. If the main chemical composition is different between the slags, also the mineralogy composition is different [14]. Each facility produces slags which have their own constitution as exemplarily shown in Table 1.

Table 1: Chemical composition of copper slags from different productions measured by X-ray fluorescence.

producer		Nkana smelter [15]	Lupin-Glogow copper mine region [16]	Aurubis [12]
repetition		n = 2	n = 1	n = 4
SiO_2	%	38 ± 1	40	30 ± 1
Al_2O_3	%	6.1 ± 0.1	15	4.3 ± 0.8
Fe_2O_3	%	8.6 ± 0.2	-	-
FeO	%	24 ± 1	-	-
Fe_{total}^{*}	%	-	7.9	60 ± 1
MgO	%	2.6 ± 0.1	2.8	1.0 ± 0.5
CaO	%	11 ± 1	25	1.0 ± 0.5
S_{total}	%	0.7 ± 0.1	1.2	0.3 ± 0.1

*species analysed Fe_2O_3

In Germany approximately 700 000 – 800 000 tonnes of copper slag are produced annually [11, 17, 18] and the main application is hydraulic engineering. Therefore, copper slag is an appropriate material to study the environmental impact of construction materials in water ways.

The main composition (10–100 wt.%) of the German copper slags are quite constant (Table 1). The slag is produced with Flash Smelting and Slag Cleaning Furnaces [11]. In Flash Smelting the concentrate, sand, oxygen and air are heated. Therefore, the sulphide minerals react rapidly with the oxygen. This results in (i) controlled oxidation of the concentrates Fe and S, (ii) a large evolution of heat and (iii) the melting of the solids [19]. The products of this process are molten Cu-matte, molten iron-silicate slag and hot dust-laden off-gas (Equation 1).

$$CuFeS_2 + 3O_2 + SiO_2 \rightarrow Cu + FeO_2 \cdot SiO_2 + 2SO_2 \qquad (1)$$

Due to this, the slag is dominated by molten oxides containing small amounts of sulphides. With the slag cleaning furnace the copper and sulphide concentration is decreased. The molten slag is cooled down slowly in large cast iron pots and a high-grade crystalline stone is produced.

However, many minor components (1–10 wt.%) and trace components (< 1 wt.%) of the concentrate are enriched in the slag and the concentration of metal(loid)s is usually higher than in natural stones. This has been reported for different copper slags worldwide (Table 2 [20-22]). Therefore, information regarding the release of metal(loid)s, total content and mineral composition are available [13, 23-25].

Table 2: Mean values of metal concentrations of two construction materials in hydraulic engineering determined by X-ray fluorescence analyses (Δx = 95% confidence interval).

	copper slag (n = 6) [12]		basaltic rocks (n = 7) [26]	
mg/kg	x	Δx	x	Δx
barium	503	92	711	176
chromium	398	731	283	160
cobalt	283	78	46	7
copper	6 842	1 552	44	11
nickel	172	34	200	126
strontium	143	59	826	109
vanadium	57	17	188	24
zinc	17 733	1 964	109	8

The main and minor constituents that form the mineral phases are fayalite, oxides, glasses and sulphides. These minerals and glasses influence the release of the metal(loid)s to a large extend. Studies financed by the producer have already shown that copper is bound mainly as sulphides. Due to this, the release to water is probable [12]; whereas chrome is bound in spinels and the release to water is very improbable. These predictions for the release are not possible for all metal(loid)s because, as examples, zinc is present in all mineral phases and for arsenic the mass content is to low for the determination by means of X-ray microanalysis.

One crucial point regarding copper slag is its high Fe(II) content. It is likely that Fe(II) released into the water phase is quickly oxidised to Fe(III), which forms iron (hydr)oxides. Other elements may be co-precipitated due to the formation of iron (hydr)oxide colloids [19] in leaching experiments and the environment.

1.3 BEHAVIOUR OF RELEVANT METAL(LOID)S FROM COPPER SLAG IN THE AQUATIC ENVIRONMENT

There are a lot of studies about the environmental behaviour of metal(loid)s in the aquatic environment. This knowledge can be taken into account to consider the environmental behaviour of the construction materials. Hence, the environmental behaviour of metal(loid)s which are relevant for copper slag (As, Cd, Cu, Ni, Pb, Sb and Zn) will be given in a short summary.

Antimony

The content of antimony in copper slag is between 0.008 and 0.065 wt.%. The major binding forms are sulphides [12].

The two common inorganic forms in natural waters are $Sb(OH)_6^-$ and $Sb(OH)_3$ [27]. The mobility of antimony in the environment is influenced by the pH value. Generally, the mobility is low for neutral pH value and increase for pH <2.7 and pH >8.3. It is not clear if antimony form any chloride-containing species in water [27].

Arsenic

Arsenic is a trace component in copper slag (0.10–0.57 wt.%). The primarily binding forms are sulphide minerals and glasses, minor binding forms are chromite, magnetite and olivine [12].

The concentration of arsenic in the environment is influenced strongly by the pH value and increase with decreasing pH-values [28]. The common inorganic forms in natural waters are H_3AsO_3, $H_2AsO_4^-$ and $HAsO_4^{2-}$ [29]. The main factor that governs the mobility of arsenic in the environment is the sorption to (hydr)oxides, especially to iron (hydr)oxides [30].

Cadmium

Cadmium is present only in trace amounts in olivine and sulphide minerals in copper slag (e.g. in ZnS [12]).

However, cadmium is a very mobile element, with a high complexation potential. In freshwater $CdCO_3$ and Cd^{2+} are predominant and in seawater $CdCl_2$ and $CdCl^+$ [29]. The solubility increases with decreasing pH [31].

Copper

The amount of copper in copper slag is 0.523–0.948 wt.%. Copper is part of the remaining melt, hence metallic copper and sulphides are formed during precipitation [12]. Therefore the leaching from copper slag is very likely.

The mobility of copper in the environment is influenced strongly by the pH value. As an overall statement, the mobility of copper is high below pH 5.5 and low above pH 6 [29]. The concentration in the aquatic environment is controlled by adsorption and the leaching of sulphides, phosphates, hydroxides and carbonates [32], whereas sorption to clay minerals, Fe-and Al-hydroxides and organic particles is the main process at low pH values. After a minimum at pH 6 the concentrations increase due to organic complexation for higher pH values. In surface waters Cu(II) are predominant. Complexes are formed with hydroxide ions, carbonate, chloride and sulphate [29].

Lead

Copper slag contains between 0.22 and 0.87 wt.% of lead. Mineral phases are olivine, magnetite, glasses and sulphides. The distribution to the mineral phase depends on the cooling conditions of the slag [12]. Hence a wide range of available fractions may occur.

In the aqueous phase free Pb^{2+} und hydroxo complexes are predominant occurring. The concentration is controlled by sorption (e.g., to clay or carbonates). Therefore, in surface waters most of the lead is bound to colloidal fractions [29].

Nickel

The content of nickel in copper slag is 0.016–0.019 wt.%. Due to the ionic radius (Ni(II) 0,78 Å, Fe(II) 0,76 Å, Mg(II) 0,65 Å) a storage at Fe- minerals is likely. Therefore a low availability is expected [12].

In the aqueous phase free Ni^{2+} and complexes are predominant. The availability of Ni increases with decreases pH. In addition, Ni trends to precipitate with Fe- and Mn-oxides [29].

Zinc

The amount of zinc in copper slag is 1.5–2.1 wt.%. Mineral phases are olivine, oxides, glasses and sulphides [12].

In surface waters most of the zinc is bound to colloids. The predominant species in surface water is Zn^{2+} for pH values lower than 7. For higher pH values hydroxides are formed [29]. The sorption and desorption of zinc depends on the pH value, whereas low pH values increase desorption.

1.4 DIRECTIVES FOR CONSTRUCTION MATERIALS IN HYDRAULIC ENGINEERING

EU Member States should aim to achieve good chemical and biological status in all bodies of surface water and groundwater by 2015 (EU-WRRL). Hence, the European Committee for Standardisation developed new testing framework recommendations for construction materials [33]. For these recommendations different technical reports were prepared. In the Technical Guidance No. 28 [34] principal components and the main routes for the transport of pollutants into surface waters were identified (Fig. 1).

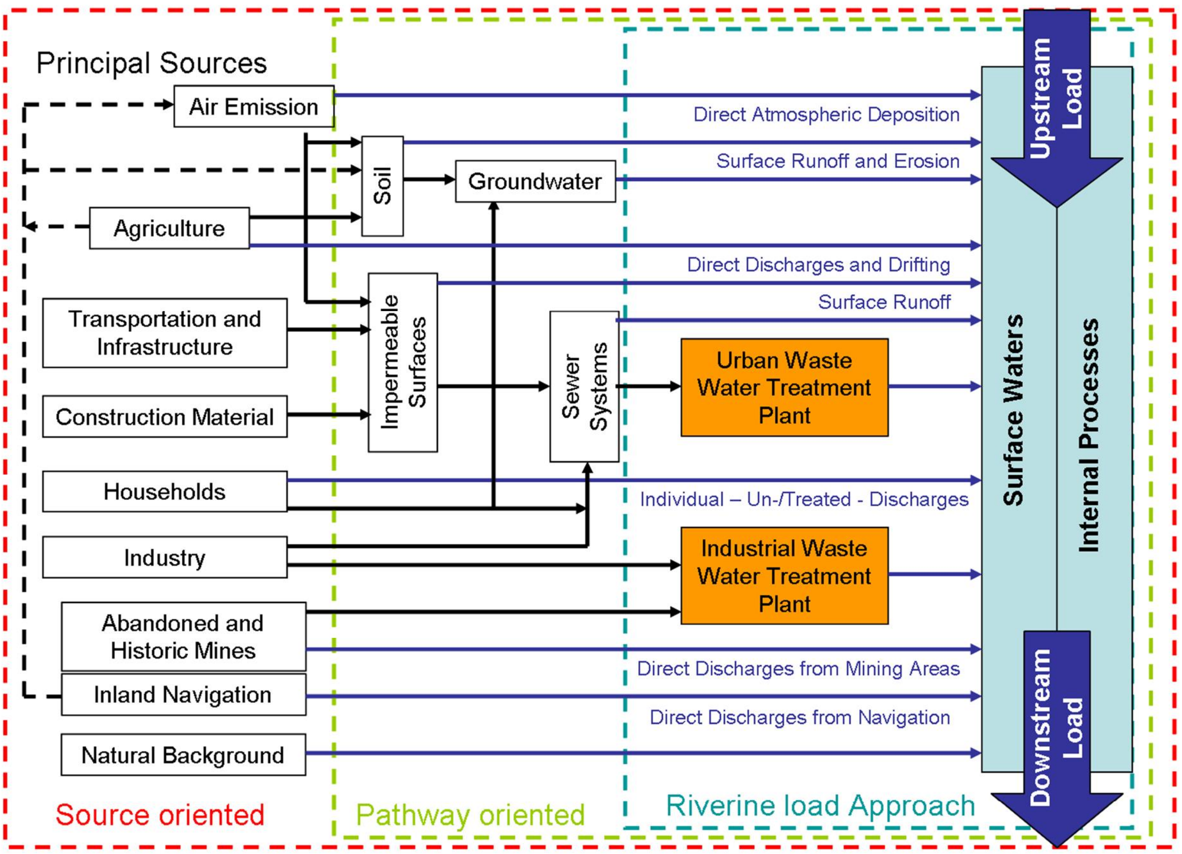

Figure 1: Sources and pathways of substances which may be released to surface water (blue arrows = direct input routes, black arrows = other transport) [34].

Construction materials were listed as a principle source. However, construction materials in hydraulic engineering are not detailed in this part. They are listed as a source in the part inland navigation (Fig. 1). Accordingly, construction materials are tested worldwide by different methods to estimate the potential release of pollutants, whereas for construction materials in hydraulic engineering the TLW [35] and the DIN EN 13383 [36] are the only specifications in Germany. These directives are not connected to any regulative values in surface water.

Neither binding forms nor environmental conditions are taking into account in these directives. However, they are important factors for the release of substances into the environment [37]. Hence, the modification in testing conditions may be evaluated separately for each product and its intended use [38-40], if clarification of mechanisms is a task. In order to be able to evaluate whether an industrial by-product used as construction material in inland navigation is a source of pollutants and to understand release mechanisms, the release of pollutants can be studied under typical environmental conditions of surface water bodies.

1.5 LEACHING TESTS

As described before the total bulk material content of metal(loid)s (Table 2) is not a robust indicator to predict the release of the metal(loid)s from construction materials. Therefore, leaching tests are necessary [41]. Mechanisms which control the release are (i) the release potential, (ii) solubility of an analyte, (iii) mass transfer and (iv) chemical speciation [42].

Worldwide a large number of standardised leaching tests can be identified (e.g., [43-48]), because not all relevant aspects of leaching behaviour can be addressed by one test method. In addition, the leaching of metal(loid)s from construction materials under environmental conditions is very complex and influenced by many factors, e.g. pH, redox potential, liquid-to-solid ratio, contact time and biological activity.

Leaching tests can be subdivided into categories under different points of view [42]: (i) the technical point of view with equilibrium conditions at the end of the test (static) or with dynamic conditions, (ii) the selection of the material (monolithic material vs. granular material) and (iii) the questions addressed, e.g., characterisation of the material or compliance of standards [49].

The European Committee for Standardisation (CEN) developed new testing framework recommendations with two categories: (i) column test and (ii) dynamic surface leaching test (DSLT) [33]. Batch tests are typically performed as static tests while dynamic conditions were performed with column tests (continuous flow) or diffusion tests (exchange of the eluent). The column test is used if a liquid is percolated though the material (e.g., road fill). These conditions are rare in hydraulic engineering (e.g., sand filters), therefore the test is not further addressed here. The dynamic surface leaching test/diffusion test is used for monolithic materials and will be performed as long-term test. The test of monolithic material is very place and time consuming due to the large amounts of eluent, but the test is important due surface wash-off and long-term release effects that can be studied with it. To avoid solution equilibriums in the eluate, an exchange of solution after different time steps is necessary. These exchanges cause an abrupt change of the physico-chemical conditions of the eluate.

Most of the release mechanisms are surface area depending processes, therefore the measurement of the surface area is an important factor. In regulatory guidelines different methods for the measurement are described, e.g., print paper method, cutting geometric forms, aluminium foil method [46, 50, 51].

Batch tests are performed with crushed or granulated material. In most cases this test is a short-term test. These tests are not space and time consuming and therefore allow to conduct different tests with varying parameters, e.g., shaking *vs.* non-shaking, particle size and liquid to solid ratio. However, these parameters have an impact on the release of metal(loid)s which counteracts the comparability of different materials or different tests. Furthermore, the equilibrium between the concentration of the metal(loid)s in the liquid and solid are from interest and often it is not possible to decide if the concentration is influenced by dynamic equilibrium.

A significant gap is that the release of metal(loid)s from crushed materials are not comparable with results from monolithic materials. If a surface depending release for metal(loid)s can be confirmed, it should be possible to compare these results via the surface area exposed in the experiments. Then, results from batch experiments with crushed material can be used to calculate the release on a construction/river basin scale.

1.6 DIFFUSIVE GRADIENT IN THIN FILMS - DGT

Long-term leaching experiments have the disadvantage that a water renewal is needed to prevent solution equilibriums. In this step the chemical conditions within the solution is abruptly changed and the formation of colloids or sorption processes cannot be studied. By adding Diffusive Gradient in Thin films (DGT) devices into the batch systems a slow depletion of the metal(loid)s in the solution takes place. Hence, the solution equilibrium may be prevented and constant chemical conditions can be achieved.

During the last 18 years DGT has been used for dynamic speciation measurements in water [52-54], soils [55-57] and sediments [58-60] and hundreds of scientific articles have been published on the development and applications of this technique [61]. It has been used for bioavailability and toxicity studies [59, 62] as well as detailed studies to quantify labile organic and inorganic trace metal species [63]. The diversity in applications implies that DGT is a useful tool for researchers from varying disciplines. In addition DGT, as an *in situ* method, has the advantage to minimise changes in speciation and it is simple to use and comparably inexpensive [61].

The DGT sampling devices contain a binding layer and a diffusion layer protected by a membrane filter (Fig. 2) [64]. They are deployed in the solutions and only the filter is directly exposed to the liquid. The metal(loid)s diffuse from the solution through the filter membrane and the diffusion gel to the binding layer, where they are accumulated (Fig. 2).

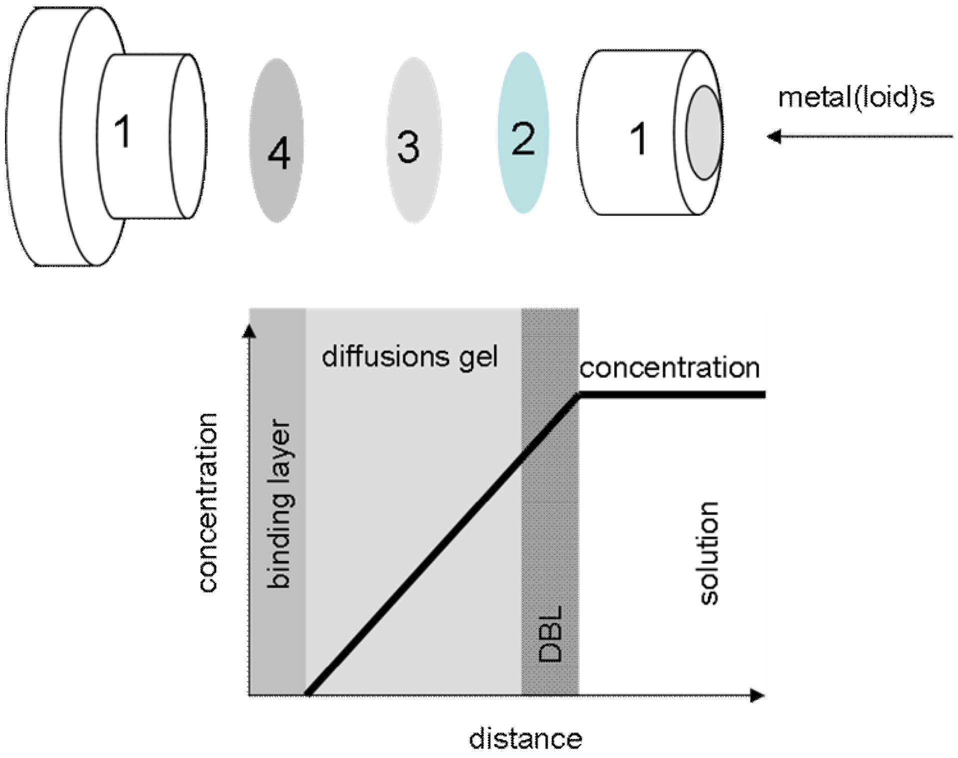

Figure 2: Design and function of DGT (1 = sampling device, 2 = filter membrane, 3 = diffusion gel, 4 = resin gel and DBL = diffusive boundary layer).

For different elements, several binding layers are available. First the technique was characterised for Ni, Zn, Mn, Fe, Cu and Cd using the chelating material Chelex as binding layer [65]. Later the Chelex binding layer was tested for 55 elements, and was found to be suitable for 24 elements [66]. With the modification of the binding layer the DGT was used for other elements. The ferrihydrite binding layer was in the beginning used for labile anionic phosphate [52] and then also for inorganic As [67], V, W, Mo, U and Sb [68-70]. In addition, several other binding layers were tested within the last years, like a mixed binding layer of Chelex and ferrihydrite [71], titanium dioxide [72], metsorb and mercapto-silica [73] and activated carbon [74].

After completion of the experiments, the accumulated metal(loid)s can be eluted from the binding layer. The DGT theoretical background includes the following calculations. The flux (J) of an ion through the gel is based on Fick's law of diffusion (Equation 2):

$$J = D\frac{dc}{dx} \qquad (2)$$

where D is the diffusion coefficient and $\frac{dc}{dx}$ *is the concentration gradient.*

By the help of Fick's first law of diffusion (Equation 2) and the assumption that (i) the diffusion coefficient of ions in the diffusion gel is equal to water, (ii) the free ions reach rapidly the equilibrium with the binding agent, and (iii) the solution is well-stirred, Equation 3 can be used to calculate the flux of ions [75]:

$$J = \frac{D \cdot c}{\Delta g} \qquad (3)$$

where Δg is defined as the thickness of the diffusion gel disc, D is the diffusion coefficient of the Diffusion layer and c the concentration of the metal(loid)s in solution [65].

The diffusion coefficient is different for each element and diffusion layer. If the diffusion coefficient for the element and binding layer is described in literature, the values can be used for the calculation. Otherwise the diffusion coefficient can be determined with a diffusion cell.

To compare this diffusion coefficient with values from literature in most cases a temperature correction is necessary, because the temperature has an influence on the diffusion coefficient. Temperature correction is achieved by the Stokes-Einstein equation (Equation 4) [75]:

$$\log D = \frac{1.37023(T-25) + 8.36 \cdot 10^{-4}(T-25)^2}{109+T} + \log\frac{D_{25}(273+T)}{298} \qquad (4)$$

where D is the diffusion coefficient, T is the temperature and D_{25} *is the diffusion coefficient at 25 °C.*

In this study only the accumulated mass in the binding layer was taken into account. DGT was used as a sink and the flux was not from interest. The mass (M) of the binding layer can be calculated by means of Equation 5 [65]:

$$M = \frac{c_e(V_g + V_e)}{f_e} \qquad (5)$$

where c_e *is the measured concentration,* V_g *the Volume of the solution,* V_e *represents the volume of the binding layer and* f_e *the elution factor for the binding layer.*

One important point for the application in leaching experiments is the accumulation capacity of the binding layers, because high amounts of ions can be released from the material and an exchange of ions takes place if the accumulation capacity is reached. The accumulation capacity can be calculate with Equation 6:

$$\sum \mathrm{X}(\frac{1}{z})_{\max} = V_{Chelex} \cdot c(\frac{1}{z})_{Chelex} \qquad (6)$$

where the Chelex discs have a thickness of 0.04 cm and a diameter of 2.5 cm and therefore a volume (V_{Chelex}*) of 0.196 ml and the maximum equivalent concentration of the Chelex gel (*$c(\frac{1}{z})_{Chelex}$ *) is 0.40 meq/ml.*

When the accumulated analyte is near to the maximum capacity of the binding layer, the accumulated analytes are released back to solution and therefore the binding layer is no longer an infinite sink [76]. The ratio of release and accumulation depends on the binding strength of the binding layer. In case of a binding layer loaded with Chelex 100 and taking into account the metal(loid)s which are enriched in copper slag, the release follows the selectivity Cu > Pb = Ni > Co = Cd = Zn > Mn [77] after the accumulation capacity is reached.

1.7 DESIGN OF EXPERIMENTS

As described before, the end use of construction materials is important and a lot of factors may influence the release and the fate of metal(loid)s. In most cases factors are tested step by step to determine the effect. A lot of factors interact with each other, which is not taken into account by step by step tests. To consider all aspects Design of Experiments (DoE) was applied which is a statistical method to study the influence of factors and their interactions. Therefore, the influence of the end use of construction material can be determined.

The DoE, also called experimental design was developed in the 1920's and is a statistical method for test series planning and evaluation [78]. First DoE was applied in the context of agriculture examinations, thereafter for military-, for industry- and for optimisation of chemical processes [79, 80]. Since 1990's it has become one of the most popular statistical techniques and was applied among different fields [81-85]. The main applications of DoE are (i) discovering interactions among factors, (ii) factor screening, (iii) establishing and maintaining quality control, (iv) optimising a process, including evolutionary operations (EVOP) and (v) designing robust products [79].

The fundamental principles of DoE are (i) randomisation, (ii) replication, (iii) blocking (iv) orthogonality and (v) factorial experimentation [79]. Randomisation is a method that protects against an unknown bias that may distort the results of the experiment. Replication is a method enhancing the precision of the experiment because it increases the signal-to-noise ratio when the noise originates from uncontrollable nuisance variables. Orthogonality in an experiment results in the factor effects being uncorrelated and therefore more easily interpreted. The factors in an orthogonal experiment design are varied independently from each other.

The first steps in the DoE are (i) state the objective and the hypothesis, (ii) determine the response variables, (iii) address the factors that might affect the variables and (iv) the levels of the factors [79]. The first three steps are displayed in Fig. 3.

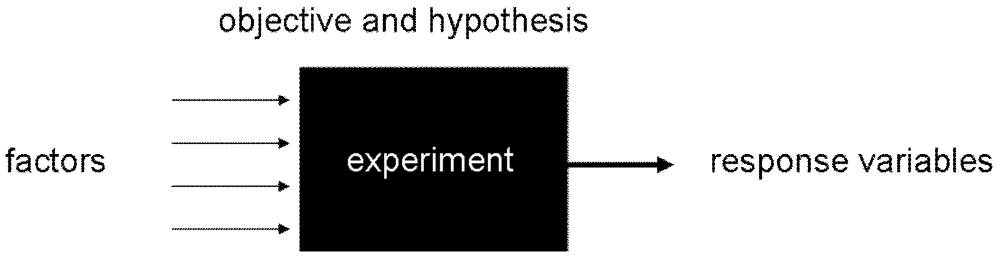

Figure 3: Scheme of a process/system with the first steps for DoE.

The levels of the factors are important to choose the design. A design with two levels, so-called two level full factorial design is a standard technique, where all factors are tested on a high and a low level. In addition, three level full factorial designs and many factorial designs with two or/and three levels exist [86]. Most of the environmental parameters are non-linear and the definition of levels is important for the results achieved with DoE. Fig. 4 shows the choice of different levels for a theoretical pH-depending concentration of cations described by van der Sloot [37].

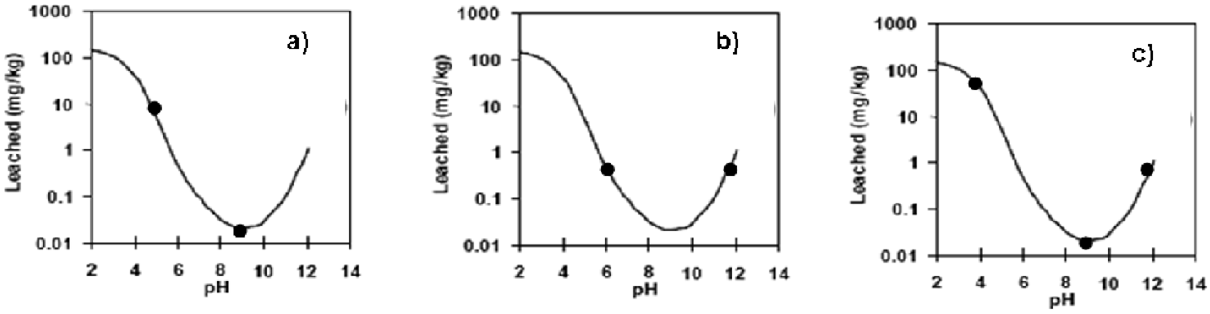

Figure 4: Theoretical pH-depending release of cations with different levels, whereas a) and b) have an upper and lower level while c) shows also a middle level.

