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SUMMARY: The European up-flow percolation leaching tests CEN/TS 14405 which has been incorporated into both EU and national regulatory waste management frameworks is carried out on granular waste materials and aggregates under conditions intended to ensure (near) local equilibrium conditions in the test and thus prevent conditionality, optimise reproducibility and provide applicable reference results that can be used as the basis for source terms in impact assessments. The need to achieve local equilibrium and the associated test requirements on particle size and flow rate have been challenged, but the test results presented in this paper on BOF steel slag, which is relatively dense, strongly indicate that they are necessary in order to obtain consistent test results. A test programme is being prepared to assess the proportion of fine particles (< 4 mm) required in a sample of granular materials to ensure fulfilment of the (near) local equilibrium assumption at the existing standard flow rate of 15 cm/day and possibly at faster flow rates.

1. INTRODUCTION

The European up-flow percolation leaching test CEN/TS 14405, which was first officially published by CEN as a technical specification, a TS, in 2004 (between 2002 and 2004 a pre-standard working version labelled prEN 14405 was circulated), has been implemented into EU legislation such as Council Decision 2003/33/EC of 19 December 2002 establishing criteria and procedures for the acceptance of waste at landfills pursuant to Article 16 and Annex II to Directive 1999/31/EC. The test method which is expected to be upgraded to a full standard (EN) in 2014, has also been incorporated (as the European standard or as different national standards with very similar test conditions) into the waste management legislation of several European countries to assess whether waste materials meet the leaching limit values associated with utilisation as substitutes for virgin raw materials (aggregates) or with acceptance at landfills, and it is used in environmental risk or impact assessments of specific waste utilisation applications. Together with a pH dependence leaching test such as e.g. CEN/TS 14429 or CEN/TS 14997, the percolation test provides a full set of leaching characteristics for granular waste materials.

In the scope of CEN/TS 14405 it is specified that the test shall be carried out under conditions that approach local equilibrium. This requirement is absolutely crucial for the applicability of the test in waste management and risk/impact assessment since the limit values both in Council Decision 2003/33/EC and in the national legislation of several countries have been derived under this assumption, and the same is true for specific assessments of the impact of utilisation or landfilling of waste materials based on percolation leaching test results.

The test conditions intended to ensure (near) local equilibrium in the percolation test CEN/TS 14405 include in particular requirements on maximum particle size and maximum flow rate as well as an initial equilibration period of up to 3 days after saturation. The fact that the test is performed in up-flow is also meant to enhance the robustness by facilitating an equal distribution of the percolating water and prevent preferential flow.

During the development of a percolation test for CE marking of aggregates, CEN/TC 351 TS-3, based on CEN/TS 14405, the necessity to achieve local equilibrium in a percolation test for regulatory use has been challenged and disregarded by some stakeholders, leading to a parallel proposal for an option with both a maximum particle size of 22.4 mm and a (required) flow rate of 45 cm/day (instead of 15 cm/day), using the argument that the material should be tested “as it is” and that the test should be quick and comply with existing national limit values for beneficial use of various aggregates. This alternative approach has recently also been proposed to be included in the percolation test for waste materials (CEN/TS 14405). The paper discusses these issues in detail, including the often repeated requirement to “test the material as it is” and the potential problems associated with size reduction (possible pH changes). The influence of changes in the various test conditions is illustrated by examples that clearly demonstrate the problems induced by even moderately larger particles (when no fines are present) and faster flow rates.

2. TEST CONDITIONS FOR CEN/TS 14405

The percolation or column leaching test CEN/TS 14405:2004 “Characterisation of waste – Leaching behaviour test – Up-flow percolation test (under specified conditions)” is carried out on largely inorganic granular or size reduced waste materials to assess the leaching behaviour of the materials as a function of the liquid/solid (L/S) ratio. The test is very similar to ISO 21268-3 (for soil). The test material is leached with demineralised water in a vertical cylindrical column operated in up-flow (15 ± 2 cm/day, based on an empty column), using a column height of 30 ± 5 cm and a diameter of 5 or 10 cm, depending on the particle size distribution, see Table 1. The particle and column size requirements are, on the one hand, intended to ensure that the test portion in the column will be representative of the laboratory and test sample from which it is taken, and, on the other hand, intended to facilitate that local equilibrium is achieved and maintained throughout the test period.

