

## Leaching experiments on the release of heavy metals and PAH from soil and waste materials

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### ABSTRACT

Leaching tests are fundamental tools for the assessment of long-term impact of contaminated waste materials on the soil-groundwater pathway. Experiments were carried out in the framework of standardization and validation of column percolation and batch test procedures, in particular concerning the stipulation of the experimental setup. The colloid release of column and batch experiments was compared and the influence of different column filling heights (12.5–50 cm) on the release of polycyclic aromatic hydrocarbons (PAH) from soil was studied, as well as the effect of varying contact times (2.5–16 h) on the release of chromium from construction and demolition (C&D) waste and municipal solid waste incineration (MSWI) bottom ash. The results indicate that filtration of the eluate, which is required for batch tests, does not always allow the simulation of the actual colloid amount in soil pore water. Medium column heights four times the inner diameter of the column seemed to provide reasonable equilibrium adjustment conditions and avoid major biodegradation. The release of chromium was only marginally affected by the contact time, varied between 0.115 and 0.150 mg/kg for demolition waste eluate at a liquid-to-solid ratio of approximately 5 L/kg.

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### 1. Introduction

Construction and demolition (C&D) waste and municipal solid waste incineration (MSWI) bottom ash constitute a significant mass percent of the waste materials produced every year around the world. In Germany alone, about 73 of the 240 million tons of mineral waste produced per year are C&D waste, with incineration and power plant ash accounting for about 15 million tons, thus representing the largest contingents of waste after excavated soil materials. Since C&D waste and MSWI bottom ash are often contaminated with inorganic and/or organic pollutants, the risk assessment of materials containing these substances is of particular importance. Laboratory leaching tests are common tools to aid the assessment of long-term impact of contaminated materials on the soil-groundwater pathway, as they determine the source term as an expression of release potential of water soluble contaminants during the use or disposal of waste materials. Different leaching tests have been developed to characterize and assess the constituents that can be released from waste materials [1–6].

Whereas column tests provide a flow-through pattern similar to that found in field conditions and enable basic characterization of waste materials, batch or tank tests present a snapshot at a certain liquid-to-solid (or to-surface area) ratio [7,8].

With the designated establishment of a new Ordinance on Waste Utilization and the amendment of the German Ordinance on Soil Protection and Contaminated Sites, leaching tests are expected to become a more important methodology for waste materials source term determination [9].

Waste materials should be tested under conditions similar to their actual application in re-use scenarios to achieve reliable results. Since the standards for leaching procedures available at an international level so far are either not validated or considered inadequate in respect to coarse-grained materials, new standards had to be developed which are applicable to coarse-grained waste materials and suitable to the new German regulations concerning waste management. Two standards, a column test (DIN 19528 2009 [10]) and a batch test (DIN 19529 2009 [11]), were developed by the responsible standardization committee of the German Standardization Organization DIN; these standards were recently validated by an interlaboratory comparison performed by BAM [12,13]. Following the outcome of the joint project “Seepage prognosis”, an agreement was reached concerning the liquid-to-solid ratio (L/S) for compliance testing: the L/S was stipulated to be set at 2 L/kg. Whereas batch tests are only suitable for compliance testing, column tests allow for both compliance testing and basic characterization.

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**Table 1**  
Test conditions for compliance tests according to DIN 19528 and DIN 19529 using BA RM and CS1 RM.