For a) the choice of levels results in a large difference between the concentration of the metal(loid), whereas for b) no effect will be detectable. In this case also three level designs can be performed (see Fig. 4 c).

The choice between full or fractional design is influenced by the number of factors or the maximum of experiments which can be performed. If four or less factors were studied the full factor design is the method of choice, because the advantages are the orthogonality and no loss of information, but if more factors are studied a lot of experiments have to be pursued. If five or more factors are studied the factorial design is useful to reduce the number of experiments. If more factors are tested, less information is lost [78].

After intense planning of the design, the design is generated by the software (e.g., JMP, Minitab, STATISTICA) and the experiments can be performed. Following the performance, the results should be analysed and evaluated.

First the effects of the factors and interactions were calculated. These effects describe the differences between the levels whereas Equation 7 calculate the main effects and Equation 8 the interactions [87]:

$$E(A) = \overline{Y}_{A+} - \overline{Y}_{A-} \tag{7}$$

$$E(AB) = \frac{1}{2}((\overline{Y}_{A+} - \overline{Y}_{A-})_{B+} - (\overline{Y}_{A+} - \overline{Y}_{A-})_{B-}) \tag{8}$$

where E(A) is the main effect of factor A, E(AB) is the effect of the interaction between A and B, $\overline{Y}$ *is the average of the high level (index A+) and the low level (index A-) while* $(\overline{Y}_{A+} - \overline{Y}_{A-})_{B+}$ *and* $(\overline{Y}_{A+} - \overline{Y}_{A-})_{B-}$ *represent the differences between the averages (upper and lower) of factor A considering the upper level of B (index B+) or the lower level of B (index B-), respectively.*

The effects are used for the multiple linear regressions with main factors and interactions. In multiple linear regression, a model attempts to describe the relationship between independent variables [81]. Equation 9 shows the formula for multiple-linear regression with two and three way interactions:

$$Y = \beta_0 + \sum_{i=1}^{n} \beta_i x_i + \sum_{i=1}^{n}\sum_{j=2}^{n} \beta_{ij} x_i x_j + \sum_{i=1}^{n}\sum_{j=2}^{n}\sum_{k=3}^{n} \beta_{ij} x_i x_j x_k + \varepsilon \tag{9}$$

where β_0 *is the offset term,* β_i *is the main effect term,* β_{ij} *is the two way interaction effect term,* β_{ijk} *is the three way interaction effect term, n is the number of the patterns,* x_i*,* x_j *and* x_k *are the coded independent variables and ε is the random error [88].*

However, all terms of the regression model have to be evaluated, to see if they are significant in comparison to the signal to noise ratio. The evaluation can be performed by an Analysis of Variance (ANOVA [79]). The parameter estimates and the ANOVA table are based on the assumption that the residuals are normally distributed, independence of model errors and equal variances. The ANOVA tests the null hypothesis, the population means of each level are equal, versus they are not all equal. The sum of squares can be used to estimate the effect of a factor. A distinction is made between the Total Sum of Squares (TSS), the Sum of Squares between Groups (SSB) and the Sum of Squares within Groups (SSW), where TSS is the sum of SSB and SSW.

To evaluate the impact of the factors the mean of squares (MS) should be considered. Therefore, the SSB will be studied in relation to the Degrees of Freedom (DF). With this information the calculation of the F-Value (Fischer variance ratio) can be performed (Equation 10):

$$F = \frac{MS_i}{MS_E} \tag{10}$$

where MS_i is the mean square of the effect and MS_E is the mean square of the error [89].

The F-test compares two variances and returns the probability (p-value) that these are not significantly different, whereas p is 0.05 in most cases [90]. The greater the F-value is from unity, the more certain is that the estimated factor effects are real [91].

The validation of the model can be performed with the goodness of fit (R^2). The R^2 described the amount of the variation of the response explained by the model.

1.8 OBJECTIVES

The overall objective of this study was to elucidate the release of metal(loid)s from construction material in hydraulic engineering. Therefore, three questions were addressed to study the environmental impact of the construction materials:

1. Can we transfer the results from batch experiments to construction scenarios/field conditions?
2. Which long-term trends exist for the release of metal(loid)s?
3. How relevant environmental conditions influence the leaching of metal(loid)s from construction material in hydraulic engineering?

The first question will be addressed in ***Chapter 2***. Therefore, the surface area depending release was studied in batch experiments. The specific surface areas of small particle sizes, used in batch leaching experiments, were compared and connected to the specific surface areas of armour stones. In addition, the comparison of different methods for the measurement of specific surface areas for armour stones was developed. Furthermore, the influence of salinity was studied to judge whether the end use of construction material in hydraulic engineering (streams or coast) has a significant effect on the release of metal(loid)s.

To answer the second question long-term leaching experiments became necessary. The aim of ***Chapter 3*** was to check whether long-term leaching experiments without water renewal are practicable, if DGTs are used. The main aim was to assess the capability of the DGT method to identify metal(loid) release mechanisms which cannot be found with other long-term leaching experiments. In addition, relevant mineral phases for the release were identified.

The influence of environmental conditions and therefore the end use of the material were considered in ***Chapter 4***. DoE was applied to investigate the influence of pH, salinity, temperature and sorption to a sediment as well as the interactions between these factors for the release of metal(loid)s.

1.9 THESIS OUTLINES

Release of metal(loid)s from construction material in hydraulic engineering in dependence on ionic strength, particle size and specific surface area.

Chapter 2 addresses the influence of ionic strength and particle size to the release of metal(loid)s from construction material in hydraulic engineering. Furthermore, measurements of the specific surface area were performed to connect results from small stones with results obtained from armour stones via a roughness factor.

Long-term release of metal(loid)s from construction material studied with DGT.

Chapter 3 describes the studies about the advantages of diffuse gradients in thin films used in long-term leaching experiments. The release of metals and metalloids was studied over a time period of 184 days without water renewal.

Release of metal(loid)s from construction material in hydraulic engineering in dependence from environmental parameters important for rivers and streams.

In Chapter 4 the influence of the environmental parameters pH, sediment content, temperature and ionic strength on the release of metal(loid)s from a construction material in hydraulic engineering was addressed. Statistical Design of Experiments (DoE) was used to study the influence of these factors and their interactions.

Final conclusions.

Chapter 5 summarises the most important findings of chapter 2 to 4, draws final conclusions on the release of metal(loid)s from construction materials in hydraulic engineering and outlines further research needs.

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2. LEACHING OF METAL(LOID)S FROM A CONSTRUCTION MATERIAL: INFLUENCE OF THE PARTICLE SIZE, SPECIFIC SURFACE AREA AND IONIC STRENGTH

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Abstract

Construction materials are tested worldwide for a potential release of dangerous substances to prevent adverse effects on humans and biota. It is crucial to identify and understand the processes which are decisive for the release of hazardous substances. The current study compares the results of different test methods. Taking copper slag as model material, the influence of material particle size, eluant composition and ionic strength was tested. Ionic strength and salinity significantly influenced the release of metal(loid)s in the water phase. Furthermore, it was elucidated that colloids can cause methodological artefacts. The available specific surface area exhibited a positive correlation with the release of hazardous substances. The specific surface areas of materials were determined by the Brunauer, Emmett and Teller model (BET) and four other methods. The aluminium foil method showed the best results with regard to the statistical uncertainty, compared to a 3D laser scanning method. With help of the roughness factor λ it is possible to compare the results from surface area measurements with different material particle sizes (0–250 mm). This comparability offers the potential to match the release of metal(loid)s from laboratory studies with field applications and catchment area calculations/modelling, based on the release per m^2.

2.1 INTRODUCTION

A variety of laboratory systems are known worldwide to elucidate the release of hazardous substances from construction materials. As an example, in Europe three types of leaching test systems can be distinguished: (i) percolation tests (e.g. [1, 2]), (ii) tank tests (e.g. [3, 4]) and (iii) shaking tests with or without adjusted pH-values (e.g. [5, 6]). Due to different input quantities (e.g. the eluant or the tested particle/stone size), the comparability of leaching results from different materials and by different test systems is limited. However, as previously pointed out by van der Sloot et al. [7], a so far underestimated point is that the combination of different leaching tests provides crucial information on the release mechanisms of certain elements (e.g. Cr, Cu or Zn). Recycled materials from various industrial processes are used, e.g. for road-, landfill- or water construction. For instance, copper slags, commercially distributed as iron silicate stones, are by-products of the industrial copper production. For 1 tonnes of copper, about 2.2 tonnes of slag material is thereby produced [8]. In Germany approximately 0.8 million tonnes of copper slag are produced per year [9] and approximately 20 million tonnes have already been used in water construction during the last 40 years in the northern part of Germany [9,10]. The copper slags are mainly used in hydraulic and coastal engineering, e.g. for groyne construction, embankments or coastal protection. The main mineral phases of the studied material are fayalite, oxides, glasses and sulphides.

Table 1: Mean values of metal(loid) concentrations of two water construction materials determined by X-ray fluorescence analyses (Δx = 95% confidence interval).

	copper slag (n = 6) [8]		basaltic rocks (n = 7) [9]	
mg/kg	x	Δx	x	Δx
barium	503	92	711	176
chromium	398	731	283	160
cobalt	283	78	46	7
copper	6 842	1 552	44	11
nickel	172	34	200	126
strontium	143	59	826	109
vanadium	57	17	188	24
zinc	17 733	1 964	109	8

Furthermore, copper slags contain high quantities of metal(loid)s, frequently exceeding those observed in natural stones (Table 1). As for the application in water construction the (i) pH, (ii) ionic strength as well as (iii) the size fraction of a construction material are relevant parameters for the metal(loid) release. The pH may range from 6 in freshwater to 9 in saline water and the ionic strength may differ from a few mmol/l (river water) up to approximately 800 mmol/l in saline environments. Indicated by some studies, the release of metal(loid)s from water construction materials may be increased significantly from ultra pure water to river water and sea water [13–15]. The particle sizes of the test materials have a major impact on the release of inorganic analytes in leaching experiments (e.g. [7, 16, 17]). This is due to (i) different surface to mass ratios, (ii) "fresh" surfaces after sample preparation, e.g. from crushing or milling, (iii) different distances over which a metal(loid) needs to travel from the centre of the particle to the water phase and (iv) variations in the release vs. sorption and precipitation/co-precipitation balances. In several directives (e.g. Toxic Characteristic Leach Procedure TCLP, Nederland Norm NEN 7383) the particle size of the materials are fixed according to the specifications of the standard for the leaching test (e.g. 0–9.5 mm [18]). However, it is very likely that even within such quite narrow particle size distributions the release of metal(loid)s will differ significantly depending on the proportion and the dominance of certain sub size fractions. Rather than on the total content, the releasing potential of a construction material for metal(loid)s depends on its mineral phase pattern. Chromium, for instance, is bound in copper slags as chromate, and hence the release of dissolved Cr fractions in laboratory experiments is very unlikely [11]. In contrast, a high amount of other analytes exists as sulphide microspots, which in turn are very prone to rapid weathering under aqueous environmental conditions. A specific property of the German copper slags is their high iron content in form of Fe(II). Since it is likely that Fe(II) released into the water phase is quickly oxidised to Fe(III), other elements may be co-precipitated due to the formation of iron (hydr)oxide colloids. As, Sb and Mo were chosen as representatives for (hydr)oxide forming elements (forming primarily anions and neutral species in water). Cd, Co, Cu, Fe, Ni, Pb and Zn are studied as representatives for elements forming cations during the release. The objective of this study was to investigate the influence of the tested particle sizes, the specific surface area and the ionic strength on the release of metal(oid)s from the model material copper slag. In order to include the surface area as basic evaluation criteria for the release of hazardous substances, five different methods to measure the surface area are compared in this study. One method is used for size fractions <5 mm (physical gas sorption) and four methods (geometrical methods) are used for stones and rocks >10 mm. The results of the physical gas sorption method measurements include the roughness of the particle surface. Whereas the geometrical methods are not suitable to include the roughness of the surface of the stones/rocks. By connecting the results from surface area measurements of size fractions <5 mm (physical gas sorption) with results from stones and rocks >10 mm (geometrical methods) via the roughness factor, it is possible to compare results from different leaching experiments and to extrapolate these results to field scenarios with, e.g. armour stones via the release per µg/m^2, on a reliable basis. Hence, this study provides information on how to further improve the connection between laboratory studies and balances/models for elements in materials in the environment.

2.2 MATERIALS AND METHODS

2.2.1 TEST MATERIAL PREPARATION

The copper slag armour stones were sampled at four different locations of the northern part of Germany (slag 1 = Elbe, slag 2 = Elbe, slag 3 = Weser and slag 4 = Elbe–Havel channel, see Table 2). The four slags are from the same production facility, but their storage time and the sampling locations are different. The basanite was donated by RPBL (Rheinische Provinzial-Basalt-und Lavawerke) and exploited at the facility Nickenich, Germany. Prior to the surface area analyses, the stones were cleaned with a soft brush and tap water and air-dried (size 40–120 mm). For BET measurements and leaching tests the stones were crushed to <5 mm by a jaw crusher (Chemisch Technisches Laboratorium Heinrich Hart GmbH). The materials then were sieved (5–4, 4–3.15, 3.15–2, 2–0.63, 0.63–0.2, 0.2–0.063 and 0.063–0 mm; Retsch, AS 200) and divided by a rotary divider (Fritsch, Laborette 27) into sub samples. The materials were characterised by X-ray fluorescence analysis (ED-XRF, Spectro Analytical Instrument GmbH, Spectro X-LAB).

Table 2: Mass concentration of selected metal(loid)s of the 4 examined copper slags and basanite measured by X-ray fluoresces analyses. The ± values display the confidence intervals (95%) according to n = 3 measurements.

	mass concentration [mg/kg]				
element	slag 1	slag 2	slag 3	slag 4	basanite
As	565 ± 25	611 ± 70	550 ± 174	590 ± 11	4 ± 3
Ba*	423 ± 11	597 ± 105	518 ± 39	697 ± 115	1 120 ± 196
Cd*	4.67 ± 1.69	16.4 ± 2.2	8 ± 2	6 ± 2	< 2
Co*	277 ± 63	194 ± 41	278 ± 84	< 100	< 100
Cr*	310 ± 94	138 ± 25	409 ± 55	202 ± 112	175 ± 56
Cu*	8 055 ± 3 646	4 917 ± 352	5 673 ± 3 202	3 859 ± 377	175 ± 77
Mo*	1340 ± 99	1195 ± 33	1 490 ± 282	2 138 ± 47	<3
Ni*	369 ± 36	< 20	218 ± 16	147 ± 15	95 ± 13
Pb*	3142 ± 59	2 673 ± 27	2 295 ± 355	2 130 ± 236	21 ± 46
Sb*	254 ± 86	580 ± 25	181 ± 24	190 ± 1	2
Sn*	775 ± 88	2 350 ± 114	730 ± 114	784 ± 1	3 ± 2
Sr*	88 ± 9	158 ± 4	171 ± 18	173 ± 15	795 ± 95
V*	53 ± 27	49 ± 12	31 ± 17	101 ± 16	402 ± 26
Zn*	15 040 ± 796	10 923 ± 915	8 563 ± 3 094	9 679 ± 691	84 ± 16

* significant different in concentration for the slags (t-test, p= 0.05)

2.2.2 SURFACE AREA MEASUREMENTS

The specific surface area of the crushed and sieved samples was determined by the method based on the Brunauer, Emmett and Teller theory (BET, Micromeritics, TriStar II 3020 V1.03) with multi point measurements and krypton as sorption gas. The method is described in detail in van Erp [19]. In DIN EN or CEN directives, the leaching rate of regulated dangerous substance for monolithic materials is used to investigate the potential environmental impact. To deliver a defined surface area of stones and rocks, a method is suggested in these directives which is based on cutting geometric forms, e.g. cylinder or square stones [5, 20].

The cutting of geometric forms from materials such as copper slags with a density >3 tonnes/m^3 is technically challenging and costly. Less time and money consuming alternatives are needed to test the materials as they are. In this study four methods to measure the surface area [m^2] were applied: the square method (used for geometric forms, e.g. moulded concrete), the print paper method (which is already practiced in some EU member states), an aluminium foil wrapping method developed in this study as well as the 3D laser scanning application (used, e.g. in archaeology [21]). All method details are reported in the SI. Since methods, based on the physical sorption of gases such as BET, tend to deliver results which are higher than measurements based on the particle/stone geometry (e.g. the aluminium foil wrapping method) the external surface area (A_{ex} [m^2/g]) of spheres can be calculated by Equation 1 [22] with the diameter d [µm] and density ρ [g/cm^3].

$$A_{ex} = \frac{6}{\rho \cdot d} \qquad (1)$$

With this equation the calculation of a roughness factor λ from the external (A_{ex}) surface area, measured with geometric methods, and the physical surface area (A_{phy}), measured with BET, is possible [23].

$$\lambda = \frac{A_{phy}}{A_{ex}} \qquad (2)$$

By introducing the roughness factor λ the specific surface area of crushed materials (measured with BET) and stones/rocks (measured with geometric methods) can be compared [23] and a correction of the results from the geometric methods with the roughness factor is possible. Then the release of metal(loid)s related to the surface area can be compared for small particles and stones.

2.2.3 LEACHING TESTS

All chemicals were at least p.a. grade (pro analysis) and all vessels were rinsed prior to their use with 10% HNO_3 (AppliChem). The leaching tests performed in this study were based on DIN CEN/TS 14997. The pH was neither modified nor adjusted. The particle size was <5 mm, the liquid to solid ratio (L/S) was 10 and the leaching time 48 h. Each leaching test was replicated 6–10 times for each eluant and each particle size. Samples were filtered by nitrogen pressure filtration (0.45 µm, 8 µm, Sartorius) and immediately acidified to 1% HNO_3 (AppliChem). Total content analyses were performed by inductively coupled plasma with sector field mass spectrometry (ICP-SFMS, Element II, Thermo Fischer). The detection limits are shown in Table SI 1. Statistica 10 (Statsoft) was used for the statistical processing and evaluation of the data. The results of the release are preferably expressed in mg/kg or mg/m^2 for leaching tests. This way of presentation enables comparison for different L/S or liquid to surface area ratios (L/A) [7]. The characteristic of the interface between particles and solution is the crucial factor for the diffusion controlled transport of metal(loid)s within the aqueous solution [24]. This correlation can be displayed in a diagram [17] of the leaching velocity v (Equation 3) vs. the leaching rate J (Equation 4), whereby the slope is the leached concentration. Therefore the leaching rate is transformed into the area dependant release r (Equation 4) with c = concentration [µg/l], V = volume of eluant [l], A = surface area of the material [m^2] and t = time [s]. At high leaching velocities the leaching rate approaches the maximum and for low leaching velocities the concentration is limited by the saturation limit [17].

$$v = \frac{V}{A \cdot t} \qquad t = \text{const.} \qquad \text{here} \quad \frac{V}{A} \qquad (3)$$

$$J = \frac{c \cdot V}{A \cdot t} \qquad t = \text{const} \qquad r = \frac{c \cdot V}{A} \qquad (4)$$

The particle size effect in the release of metal(loid)s from different particle size fractions (5–2; 2–0.63; 0.63–0.2; 0.2–0.063 and <0.063 mm) is examined here in detail. The time and the L/S ratio are constant during the leaching tests, therefore the results are presented as the release (r) vs. L/A (V/A). The slope of the curve (r vs. V/A) represents the concentration of the metal(loid)s of the slag in the eluant after leaching. This kind of diagram allows the comparison of materials with different surface areas (particle sizes) where equal slopes indicate equal release mechanisms. Furthermore, the release and the leaching rate respectively, enable the comparison between different leaching tests.

To study a potential dependence of the leaching of metal(loid)s caused by different eluants the leaching tests were performed with (i) ultra-pure water (USF ELGA, Purelab Plus), (ii) filtered (nitrogen pressure filtration, 0.45 µm, Sartorius) river Rhine water (Koblenz, 590 km) and (iii) with ultra-pure water spiked with 30 g/l sea salt (Merk). The ionic strength experiments were performed with NaCl solutions (5, 10, 20 and 30 g/l, Merck). Sodium chloride was chosen since it is a major constituent of salt water and has no significant effect on the pH.

2.3 RESULTS AND DISCUSSION

2.3.1 TOTAL CONTENT ANALYSES OF THE MATERIAL

The major components (per definition 10–100 wt.%) of the tested copper slag material are Fe, Si and O (Table SI 2). The concentrations of the minor (per definition 1–10 wt.%) and trace components (per definition <1 wt.%) with the highest abundances of the four examined slags are presented in Table 2 together with the respective data for the natural material basanite which was used for comparison purposes in this study. Even though the examined slags were from the same production facility and the percentage of the main components is very similar (Table SI 2), significant differences were found for the mass concentrations of minor components (Table 2). Therefore, the distribution patterns of the minor slag components were not comparable (e.g. concentration of Cu in slag 1 is two times higher than in slag 4, while the Cd concentration of slag 3 is exceeded by factor two in slag 2). Furthermore, the elevated statistical variation is an indication for inhomogeneous distribution in the slags (e.g. Cu in slag 1: 8 055 ± 3 646 mg/kg). In the case of copper this high variability can be ascribed to a heterogeneous distribution of sulphide mineral micro spots on the slag surface [25]. This is the prevalent mineral phase to which copper is bond to in the slags [26].

High concentrations for most of the metal(loid)s were found compared to the basanite material which is also a common water construction material in Germany and the Netherlands. The highest excesses were detected for Cu, Mo, Pb, Zn and Sn.

However, according to the environmental impact of a material, the total content is less relevant and the leachable fraction is more important [8]. From a material chemical point of view the leachable fraction is dominated by the mineral phase composition of a material [27]. The mineral pattern is governed by the mineral formation sequence which is depending on, e.g. the cooling temperature (cooling speed) as well as on the total metal(oid) content of the hot slag [28]. Hence, even though the major component content suggests a homogenous composition of the material, the leaching behaviour of an industrial by-product may differ significantly, if the feed materials and the cooling conditions are not kept within narrow confines. However, on an industry scale this demand is often not realistic and hence it seems to be necessary that materials are tested in regular intervals, depending on the application and the industrial processes.

2.3.2 COMPARISON OF SURFACE AREA MEASUREMENTS WITH DIFFERENT METHODS

The specific surface area of a copper slag stone and a basanite stone calculated by the four different methods is shown in Table 3.

The mass of the slag stone (slag 1, mass = 1 756 g) and the basanite stone (mass = 1 581 g) is comparable, and hence the stones are suitable to investigate the influence of the porosity and the surface roughness.

Table 3: Specific surface areas of copper slags and basanite stones determined by four different methods (for methods see SI).

	slag 1			basanite		
method	specific surface area [m^2/g]	confidence interval (95%)	n	specific surface area [m^2/g]	confidence interval (95%)	n
3D laser scan	$2.24 \bullet 10^{-5}$ $2.15 \bullet 10^{-5}$	-	2	$2.72 \bullet 10^{-5}$	-	1
aluminium foil	$2.46 \bullet 10^{-5}$	$0.04 \bullet 10^{-5}$	8	$2.86 \bullet 10^{-5}$	$0.03 \bullet 10^{-5}$	8
print paper	$2.51 \bullet 10^{-5}$	$0.07 \bullet 10^{-5}$	8	$2.87 \bullet 10^{-5}$	$0.09 \bullet 10^{-5}$	8
square	$3.18 \bullet 10^{-5}$	$0.25 \bullet 10^{-5}$	8	$3.65 \bullet 10^{-5}$	$0.33 \bullet 10^{-5}$	8

First of all, the results of the different methods are within the same order of magnitude. It is shown that the most simple methods (compare SI) reveal the highest surface area results as well as the highest confidence intervals. The 3D laser scan method as a labour and cost intensive "high tech" method was used as a reference. The best "low tech" method for the studied materials is the aluminium foil method, with a divergence from the reference method of 0.26×10^{-5} m^2/g ($\pm 0.04 \times 10^{-5}$) for copper slag and 0.14×10^{-5} m^2/g ($\pm 0.04 \times 10^{-5}$) for the basanite. The print paper method also shows a good comparability, but with higher deviations. Taking into account the need for a quick, cheap, non-invasive and reliable method to determine the specific surface area of stones/rocks (e.g. CEN TC 351, TS-2), from the authors' perspective the aluminium foil method displays the best results among the tested low tech methods.

Table 4 shows the results of the BET measurements of the seven particle size fractions of the two in detail studied copper slags (slag 1 and 2) and of six particle size fractions of the basanite sample.

Table 4: Results of the BET measurements (n = 1).

grain size	Specific surface area [m²/g]				
	slag 1	slag 2	slag 3	slag 4	basanite
5–4 mm	0.0184	0.0693			0.5112[1]
4–3.15 mm	0.0173	0.0659			
3.15–2 mm	0.0196	0.0795			1.5532
5–2 mm	0.0184	0.0716	0.0221	0.0196	
2–0.63 mm	0.0400	0.1259			1.2908
0.63–0.2 mm	0.2287	0.2619			1.6475
0.2–0.063 mm	0.5184	0.5434	0.4043	0.2115	1.7070
<0.063 mm	0.8401	0.9592			2.0583

1) value for the particle size 5 – 3.15 mm

Because of the insignificant small differences between the specific surface areas of the size fraction of 5–4 mm, 4–3.15 mm and 3.15–2 mm the fractions from 5 to 2 mm are treated as one fraction in the following study (insufficient resolution of the method, including sieving and BET). Since the specific surface area measurements results differed statistically significantly for the 5–2 mm particle size fraction of slag 1 and 2 (t-test between 0.0184 ± 0.0012 and 0.0716 ± 0.0071, $\alpha = 0.05$ and $p = 0.0002$) in addition two other copper slags (slag 3 and 4) with two particle size fractions (5–2 mm and 2–0.063 mm) were examined to verify the results from slag 1 and 2. The fraction 5–2 mm was chosen as representative for the larger particles (limited BET cuvette capacity and influence of micro cracks, etc.) and the fraction 2–0.063 mm was chosen to be representative for the small particle sizes ("ideal" mass to surface ratio in BET measurements). Supported by these results it is shown that all the slags display overall comparable BET results. The exceptions, slag 2 (for 5–2 mm) and slag 4 (for 0.2–0.063 mm), can be ascribed to an insufficient separation of the three fractions by the sieving method (slag 4) and to a limited material capacity of the standard vessels in BET measurements with size fractions >2 mm, if no significant porous structure is given. The consequence is that BET measurements for nonporous materials have to be verified carefully even for particle sizes <2 mm due to methodological artefacts caused by sieving.

However, the overall results display a clear increase in the surface area of the slags with decreasing particle sizes <2 mm. This is due to the fact that there is no impact of the inner surface on the results and hence, a change in particle size directly affects the specific surface of the material [29]. For basanite only for the step between 5–3.15 mm and 3.15–2 mm a significant increase in surface area was detected.

