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

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HIGHLIGHTS

- ► The link between laboratory studies (<5 mm) and field scenarios (>45/125 mm) is presented.
- ► This link is strongly needed in administration and environment protection work (mass balances).
- ► Significant method artefacts causing an underestimation of the release of analytes.
- ► In water construction the impact of the ionic strength needs to be examined.
- ► Two methods are introduced to determine the geometric surface area in leaching tests.

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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.

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.

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

mg/kg	Copper slag ($n = 6$) [11]		Basaltic rocks ($n = 7$) [12]	
	x	Δx	x	Δx
Barium	503	92	711	176
Chromium	398	731	283	160
Cobalt	283	78	46	7
Copper	6842	1552	44	11
Nickel	172	34	200	126
Strontium	143	59	826	109
Vanadium	57	17	188	24
Zinc	17733	1964	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. Materials and methods

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 = Elbe–Havel channel and slag 4 = Weser, 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).

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 Eq. (1) [22] with the diameter d [μm] and density ρ [g/cm^3].

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

With this equation the calculation of a roughness factor λ from the external (A_{ex}) surface area, measured with geometric methods,