| Test conditions DIN 19528             | BA RM<br>(≤32 mm) | CS1 RM<br>(≤10 mm) |
|---------------------------------------|-------------------|--------------------|
| Internal diameter of the column (cm)  | 10.00             | 5.86               |
| Sample filling height in column (cm)  | 40.0              | 25                 |
| Filling volume (cm <sup>3</sup> )     | 3.142             | 674                |
| Dry mass (kg)                         | 5.2               | 1.2                |
| Particle density (g/cm <sup>3</sup> ) | 2.50              | 2.60               |
| Bulk density (g/cm <sup>3</sup> )     | 1.65              | 1.77               |
| Porosity <i>n</i> (-)                 | 0.35              | 0.33               |
| Contact time eluent/sample (h)        | 5.0               | 5.0                |
| Flow rate (ml/min)                    | 3.56              | 0.75               |
| Eluate volume up to L/S 2 (L)         | 10.4              | 2.4                |
| Test duration until L/S 2 (h)         | 48.5              | 52.8               |
| Test conditions DIN 19529             |                   |                    |
| Dry mass (kg)                         | 2.5               | 0.25               |
| Eluate volume at L/S 2 (L)            | 5                 | 0.5                |
| Agitation duration (h)                | 24                | 24                 |

As opposed to CEN/TS 14405 (2004) [14] and ISO/TS 21268-3 (2007) [15], the new column test procedure stipulates a certain contact time between leachant and sample material instead of a fixed flow rate. This new approach enables the use of different column dimensions by applicants depending on their specific requirements and most importantly, on the maximum grain size of the materials under investigation.

Additionally, DIN 19528 and DIN 19529 allow the testing of materials with a maximum grain size of 32 mm, which is not considered in other existing standards (CEN/TS 14405 (2004) [14], ISO/TS 21268-3 (2007) [15], EN 12457-1 2002 [16]; ISO/TS 21268-1 2007 [17]).

The new batch test procedure [11] has been validated only for inorganic substances. An analogous standard for batch testing is being prepared by DIN, which stipulates a special procedure for the liquid/solid separation step in the case of organic compounds. BAM currently conducts ruggedness testing for this batch test procedure taking into account regulated organic contaminants of high priority.

In addition to the validation interlaboratory comparisons, investigations on the variation of boundary conditions for batch and column tests were carried out for several years. Exemplary results concerning the stipulation of the experimental setup are presented. The colloid amount of the eluates from column and batch experiments considering different sample pre-treatment procedures are compared. The influence of test duration of column experiments in terms of equilibrium establishment between sample and eluate, as well as biodegradation using PAH contaminated soil, was studied. The impact of contact time on heavy metal release from C&D waste and MSWI bottom ash in column experiments was investigated.

## 2. Experimental

The test materials were obtained from materials previously prepared for two different interlaboratory comparisons [12,13]. CS1 RM (contaminated soil, reference material), BA RM (MSWI bottom ash, reference material), and DW1 RM (construction and demolition waste, reference material) were taken from the former, and CS2 RM (contaminated soil, reference material) and DW2 RM (construction and demolition waste, reference material) from the latter interlaboratory comparison.

Batch and column percolation tests were carried out according to [10] and [11] respectively using CS1 RM, CS2 RM, BA RM, DW1 RM, and DW2 RM. Experimental conditions for compliance testing of two different materials are given in Table 1.

Batch test were performed by agitating sample and demineralized water for 24 h in an end-over-end tumbler followed by sample preparation consisting of settling, centrifugation, and pressurized filtration through a glass fiber filter.

Column tests were performed with glass columns of 5.86 cm internal diameter. The test samples were filled into the columns and compacted slightly so that the bulk density was very similar for all columns. On bottom and top of the columns a quartz sand filter layer was placed (0.6–1.2 mm grain size). The columns were saturated with demineralized water within 2 h directly prior to the test.

Additionally, the column test allows basic characterization experiments, whose conditions differ from those for the compliance tests. Instead of one eluate, four fractions at different L/S ratios (0.3, 1, 2, and 4) have to be collected. The results for the respective compliance test can be calculated by cumulating the released amount of the first three fractions for the components analyzed and back-calculating it as a concentration at L/S 2 L/kg.

Fig. 1 shows the workflow for compliance testing and the relevant experimental conditions. The pre-treatment of the eluates prior to the analysis depends on whether organic or inorganic substances will be analyzed.