Comparing the BET results of the basanite with those of the slags, the influence of the pore volume connectivity is visible by causing a significant increase of the available inner surface in the fraction <2 mm of the porous material by connecting micro pores in the small basanite fraction. However, even though the inner surface area of the slag is low the roughness factor λ is needed to connect the results from BET measurements (physical gas sorption) with the measurements from geometry based methods for bigger stones/rocks. The roughness of the slags is dominated by (i) material inherent microcracks, (ii) mineral phases and hence the cooling temperature as well as from (iii) physical forces from crushing the material [23]. Caused by this, λ is getting smaller with smaller particle sizes (Fig. SI 4). As an example, for naturally weathered silicates λ was between 20 and 200 [22].

In order to display the capability of the aluminium foil wrapping method the specific surface area of different stone sizes were determined exemplarily for copper slag 1 and the basanite sample (Fig. SI 5). By Equation 1 the external specific surface area was calculated. The external and the physical surface area are clearly different. Therefore, the values of λ were between 40 and 1000 for basanite, caused by the differences in the available inner surface of the different size fractions and between 15 and 150 for the slags. By connecting the results from the aluminium foil wrapping method with the BET measurements the biggest particle size fraction was used because the surface structure is similar to the surface structure of the stones. For the basanite and for copper slag λ is 780 and 30, respectively. As previously mentioned, via λ it is possible to correct the aluminium foil wrapping method measurements for the roughness, as displayed in Fig. 1. The coefficients of determination

(r^2) for basanite and copper slag are as high as 0.99. In contrast to the BET method all geometry based methods do not take the inner surface area into account. By correcting the results of the geometric methods via the roughness factor λ derived from the BET measurements, it is possible to connect results derived from particle size fractions of a few µm (used, e.g. in laboratory studies) to results from stones/rocks in a centimetre or even metre size range (from, e.g. field applications).

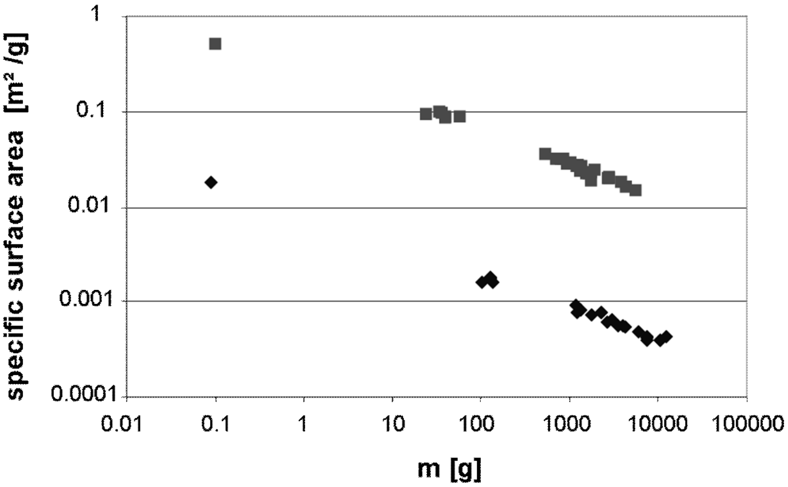

Figure 1: Specific surface area of small stones/stones/rocks vs. the mass determined by BET and the λ corrected aluminium foil method (square = basanite, rhombus = slag 1).

This has a potential to significantly increase the reliability of material cycle calculations/ modelling, e.g. at a catchment scale. Hence, the combination of the aluminium foil wrapping method with BET measurements offers the potential to directly link results from laboratory studies with field applications via the specific surface area.

2.3.3 INFLUENCE OF THE MATERIAL PARTICLE SIZE AND SPECIFIC SURFACE AREA TO THE METAL(LOID) RELEASE IN LEACHING TESTS

The results from the leaching of different particle sizes are shown in Fig. 2. The results for the other metal(loid)s are shown in Fig. SI 6. For slag 1 two different tendencies are shown in Fig. 2 and Fig. SI 6. The overall metal release increased with decreasing particle sizes (correlation coefficient r = −0.45 to −0.66). However, the aqueous concentrations of elements forming oxides tend to decrease with decreasing particle sizes (r = 0.04–0.94, slag

1). In contrast to slag 1, slag 2 shows an increase in the concentration for all analytes with decreasing particle sizes. For Pb, Cu and As the correlations are characterised by r = −0.65 to −0.94, while for Cd, Co, Ni and Sb a correlation coefficient of r = −0.47 to −0.72 was calculated. For Zn and Mo no significant correlation of the concentrations in the eluant with the examined particle sizes was detected.

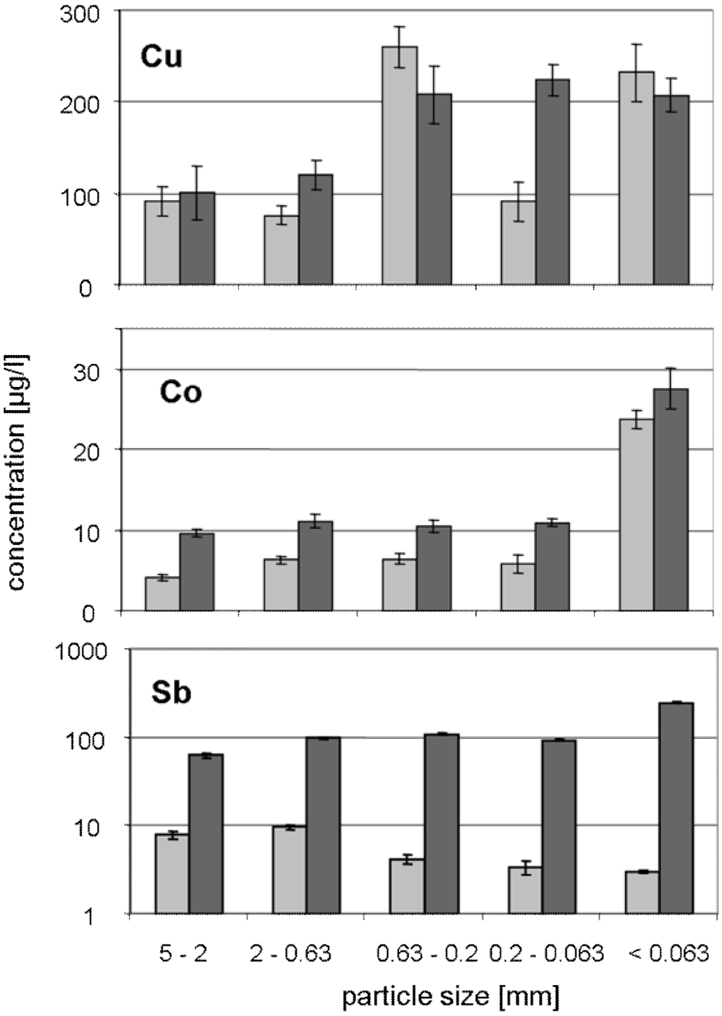

Figure 2: Concentration/release of selected metal(loid)s vs. different particle sizes (light grey = slag 1, dark grey = slag 2).

A general comparison based on the t-test between the metal(loid) concentration of the different particle sizes of slag 1 and 2 together, displays a significant difference between the fraction 5–2 mm and those <0.2 mm (Table SI 5).

Based on the release concentration patterns two groups of metal(loid)s were identified. The first group consists of the elements Cd, Co, Cu, Ni, Pb and Zn, showing a maximum concentration with the smallest particle sizes. The second group contains the elements that form hydr(oxi)des under oxygen-rich aquatic conditions (As, Mo and Sb). For this group, slag 2 shows a maximum release concentration for the particle size <0.063 mm which is comparable to the results of the other analytes and for slag 1 a maximum metal(loid) concentration was detected for the particle sizes >0.63 mm.

Considering the Fe(II) content of the tested slag and also the decreasing concentrations of the hydr(oxid)e forming elements As, Sb and Mo, the "loss" of oxide forming elements caused (i) by sorption and (ii) by formation of colloids is hypothesised. The formation of colloids was tested by filtration with 8 µm and 0.45 µm cut offs.

A significant formation of Fe, As and Pb containing colloids is proven by the results from Table SI 3 indicating that the oxidation of Fe(II) from the bulk material to Fe(III) in the media causes significant methodological artefacts for these elements. Thus, leaching studies on copper slags might underestimate the release of these elements being relevant also in terms of the EU Water Framework Directive (Pb, As). The release of selected metal(loid)s vs. the V/A (L/A ratio) is displayed in Fig. 3. The results of the other analytes are shown in Fig. SI 7.

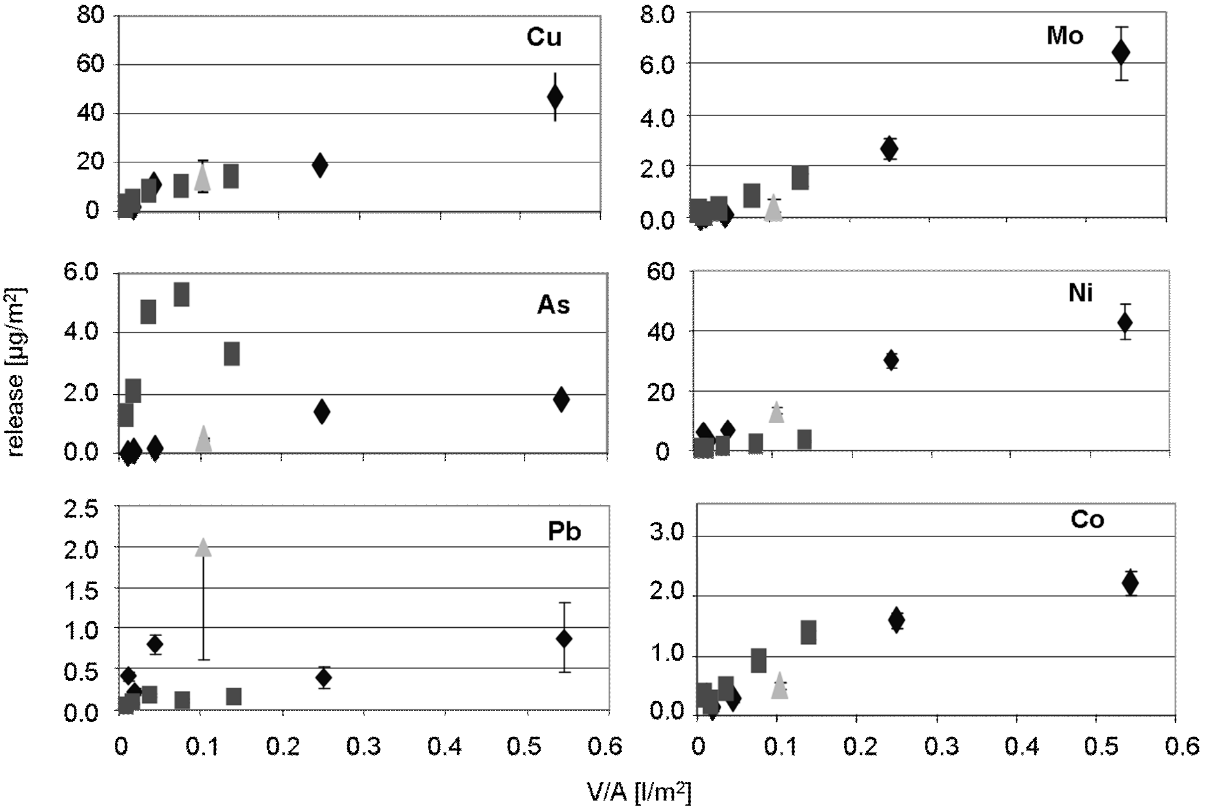

Figure 3: Release in µg/m² vs. V/A in l/m² calculated from the results of Table 4 by Equation 3 and 4 (square = slag 1, rhombus = slag 2, triangle = slag 1 mixed particle sizes (0 - 5 mm)).

The copper release is demonstrated in Fig. 3. It correlates well with Cd, Co, Mo, Ni and Zn. All elements except As, Sb and Pb correlate positively with the L/A ratio (r = 0.82–0.99). For As and Sb only for slag 1 a positive correlation between the release and the L/A ratio is given. For Pb no correlation with L/A was found. For Co, Ni, Cd and Sb the slopes decrease for high L/S and high concentrations because the release values approach to the maximum. The mixed sample (particle size 0–5 mm) matches well with the release of the sieved particle sizes of slag 1, except for Pb. The different slopes between slag 1 and 2 (except for As) are comparable with the differences in mass concentrations. Including the results of Fig. 3 and Fig. SI 7, for copper slags an overall particle size/specific surface area dependent release of metal(oid)s was measured. It can be explained by the high density and low porosity of the material. However, As, Sb and Mo who tend to form negatively charged species in the eluant, displayed additionally (i) a concentration dependent release (e.g. high bulk concentration = high release) and hence (ii) sorption (e.g. on the bulk material or colloid surface) as well as a (iii) precipitation (e.g. colloids) dependence (Fig. 2 and Fig. SI 6 for slag 1). The release curve of As (Fig. 3) is a good example for the benefit of the graphical description of the releases. Even though the mass concentrations of the two slags are very comparable, a different curve shape/release pattern appears. By the other analyte patterns it can be concluded that As is bound to different mineral phases (e.g. sulphides and glassy phase) in the two slags [11].

2.3.4 INFLUENCE OF ELUANT COMPOSITION AND IONIC STRENGTH TO THE METAL(LOID) RELEASE IN LEACHING TESTS

Leaching was performed with ultra-pure water, native water of the river Rhine and ultra-pure water spiked with 30 g/l sea salt. The results are shown in Table 5.

Table 5: pH of the eluant and concentration of the examined metal(loid)s [µg/l] of slag 1 extracted with three different types of water (n = 8, ± 95% confidence interval).

element	concentration [µg/l]		
	river Rhein water[1)]	Ultra pure water with sea salt	ultra pure water
As	5.89 ± 0.30	11.8 ± 5.1	8.29 ± 0.57
Cd	0.50 ± 0.09	3.14 ± 0.22	0.72 ± 0.05
Co	2.64 ± 0.18	3.59 ± 0.20	3.18 ± 1.00
Cu	133 ± 19	430 ± 108	18.0 ± 3.6
Mn	141 ± 11	1 025 ± 45	206 ± 59
Mo	45.2 ± 7.0	39.6 ± 10.0	158 ± 19
Ni	60.1 ± 5.3	161 ± 25	92.1 ± 27.6
Pb	12.2 ± 6.1	10.3 ± 4.2	2.34 ± 0.89
Sb	10.7 ± 1.3	9.63 ± 1.09	30.9 ± 3.2
Zn	27.1 ± 5.2	21.2 ± 6.0	16.7 ± 6.3

[1)] River Rhine water data was corrected on the initial analyte concentration of the native water sample.

The pH after leaching was 8.3 for river Rhine water and ultra-pure water spiked with 30 g/l sea salt and 7.9 for the ultra-pure water.

According to the extraction patterns of the metal(loid)s three groups can be distinguished. The analytes from the first group (As, Cd, Co, Cu and Ni) reveal a maximum release with ultra-pure water spiked with 30 g/l sea salt. The second group includes the elements Pb and Zn (r = 0.6). Pb and Zn revealed the highest concentration by leaching with native water from the river Rhine. The third group consists of Mo and Sb (r = 0.99), for which the highest concentrations were found by leaching with ultra-pure water. With the exception of Cd high variations between the different repetitions were found for all analytes. The results are an additional indicator of the impact of the eluant on the releasing balance. Since the pH values of the three eluants are very comparable (pH 7.9–8.4), the ionic strength and native river Rhine water components (e.g. dissolved organic carbon) govern the different release pattern of the three analyte groups. Hence, it is quite obvious that only for Mo and Sb a "worst case" estimation is possible by using ultra-pure water. For all other analytes a significantly higher release was found with ultra-pure water spiked with sea salt.

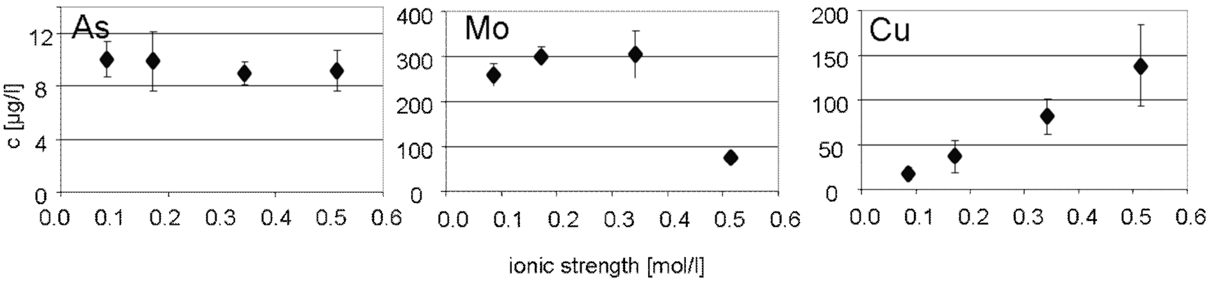

Figure 4: Concentration of As, Mo and Cu vs. the ionic strength (n = 11, 95% confidence interval).

Finally in Fig. SI 8 and Fig. 4 the results from the ionic strength dependent leaching experiments with NaCl from 5 g/l to 30 g/l are presented. The leaching patterns can be sorted again in three groups. The first group contains the elements As and Cd, for which no shift in concentration-dependence from the ionic strength was detected. The second group is formed by Mo and Sb, for which an increase in concentration up to 20 g/l NaCl was detected and for which a reduced release was found with 30 g/l. The third group contains the analytes Pb, Co, Cu, Ni and Zn for which a clear correlation in release with increasing ionic strength was shown (r = 0.54–0.81).

In summary, for the metals Pb, Co, Cu, Ni and Zn, the results shown in the Fig. 4 and Fig. SI 8 demonstrate a clear correlation between the released concentration and the ionic strength of the eluant. Hence, as an example, the release of copper might increase by a factor of 3 between fresh water and salt water environment. For the other analytes (As, Cd = no concentration shift and Mo, Sb = reduced concentration at 0.5 mol/l) it can be suspected that, as previously mentioned in Section 3.3, the formation of colloidal fractions is enhanced by counter ions from the media and the bulk material. This needs to be confirmed in future studies.

2.4 CONCLUSIONS

In general, the increased release caused by an increase in ionic strength is mainly caused by (i) exchange processes, (ii) complex formation and (iii) colloid formation. The ionic strength is an important factor but the composition of the water (e.g. the HCO_3^- – content) may superimpose this effect and therefore the concentrations of the metal(loid)s in the experiments with ultra-pure water spiked with sea salt or native river water and the ultra-pure water spiked with NaCl were significantly different. As an overall result the ionic strength is an important parameter for the release.

The results emphasise the need for a regulation accounting for the environmental conditions of the intended end use of a construction product and for accordingly adaptive test procedures. The application of a new method to determine the surface area of stones/rock was tested with the best results in comparison to the known/established methods. This method can be connected to BET based results when applying of a roughness factor. This connection offers the potential to directly link, via the specific surface area, results from laboratory studies with field applications. The specific surface area is an adequate tool to study the release of metal(oid)s from construction materials. The leaching test with different surface areas shows, that As is bound in different mineral phases in the examined slags. Methodological artefacts such as the formation of colloids in leaching experiments may cause misleading interpretations in studies on copper slags for the water frame directive relevant elements As and Pb. The leaching experiments emphasise the impact of the eluant composition on the metalloid release from construction materials, indicating an important influence of the ionic strength, if the intended end use is water construction.

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3. Determination of the long-term release of metal(loid)s from construction materials using DGTs

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Abstract

Long-term leaching experiments are crucial to estimate the potential release of dangerous substances from construction materials. The application of Diffuse Gradients in Thin film (DGT) in static-batch experiments was tested to study the long-term release of metal(loid)s from construction materials for hydraulic engineering, for half a year. Long-term release experiments are essential to improve calculations of the life-time release for this materials. DGTs in batch experiments were found to be a space and labour efficient application, which enabled (i) to study, in a non-invasive manner, the total release of nine metal(loid)s for half a year, (ii) to differentiate between release mechanisms and (iii) to study mechanisms which were contrary to the release or caused experimental artefacts in the batch experiments. For copper slag (test material) it was found that eight metal(loid)s were released over the whole time period of 184 d. Cu, Ni and Pb were found to be released, predominantly caused by (the) weathering of sulphide minerals. Only for Zn a surface depletion mechanism was identified. The results from the long-term batch experiments deliver new information on the release of metal(loid)s during the life cycle of construction materials with regard to river basin management objectives.

3.1 INTRODUCTION

Long-term leaching experiments are crucial to estimate the potential release of dangerous substances from construction materials [1]. Recently, the European Committee for Standardisation developed new testing framework recommendations for construction materials. These intend to evaluate the influence of intrinsic release parameters (e.g., the diffusion coefficient), to predict surface wash-off effects and to assess the long-term behaviour in the aquatic environment (e.g., mineral transformation [2]). However, the current long-term tank tests have certain limitations: (i) the maximum time scale is only 60 days, (ii) they are labour intensive and need a relative large work space and (iii) they are based on the exchange of the eluent. The renewal of the eluent includes an unaffordable abrupt change of the experimental conditions and of the accompanying parameters. If the eluent is not replaced, the total release potential of metal(loid)s might be underestimated [3]. This is, due to the formation of solution equilibriums between aqueous and solid phase. Since it is known that under submerged conditions certain construction materials release continuously significant quantities of pollutants over time, it is urgent to estimate the total release potential of priority pollutants (e.g., Cd) into the surface water. To facilitate calculations on the release during their life cycle in water construction, time scales of half a year or longer need to be investigated [4].

To enable constant experimental conditions, Diffuse Gradients in Thin films (DGTs) were applied to elucidate the release of metal(loid)s from construction materials. DGT is an in situ method developed for the measurement of metal(loid)s in water, sediments and soils [5]. In principle, the metal(loid)s diffuse from a solution through a diffusion layer to a binding layer, where they are accumulated, which prevent the establishment of solution equilibriums of metal(loid)s during the long-term experiments. The DGT technique has already been used to elaborate the behaviour of trace elements in a variety of environmental matrices [5–7].

Worldwide, construction materials are used in rivers and streams for river bank reinforcement to maintain the desired shipping and transportation conditions as well as to protect the shores and the surrounding land. As a simplification, in this study construction materials for hydraulic engineering are named as water construction materials. For instance, several million tonnes of copper slags (CUS) have already been applied in Germany as water construction material [8]. In this study, CUS (product name: ironsilicate stone) was used as a model material to elucidate the release of metal(loid)s into the water phase. The main mineral phases are fayalite, oxides, glasses and sulphides [9]. A specific property of CUS is their elevated Fe(II) content. Fe(II) is likely to be released into the surrounding water phase. After oxidation to Fe(III), further elements may be co-precipitated or absorbed due to the formation of iron (hydr)oxide colloids. The colloid formation in leaching experiments may cause misleading interpretations of eluent analyses. In addition to the high Fe(II) content, CUS contains significant quantities of metal(loid)s, exceeding significantly the total content of natural stones [9].

In addition to the release of the metal(loid)s, leaching experiments enable to investigate release mechanisms. In this study As, Sb and Mo were chosen as representatives for (hydr)oxide forming elements, while Cd, Co, Cu, Ni, Pb and Zn are studied as representatives for elements that form cationic species after the release into the water phase. Fe was included to study potential colloid formation during the leaching experiments. Since Mn is not bound as sulphide, it was measured in the sulphide leaching experiments. The aim of this study was (i) to test the applicability of DGTs in long-term batch experiments to quantify the release of metal(loid)s from construction materials for at least half a year, (ii) to assess the capability of this method to identify significant metal(loid) release mechanisms and to (iii) transfer the results of the experiments to an exemplary field emission scenario for the tested model material. The over all goal was to improve life-cycle predictions of water construction materials.

3.2 METHODS

3.2.1 TEST MATERIAL AND LEACHING EXPERIMENTS

CUS stones were sampled close to the city of Wedel at the river Elbe (Germany). The stones were crushed (<5 mm) by a jaw crusher (Chemisch Technisches Laboratorium Heinrich Hart, Germany) and divided into sub-samples of 25 g using a rotary divider (Laborette 27, Fritsch, Germany). The specific surface area of the sub-samples was determined by the method of the Brunauer, Emmett and Teller theory (TriStar II 3020 V1.03, Micromeritics, Germany) as described elsewhere [10].

Static leaching batch experiments were used without adjusting the pH of the eluent. The experimental setup is shown in Fig. SI 1. Three different experiments were carried out for leaching periods between 48 h and 184 d (Table SI 1): (i) without DGT, (ii) with $\mathrm{DGT}_{\mathrm{Chelex}}$ (DGT with a Chelex 100 binding layer for cations) and (iii) with $\mathrm{DGT}_{\mathrm{Fe\text{-}oxide}}$ (DGT with a Fe-oxide binding layer for anions). All experiments were performed in triplicate. Additionally, one blank sample was added in each series (Fig. SI 1). The slag sub-samples (0–5 mm, 25 g) were leached with 0.25 l (liquid/solid ratio 10:1) of ultra pure water (Purelab Plus, USF ELGA, Germany) and stored in the dark with an average temperature of 22.9 ± 0.8 °C. After different leaching periods the experiments were sacrificed and the eluent was filtered (nitrogen pressure filtration, 0.45 µm and 8 µm cut-off cellulose nitrate membrane filters, Sartorius, Germany). In total, 156 batch experiments were carried out. The difference in concentration of metal(loid)s in the eluent between 0.45 µm and 8 µm cut-off were used as an indicator for the colloid formation. Therefore, the concentrations of the analytes after the filtration with 8 µm were only used for the results of the colloid formation. All samples were immediately acidified by adding HNO_3 to a percentage of 1% (subboiled, dst-1000, savillex, USA).

The metal(loid) concentrations were quantified by means of Inductively Coupled Plasma-Quadrupole Mass Spectrometry (ICP–QMS, Agilent 7700 series ICP–MS, Agilent technologies, Japan) and Inductively Coupled Plasma – Optical Emission Spectrometry (ICP–OES, JY 238 Ultratrace, Horiba Jobin Yvon, Germany). Limits of detection are listed in Table SI 2. Statistica 10 (Statsoft, Germany) was used for the statistical processing and evaluation of the data. All chemicals were per analysis grade or higher quality. Furthermore, all vessels were rinsed prior to use with 10% or 1% HNO_3.

3.2.2 DGT MEASUREMENTS

DGT units were purchased from DGT Research Inc. (UK). Detailed information is available in the Supporting Information (page A13). The DGT units were fixed on the bottom of the bottles with a mounting tape (3 M, Scotch, USA). After the leaching periods, the DGT units were thoroughly washed with ultra-pure water. The diffusion layer and the filter membrane (0.45 µm, Sartorius, Germany) were peeled off and the binding layer was placed in a cleaned 15 ml polypropylene tube (VWR, Germany). A 2 ml aliquot of 1 M HNO_3 was added to the tube to extract the metal(loid)s from the binding layer. After an extraction period of 24 h the concentrations of the metal(loid)s within the extraction solution were measured by ICP–QMS/OES. The analyte mass (M) can be calculated with Equation 1 [6].

$$M = \frac{C_e(V_g + V_e)}{f_e} \qquad (1)$$

Ce: measured extraction concentration [µg/l], V_g: volume of the extraction solution [l]. V_e: volume of the binding layer [l]; f_e: elution factor.