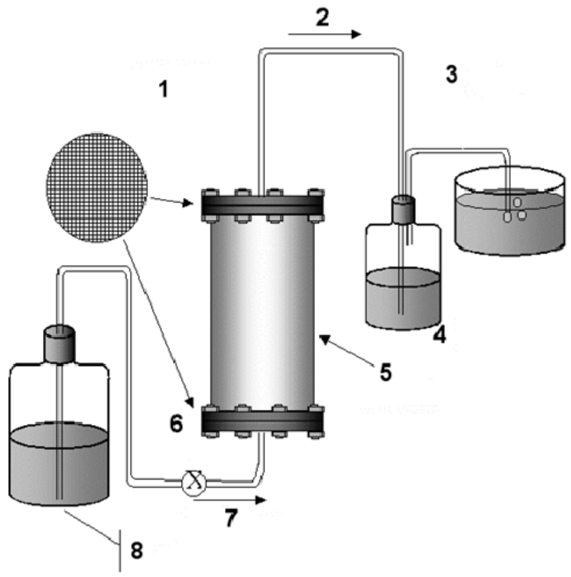
At the top and bottom the column is equipped with a filter plate or a thin layer of quartz sand separated from the test material by a pre-filter. This is intended to distribute the water evenly at the inlet and prevent entrainment of fine particles with the eluate at the outlet. In this column test 7 eluate fractions are collected within the range of L/S = 0.1-10 l/kg (L/S = 0-0.1, 0.1-0.2, 0.2-0.5, 0.5-1.0, 1.0-2.0, 2.0-5.0 and 5.0-10.0 l/kg). An example of a percolation test set-up is shown in Figure 1.

The duration of the percolation test depends on the bulk density of the material tested – for a bulk density of 1.5 g/cm^3 it will be approximately 30 days following a 16 to 72 hour pre-equilibration period under saturated conditions. The pre-equilibration is intended to ensure (near) equilibrium between the leached substances in the aqueous and solid phases, respectively, prior to testing. If necessary, the eluates can be collected under nitrogen or argon to prevent e.g.

oxidation of reduced species and/or uptake of atmospheric CO_2 which could lower the pH of alkaline eluates. The eluate fractions are filtered through 0.45 µm membrane filters and analysed. Results are reported as concentrations or released amounts as a function of L/S.

Table 1. Use of column type, related to particle size of the waste to be tested (from CEN/TS 14405).

Fraction < 4 mm	*Fraction ≥ 10 mm*	*Column to be used*
≥ 95 % (w/w)		5 or 10 cm column without size reduction
80 % to 95 % (w/w)	≤ 5 % (w/w)	5 cm column with size reduction of the material fraction > 4 mm, or 10 cm column (without size reduction)
≤ 80 % (w/w)	≤ 5 % (w/w)	10 cm column (size reduction not required)
-	> 5 % (w/w)	10 cm column (size reduction of the fraction > 10 mm required)



1. Support filter (could also be a layer of quarz sand)
2. Flow direction
3. Air lock (optional)
4. Eluate collection
5. Column filled with granular waste
6. Pump
7. Flow direction
8. Leachant

Figure 1. Example of a column test set-up (from CEN/TS 14405).