The contact time between eluent and test material ( $t_c$  [h]) is calculated according to [10] by Eq. (1):

$$t_c = \frac{V \cdot n}{q \cdot 60} \quad (1)$$

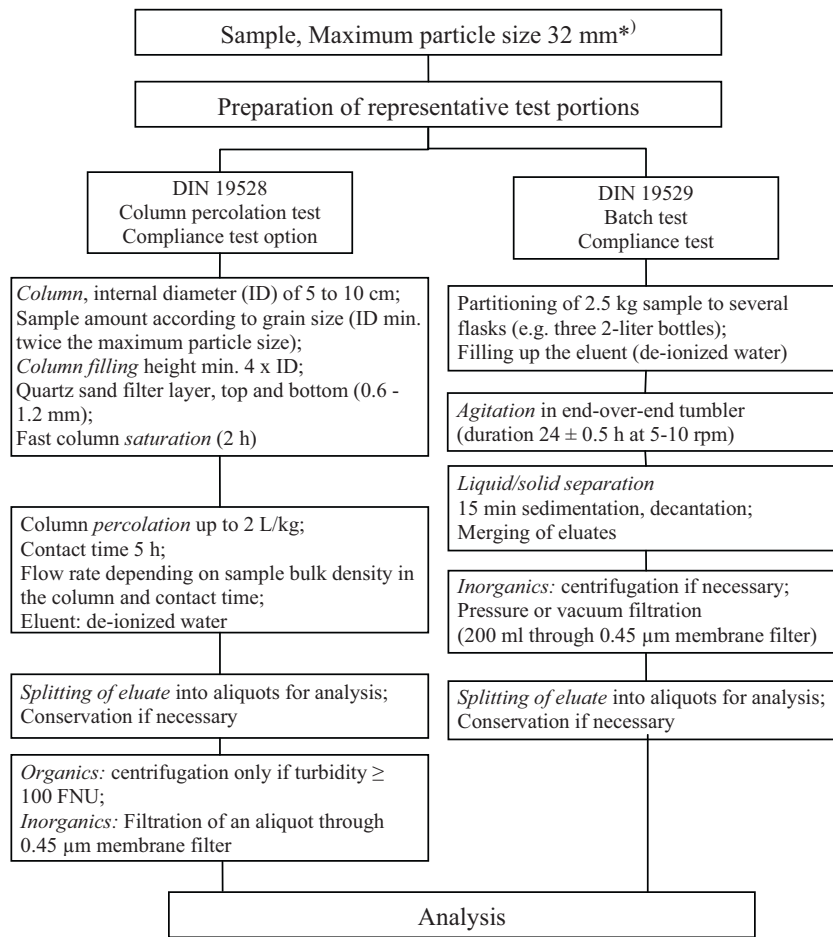
where  $V$  (mL) is the filling volume of the column,  $n$  (-) is the porosity,  $q$  (mL/min) is the applied flow rate and 60 is used as time unit conversion factor from minutes to hours.

The turbidity of the eluates was measured with a Hach 2100 IS turbidity meter according to DIN EN ISO 7027 [18]. PAH concentrations were measured by liquid–liquid extraction of the eluates followed by HPLC with fluorescence detection, according to DIN EN ISO 17993 [19]. The HPLC was a Waters 625 system, equipped with a Waters 470 fluorescence detector. The column used was a Supelcosil LC-PAH of 5 μm particle size, 25 cm length, and an internal diameter of 4.6 mm. A mixture of acetonitrile and water was used as mobile phase. After 5 min of 40% acetonitrile fraction, the gradient was changed within 25 min to 100% acetonitrile, which was kept for 6 more minutes. The PAHs investigated were those identified by the United States Environmental Protection Agency (US-EPA) as priority pollutants. Since acenaphthylene is not accessible through fluorescence detection, all results refer to the remaining 15 of the 16 EPA-PAH. The concentrations of chromium were measured with Inductively Coupled Plasma Optical Emission Spectrometry (ICP OES), following DIN EN ISO 11885 [20] and using a Thermo Scientific Iris Intrepid II XSP spectrometer.