Several binding layers are available for a variety of elements. While many of the cationic metal ions (e.g., Cu, Zn) accumulate onto the Chelex layers, the anionic and neutral species of As, Sb and Mo do not bind. However, the anionic species show high affinities to Fe-oxide layers [11–13]. Therefore, the metalloids accumulated in Fe-oxide binding layers. Due to the diffusion through the diffusion layer, the accumulation of the metal(loid)s is slow and the physicochemical conditions of the eluent do not change abruptly in the course of the experiments.

3.2.3 ELUTION FACTORS FOR FE-OXIDE BINDING LAYERS

The elution factors for the extraction with 1 ml 1 M HNO_3 of the Chelex binding layer were already reported by Zhang [14]. Preliminary experiments indicated that significant Cu and Pb quantities are also present in the Fe-oxide binding layers (data not shown). However, neither the accumulation of Cu and Pb in Fe-oxide binding layers nor the respective elution factors are reported in literature. Therefore, in this study the elution factors for the accumulated metal(loid)s were determined empirically by application of two methods. In the first approach, the elution factors were determined by loading the binding layers with a known mass of metal(loid)s [15]. For that, three Fe-oxide binding layers were placed in 10 ml of standard solution (SI page A12) and shaken for 24 h. Subsequently, the Fe-oxide gel was extracted with 2 ml of 1 M HNO_3 for 24 h. In a second experiment 6 DGT units with a Fe-oxide binding layer were placed in a solution of the respective metal(loid)s prepared from CUS (SI page A12) and shaken for 72 h. Since the properties (especially the speciation characteristics) of a CUS solution can not be simulated by an artificially prepared mixture of metal(loid)s, the CUS solution was used to determine the elution factors. After 72 h the Fe-oxide gel was extracted with 2 ml of 1 M HNO_3 for 24 h. The extraction of the binding layer was repeated until all measured concentrations of the metal(loid)s in the extract were below the limit of detection (Table SI 2). Detailed information about the CUS solution as well as the calculations are given in the Supporting Information (page A13 and Table SI 3).

3.2.4 SULPHIDE LEACHING

As displayed in the results, different metal(loid)s from CUS were found to be most likely released from sulphide minerals over a long period. No extraction method is available to exclusively leach sulphides [16]. As a compromise, the sulphide phases were extracted with a mixture of H_2O_2 and HNO_3. H_2O_2 is an oxidising agent which dissolves the sulphide phases with enhanced selectivity, while the purpose of the HNO_3 was to improve the H_2O_2 efficiency. Unfortunately, HNO_3 also attacks other minerals to a certain extent [16]. To compare the results after the experiments for the unintended leaching of silicates, the CUS was also extracted in parallel experiments with HNO_3 only. HNO_3 is normally used to extract metal(loid)s from oxides, therefore in experiments without H_2O_2 the elements which were bound as oxides were released in higher extend [17].

The sulphide extraction experiment was carried out using a rack with 50 ml syringes (Terumo, Belgium), the housings of the syringes were used as mini columns. The CUS was sieved (4–5 mm, AS 200, Retsch, Germany) and divided by a rotary divider into sub samples of 25 g and filled into the mini columns. The two different eluents – (i) 20 ml 0.1 M HNO_3 + 20 ml ultra-pure water (eluent 1, three replicates) and (ii) 20 ml 0.1 M HNO_3 + 20 ml 30% H_2O_2 (eluent 2, three replicates) – were added over a time period of four days. The eluent was exchanged daily. After extraction, the eluent was filtered (0.45 µm syringe filter, Satorius, Germany) and acidified to 1% HNO_3. While the metal(loid) concentrations were measured by ICP-QMS/OES, the sulphate concentration was determined photometrically using a cuvette test (barium chloride [18], LCK153 and DR 5000, Hach Lange, Germany).

3.3 RESULTS AND DISCUSSION

3.3.1 DETERMINATION OF ELUTION FACTORS AND BINDING STRENGTH OF CU AND PB

Two different binding layers (Chelex and Fe-oxides) were used to examine the leaching behaviour of different elements. According to their accumulation characteristics, it was possible to distinguish three groups of analytes: (i) As, Sb and Mo were bound to the Fe-oxide binding layers, (ii) the metals Zn, Cd, Co and Ni were accumulated in the Chelex binding layers, whereas (iii) Pb and Cu were detected in both binding layers. The elution factors for the Fe-oxide binding layer are shown in Table 1. The pH (not adjusted) in all experiments was 6.8 ± 0.1 (Table SI 4).

Table 1: Elution factors (f_e, n = 6) for elution with 1 M HNO_3 determined for Fe-oxide binding layer by application of two different methods and compared with fe from the literature.

f_e (methode)	Cu	As	Mo	Sb	Pb
f_e (step-wise)	0.89 ± 0.01	0.73 ± 0.05	0.73 ± 0.04	0.86 ± 0.03	0.90 ± 0.02
f_e (by Zhang [15])	0.91 ± 0.01	0.75 ± 0.07	0.75 ± 0.03	0.82 ± 0.08	0.88 ± 0.03
f_e (from Lit. [13])		0.78 ± 0.05		0.85 ± 0.03	

The elution factors (recovery) for $DGT_{Fe\text{-}oxide}$ differed between the elements: For Cu and Pb a relative recovery of approximately 90% was calculated, while for Sb 85% and for Mo and As 75%, were found respectively. Since the results of the two methods conducted are comparable to each other and to the elution factors given in the literature [13], it can be concluded that the elution factor is neither affected by the speciation of the metal(loid)s nor by the competition between the different elements (Table 1).

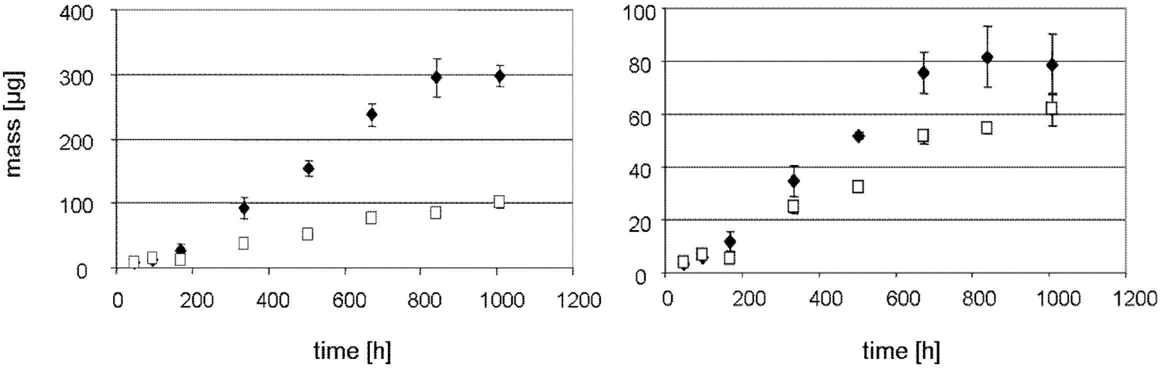

Figure 1: Mass of Cu and Pb accumulated in the Chelex (diamonds) and the Fe-oxide binding layer (squares) vs. time.

After six month, the Cu accumulated on the Chelex binding layer was three times higher than that found in the Fe-oxide binding layer. Therefore Fe-oxide is not an infinite sink. In case of Pb, the masses determined in the Fe-oxide binding layers after longer time periods (>350 h) were only slightly lower than in the Chelex binding layers.

3.3.2 COLLOID FORMATION

The filtration with the 0.45 µm and the 8 µm cut-off displayed statistically significant differences (t-test, α = 0.05) for the concentration of Fe in all three setups (with $\mathrm{DGT}_{\mathrm{Chelex}}$, $\mathrm{DGT}_{\mathrm{Fe\text{-}oxide}}$ and without DGT), without significant differences between the experiments with or without DGT. The concentration of As, Mo and Sb showed only significant differences in certain experiments. The measured concentrations are shown in Fig. 2 and SI 2. For the other metals, the concentrations of 0.45 and 8 µm filtered samples were not significantly different.

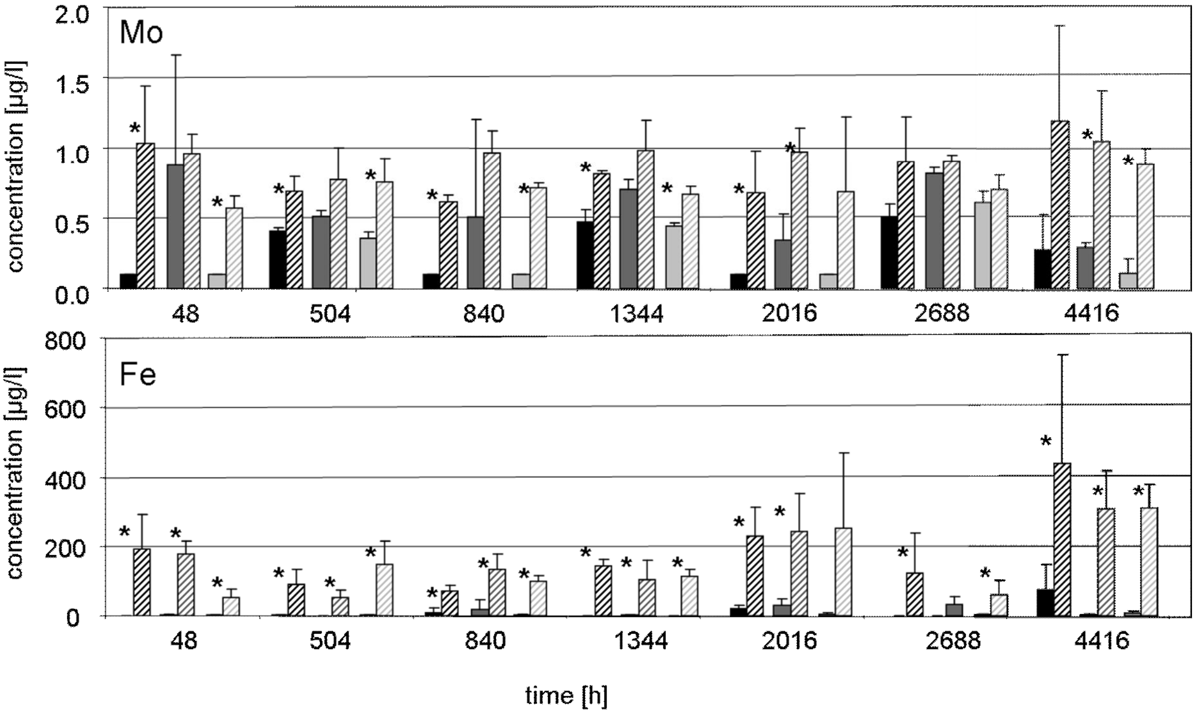

Figure 2: Concentration of metal(loid)s in the eluent measured after filtration with different pore sizes (plain = 0.45 µm and striped = 8 µm) for leaching experiments (CUS) without DGT (black), with $\mathrm{DGT}_{\mathrm{Chelex}}$ (dark grey) and $\mathrm{DGT}_{\mathrm{Fe\text{-}oxide}}$ (light grey). * significant differences (t-test, Ŭ = 0.05).

The significant difference in Fe concentrations between the two cut-offs are a clear evidence that there was not a suppression of colloid formation by the DGTs. A possible explanation might be that the colloid formation took place on or close to the surface of the CUS and that oxidation and precipitation occur very rapidly within a few minutes [19].

For Mo the differences in the filtration experiments were more pronounced than for As and Sb. The lowest cut off/filtration effect was observed in the DGT_{Chelex} experiments, which can be explained either by the formation of molybdate complexes, built between Mo and cations (like Cu, Pb and Ca [20–22]) or by a higher absorption of cations to the Fe-colloids resulting in higher amounts of Mo in the solution [23]. It can be assumed that the significantly lower concentrations of cations in the solutions of the DGT_{Chelex} experiments prevented the precipitation of Mo.

3.3.3 LONG-TERM LEACHING WITHOUT DGT

Fig. 3 displays changes in the release of the metal(loid)s by plotting the mass in solution vs. time and the mass released per area vs. time on a double-log scale. The specific surface area of the CUS ($0.096\ m^2/g$) was used to calculate the release of the metal(loid)s in $\mu g/m^2$ for the experiments with and without DGT.

Except As, Mo and Sb, the mass of metal(loid) plotted vs. time exhibited a positive correlation ($r > 0.60$), suggesting a continuous release. As and Sb showed a negative correlation ($r < -0.74$), since the mass decreased within the first 48 h, while for Mo no correlation was obtained at all (Fig. 3). In most cases, the mass of Fe was below limit of detection (Fig. 2, filtration with 0.45 µm cut off). As mentioned in the previous paragraph, this is probably due to the formation of Fe colloids and/or of molybdates with a low solubility. The slope of the log release/log time plot indicates different leaching processes [24]. Detailed information about leaching processes identified (e.g., dissolution and diffusion) are given in the Supporting Information (page A15).

After 672 h the slope for Cu decreased from 0.45 ± 0.03 to zero. For Ni and As over the whole experimental period the slope was 0.48 ± 0.01 and -0.31 ± 0.03, respectively. Except for Sb (slope: -0.45 ± 0.04), the slope of all other elements was positive and varied between 0 and 0.23 (Fig. 3).

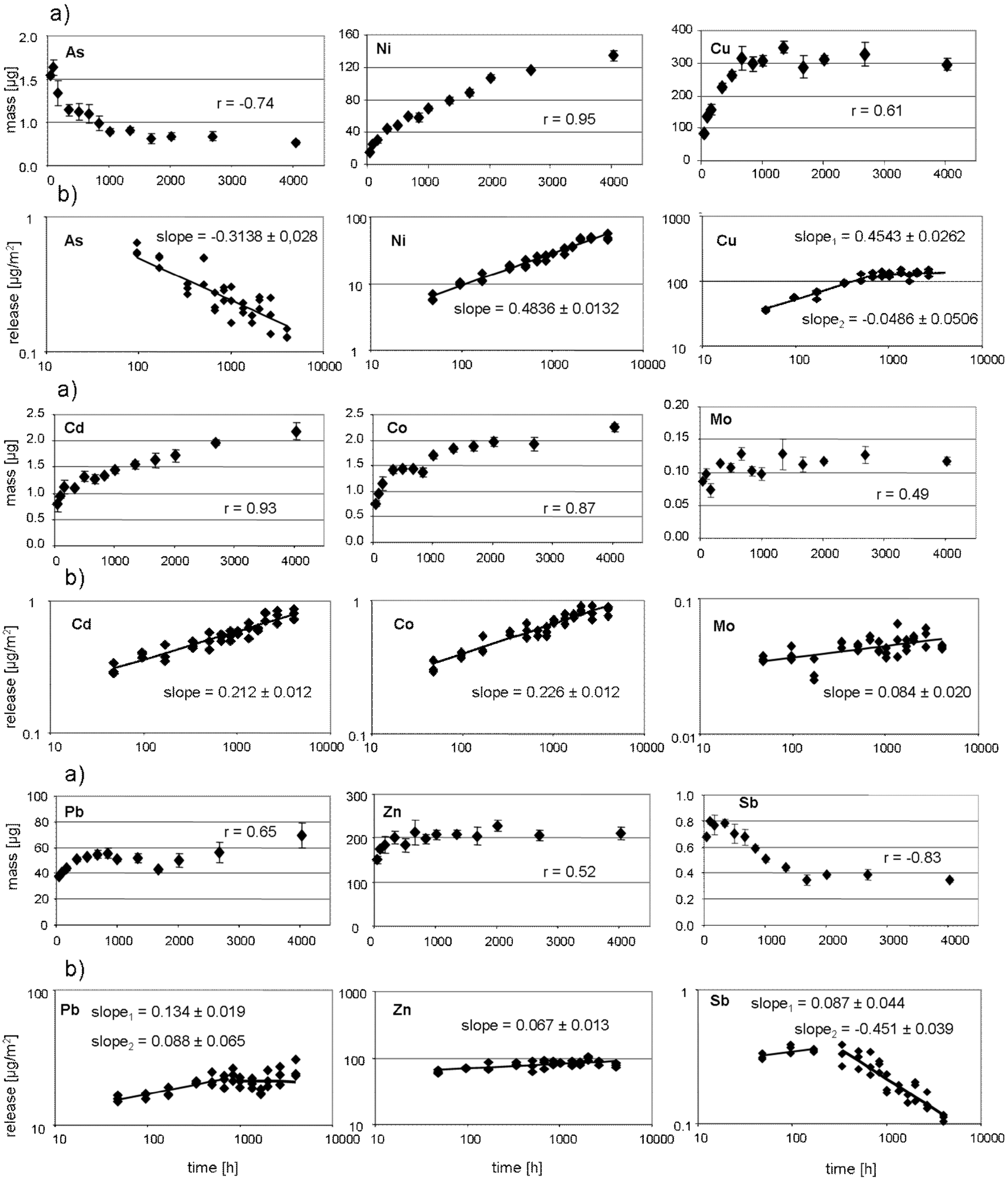

Figure 3: DGT free CUS leaching experiment. Row a) mass of metal(loid)s in eluent vs. time and row b) release vs. time on a double-log scale.

Cd, Co and Ni showed an unhampered time-dependent release in all experiments, so that in this case the application of DGT exhibited no additional advantages. The amounts of Zn, which was leached during the first seven days, was relative high (184 µg within 168 h), but then remained constant on a mass range (209 µg within six months). For Cu and Pb a decrease of the release after 1008 h was observed (Fig. 3). Possible explanations are the depletion of the surface of the slag (wash up effect) and/or that the solution equilibriums for the relevant mineral phases is reached.

The masses of As and Sb in the eluent decreased after a few days suggesting sorption-controlled processes for these elements (Fe-oxides on the CUS surface and to freshly formed Fe-oxide colloids in the water phase). There was no Mo release found in the experiments without DGT. In addition to the surface release/sorption equilibrium this suggests falsely (as explained later) the possibility that Mo was not released at all. The sorption of Mo, As and Sb starts after a few days. Thus, Fe-oxides could be the sorbent when Fe(II) from the slag being oxidised to Fe(III). Generally, these results show that the masses of the analytes in the eluent do not comply with the total release from the test material in experiments without DGT.

3.3.4 LONG-TERM LEACHING WITH DGT

As described in Section 2, the long-term experiments with DGT deliver (i) the total masses of the metal(loid)s in the water phase and (ii) the mass of the metal(loid)s accumulated in the Chelex or Fe-oxide binding layer over a time period of up to 184 d. Significantly lower masses of Cu, Zn, Cd, Co and Ni (Fig. SI 3) were found in the eluent in the experiments with DGT_{Chelex} than in those without DGT. After a time period of 1008 h the released masses equalised in both experiments, due to a saturation of the Chelex binding layer. Detailed information on the capacity and the overload of the binding layers is available in the Supporting Information (Fig. SI 4). It was also secured that no release/sorption effects for the analytes are caused by the DGT units themselves (SI page A16).

For Pb and Cu the trend of mass patterns in the eluent with and without DGT was found to be identical even though an accumulation in the binding layer took place (Fig. SI 3). The maximum mass was for Cu 350 µg and for Pb 60 µg in the eluent. For As and Sb, all experiments showed an increase of the masses within the first two days and a decrease of the masses found in the eluent by the end of the experiment. For Mo the masses were constant in the eluents in all experiments. The comparison of the total mass of the different metal(loid)s (mass in DGT calculated by Equation 1 + mass in the eluent) leached over the different time steps is shown in Fig. 4 and SI 5.

After 184 d, the mass of Cu and Pb released from CUS was three times higher in the presence of DGTs, indicating that solution equilibrium was reached after 1344 h in the experiments without DGT. The DGTs disturbed equilibrium formation and enabled a further release of the analytes.

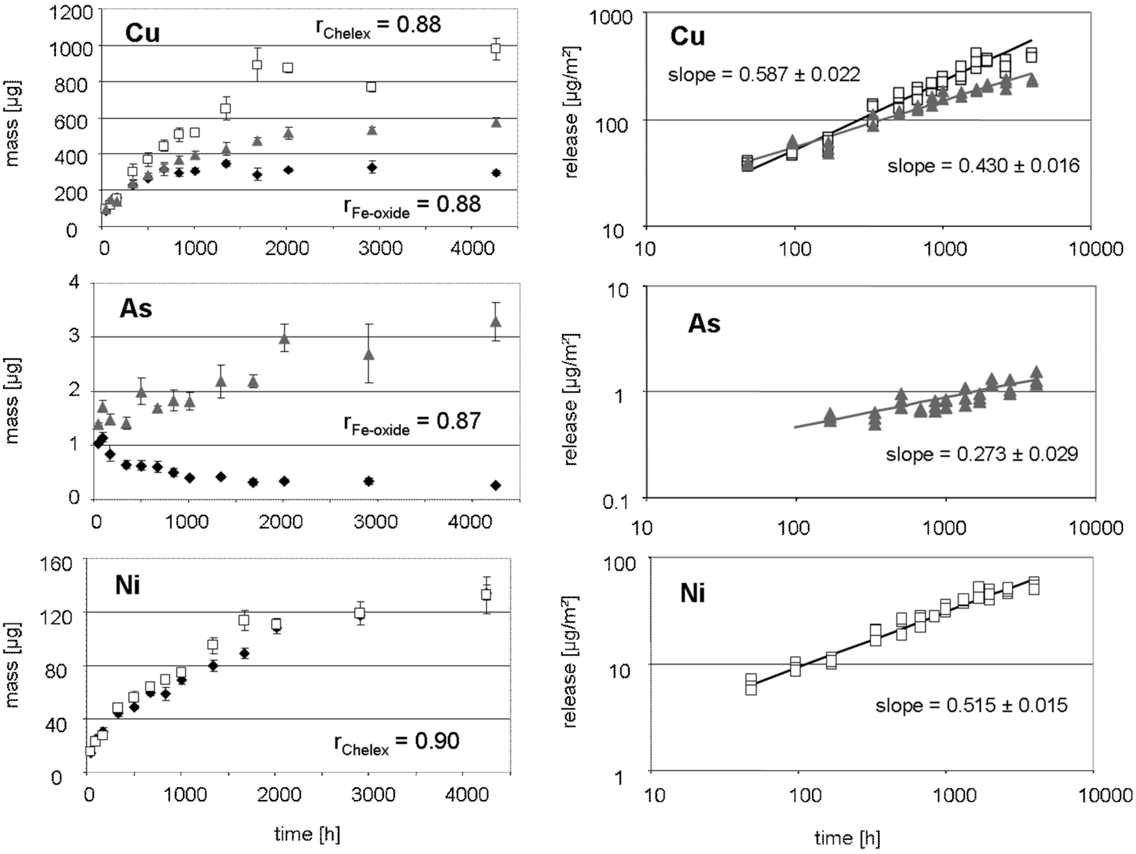

Figure 4: Mass of metal(loid)s released from CUS vs. time (left side) and the release vs. time on a double log-scale (right side). The slope of the fitted curve is indicated (black diamonds = without DGT, white squares = eluent and DGT_{Chelex}, grey triangles = eluent and $DGT_{Fe\text{-}oxide}$).

Due to an overload of the binding after 1680 h, Pb tended to precipitate after desorption from the binding layer. For Cd, Co, Ni and Zn the results of the leaching experiments with and without DGTs are comparable (Fig. 3, 4 and SI 5). Hence, we conclude that the low release of Cd, Co and Zn is caused by the formation of a depletion zone on the surface of the slag for these analytes and that the reduced release was based on a surface driven effect.

For the (hydr)oxide forming analytes As, Mo and Sb, the masses in the eluents of the experiments with and without DGT were close to each other (Fig. SI 3). It is most likely that after the first few days, sorption processes to the Fe-oxides formed on the surface of the slag occurred. This indicates that the formation of an equilibrium was not sufficiently suppressed for the (hydr)oxide forming analytes. Taking the $DGT_{Fe\text{-}oxide}$ mass into account, an accumulation to the binding layer was observed at the same time. Since the mass of As, Mo and Sb increased over time in the DGTs, it was shown that a continuous release from the slag during the course of the experiment occurred, which was masked in experiments without DGT (Fig. 4 and SI 5).

As previously mentioned, the release of Cd, Co, Ni and Zn was comparable in all three test systems, whereas Cd and Co showed a lower release rate than Ni. For Cu the release mechanism is the same over the whole time period, whereas the release measured with DGT_{Chelex} is higher than in the experiments with $DGT_{Fe\text{-}oxide}$, since the sorption of copper is higher for the DGT_{Chelex}. For Pb the release was identical between DGT_{Chelex} and $DGT_{Fe\text{-}oxide}$ until the overload of the Chelex binding layers occurred after which the total released mass of Pb decreased.

3.3.5 SULPHIDE LEACHING

For Cu only one release mechanism was found to be relevant for the release during the long-term experiments. Due to the well known composition of the CUS, it seemed very likely that the weathering of sulphides is mainly causing the copper release. To confirm this hypothesis, sulphide leaching experiments were performed.

The sulphate concentration in the eluent was significantly higher after the extractions with H_2O_2 (Table SI 5). The pH of all fractions was comparable and the redox potential was higher after the extraction with H_2O_2, proving oxidising conditions after the experiment. The H_2O_2 is suitable to provoke efficiently the release of sulphur from CUS, and hence also of the associated metal(loid)s.

The comparison of the sum of the element concentrations extracted with and without H_2O_2 showed significant differences in concentrations for the different elements (Table SI 6). For Fe and Mn the extraction with H_2O_2 is very low, whereas Ni, Cu, Mo, Cd, and Pb showed very high extraction efficiency with H_2O_2. Therefore, compared to Fe and Mn – Cd, Cu, Ni, Pb and Mo are mainly released from rapidly oxidised fractions.

For Zn the extraction with H_2O_2 was very high on the first day but declined to results comparable to the other eluent afterwards (Table SI 6). This confirms that Zn is bound in different mineral phases in the test material, also as sulphides [9]. For Cu the initial concentration was comparable between the two eluents while from day two onwards the concentration significantly increased in the experiment with H_2O_2. This emphasises that within 24 h copper is released via a wash up effect and after 48 h by sulphide weathering. This shows that short-term experiments are not suitable to evaluate the Cu release from slag.

The sulphide leaching experiments did not explain the binding forms of Co, Zn and Sb in the slag. The high amount of Zn in the CUS suggests the presence of this element in different mineral phases [9]. The comparison between the release observed in the long-term experiments and the binding of the metal(loid)s in the slag, examined by sulphide extraction, indicates the relevance of the sulphide mineral weathering, especially for the Cu release. As a consequence, sulphide mineral micro spots on the slag surface are an important source for the release of metal(loid)s to the environment.

3.3.6 BEHAVIOUR OF COPPER SLAG IN THE ENVIRONMENT

Within the first two days all studied elements were released from the slag (by wash up and ion exchange). Afterwards, the elements mainly bound in the sulphide phases (Cu and Pb) were released in the experiments over a very long period of time. For these elements a surface dependant elution for different particle sizes was shown before [8]. Furthermore, the iron oxidation, and thus the associated colloid formation, are also of environmental relevance. These colloids have the potential either to be spread in the water phase or to accumulate in sediments [25]. Considering the roughness factor of 30 and the specific surface area of copper armour stones with 2.46×10^{-5} m^2/g [8] the release of elements from CUS armour stones can be calculated based on the long-term experiments with DGTs. For instance, in a standard midsize water construction activity in a channel 10 000 t of CUS can be used. In that case 2 900 g of Cu, 700 g of Zn and 500 g Pb per six months would be emitted into the river.