3. LOCAL EQUILIBRIUM

3.1 What is local equilibrium?

Granular waste materials generally consist of a number of particles that together comprises a large surface area to volume ratio which increases with decreasing particle size. The smaller the particle sizes, the larger the surface area with which percolating water can be in contact. Due to the large surface area, chemical (dissolution) processes that can cause transfer of substances from the solid material into the percolating water proceed relatively fast, and due to the small diameters of the particles diffusion of substances from the inner part to the surface of the particles and into the percolating water are also relatively fast. Often these processes occur fast enough compared to the flow rate of the percolating water for “equilibrium” conditions between the solid matrix and the percolating water to exist for many substances. Equilibrium means that the dissolved concentrations of the substances in question in the aqueous phase do not increase or decrease further as a function of time. In a percolation test the equilibrium condition is referred to as "local equilibrium". The equilibrium is only the same everywhere in the column at the starting point, after pre-equilibration (global equilibrium). When the percolation starts, equilibrium conditions will still exist locally within the column, provided that the contact time is sufficiently long, i.e. the release of substances from the particles is sufficiently fast compared to the bulk (plug) flow of the water percolating through the column, but the conditions will change with time and generally be different at different points along the column due to the depletion, transport and removal of substances with the eluate.

If the contact time becomes too short to ensure local equilibrium conditions due to either too large particle sizes or too fast flow rates, the controlling release mechanism changes to diffusion/surface dependent release and even small differences in flow rate or particle size distribution will produce differences in test results, i.e. the test procedure becomes less robust and more sensitive to changes in test conditions. Chemical non-equilibrium caused e.g. by contact times that are too short to allow dissolution of a mineral phase to reach saturation may cause both over- and underestimation of the release of a substance compared to the release of the substance under local equilibrium conditions. Physical non-equilibrium caused e.g. by contact times that are too short to eliminate a gradient in the concentration between the concentrations of soluble salts in the particles and in the pore water will result in an underestimation of the release compared to the release under local equilibrium conditions.

The flow rate should be slow enough to fulfil the local equilibrium assumption (LEA) even though the actual contact time for a given granular material can vary due to different particle size distributions and hence different porosities of the packed material. If a percolation test run at two different flow rates produces the same results, then the LEA is fulfilled for both.

3.2 Why is local equilibrium important?

As already indicated, CEN/TS 14405 and other percolation tests are becoming more and more widely used as regulatory tools in waste management (and in the environmental management of several other materials, including e.g. soil and construction materials). The applicability of percolation test results within regulatory frameworks depends on the fulfilment of the following requirements (based on Dijkstra and van Zomeren, 2012):

- Conditionality of the test results must be avoided to the extent possible
- The reproducibility should be as good as possible
- The test results should provide a reference upon which scenario assessments can be based

The performance of a percolation test under local equilibrium conditions is a precondition for the fulfilment of these requirements.

Conditionality: Under local equilibrium conditions the release of substances from a granular material is not a function of residence time but merely a function of the amount of water that has percolated through the column (L/S). The results when presented as a function of L/S have become independent of variations in size (length, width), particle size distribution and flow rate. They no longer represent only one unique combination of these parameters, i.e. they are no longer conditional. If they were, they would only represent one out of the many different possible scenarios that exist in the field. Conditionality should therefore be avoided. Results that are not conditional have a broader applicability and may allow translation of laboratory test result to release under various full scale/field conditions. Factors and conditions that influence the release in practice and are not/cannot be taken sufficiently into account in the reference leaching test can be addressed (in a generic or site-specific manner) when developing regulatory emission criteria or setting conditions for compliance with such criteria, e.g. by factoring them into the relevant scenario calculations. Avoiding conditionality also allows some degree of comparison of results from different test methods performed on the same material under local equilibrium conditions (e.g. percolation leaching tests (CEN/TS 14405) and batch leaching tests (EN 12457-1, -2 and -3)).

Reproducibility: As already mentioned, a test results produced under local equilibrium conditions is insensitive to variations in column size, filling height, particle size distribution, and flow rate, i.e. the test exhibits maximum robustness under these conditions. This will have a favourable influence on the in-lab repeatability and the between-lab reproducibility of the test results. This is particularly important when assessing test results close to a regulatory limit value.

Reference results: Scenario calculations are made for specific risk assessments, but also for generic risk assessments e.g. to establish a consistent set of regulatory limit values. A percolation test provides an important part of the information upon which such assessments in principle are based (the “source term”). It is important that such information – after correct translations have taken place from test result to the relevant field conditions - does not severely under- or overestimate the release under all those different conditions, and not just represents a single condition (namely the laboratory test conditions).