## 3. Results and discussion

In order to explain the selection of the new specifications in the German leaching standards recently published, examples including interlaboratory test results are given below.

Batch tests often lead to enhanced mobilization of colloids due to the agitation. Those particles often contain colloidal-linked pollutants [21], and therefore the eluate has to be centrifuged and/or filtrated in order to avoid an overestimation of contaminant release. However, determining the cut-off for filtering and/or centrifugation to simulate realistic soil water remains a difficult step. In the case of column tests, the packing of the sample material and quartz sand filter layers results in a self-filtration capacity that usually renders unnecessary an additional subsequent sample preparation. Fig. 2 compares the turbidity of DW2 RM and CS2 RM eluates obtained from column tests without subsequent filtration and from batch tests using a 0.45-μm mem-



\*) Particles >32 mm can be crushed

Fig. 1. Workflow for compliance testing according to DIN 19528 and DIN 19529.

brane during filtration; the numbers on the x axis each represent a laboratory that participated in the interlaboratory comparison test. The filtration at 0.45 µm in the batch test procedure is not always appropriate to simulate the actual colloid amount in soil pore water due to additional pH dependence of colloid mobilization. The turbidity of column test eluates is very low in the case of DW2 RM, indicating that the self-filtration of the column is working in a similar way to that found in field conditions,

where a range of turbidity measured in soil water showed low levels [22]. However, the effect of soil pH on the colloid mobilization is not considered, which can be seen in the case of CS2 RM. The turbidity of the eluates obtained from column experiments using soil (initial pH value 8.5 [23]) is significantly higher than those from DW2 RM (pH value 10.9).

The particle size of the quartz sand filter layer has to be strictly adhered to in order to ensure some retention of the finest parti-

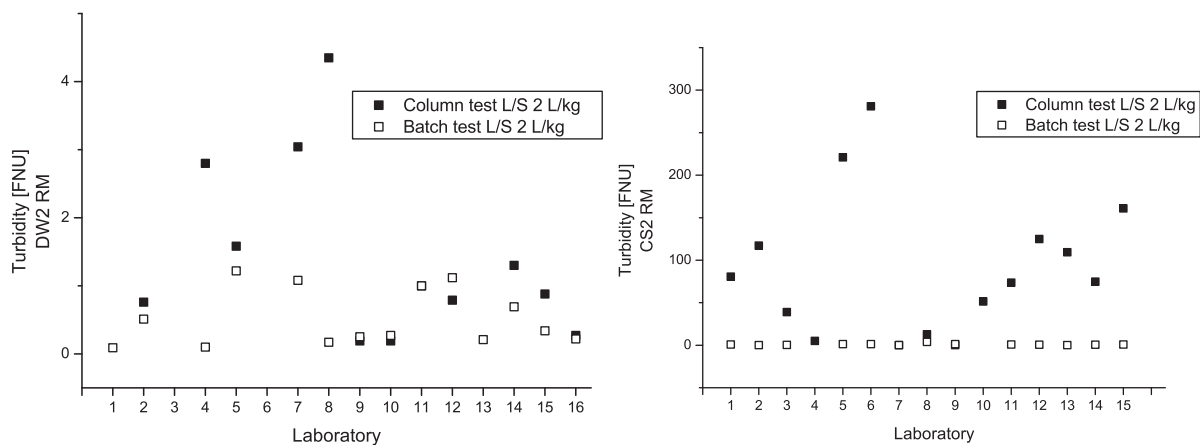
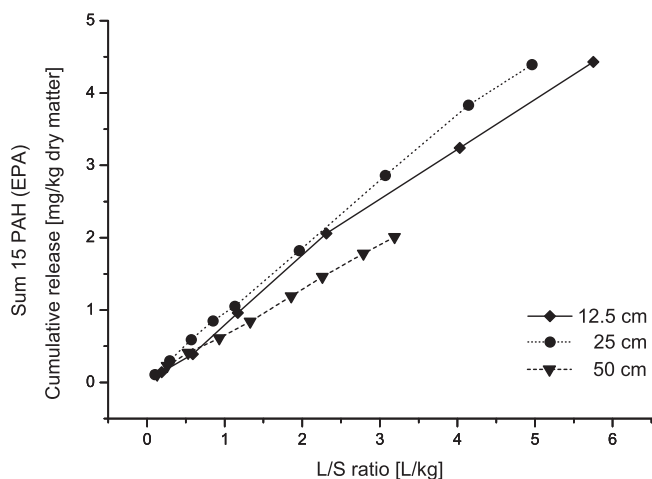