3.4 CONCLUSIONS

As mentioned in the introduction, the longest standard leaching test, suitable for construction materials in water construction, has a duration of 60 d [26]. Experiments that integrate time scales of at least half a year are an urgent need for life cycle considerations of construction material. By using DGTs in long-term leaching experiments it was possible to study the leaching behaviour of the model material CUS for half a year. The experiments undertaken in this study are not only space and labour efficient as well as non invasive (no media exchange needed), they have also the potential to integrate time scales up to one year or more by adapting the ion exchanger to test material ratio or by exchanging the DGT sampling devices during the experiment. At a first glance, testing time scales of half a year or a year sound impracticable. But on a second glance, compared to the intended life time of a construction material (far above 50 years) and the potential economic side effects (e.g., remediation costs), an assessment study with a run time of often more than two years must include reliable information on the long-term release of potential pollutants.

In addition to the information on the total release of the amount of pollutants in terms of the Water Framework Directive, static batch experiments with DGT enable (i) to differentiate between the depletion of the material surface and the solution equilibriums and (ii) to study sorption processes with or without a further release of the analytes. This means for the practically relevant model material copper slag that: (i) the cations Cd, Co, Cu, Ni and Pb are confirmed to be released from the slag over the whole time period of six months (mainly by sulphide weathering), (ii) a surface depletion of Zn (mainly exchange processes) was detected, and (iii) that the (hydr)oxide forming elements As, Mo and Sb were also released over the whole time period.

These (hydr)oxide forming analytes were adsorbed to Fe-oxide colloids in standard batch systems, masked by experimental artefacts. As a general benefit, it was confirmed that not only As, Sb and Mo were adsorbed to the Fe-oxide DGTs but also Cu and Pb. The binding strength for Pb in $DGT_{Fe\text{-}oxide}$ experiments was as high as for the Chelex binding layers, which indicates that Fe-oxide binding layers could be an appropriate tool to examine Pb in DGT experiments. However, for standardised measurement procedures of Pb with $DGT_{Fe\text{-}oxide}$ more research is necessary.

The sulphides were found to play a significant role in the metal(loid) release during the long-term experiments with CUS. After 184 d, no decrease in Cu, Ni and Pb release was detected. Based on calculations on the specific surface area and of the tested size fractions, it is now possible to significantly improve the estimation of the emission of elements relevant in terms of the Water Framework Directive due to water construction projects. In general, this is a major step forward, towards life cycle calculations of water construction products, which is asked for by different governmental and non-governmental interest groups, as e.g., explicitly mentioned in the EC Guidance Document No. 28 [4].

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4. Influence of environmental parameters and their Interactions on the release of metal(loid)s from construction materials

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Abstract

Besides the leaching behaviour of a construction material under standardised test-specific conditions with laboratory water, for some construction materials it is advisable to test their environmental behaviour also under close to end use conditions. The envisaged end use combined with the product characteristics (e.g., mineral phases) is decisive for the choice of environmental factors that may change the release of substance that potentially cause adverse environmental effects (e.g., fertilisation or ecotoxicity). At the moment an experimental link is missing between mono-factorial standardised test systems and non standardised complex incubation experiments such as mesocosms which are closer to environmental conditions. Multi-factorial batch experiments may have the potential to close the gap. To verify this, batch experiments with copper slag were performed which is used as armour stones in hydraulic engineering. Design of Experiments (DoE) was applied to evaluate the impact of pH, ionic strength, temperature and sediment content on the release of As, Cu, Mo, Ni, Pb, Sb and Zn. The study shows that release and sediment-eluent partitioning of metal(loid)s are impacted by interactions between the studied factors. Under the prevalent test conditions sediment acts as a sink enhancing most strongly the release of elements from the material.

4.1 INTRODUCTION

In several studies the leaching behaviour of waste materials was already addressed [1-4]. The U.S. environmental protection agency (EPA) as well as the European Committee for Standardisation (CEN) adopted testing framework recommendations for solid waste and construction materials. However, the "real" environmental physicochemical conditions differ substantially from those used in the standardised test systems [5, 6]. Since the leaching behaviour of construction materials is impacted by a variety of physical (e.g., particle size, liquid to solid ratio, leaching time) and chemical parameters (e.g., leaching media, pH-value) the choice of experimental conditions is crucial for evaluating the mass of a substance released in a specific test system [7]. Standardization is required for regulatory aspects to prepare reproducible and comparable results. Nevertheless, due to the high variety of specific environmental situations, the conditions used in the standardized test systems can hardly reflect the entire environmental risk caused by a certain material [8]. For instance, depending on the intended use of a construction material in rivers and streams, different environmental factors in varying degrees may be relevant for the release of metals and metalloids (metal(loid)s).

With respect to the release of metal(loid)s from construction materials in hydraulic engineering, key factors of mobilisation like the pH value, the salinity and the temperature have to be considered as well as sorption/release processes caused by sediments.

In general, most of the environmental parameters were already tested in single parameter studies. For example, leaching experiments with different materials were implemented varying the pH (e.g., [8, 9, 10]), the ionic strength (concentration of NaCl, e.g., [9, 11]), the temperature (e.g., [12-14]) and the composition of the leaching media (e.g., [15, 16]). But only a few studies addressed the impact that interactions between several parameters may have on the release of the metal(loid)s (e.g., [12, 13]). As an example a significant influence was already identified for the interaction of temperature and pH [13]. The basic interactions of the examined parameters of this study are presented in Fig. 1.

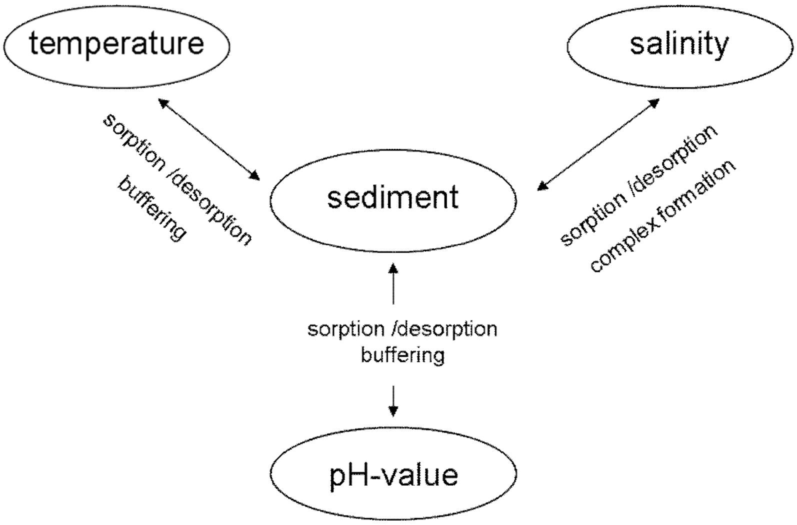


Figure 1: Potential interactions between the investigated parameters by taking the sediment as central objective.

The statistical method 'Design of Experiments' (DoE) was developed in the 1920's for the planning and evaluation of test series [17]. DoE is a tool to study the impact of different factors on a certain process as well as the interactions between the individual factors. It has already been used in technical and chemical process optimisation [18-20], and a few studies also used DoE to gain in depth information on the release of metal(loid)s in leaching processes [13, 14, 21]. DoE was applied to optimise leaching parameters like pH, the particle sizes of the test material or the liquid to solid ratios.

The objective of the study presented here was to rank the impact of pH, salinity, temperature and the presence of native sediment on the metal(loid) release from a construction material in hydraulic engineering. The influence of these factors on the metal(loid) release was tested to attain in depth information on the environmental behaviour of the selected material. The statistical method of DoE was checked for its suitability to rank the impact of the interactions of the factors pH, ionic strength, temperature and presence of sediment on the metal(loid) release. Copper slag (CUS) was used as test material for the following reasons. In Germany, CUS is mainly used to stablize and protect the embankments of inland waterways and of the coast line. Recently, results have been published on the behaviour of CUS in short and long-term studies [22, 23], and detailed information on the composition of CUS are given elsewhere [24]. However, CUS consists of different mineral phases like fayalite, oxides, glasses and (mixed) sulphides. Unfortunately the precise binding forms of the metal(loid)s are not yet precisely detailed. As analytes As, Sb and Mo were chosen as representatives for (hydr)oxide forming elements (forming primarily anions and neutral species in water) and Cu, Ni, Pb and Zn as representatives for elements forming cations after their release.

4.2 METHODS

4.2.1 LEACHING EXPERIMENTS

The test material (armour stones of copper slag) was cleaned with a soft brush and crushed by a jaw crusher (Chemisch Technisches Laboratorium Heinrich Hart GmbH, Germany). Then the test material was sieved (1–4 mm, AS 200, Retsch, Germany,) and divided by a rotary divider (Laborette 27, Fritsch, Germany) into sub-samples of 7.5 g. The sediment was sampled at the river Lahn (stream km: 136, water gate Lahnstein, Germany). The sampled sediment was directly transferred to the laboratory, shock frosted with liquid nitrogen, freeze-dried (Gamma 1-16 LSC, CHRIST, Germany) and sieved (<2 mm, AS 200, Retsch, Germany). The experiments with CUS (0 g and 7.5 g), sediment (0 g, 0.75 g and 3.75 g) and NaCl (0 g, 0.21 g, 0.42 g, Merck, Germany, p.a.) were performed in 50 ml tubes (SuperClear, VWR, Germany). The test materials were mixed overhead with the eluent, 14 ml ultra-pure water (USF ELGA, Purelab Plus, Germany). After mixing, pH 4 and 10 were adjusted by addition of HNO_3, (subboiled 65%, dst-1000, Savillex, USA) and NaOH (50%, p.a., Merck, Germany), respectively. As copper slag is usually causing in aqueous solutions a pH between 7 and 8 [22], no adjustment was needed in experiments in this pH range. The temperature was adjusted by a climatic chamber (Light Thermostat 1301, RUMED, Germany). After 24 h the pH values of the eluates were measured and, if the resulting pH differed by more than 0.5 units from the initial value, the pH value was corrected. Subsequently the batch experiments were stored in the climatic chamber for further 24 h. After 48 h the eluates were filtered with syringe filters (0.45 µm, Minisart (SFCA), Sartorius, Germany) and acidified to 1% HNO_3 (subboiled, 65%, dst-1000, Savillex, USA). The metal(loid) concentration was detected by means of Inductively Coupled Plasma-Quadrupole Mass Spectrometry (ICP-QMS, Agilent 7700 series ICP-MS, Agilent Technologies, USA) and Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES, JY 238 Ultra trace, Horiba Jobin Yvon, Germany).

4.2.2 DESIGN OF EXPERIMENTS

A full factorial design was used to design the leaching experiments (Table SI 1). The factors and levels tested in this study were pH (4, 7 and 10), temperature (T = 4 °C and 36 °C), NaCl content (c_{NaCl} = 0 g/l and 30 g/l) and the sediment content ($m_{sed.}$ = 0 g, 0.75 g and 3.75 g). Intermediate levels were included for the pH and the sediment content in order to better account for the non-linearity of pH and for the potential sorption capacity of the sediment possibly resulting in a complete disappearance of a certain analyte at the highest level. The planning and the statistical analysis were performed with STATISTICA 10 (Statsoft, Germany). Each leaching experiment was performed in triplicate. One blank sample was added in each leaching experiment without sediment and three in experiments with sediment. In total, 360 batch experiments were carried out. Despite the fact that randomisation is a fundamental principle in DoE, all experiments with the same temperature were performed simultaneously, because only one climate chamber was available to adjust the temperature. The amount of the metal(loid)s released from the sediment was subtracted as background from the metal(loid) concentrations caused by leaching from the CUS.

If factors were tested with two levels, a model with three-way linear interaction between the factors can be analysed. Otherwise the determination of quadratic effects was possible. The significance of the main effects (pH, sediment content, temperature and NaCl content) and their interactions was tested by means of the analysis of variance (ANOVA, F-value and p-value [17]), whereas not significant effects and interactions were ignored. ANOVA is based on the assumption that the residuals are normally distributed what was tested with the Shapiro-Wilks test (SW-test, $p = 0.05$). The validation of the model was performed with the goodness of fit. The R^2 described the amount of the variation of the response explained by the model. For visualisation purposes and for the analysis of the results, the Pareto charts and the plots of marginal means were generated.

4.2.3 SEDIMENT

A separation between the test material CUS (1–4 mm) and the sediment (<2 mm) was necessary at the end of the leaching experiments, to enable the determination of the amount of metal(loid)s sorbed to the sediment. Since copper slag contains a high amount of magnetite, this was achieved by magnetic separation [24]. The quantitative recovery of the magnetic separation was determined by analysing defined mixtures of CUS and sediment.

At the end of the experiments the mixture of CUS and sediment was freeze-dried (Gamma 1-16 LSC, CHRIST, Germany), thoroughly shaken and filled into large round boxes (150 mm, PS, Bock, Germany). A small round box (73 mm, PS, Bock, Germany) mounted on a NdFeB magnet (N40, Q-51-51-25N, Chen Yang Technologies, China) was moved across the mixture. The distance between the CUS/sediment mixture and the magnet was reduced step wise. The magnetic separation was also performed with sediments containing no slags to assess the amount of magnetisable sediment. The separated sediments were digested with 65% HNO_3 (suprapur, Merck, Germany, 0.5 g Sediment/10 ml HNO_3) in a microwave (200 °C for 20 min, turbo wave, MLS, Germany) and the quantification of the metal(loid)s was performed by means of ICP-QMS (Agilent 7700 series ICP-MS, Agilent Technologies, USA).

4.3 RESULTS AND DISCUSSION

4.3.1 METAL(LOID)S LEACHING FROM THE SEDIMENT VS. LEACHING FROM CUS

Principally, the studied metal(loid)s may origin from CUS or from the sediments. Therefore, the metal(loid) amount released from the sediment and from the CUS is compared first. In general, the release of the metal(loid)s from the sediment increased with increasing mass of sediment added in the experiment (Fig. SI 1). This is a simple proof of the method robustness.

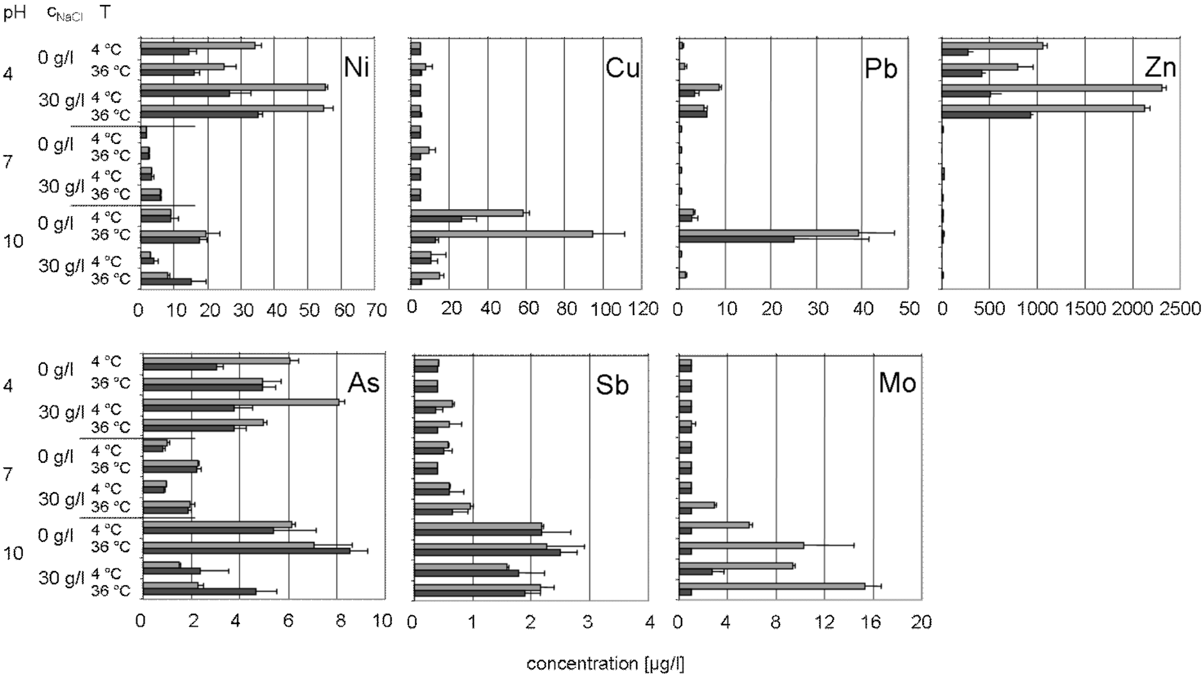


Figure 2: Concentrations of the metal(loid)s in the eluates in leaching experiments with different factor levels and with 3.75 g sediment (light grey = experiments with CUS, dark grey = experiments without CUS).

Four groups of analytes can be distinguished based on the leaching results (Fig. 2 and Fig. SI 2). The first group contains only the element Mo. In all experiments without CUS the Mo concentrations were below the limit of detection (LoD, Table SI 2). Thus, Mo was not released from the sediment. In contrast, Sb, Pb and Cu, the elements of the second group, were predominantly released from the sediments at pH 10. The increase of Cu and Pb at high pH values depends on the higher DOC in the eluent. In addition, the organic matter appears to govern the solubility of Cu and Pb under low pH conditions [25]. The leaching behaviour for Sb is typical for an oxyanion [26]. For instance, Pb was found to be released significantly in absence of NaCl at pH 10 and 36 °C. The third group, containing only Zn, exhibited elevated eluate concentrations mainly at pH 4, whereas the concentration in the eluates in experiments with CUS was significant higher than without. The high release at low pH values occurs due to the higher ion exchange capacity. The fourth group (As and Ni) was released at pH 4 and pH 10 from the sediment, whereby the concentration at pH 10 was comparable in experiments with and without CUS. The release of Ni at pH 4 occurs due to the higher ion exchange capacity, but in contrast to Zn for Ni the complex formation with DOC is more pronounced. Arsenic as an oxyanion tends to be release at high pH values, the release at pH 4 may be caused by a decreased sorption of arsenate on clay minerals [27]. The arsenic release from the sediment at pH 10 was in three 3.75 g sediment experiments higher than in experiments with CUS (data not detailed, mean values presented in Fig. 2). This can be explained by the prevalent speciation of arsenic at pH 10 $HAsO_4^{2-}$ [28] and its sorption to iron(hydr)oxides surfaces on/from the CUS [22, 23].

In addition, the concentration of metal(loid)s in the eluates that displayed a high release at pH 4 (Ni, As and Zn) was also higher at 4 °C than at 36 °C. This is due to the higher buffer capacity of the sediment at 36 °C than at 4 °C (SI page A22 and Table SI 3).

4.3.2 FACTORS AND LEVELS FOR THE ANALYSE OF THE FULL FACTORIAL DESIGN

In the evaluation of all following results the metal(loid) "sediment background" was subtracted. If the concentration of the metal(loid)s in the experiments with and without CUS was the same within the statistical error, the concentration was set to one half of the limit of detection of the ICP-QMS analyses for further statistical calculations (Table SI 2). This occurred predominantly in experiments with 3.75 g sediment (Fig. 2). Therefore the statistical analysis was only reasonable to be performed for the experiments without sediment and in the experiments with 0.75 g sediment, except for Ni and Zn. In addition, the influence of the factor pH was analysed from 4 to 7 and from 7 to 10 to study the influence of the other factors in detail. The factor levels for the leaching experiments included in the statistical analyses are shown in Table 1.

Table 1: Design of the experiments and factor levels of the main leaching tests for the different metal(loid)s.

	pH		sediment content [g]			temperature [°C]		c_{NaCl} [g/l]		elements
	-	+	-	=	+	-	+	-	+	
design 1	4	7	0		0.75	4	36	0	30	Cu, Mo, Pb, Sb, As
			0	0.75	3.75	4	36	0	30	Ni, Zn
design 2	7	10	0		0.75	4	36	0	30	Cu, Mo, Pb, Sb, Zn, As
			0	0.75	3.75	4	36	0	30	Ni

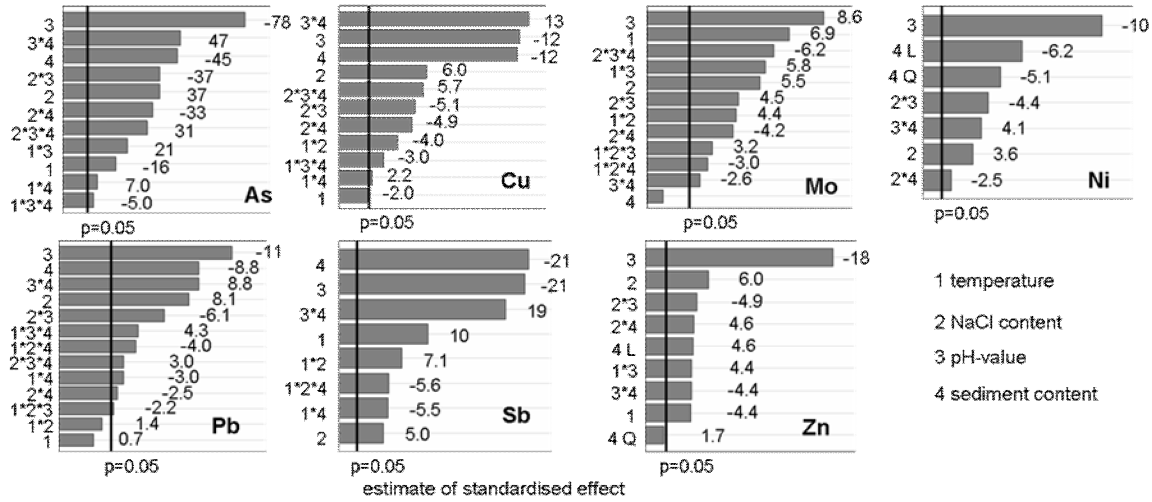
- low level, = medium level, + high level

The results of the ANOVA and the Shapiro-Wilks test are shown in Table SI 4. All p values of the Shapiro-Wilks test were not significant, therefore the null hypothesis (normal distribution) was assumed. The R² was 0.8 or higher for all metal(loid)s, except for Ni, for which no significant effect was found in design 2. The three way interactions are needed to describe the concentrations of the metal(loid)s in the leaching experiments. The R² of the models with quadratic interactions (0.90 - 0.80) were slightly lower than the R² from the models with three way interactions (0.99 - 0.90, Table SI 4).

4.3.3 ELUATE ANALYSES

As described in literature the pH has a strong impact [8, 15] on the metal(loid) mobility. In addition, distinct differences between experiments with and without sediment were visible. In experiments without sediment the release of the metal(loid)s from CUS can be directly studied. In experiments with sediment the partitioning between the sediment and the eluent can be evaluated. The sediment acts as sink for metal(loid)s and a source of organic substances therefore the changed solubility in presence of organic substances as well as the sorption to sediment can be studied. The Pareto charts from the statistical analysis are shown in Fig. 3, whereas the x-axis shows the factors and factor interactions represented by numbers (e.g., 1 = Factor temperature, 1* 2 = Interaction between the factor temperature and NaCl content) and the numbers within the diagrams are a measure for the effect of the factors and of their interactions. No significant effects for Ni were identified in design 2, thus the Pareto chart was not included.

Design 1



Design 2

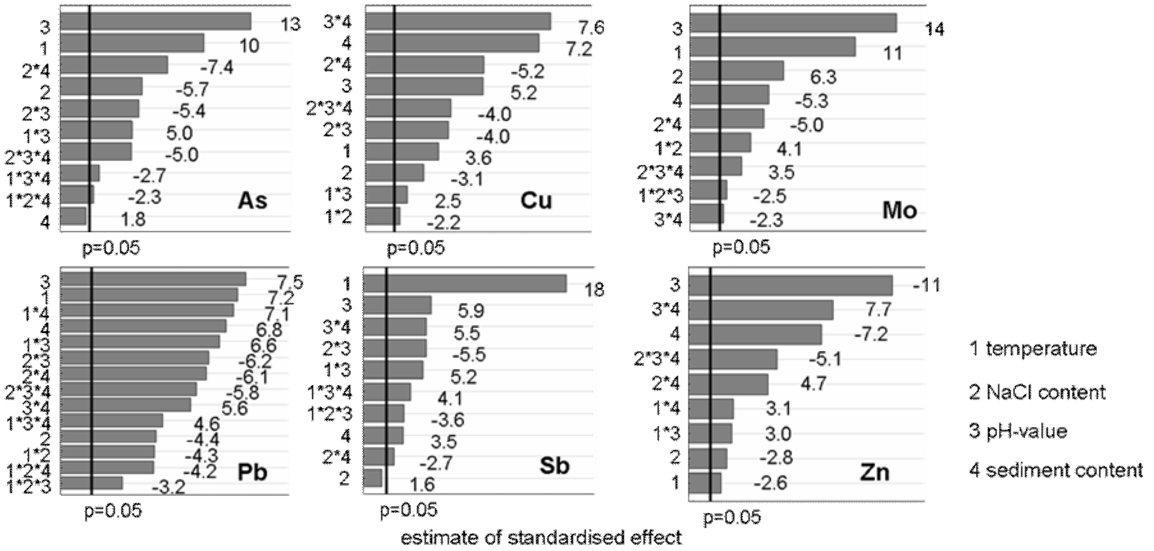


Figure 3: Pareto charts of the effect estimate from the concentrations of the metal(loid)s in the eluates in design 1 (pH 4 and 7) and design 2 (pH 7 and 10).

In experiments without sediment the concentration of the metal(loid)s decreased with increasing pH-values (Fig. 4), whereas strong differences of the concentration of metal(loid)s in the eluates were observed between pH 4 and 7 and small differences between pH 7 and 10. Only the concentration for Mo increased with increasing pH-values from 4 - 10. This leaching behaviour is typical for an oxyanion [26]. Hence, in experiments without sediment and low pH the ion exchange on the surface of the slag is an important mechanism.

Like the pH-value, the sediment content displayed a strong impact on the concentration in the eluates. The concentration decreased with increasing sediment content, proving that the sediment acts as an efficient catcher of metal(loid)s released from the test material (except for Zn and Mo).

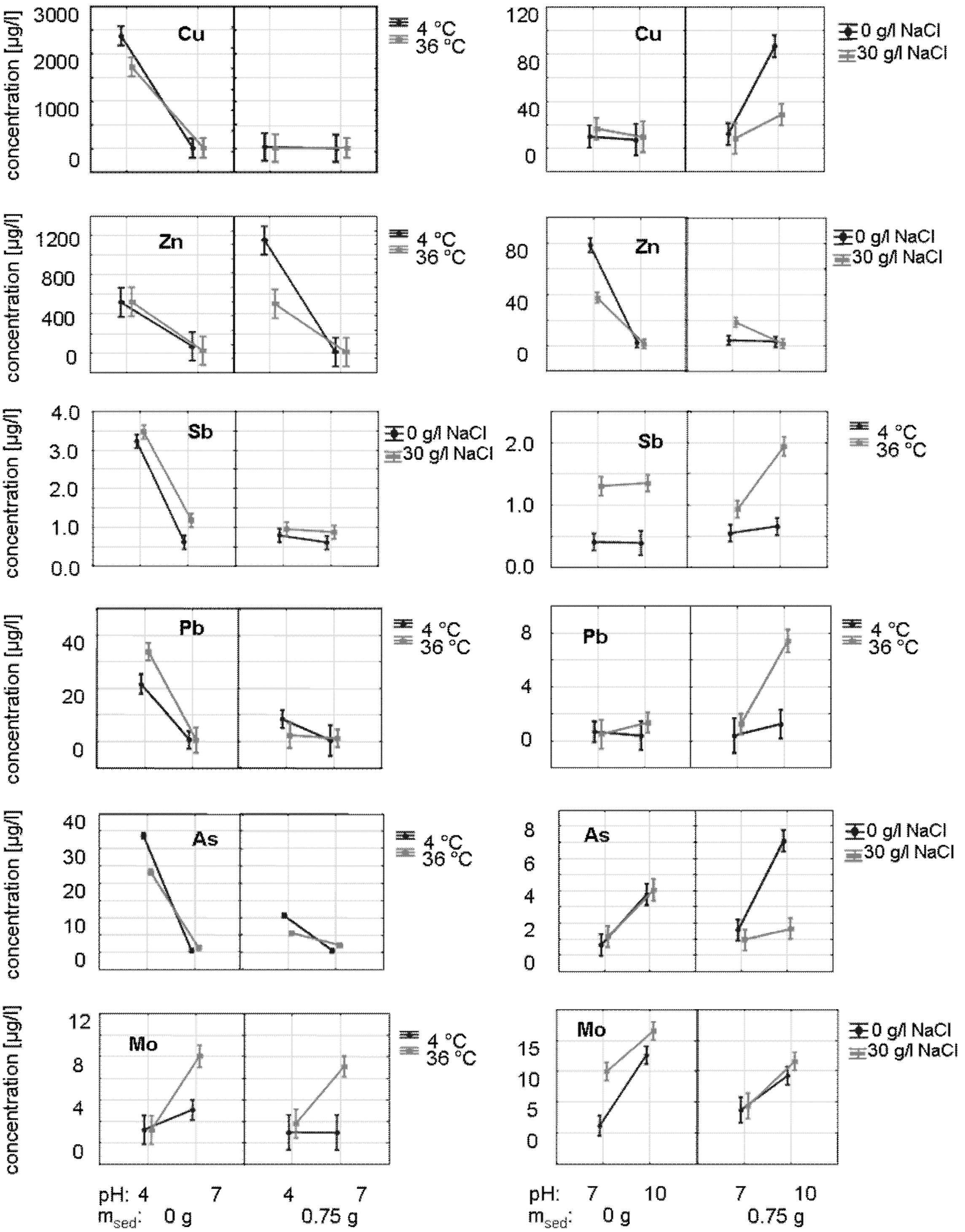


Figure 4: Plot of marginal means for the concentration of the metal(loid)s in the leaching experiments with different factor combinations.

The interaction between sediment and pH value occurs since more metal(loid)s were released from the CUS at low pH and hence, more metal(loid)s were sorbed to the sediment (Fig. 4). At pH 7 a minimum of the concentration of the metal(loid)s was observed and afterwards the concentrations in the eluates increased again with the increase of pH (except for Zn and Mo, Fig. 4). This might be caused by an equilibrium shift between slag and sediment (release and sorption) and/or the higher solubility of the metal(loid)s when more organic carbon or complexing agents were released from the sediment [25, 27].

Based on the results, in Table 2 the most important effects and interactions are hypothesised together with the metal(loid)s for which the effects were observed.

Table 2: Effects related to factor interactions on metal(loid) elution within design 1.

effect	interaction	impacted elements
sorption	pH-sediment	As, Cu, Ni Pb, Sb
buffering of the pH	temperature-pH-sediment	As, Cu, Ni, Pb, Zn
equilibrium release/sorption and /or humic acid driven release	NaCl-pH-sediment	As, Cu, Pb, Zn
ion exchance-solubility	NaCl-pH-sediment or temperature-NaCl	As, Cu, Mo, Ni, Pb, Sb

Besides the sediment and the pH-value, also the temperature, the NaCl content and the interactions between these parameters show significant effects on the concentration of the metal(loid)s in the eluates. The NaCl-pH interaction can be explained by the higher solubility of metal(loid)s due to complexation or by a higher exchange of ions due to the higher ionic strength. However, in all experiments with sediment the NaCl content was a negligible factor, therefore in presence of other complexing agents from the sediment the Cl-complexation plays a minor role. The interaction temperature-pH was caused by pH differences based on slight differences of the buffer capacities of the sediment (Table SI 3, pH 4). However, this effect is negligible under environmental conditions and has rather to be accounted for future experiments. For higher pH values for Sb, Pb and Mo the increase of temperature caused an increase in concentration of the metal(loid)s in the eluates (see Fig. 4). Therefore the equilibrium between sorption and release or the solubility was changed.

Especially for Mo no differences between the concentrations in the eluates were observed in experiments with and without sediment, but higher temperatures and NaCl caused an increase in Mo concentration in the eluates (Fig. 4 and Fig. SI 3). Therefore, the concentration of Mo in the eluates was affected preferentially by changes in the solution equilibrium.

4.3.4 SEDIMENT ANALYSIS

To investigate the sorption of the metal(loid)s released from CUS, a magnetic separation was performed to separate slag particles from the sediment. The recovery of the magnetic separation was examined with and without sediment (Table SI 5). The recovery of the pure CUS was as high as 99.5%. The small not separated rest of 0.5% fall in the class of less than 1 mm. Therefore, a second recovery experiment with a particle size <63 µm was performed. The recovery was 93%. Thus, it was shown that a large amount of small particles can be separated with this technique with a satisfying recovery. If a mixture of slag and sediment was used for the separation, the recovery of the slag was > 99%, but small amounts of magnetic sediment particles were also removed. Due to this the recovery of the sediment was 97% for 0.75 g sediment added and 98% with 3.75 g sediment added. To make sure that CUS residues (<1%) which were not removed, do not affect the mass content of the metal(loid)s in the sediment, the mass content of Cr was also measured and was used as an indicator for CUS. Cr has a high mass content in the copper slags but the availability in leaching experiments is very low due to its binding form (Cr-spinel). Hence, the Cr mass content in experiments with and without CUS should not differ significantly if no CUS is present after magnetic separation.

Experiments with different sediment masses and different pH-values were chosen to examine the sorption of the metal(loid)s to the sediments in the leaching experiments. Experiments with NaCl were not included, since the magnetic separation was disturbed by salt encrustations and after drying a sufficient dry dispersion was impossible with the small sample amounts. Table 3 shows the results of the sediment analyses for the different sediment masses. The mean values were compared with t-test (α = 0.05).

Table 3: Mass content of metal(loid)s in the sediment for the experiments with and without copper slag (t-test, α = 0.05).

	0.75 g sediment			3.75 g sediment		
	mass content [mg/kg]		p	mass content [mg/kg]		p
	experiment without CUS (n = 3)	experiment with CUS (n = 9)		experiment without CUS (n = 3)	experiment with CUS (n = 9)	
Cr	56.1 ± 1.8	56.8 ± 2.9	0.69	59.6 ± 7.0	59.9 ± 4.3	0.93
Ni	50.4 ± 2.8	54.9 ± 1.7	0.01*	54.6 ± 3.4	55.8 ± 1.9	0.47
Cu	53.1 ± 7.2	431 ± 113	0.01*	53.4 ± 3.2	131 ± 30	0.01*
Zn	871 ± 68	1276 ± 82	0.01*	889 ± 53	969 ± 47	0.03*
As	5.70 ± 0.50	11.9 ± 1.7	0.01*	4.78 ± 0.22	5.91 ± 0.30	0.01*
Mo	0.51 ± 0.03	27.4 ± 4.9	0.01*	0.50 ± 0.05	3.62 ± 0.60	0.01*
Sb	<LOD	<LOD	-	<LOD	<LOD	-
Pb	126 ± 9	144 ± 9	0.01*	125 ± 4	124 ± 4	0.60

* significantly different $p < 0.05$

For Sb the mass content of the sediment was below the limit of detection (Table SI 6). No sorption was detected. The metal(loid)s Ni, Cu, Zn, As, Mo and Pb show a significant higher mass content in the sediments (0.75 g) after leaching with CUS, whereas the differences of the mass content for Ni and Pb were very small. These elements were sorbed to the sediment. In the 3.75 g sediment experiments the release of Cu, Zn, As and Mo was high enough to show a statistically significant sorption above the sediment background. For the other elements the released masses were too low.

While in experiments without sediment the release of metal(loid)s increased at low pH values, the mass fraction in the sediment did not depend on pH (Table SI 7). This may be caused by (i) the buffer capacity of the sediment, (ii) masking effects from the high variation of the metal(loid) content in the sediment or (iii) the strong sorption of the metal(loid)s to the sediment. Therefore no solution equilibrium in the eluates occurs and the slag released continuously significant quantities of metal(loid)s over time.

The high mass content of Cu, Zn, As and Mo shows (i) that the concentration in the water phase does not correlate with the total release, if sediment was included in the experiments,

(ii) that there is a significant and high potential for these elements to be enriched in sediments after the release from the slag also under environmental conditions, (iii) that the sorption to the sediment may mask effects caused by other factors and (iv) that the test material to sediment ratio was a crucial factor in the experiments.

4.3.5 DISCUSSION: ENVIRONMENTAL BEHAVIOUR OF THE TEST MATERIAL

Apart from some micro environments, from the low pH tests direct conclusions for environmental applications are not possible, since pH 4 is an extreme pH-value for fresh- and seawater. However, basic release mechanisms can be identified. All metal(loid)s except Mo showed a very high release at low pH value in the experiments without sediment. It was shown that pH changes can significantly impact the metal(loid) release (e.g., the impact on the combination buffer capacity and temperature). At low pH conditions the increase of NaCl caused a strong increase in the metal(loid) concentration of the eluates. The pH and the NaCl content increased the ion exchange on the surface of the CUS. The metal(loid) concentrations of the eluates in experiments with sediment were in general very low, except for Mo. This confirmed, in combination with total content analyses of the sediments, that significant amounts of the metal(loid)s were directly sorbed to the sediment. Hence, the ratio of test material to sediment is crucial for the results attained by the multi factorial batch experiments and in environmental studies. In addition, for Mo the sediment as a sink was the most important factor, since the sediment caused a continuous depletion of the eluates and hence, high amounts were released from the slag. This was not detected before in other leaching experiments with CUS.

A pH ranging from 7 to 10 applies to many streams and rivers [29]. Strong differences between experiments with and without sediment were visible and the sorption to the sediment was confirmed for all metal(loid)s. Despite sorption, the concentration of the metal(loid)s in the eluates depended on the interaction of different factors. Without sediment neither the NaCl concentration nor the temperature showed significant effects on the metal(loid) content of the eluates for Cu, Pb, As and Zn but Sb and Mo were strongly impacted by the factor temperature. In terms of eluates concentration plus enrichment in the sediment, in the presence of sediment in the batch experiments a high total metal(loid) mobilisation was observed. The higher temperatures increased the solubility. For Mo a dynamic equilibrium between eluent and CUS is a potential explanation, whereas in this case the sediment acts as a binding layer. The temperature and the pH may have changed this equilibrium.

4.4 CONCLUSIONS

DoE supported experiments are a valuable tool to enable a mechanistic understanding of the metal(loid) release from a test material taking into account also synergistic or antagonistic effects of several factors.

In general the DoE supported experiments have shown: (i) leaching experiments in the absence of a sediment fraction showed significantly different effects from those with sediment or in the presence of other binding layers [23], (ii) sediment has proven to be the most important factor in the experiments via depletion of the eluates and release of chelating agents. Therefore the potential release of metal(loid)s in leaching experiments without a binding layer may underestimate the potential environmental impact, also in short term experiments. (iii) To study these interrelations in detail lower sediment to CUS ratios will be needed in future studies, to increase significantly the mass content of the metal(loid)s in the sediment.

For the application of CUS in hydraulic engineering the results show that (i) the separation technique described in this paper displayed good recoveries for CUS particles due the high magnetite content, (ii) the end use or intended use have a direct impact on the release of the metal(loid)s as well as on the distribution/partitioning between sediment and the water phase, (iii) the material has the potential to change the total content of As, Cu, Mo, Ni, Pb and Zn of sediments in direct contact with the armour stones. Hence, a mass transfer calculation for the metal(loid)s is needed to assess the ecological and economical relevance, since each year several hundred thousand tons of this construction material are used in hydraulic engineering.

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5. FINAL CONCLUSIONS

The release of hazardous substances from construction materials within the scope of their end use in hydraulic engineering is a complex issue. Standard test systems as well as new methods were used to transfer the results from batch experiments to construction scenarios to increase the knowledge of long-term trends and artefacts for the release of metal(loid)s from the test material copper slag. In addition, the effects of relevant environmental conditions on the leaching of metal(loid)s from construction material in hydraulic engineering were investigated to increase the knowledge of pertinent mechanisms influencing the release of metal(loid)s.

It was possible to show with standard batch tests that the release of some metal(loid)s is dependent on material surface. This surface depending release of metal(loid)s is a prerequisite to link their release in lab studies and field scenarios with the roughness factor. Therefore the cost-, time efficient long-term or short term experiments with small or granulated stones can be used to study the release of metal(loid)s from construction materials, if the results of the release are connected via the roughness factor (BET measurement and aluminium foil method) to conditions relevant for construction projects in hydraulic engineering.

The solution equilibrium of metal(loid)s in the eluate are a main reason for underestimating the potential release of metal(loid)s from construction materials. DGT as well as the addition of sediment has shown a significant higher release of most metal(loid)s from test material. DGT as a novel cost-, time efficient method for leaching experiments enables new perspectives in studying release mechanisms of pollutants from granular construction materials and in distinguishing between long-term release and wash up effects. Therefore, DGT should be used for the assessment of construction materials in hydraulic engineering.

In particular, construction materials which contain sulphide minerals should be closely examined under long-term conditions before they are used in hydraulic engineering, because sulphide mineral weathering was identified as a long-term source in the release of some metal(loid)s from copper slag and most leaching tests are underestimate this source.

The salinity as well as three other factors were tested supported by DoE as environmental factors to study the influence of end use conditions on the release of metal(loid)s from copper slag. It was shown that environmental factors and therefore end use conditions significant influence the release of metal(loid)s from construction materials. In order to avoid negative environmental effects construction materials which have shown in previous leaching tests the potential to release high amounts of metal(loid)s should be tested under end use conditions. If the conditions in construction projects differ, DoE is an appropriate tool to simplify the design of leaching experiments.

In the experiments with sediment a sorption to the sediment was confirmed for almost all examined metal(loid)s and a higher potential than in other leaching tests for the release of some metal(loid)s from the slag was determined. The experiments increase the knowledge on the partitioning of the metal(loid)s between slag and sediment and have shown that the interaction between sediment and construction material need further research to estimate the potential environmental risk of construction materials in hydraulic engineering.

Finally, as a potential artefact in most standard test systems, this thesis also addressed the colloid formation in leaching experiments. The colloid formation (size range 0.1 – 8 µm) has the potential to decrease the metal(loid) concentration in the eluates which is detected after the filtration step (<0.45 µm) and therefore the mass released might be underestimated.

Consequently, in order to avoid potential artefact, the filtration of the eluate should only be performed if granular construction materials with small particle sizes (<63 µm) are used in leaching experiments or shaking is part of the leaching experiments.

In summary, the following overall conclusions can be drawn:

i. Batch experiments with granulated stones can be used to study the release of metal(loid)s from construction materials, if results were transferred via the roughness factor.

ii. DGT as a novel cost-, time efficient method for leaching experiments could be used for the assessment of construction materials in hydraulic engineering.

iii. Construction materials which contain sulphide minerals should be closely examined under long-term conditions before they are used in hydraulic engineering.

iv. In order to avoid negative environmental effects construction materials with potential to release high amounts of metal(loid)s should be tested under end use conditions.

v. The interaction between sediment and construction material has been identified as crucial factor to estimate the potential environmental risk of construction materials and further research is necessary.

vi. The filtration of the eluate after the leaching of construction materials should be avoided.

The thesis may significantly support ongoing scientific discussions on the use of industrial by-products in hydraulic engineering and the evaluation process on their environmental impact.

APPENDIX

A.1 SUPPORTING INFORMATION OF CHAPTER 2

Leaching of metal(loid)s from a construction material: influence of the particle size, specific surface area and ionic strength.

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Figure SI 2:	Figure SI 2: Pictures of the performance of a) the aluminium foil method and b) the print paper method.
Figure SI 3:	USB Microscope pictures a) slag 1 and b) slag 2, the roughness of slag 2 is significantly higher.
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Figure SI 6:	Concentration/release of metal(loid)s vs. different particle sizes (light grey = slag 1, dark grey = slag 2, n = 8, ± 95% confidence interval).

Tables:

DESCRIPTION OF THE FOUR SPECIFIC SURFACE AREA METHODS FOR ARMOUR STONES

One armour stone for basalt and one for copper slag were used to compare the four methods.

3D LASER SCAN METHOD

The scans were done with an ATOS Compact Scan (GOM) by Topometric, Germany. The method is based on producing a triangular transformation network from a data point cloud where the surface area is calculated from. For more details please refer to: http://www.gom.com/metrology-systems/system-overview/atos-compact-scan.html.

ALUMINIUM FOIL METHOD

For the aluminium foil method the stone was wrapped in aluminium foil (Koff AG), while the aluminium foil was pressed on the surface to include micro relief, but without overlaps and folds (Fig. SI 2). Thereafter the stone was unwrapped and the aluminium foil was weighed. For the calculation the density of the aluminium foil was measured (~2.8 g/cm³). With the weight, the density and the thickness of the aluminium foil the calculation of the surface area of the stone is possible.

PRINT PAPER METHOD

The print paper method (Fig. SI 3) is comparable to the aluminium foil method, only the calculation is different because the surface related mass of the print paper is known (80 g/m²).

SQUARE METHOD

For the square method the height, length, width of the stone was measured in order to calculate the surface area.

Table SI 1: Detection limits ICP-SFMS (3 Sigma criterion).

Element	Detection limit [µg/l]
As	1
Cd	0.08
Co	0.2
Cu	1
Fe	5
Mo	0.5
Ni	1
Pb	0.1
Sb	0.2
Zn	2

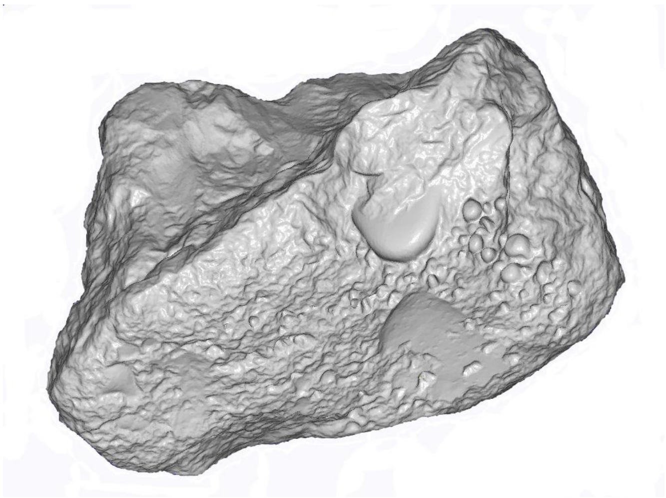

Figure SI 1: Replica of the stone with the 3D Laser.

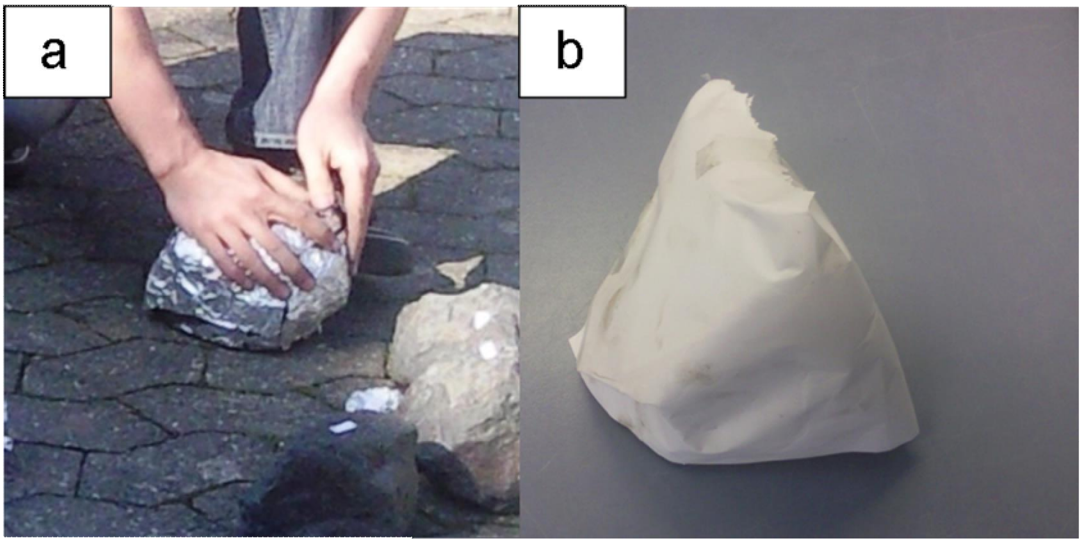

Figure SI 2: Pictures of the performance of a) the aluminium foil method and b) the print paper method.

Table SI 2: Chemical composition of copper slag in wt.% measured by x-ray fluoresces.

		slag 1			slag 2		
Repetition		1	2	3	1	2	3
Na_2O	%	2.2	1.2	1.2	<2	2.2	<2
MgO	%	1.6	1.6	1.6	1.6	2.6	0.6
Al_2O_3	%	5.8	5.5	5.3	6.4	6.2	6.2
SiO_2	%	30.0	30.4	30.6	30.6	30.2	30.8
P_2O_5	%	0.3	0.3	0.4	0.2	0.2	0.2
K2O	%	0.7	0.6	0.6	0.8	0.8	0.8
CaO	%	3	3	3	3	3.1	3.1
TiO_2	%	<0.1	<0.1	<0.1	0.2	0.2	0.2
Fe_2O_3	%	49.6	51.3	50.7	50.8	50.2	51.8

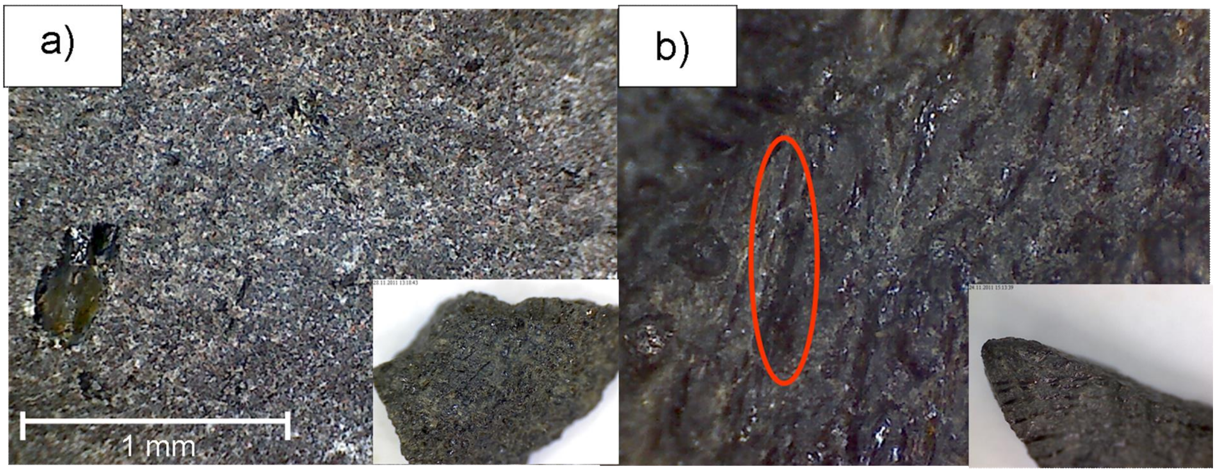

Figure SI 3: USB Microscope pictures a) slag 1 and b) slag 2, the roughness of slag 2 is significantly higher.

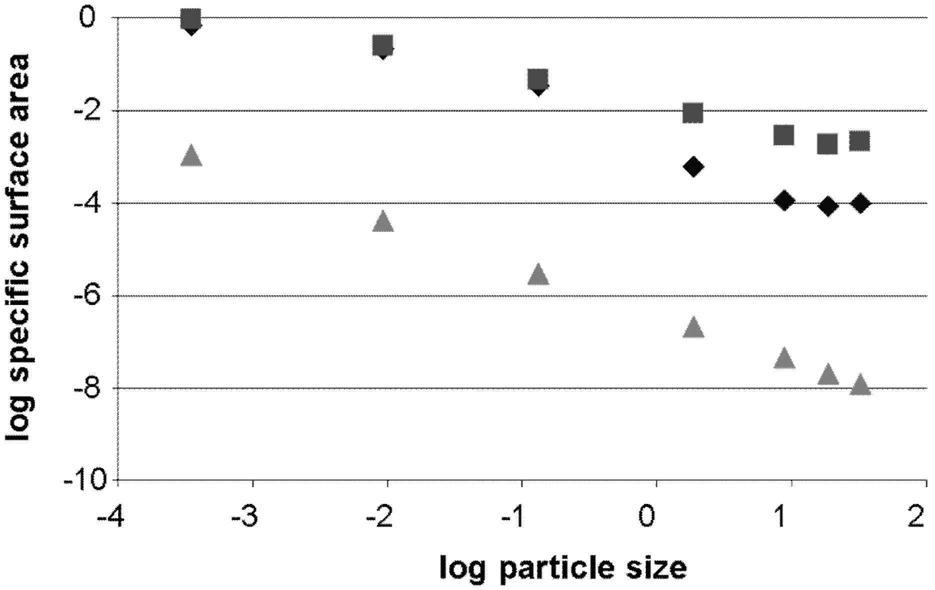

Figure SI 4: Log-log-diagram of the physical specific surface area of copper slag 1 (diamonds) and slag 2 (squares) measured with BET and the external surface area calculate with Equation 1 (triangles).