Fig. 2. Turbidity results from interlaboratory tests: comparison of column and batch testing of DW2 RM (left) and CS2 RM (right).



**Fig. 3.** Cumulative release of PAH from CS1 RM versus L/S from columns with different filling heights and fixed flow rate.

**Table 2**

Comparison of contact time and L/S ratio related to test duration for column test with different filling heights and fixed flow rate.

| Filling height (cm) | Contact time (h) | L/S ratio for 168 h test duration (L/kg) |
|---------------------|------------------|--|
| 12.5                | 10.3             | 4  |
| 25                  | 18.9             | 2  |
| 50                  | 35.2             | 1  |

cles from columns for two reasons: the wide variety of sample materials and the reproducibility of results between laboratories. A turbidity of <100 FNU is considered to be achievable and adequate for analytical purposes in DIN 19528 (2009) [10].

Fig. 3 illustrates the effect of different column filling heights on the cumulative release of polycyclic aromatic hydrocarbons (PAH) from CS1 RM; the average of three replicates is shown. A fixed flow rate of 0.22 mL/min was used in all cases. The internal diameter of all columns was 5.86 cm. Applying the same flow rate leads to different contact times (Eq. (1)) and therefore to significantly varying test durations [24], i.e. the larger the filling height the longer the test duration, or expressed diversely, the same L/S ratio is achieved earlier for shorter filling heights. Table 2 shows the relationship of contact time and L/S ratio as a function of the filling height for these column tests.

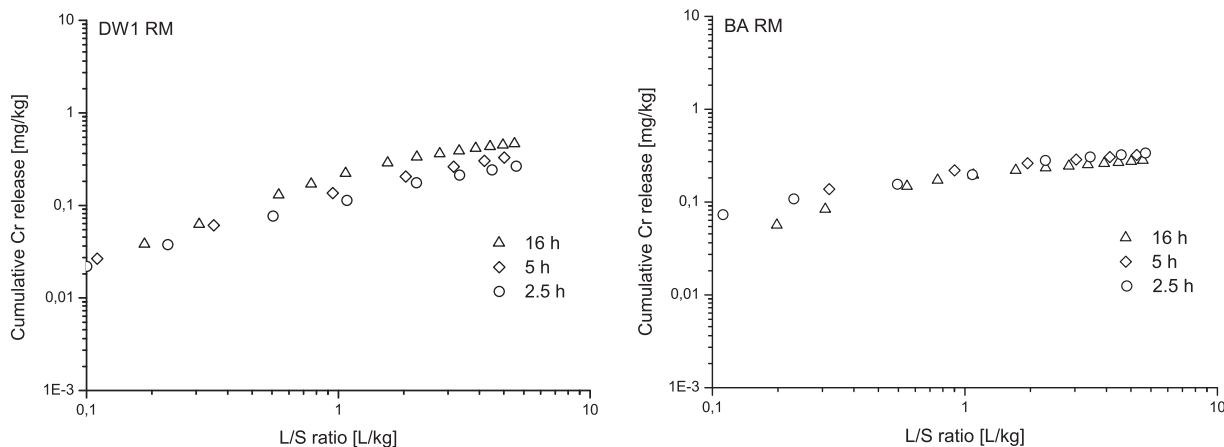
The contact time may not be enough to ensure a sufficient equilibration adjustment in the case of the 12.5-cm column, thus leading