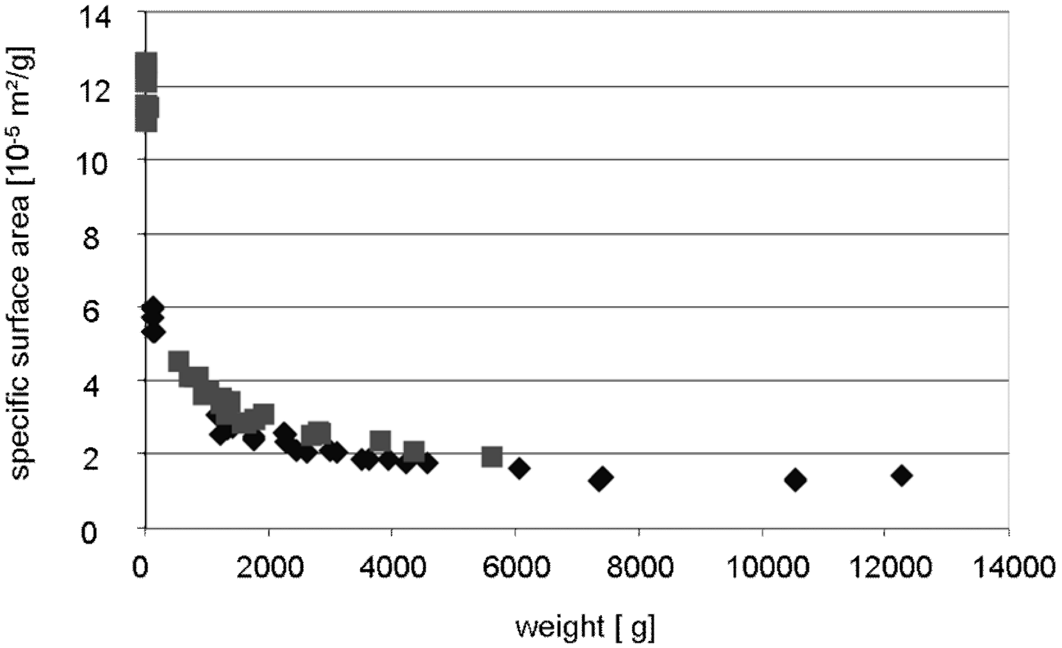

Figure SI 5: Specific surface area of copper slag (diamonds) and basalt (squares) measured with the aluminium foil method.

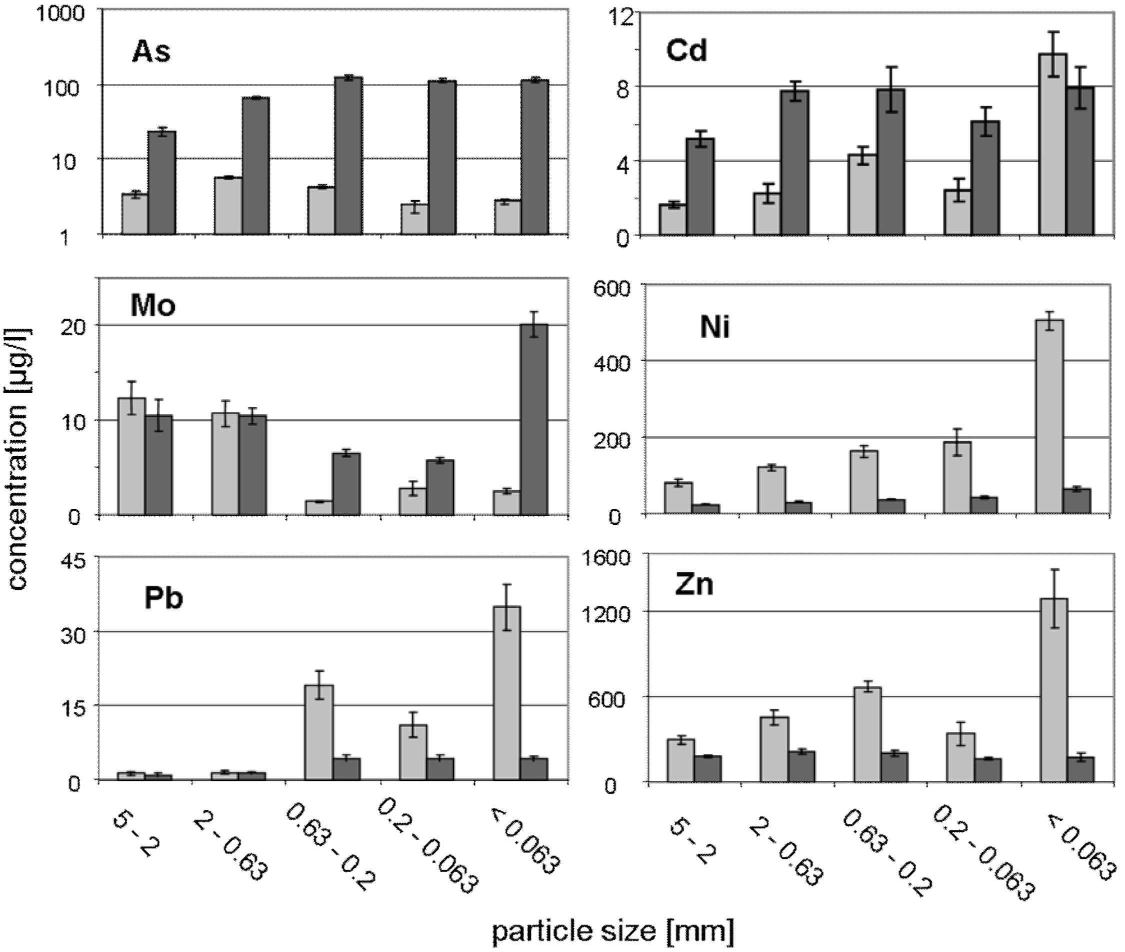

Figure SI 6: Concentration/release of metal(loid)s vs. different particle sizes (light grey = slag 1, dark grey = slag 2, n = 8, ± 95% confidence interval).

Table SI 3: Metal(loid) concentrations of samples filtered with different filter cut offs, t-test with p=0.05, (n = 8, ± 95% confidence interval).

	c [µg/l]		p
	0.45µm	8µm	
Cd	2.90 ± 0.42	2.88 ± 0.33	0.946
Pb	20.7 ± 14.4	42.4 ± 18.5	0.048
Mn	308 ± 28	316 ± 29	0.693
Fe	< 5	790 ± 655	-
Co	5.06 ± 0.66	5.67 ± 1.02	0.278
Ni	137 ± 11	139 ± 13	0.835
Cu	191 ± 93	231 ± 95	0.506
Mo	4.47 ± 2.71	6.68 ± 3.98	0.319
Sb	5.41 ± 0.99	5.94 ± 1.27	0.478
Zn	529 ± 68	547 ± 67	0.681
As	5.06 ± 0.41	6.28 ± 126	0.049

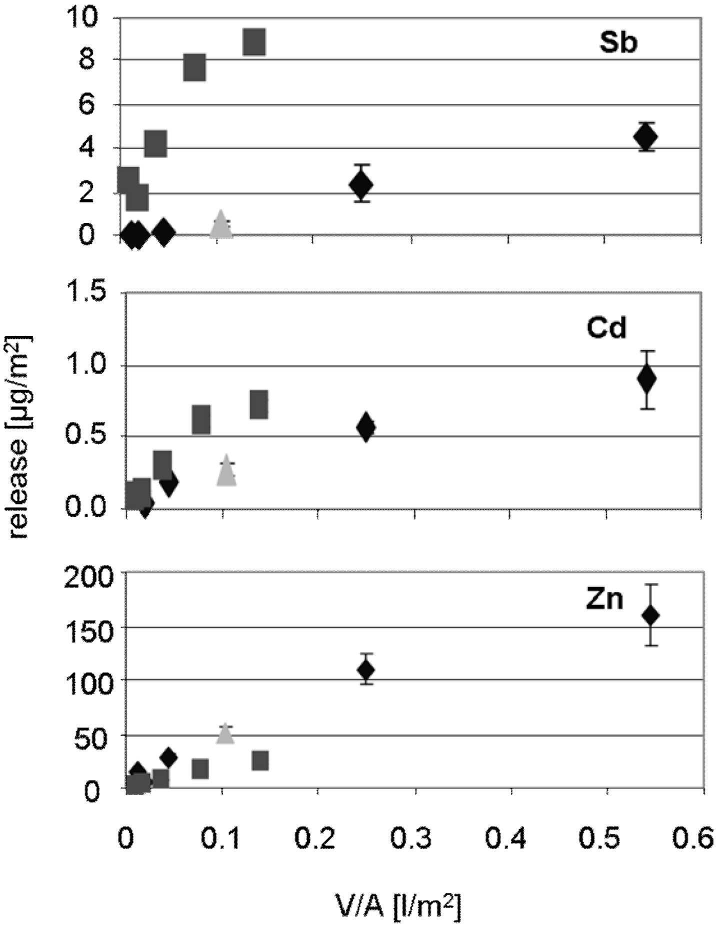

Figure SI 7: Cumulative release in µg/m² vs. the V/A ratio in l/m² calculated from the results of Table 4 by Equation 3 and 4 (square = slag 1, diamonds = slag 2, triangle = mixed sample slag 1 (0-5 mm), n = 8, ± 95% confidence interval.

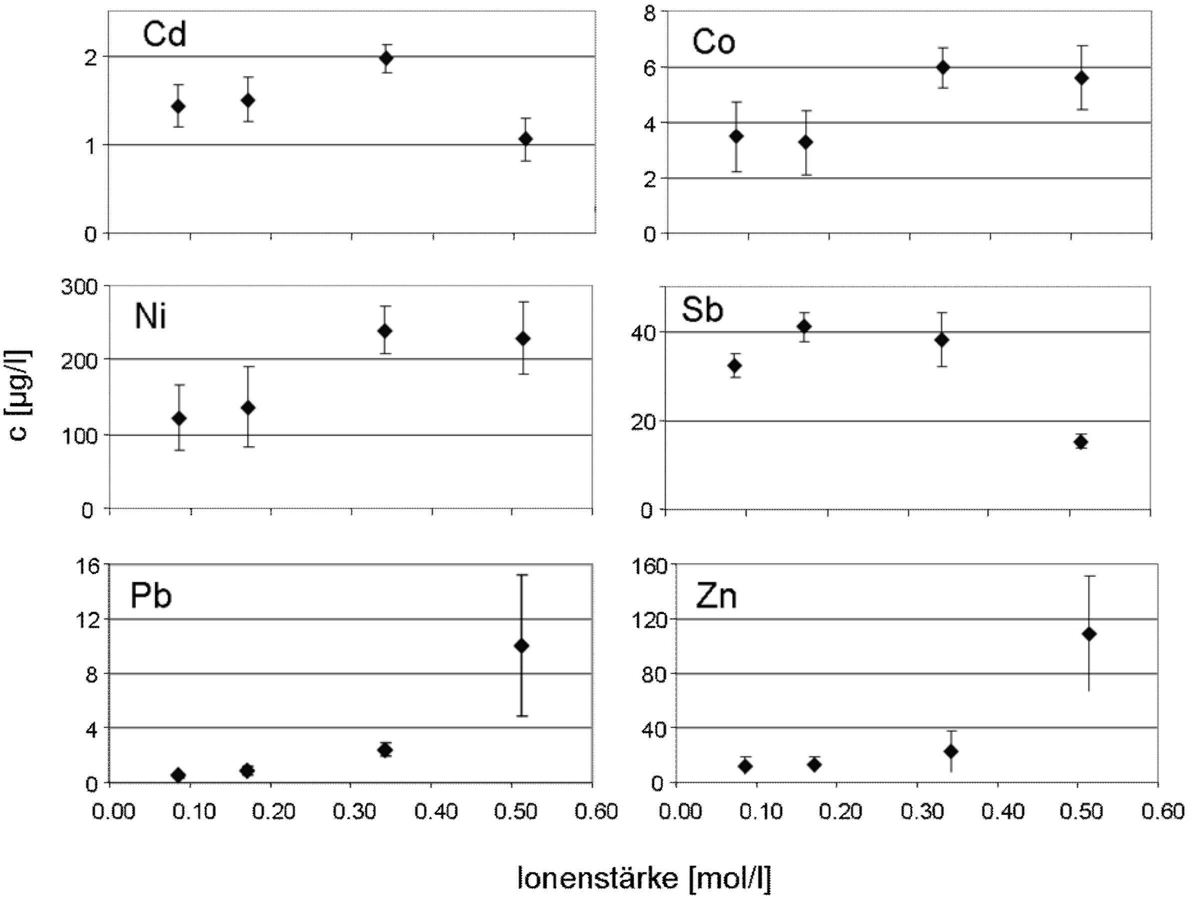

Figure SI 8: Metal(loid) concentrations vs. the ionic strength in the ionic strength experiments (n = 11, ± 95% confidence interval).

Table SI 4: Metal(loid) concentrations from leaching experiments with $CaCl_2$ solution (20 g/l, n = 6, ± 95% confidence interval).

Element	Concentration µg/l
As	5.04 ± 1.12
Cd	2.92 ± 0.49
Co	8.31 ± 0.72
Cu	125 ± 46
Mo	54.6 ± 5.6
Ni	378 ± 35
Sb	17.9 ± 1.7
Zn	255 ± 73

A.2 SUPPORTING INFORMATION OF CHAPTER 3

Determination of the long-term release of metal(loid)s from construction materials using DGTs

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Content:

Detailed information about the DGT units and disks.

Detailed information about the solution for determine the elution factor.

Detailed information about the slope of log release / log time plots.

Accumulation capacity of Chelex- and Fe-oxid binding layers.

Influence of the experimental design of DGT experiments for the mass of metal(loid)s in the eluent.

Figures:

Figure SI 1:	Experimental setup for static batch experiments. This setup was performed for each time period.
Figure SI 2:	Concentration of metal(loid)s in the eluent measured after filtration with different pore sizes (plain = 0.45 µm and striped = 8 µm) for experiments without DGT (black), with DGT_{Chelex} (dark grey) and $DGT_{Fe\text{-}oxide}$ (light grey). * significant differences (t-test, α = 0.05).

Figure SI 3:	Mass of the metal(loid)s measured in the eluent for the three different experiments (black diamonds = without DGT, white squares= DGT_{Chelex}, dark grey triangles = $DGT_{Fe\text{-}oxide}$) for different leaching times.
Figure SI 4:	Mass of metal(loid)s in the Chelex binding layer vs. time.
Figure SI 5:	CUS leaching experiment with DGT_{Chelex} or $DGT_{Fe\text{-}oxide}$. Row a) mass of metal(loid)s in eluent vs. time and row b) release vs. time on a double-log scale (black diamonds = without DGT, grey triangles = results from $DGT_{Fe\text{-}oxide}$, white squars = results from DGT_{Chelex}).

Tables:

Table SI 1:	Time periods for the long-term leaching experiments.
Table SI 2:	Detection limits for ICP-QMS and ICP-OES in µg/l (blank + 3 sigma).
Table SI 3:	Mass of the metal(loid)s for different re-elution steps for the calculation of the elution factor (SD = standard deviation).
Table SI 4:	Accompanying parameters of the long-term experiments (n = 39).
Table SI 5:	pH values, redox potentials and sulphate concentrations of the eluents after the sulphide leaching experiments (the recovery of the sulphate test was 86 ± 7%).
Table SI 6:	Concentrations of metal(loid)s after extraction with HNO_3 (eluant 1) and HNO_3 mixed with H_2O_2 (eluant 2 50/50).

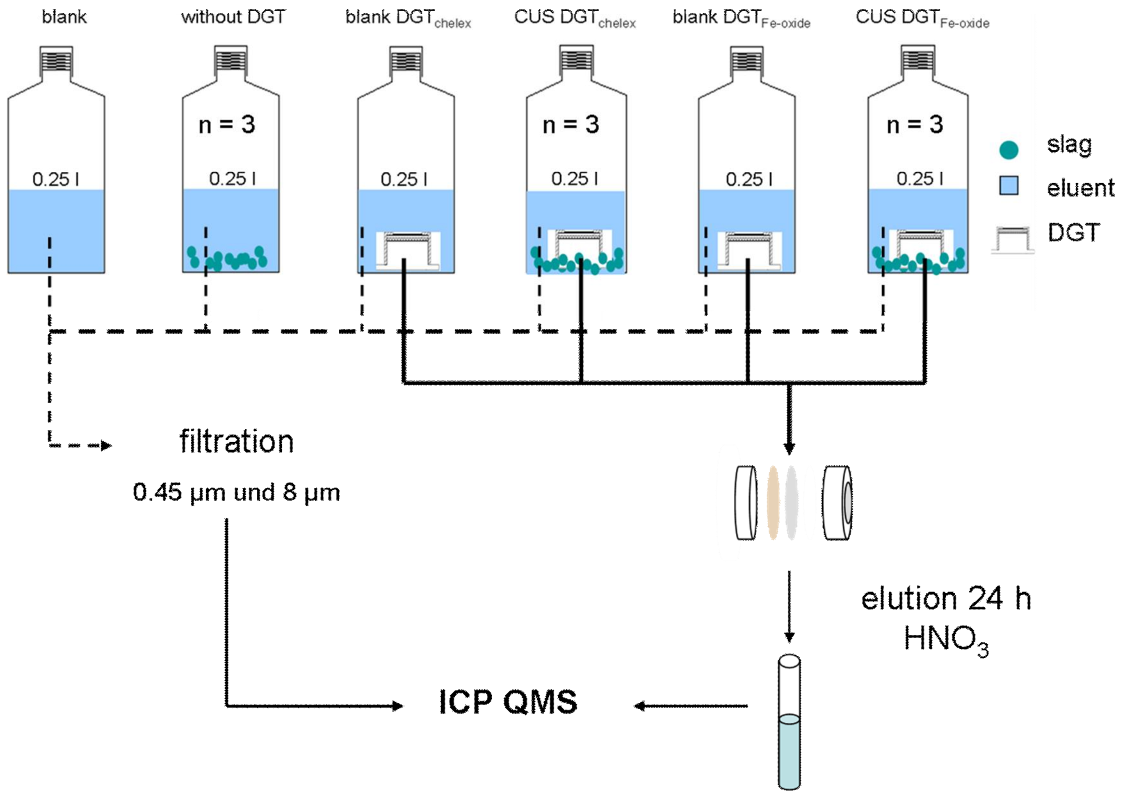

Figure SI 1: Experimental setup for static batch experiments. This setup was performed for each time period.

Table SI 1: Time periods for the long-term leaching experiments.

sampling time	time h
2 days	48
4 days	96
7 days	168
14 days	336
21 days	504
4 weeks	672
5 weeks	840
6 weeks	1008
8 weeks	1344
10 weeks	1680
3 months	2016
4 months	2952
6 months	4416

Table SI 2: Detection limits for ICP-QMS and ICP-OES in µg/l (blank + 3 sigma).

	Mn	Fe	Co	Ni	Cu	Zn	As	Mo	Cd	Sb	Ba	Pb
ICP-QMS	0.13	1.28	0.06	0.10	0.72	0.43	0.13	0.30	0.06	0.52	0.56	0.64
ICP-OES					10	2						50

Detailed information about the DGT units and disks

All disks have a diameter of 2.5 cm while the caps of the units show a diameter of 2 cm. The thickness of the discs is: (i) 0.078 cm in case of the diffusion gels; (ii) 0.04 cm for the Chelex gels and (iii) 0.06 cm for Fe-oxide gels. The thickness of the filter membrane is 0.013 cm.

The DGT sampling devices contain a binding layer and a diffusion layer protected by a membrane filter. They are deployed *in situ* and only the filter is directly exposed to the aqueous phase. The metal(loid) diffuse from the aqueous phase through the filter membrane and the diffusion gel to the binding layer, on which they are accumulated. After completion of the accumulation, the metal(loid)s can be eluted from the resin layer by HNO_3.

Detailed information about the solution for determine the elution factor

The standard solution was prepared from ICP-Standards (Merck, Germany) with a total mass of 20 µg of As, Cu, Mo, Sb and Pb.

To be as close as possible to the experimental set-up described before, for the CUS-solution CUS (600 g, particle size 0-5 mm) was leached with 3 l ultra-pure water for a period of three weeks. The solution was filtered (0.45 µm) and the concentration of the metal(loid)s was determined by ICP-QMS/OES.

Table SI 3: Mass of the metal(loid)s for different re-elution steps for the calculation of the elution factor (SD = standard deviation).

	mass [ng]					
	Cu	As	Mo	Sb	Pb	Fe
Step 1	3 249	19.6	25.1	31.9	467	467
Step 2	358	7.2	9.2	5.0	46	46
Step 3	40	<LOD	<LOD	<LOD	5	5
sum	3 647	26.7	34.3	36.9	518	518
f_e	0.89	0.73	0.73	0.86	0.90	0.90
SD	0.01	0.06	0.08	0.03	0.02	0.02

Table SI 4: Accompanying parameters of the long-term experiments (n = 39).

	pH	redox potential
without DGT	6.8 ± 0.1	348 ± 8
DGT_{Chelex}	6.8 ± 0.1	343 ± 5
$DGT_{Fe\text{-}oxide}$	6.8 ± 0.1	338 ± 6

The results of the accompanying parameters are summarised in Table SI 3. There is no significant difference between the experiments (t-test, α = 0.05).

Therefore the conditions during the experiments without DGT, DGT_{Chelex} and $DGT_{Fe\text{-}oxide}$ are comparable. The pH increased during the first 168 h, then the pH is constant. The redox potential was constant over the time.

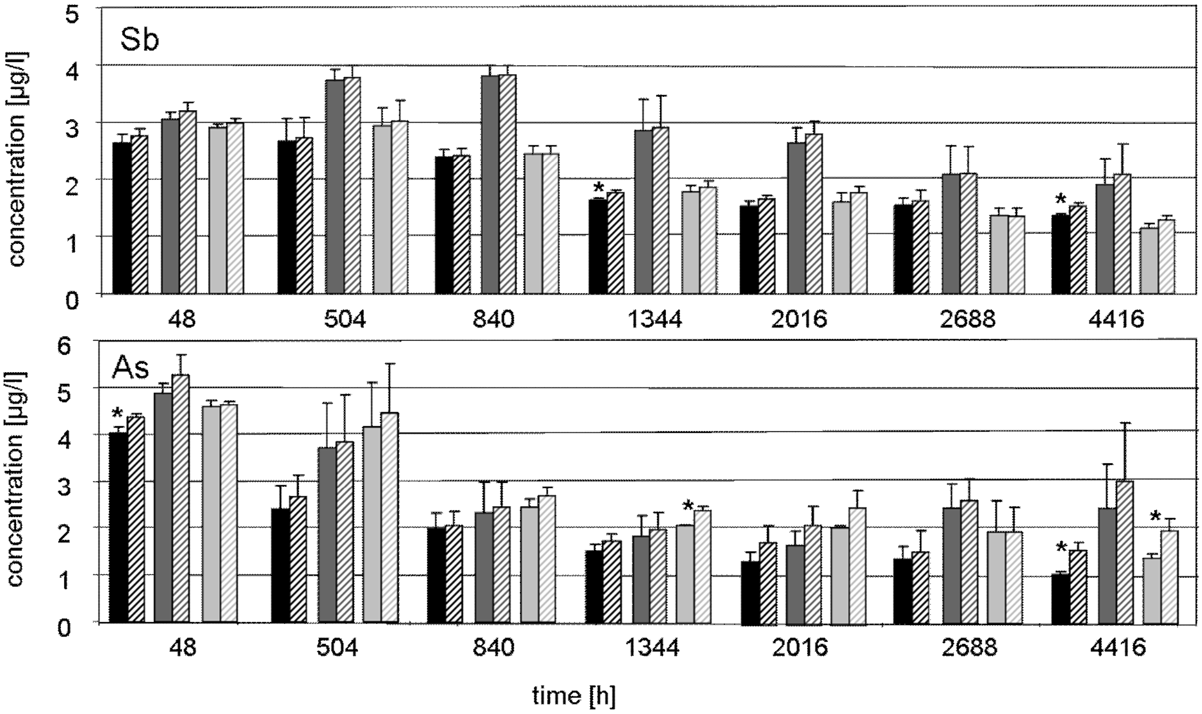

Figure SI 2: Concentration of metal(loid)s in the eluent measured after filtration with different pore sizes (plain = 0.45 µm and striped = 8 µm) for experiments without DGT (black), with DGT_{Chelex} (dark grey) and $DGT_{Fe\text{-}oxide}$ (light grey). * significant differences (t-test, α = 0.05).

Detailed information about the slope of log release / log time plots

Theoretically, a 100% surface driven dissolution process displays a slope of 1 in the log release / log time plot. A slope of 0.5 in the log release / log time plot indicates a diffusion controlled process [1]. A slope of zero indicates in this study either no release or opposing processes such as release and sorption onto the test material surface. A negative value for the slope is obtained when sorption is the dominant process.

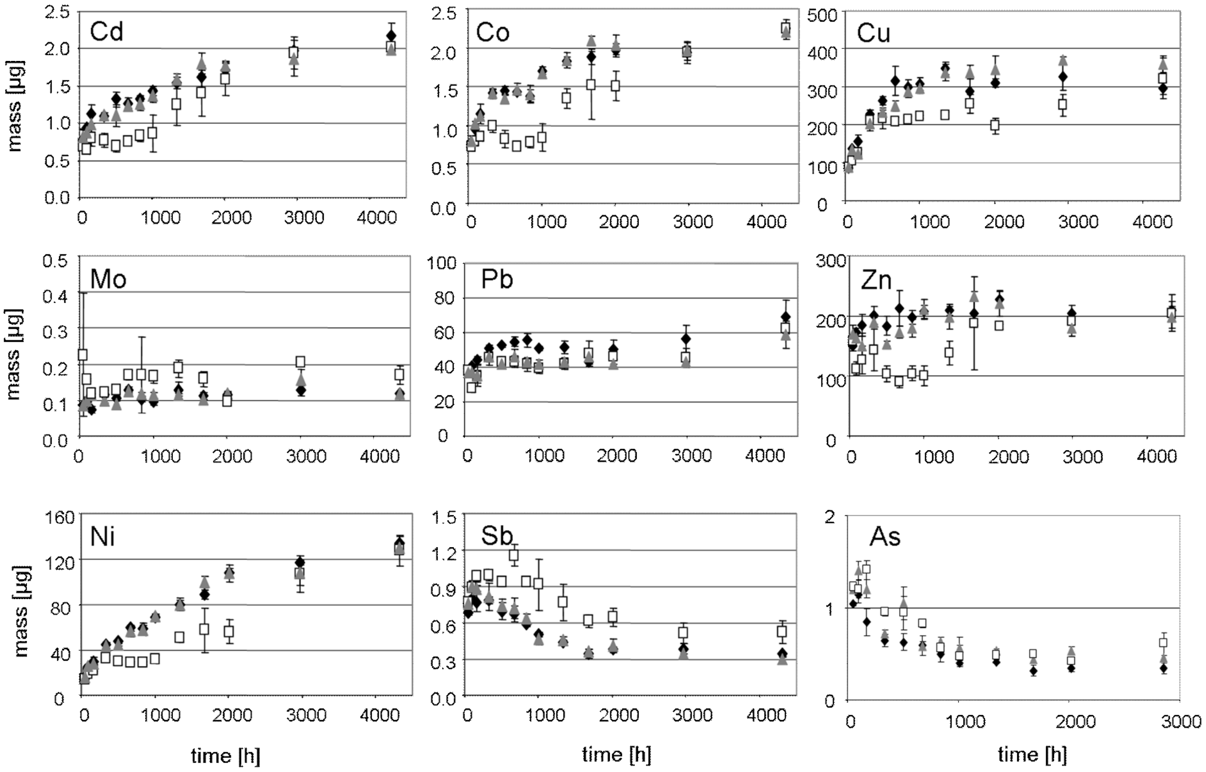

Figure SI 3: Mass of the metal(loid)s measured in the eluent for the three different experiments (black diamonds = without DGT, white squares= DGT$_{\text{Chelex}}$, dark grey triangles = DGT$_{\text{Fe-oxide}}$) for different leaching times.