to a somewhat lower release (Fig. 3). However, longer test duration, as is the case of the 50-cm column, may lead to biodegradation of organic contaminants, like PAH, and therefore to an underestimation of pollutant release (Fig. 3). Therefore, a column height approximately four times of the inner diameter of the column was suggested for the standard procedure, allowing the required L/S ratios to be reached in a reasonable time and ensuring a certain level of local equilibrium between test material and eluent. Applying this specification and the stipulation that the inner diameter of the column must be at least twice the maximum grain size, the representativeness of the test material amount is always ensured. This is an advantage over batch testing, particularly for coarse-grained material, since the sample quantity needed for analysis depends on the maximum grain size. Furthermore, in the case of batch testing of material with larger particle sizes, this would result in using very large bottles, e.g., a maximum grain size of 32 mm requires a test sample amount of 2.5 kg, which in addition to being difficult to handle, especially considering that appropriately-sized tumblers need to be used. Partition of the sample amount to smaller bottles and recombination of the eluates is allowed, but this would result in additional tumblers needed, especially in routine analysis. In the case of column tests, the approach of a standardized contact time enables comparable results despite different column dimensions [12,13]. Due to practical considerations it is virtually impossible to simulate field conditions in laboratory experiments. However, the results obtained from column tests should be as reliable as possible, and a compromise has to be found. One major problem is a long contact time, which would lead to very long test durations. For this reason, several tests have been conducted to evaluate the effects of reduced contact time on the reliability of leaching results, and it was found that a slight decrease in contact time has no significant effect in the release of contaminants [25].

The effect of different contact times on the release of chromium from BA RM and DW1 RM respectively is demonstrated in Fig. 4. Column dimensions, filling heights, sample amounts, and grain sizes were identical in all cases; the experiments varied only in flow rate and thus in contact time.

In the case of chromium, 0.23 mg/kg was released from DW1 RM using batch test and 0.14 mg/kg using column test. For BA RM the respective averaged results were 0.07 mg/kg for batch tests and 0.09 mg/kg for column tests. For this comparison, the calculated release rates of the column tests eluates up to L/S 2 L/kg were cumulated. The difference between column and batch test results might be due to varying sample properties and test conditions [8].

In general, the results indicate only a minor impact of the contact time on the release of chromium from the investigated sample



**Fig. 4.** Cumulative release of Cr from DW1 RM (left) and BA RM (right) in column tests with different contact times.

materials, thus providing justification for a shorter contact time. This has also been shown for copper [25]. Theoretical considerations regarding this topic have been given elsewhere [8].

#### 4. Conclusions

Leaching tests as a tool for the accompanying assessment of waste materials intended for re-use have to be as cost and time efficient, practical, and realistic as possible. This applies in particular to routine work of analytical laboratories. In the framework of German research and standardization projects, it has been shown that this requirement can be fulfilled by appropriate stipulations even if coarse-grained material is considered. The decision of whether batch or column tests are the best option depends in particular on the maximum grain size of the waste material investigated, e.g. from a practical stand point, batch tests are more appropriate for materials with a grain size up to 10 mm.

Column experiments offer the advantage to perform basic characterization and compliance testing within one test. With the requirements on the column dimensions (see Fig. 1), the representativeness is guaranteed and a sufficient eluate volume for both inorganic and organic analysis is available. Compared to batch tests, where a filtration step is required, no solid/liquid separation step is needed prior to analysis. Furthermore, the investigation of materials containing colloid-linked contaminants provides more reliable results.

A reduction of contact time seems to be a reasonable compromise between field-like conditions and practicability in terms of the release of some heavy metals that, in the case of waste material reuse tend to have representative behaviour, such as chromium and copper, but this has to be further studied for other contaminants.

An international harmonization of leaching procedures concerning L/S ratio, type of eluent, and sample pre-treatment is necessary and currently in progress. Furthermore, the waste materials should be investigated in the same condition as in the designated re-use scenario (especially regarding grain size).

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