Accumulation capacity of Chelex- and Fe-oxid binding layers

The accumulation of the different elements in the Chelex and Fe-oxide binding layer is a time-dependent process which can be displayed by means of mass of metal(loid)s in the binding layer vs. time.

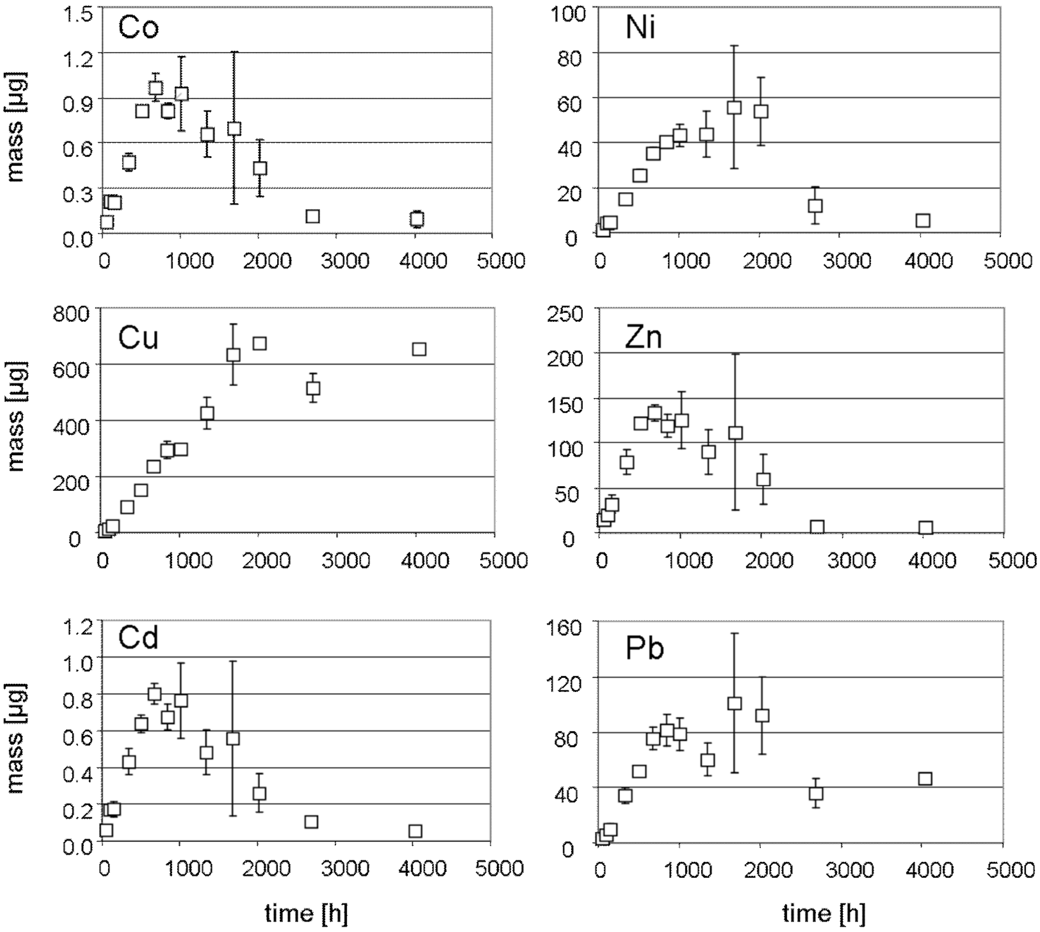

Figure SI 4: Mass of metal(loid)s in the Chelex binding layer vs. time.

Fig. SI 4 shows that during the first 1008 h all measured metals are accumulated to the Chelex binding layer. After a period of ~1008 h (six weeks), a saturation of the Chelex binding layers can be observed which causes a re-dissolution of the metals. After this time the mass of the metals in the Chelex binding layer start to decrease, except for Cu (Fig. SI 4). Only Cu is accumulated over the whole time period. The exchange from the Chelex binding layer follows nearly the selectivity of the Chelex with Cu > Pb = Ni > Co = Cd = Zn > Mn [2]. Using DGT$_{\text{Fe-oxide}}$, an overloading of the Fe-oxide binding layer is not observed (data not shown).

Influence of the experimental design of DGT experiments for the mass of metal(loid)s in the eluent

For analytes which form predominantly cations in the water phase, DGT$_{\text{Fe-oxide}}$ was added to insure that no effects for the mass of metals in the eluent are caused by the use of DGT units (potential influence of the housing, the gel or the 3M tape). A comparison of the metal mass of the eluents from experiments without DGT and DGT$_{\text{Fe-oxide}}$ exhibited that the use of DGT units were not impacting the release of the metals (Fig. SI 5). The same applies to the mass of metalloids from experiments without DGT and DGT$_{\text{Chelex}}$. This was also supported by extraction results of the DGT$_{\text{Fe-oxide}}$ where no metals (except Cu and Pb) were detected (data not shown).

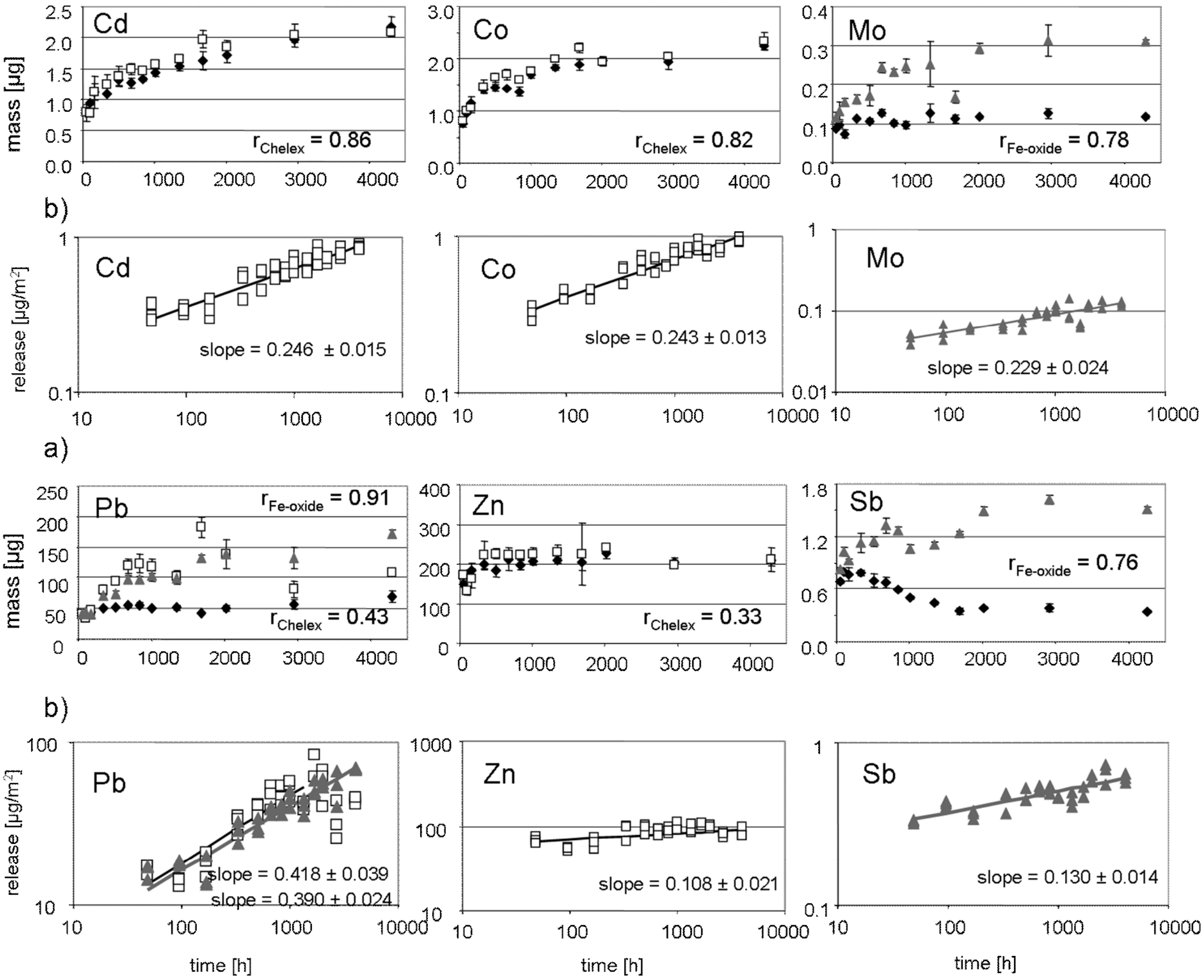

Figure SI 5: CUS leaching experiment with DGT$_{\text{Chelex}}$ or DGT$_{\text{Fe-oxide}}$. Row a) mass of metal(loid)s in eluent vs. time and row b) release vs. time on a double-log scale (black diamonds = without DGT, grey triangles = results from DGT$_{\text{Fe-oxide}}$, white squares = results from DGT$_{\text{Chelex}}$).

Table SI 5: pH values, redox potentials and sulphate concentrations of the eluants after the sulphide leaching experiments (the recovery of the sulphate test was 86 ± 7%).

fraction	eluant	pH	redox [mV]	SO_4 [mg/l]
1	HNO_3	5.4	240	< 40
	$HNO_3 + H_2O_2$	5.3	334	198
2	HNO_3	3.2	380	< 40
	$HNO_3 + H_2O_2$	3.3	453	137
3	HNO_3	2.9	395	< 40
	$HNO_3 + H_2O_2$	3.0	473	110
4	HNO_3	4.2	316	< 40
	$HNO_3 + H_2O_2$	3.2	458	95

Table SI 6: Concentrations of metal(loid)s after extraction with HNO_3 (eluant 1) and HNO_3 mixed with H_2O_2 (eluant 2).

	Concentration [µg/l]									
	HNO_3					$HNO_3 + H_2O_2$				
fraction	1	2	3	4	**sum**	1	2	3	4	**sum**
Mn	8.52	16.4	14.6	17.1	**56.7**	4.23	0.88	0.80	1.49	**7.40**
Fe	1 253	8 741	8 481	10 173	**28 648**	7.61	29.9	74.2	61.0	**173**
Co	3.42	7.34	7.10	8.98	**26.8**	4.49	4.22	4.32	7.01	**20.0**
Ni	25.4	38.3	29.5	49.8	**143**	115	198	216	361	**890**
Cu	466	710	416	718	**2 309**	491	12 627	9 322	16 597	**39 037**
Zn	273	433	411	485	**1 602**	1 186	599	386	676	**2 847**
As	1.16	9.06	6.27	4.50	**21.0**	4.01	8.46	9.47	10.97	**32.9**
Mo	1.50	1.72	1.78	0.80	**5.80**	82.2	31.3	36.5	76.3	**226**
Cd	1.46	0.77	0.46	0.59	**3.28**	7.25	5.98	4.25	7.42	**24.9**
Sb	0.73	1.99	1.51	0.70	**4.93**	2.45	0.95	0.85	1.06	**5.31**
Pb	27.7	61.1	22.9	16.0	**128**	7.07	266	199	153	**625**

References:

[1] H.A. van der Sloot, Leaching behaviour of waste and stabilized waste materials; characterization for environmental assessment purposes, Waste Management and Research, 8 (1990) 215-228.

[2] Nobel, A. (2000) Chelex 100 and Chelex 20 Chelating Ion Exchange Resin Instruction Manual. Bio-Rad Laboratories.

A.3 SUPPORTING INFORMATION OF CHAPTER 4

Influence of environmental parameters and of their interactions on the release of metal(loid)s from a construction material in hydraulic engineering

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Content:

pH measurements.

Figures:

Figure SI 1:	Mean concentrations of the metal(loid)s in the eluates in leaching experiments without CUS and two different sediment contents.
Figure SI 2:	Concentrations of the metal(loid)s in leaching experiments for different factor combinations with 0.75 g sediment (light grey = experiments with CUS, dark grey = experiments without CUS).
Figure SI 3:	Plot of marginal means for the concentration of the metal(loid)s in the leaching experiments with different factor combinations.

Tables:

Table SI 1: Full factorial design for the leaching experiments.

design 1					design 2				
sample number	temperature [°C]	NaCl [g/l]	pH	sediment content [g]	sample number	temperature [°C]	NaCl [g/l]	pH	sediment content [g]
K 91	4	0	4	0.75	K 37	4	0	7	0.75
K 37	4	0	7	0.75	K 64	4	0	10	0.75
K 19	4	0	4	3.75	K 46	4	0	7	3.75
K 46	4	0	7	3.75	K 73	4	0	10	3.75
K 97	4	30	4	0.75	K 43	4	30	7	0.75
K 43	4	30	7	0.75	K 70	4	30	10	0.75
K 25	4	30	4	3.75	K 52	4	30	7	3.75
K 52	4	30	7	3.75	K 79	4	30	10	3.75
K 82	4	0	4	0	K 28	4	0	7	0
K 28	4	0	7	0	K 55	4	0	10	0
K 88	4	30	4	0	K 34	4	30	7	0
K 34	4	30	7	0	K 61	4	30	10	0
K 93	36	0	4	0.75	K 39	36	0	7	0.75
K 39	36	0	7	0.75	K 66	36	0	10	0.75
K 21	36	0	4	3.75	K 48	36	0	7	3.75
K 48	36	0	7	3.75	K 75	36	0	10	3.75
K 99	36	30	4	0.75	K 45	36	30	7	0.75
K 45	36	30	7	0.75	K 72	36	30	10	0.75
K 27	36	30	4	3.75	K 54	36	30	7	3.75
K 54	36	30	7	3.75	K 81	36	30	10	3.75
K 84	36	0	4	0	K 30	36	0	7	0
K 30	36	0	7	0	K 57	36	0	10	0
K 90	36	30	4	0	K 36	36	30	7	0
K 36	36	30	7	0	K 63	36	30	10	0

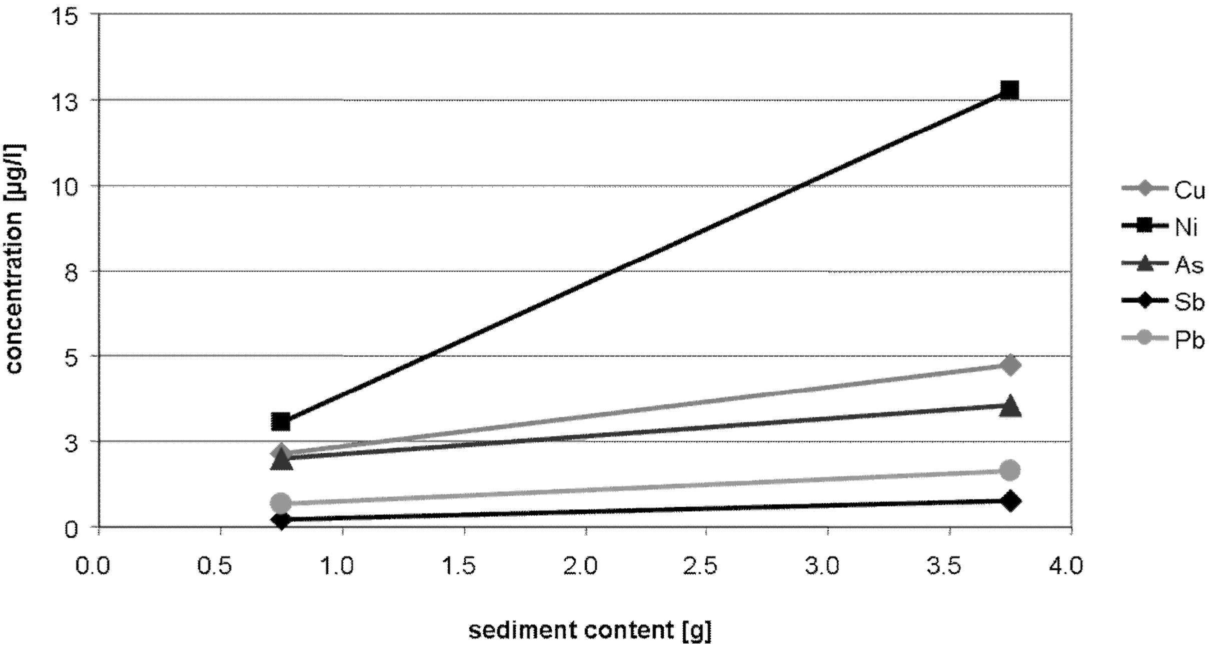

Figure SI 1: Mean concentrations of the metal(loid)s in the eluates in leaching experiments without CUS and two different sediment contents.

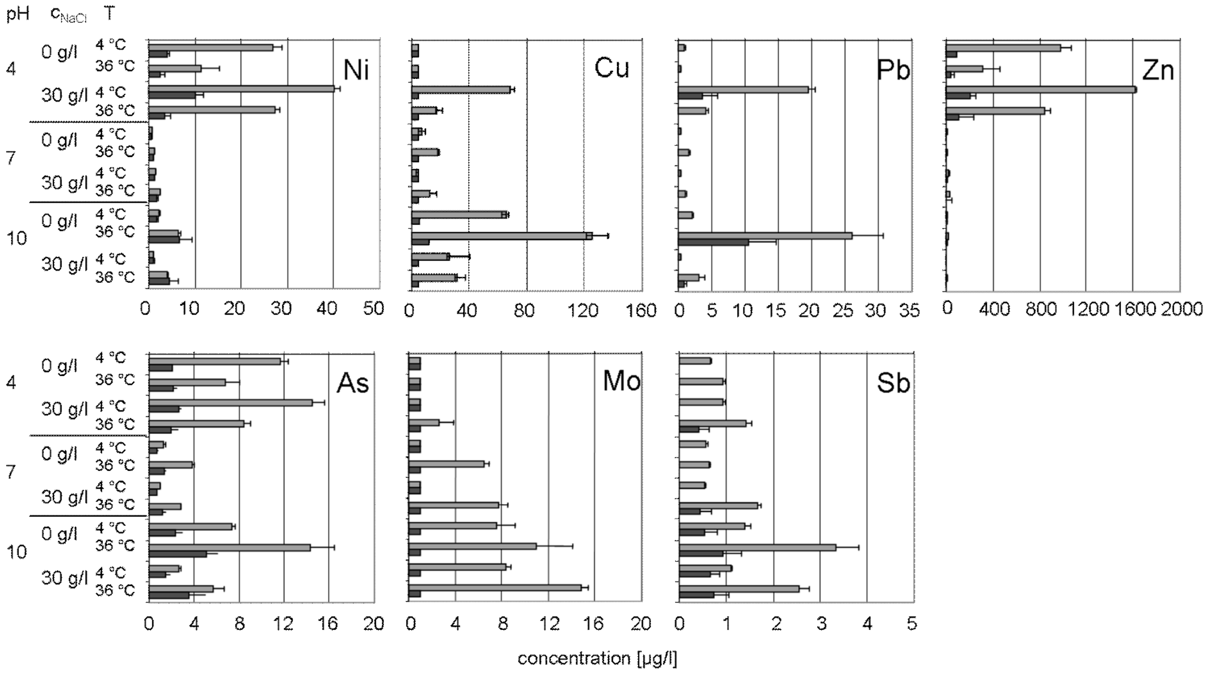

Figure SI 2: Concentrations of the metal(loid)s in leaching experiments for different factor combinations with 0.75 g sediment (light grey = experiments with CUS, dark grey = experiments without CUS).

Table SI 2: Limit of detection for ICP-QMS and ICP-OES in µg/l (blank + 3 sigma).

element	As	Cu	Mo	Ni	Pb	Sb	Zn
LoD [µg/l]	0.30	1.50	1.00	0.15	0.40	0.40	0.15

pH measurements

The pH value was measured in the experiments after 24 h and 48 h in order to check for a potential impact of the buffer capacity of the sediment and of the CUS and of their interactions. The results (Table SI 3) show that the pH values of the eluates were influenced by the temperature, the CUS and the sediment at the lower (pH 4) and the upper limit (pH 10). The more sediment was applied; the lower was the difference to pH 7. Whereby, the effect was more pronounced at higher temperatures. Thus the buffer capacity of the sediment is higher than the capacity of the CUS and a higher temperature increased the buffer capacity of both the sediment and CUS. The NaCl concentration did not impact the pH value, since NaCl is a neutral salt and did not cause any significant H^+ release from the other matrices.

Table SI 3: pH measurements for different time steps for the leaching experiments at different factor combinations.

temperature	time	pH 4 with 0.75 g sediment	pH 4 with 3.75 g sediment	pH 10 with 0.75 g sediment	pH 10 with 3.75 g sediment
	0 h	3.5	3.9	10.2	10.3
4	24 h	4.9	4.7	10.0	9.5
	48 h	5.4	5.0	9.7	9.6
	0 h	3.5	3.9	10.2	10.0
20	24 h	4.4	5.0	9.0	9.0
	48 h	5.0	4.9	9.7	8.9
	0 h	3.5	3.9	10.2	10.3
36	24 h	4.5	5.3	9.1	8.1
	48 h	6.0	5.1	9.5	9.3

Table SI 4: p-values of the Shapiro-Wilks-test (SW) and R² for the full factorial design of the main experiments (p = 0.05).

	design 1 R^2	design 1 p (SW)	design 1 model	design 2 R^2	design 2 p (SW)	design 2 model
As	0.99	0.06	three way	0.90	0.08	Q
Cu	0.96	0.72	three way	0.89	0.10	three way
Mo	0.96	0.15	three way	0.93	0.59	three way
Ni	0.80	0.07	Q	-	-	no effect
Pb	0.96	0.21	three way	0.94	0.19	three way
Sb	0.97	0.72	three way	0.93	0.25	three way
Zn	0.89	0.24	Q	0.89	0.09	three way

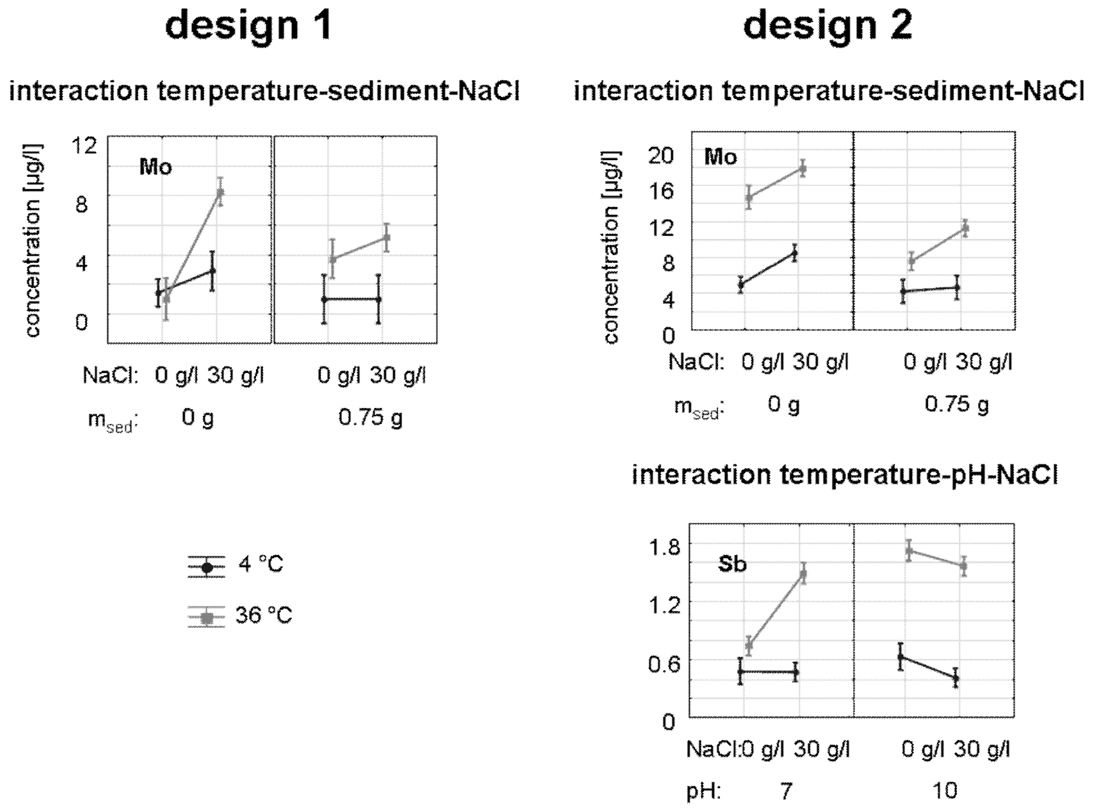

Figure SI 3: Plot of marginal means for the concentration of the metal(loid)s in the leaching experiments with different factor combinations.

Table SI 5: Separation and recovery of CUS particles from sediments with a NdFeB magnet (n = 6).

CUS / Sed	copper slag			sediment		
	initial weight [g]	back weight [g]	recovery [%]	initial weight [g]	back weight [g]	recovery [%]
1 / 0	7.500 ± 0.035	7.459 ± 0.013	99.5 ± 0.3	-	-	-
1 / 0*	0.558 ± 0.028	0.523 ± 0.026	93.8 ± 0.3	-	-	-
10 / 1	7.500 ± 0.035	7.442 ± 0.036	99.2 ± 0.6	0.863 ± 0.171	0.834 ± 0.150	96.9 ± 1.7
2 / 1	7.500 ± 0.035	7.426 ± 0.036	99.0 ± 0.7	3.689 ± 0.063	3.615 ± 0.074	98.0 ± 0.4

* particle size < 0.063 mm

Table SI 6: Limit of Detection for sediment measurements with ICP-QMS (blank + 3 sigma).

element	Cr	Ni	Cu	Zn	As	Mo	Sb	Pb
LoD [µg/l]	1.33	1.15	1.10	3.18	0.41	0.70	1.70	0.74

Table SI 7: Mass content of metal(loid)s in the sediment for the experiments with copper slag and 0.75 g sediment.

analyte	mass content [mg/kg]		
	pH 4	pH 7	pH 10
Fe	39 600 ± 1 300	40 000 ± 1 800	37 700 ± 1 300
Co	21.7 ± 0.5	22.1 ± 0.8	20.7 ± 0.5
Ni	54.6 ± 0.7	56.7 ± 1.0	53.3 ± 0.7
Cu	446 ± 13	526 ± 86	319 ± 68
Zn	1 310 ± 30	1 320 ± 60	1 190 ± 50
As	13.5 ± 1.4	11.9 ± 0.4	10.3 ± 0.7
Mo	30.6 ± 3.8	28.3 ± 3.9	23.3 ± 2.4
Cd	1.89 ± 0.08	1.90 ± 0.05	1.80 ± 0.20
Sb	<LoD	<LoD	<LoD
Pb	148 ± 5	151 ± 4	135 ± 3

Curriculum Vitae

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