A result produced under local equilibrium will result in a reliable “reference” measurement, namely an “upper estimate” for release for less reactive substances such as soluble salts that can be released over prolonged contact times in practice. For chemically reactive substances (metals, oxyanions), the estimate can be an upper estimate or a lower estimate – but always an estimate that is no longer dependent on a unique combination of contact time, particle size, flow rate and application dimensions.

For many scenarios, such as a quick rain event on a thin layer of coarse grained material, local equilibrium may not be reached in practice. In that case, the test result conducted at local equilibrium is an upper estimate of what the release could be. However, a more precise estimate can be made as equilibrium test results are easier to “translate” to non- equilibrium conditions than vice versa. A non-equilibrium test result is very hard to interpret, as one never quantitatively knows what the release would become at longer contact times.

For other scenarios, such as a granular material that is used below the groundwater table (e.g., a filler material), the test should provide the results that account for the long contact times. In those cases, the test should provide equilibrium results and is not an “upper estimate”.

The latter two examples illustrate that the percolation test should not just represent a result representative for a single condition (e.g. lab conditions, or a simulation of a specific practical condition). A percolation test should provide the information from which the translation can be made to other scenarios, and local equilibrium is therefore the best point of departure

3.3 Particle size and flow rate

From the above it is evident that particle size or particle size distribution and flow rate (contact time) are extremely important factors that largely can determine whether or not local equilibrium conditions will prevail in a percolation test on a granular material. They are interdependent – for finer granular materials local equilibrium can be achieved even at higher flow rates while (much) lower flow rates/longer contact times will be required to ensure local equilibrium if coarser aggregates are tested. For heterogeneous granular materials with a substantial amount of small particles (e.g. 50 to 100 % < 4 mm or < 10 mm with a large proportion of particles < 4 mm) it has been shown that local equilibrium are fairly well achieved within a contact time of approximately 15 hours (Dijkstra et al., 2008; Susset and Leuchs, 2008a and 2008b). 15 hours correspond approximately to the lower end of the contact time for most granular materials when tested in CEN/TS 14405 under the existing standard conditions (15 cm/day and an assumed porosity of approximately 0.30). For porous granular materials with a large portion of small particles such as e.g. MSWI bottom ash shorter contact times will often be sufficient to reach (near) local equilibrium (Dijkstra et al., 2008), but this may not be the case for more dense materials with lower porosity such as steel slag. The standard conditions of the percolation leaching test should ensure that near local equilibrium is reached for all granular materials falling within the scope of the test, and since steel slag is one of the critical materials in this respect, it provides a suitable test material that can be used to assess the limitations and set/adjust the standard conditions for CEN/TS 14405.

The influence and interdependence of particle size and flow rate are illustrated in Figure 2a and Figure 2b which show results (in terms of accumulated release as a function of L/S) of percolation tests on basic oxygen furnace (BOF) steel slag carried out in columns of 30 cm length and 5 cm diameter under standard conditions for CEN/TS 14405 (100 % < 4 mm, 50 % < 0.7 mm, and 15 cm/day), on a larger particle size fraction (6 to 10 mm) of the same BOF slag in a 10 cm diameter column still with a flow rate of 15 cm/day, and on the same larger particle size fraction using a flow rate of 30 cm/day, also in a 10 cm column. Compared to the conditions proposed by some stakeholders in CEN/TC 351 these deviations are quite moderate, and the larger particle size distribution actually falls within the envelope allowed for CEN/TS 14405, but it contains no particles < 4 mm. The higher flow rate is twice as fast as the prescribed flow rate.

If the induced non-equilibrium conditions were purely physical, decreasing release would be expected in the order (4 mm, 15 cm/day), (6-8 mm, 15 cm/day) and (6-8 mm, 30 cm/day). This is seen to be the case for sulphate, chloride, Na, Sr, and Ba, but not for Cr and Zn which are sensitive to changes in redox and pH conditions. Figure 2b shows that pH appear to be influenced by the changed conditions but in a way that may have been caused by carbonation of the highly alkaline eluates during the tests.

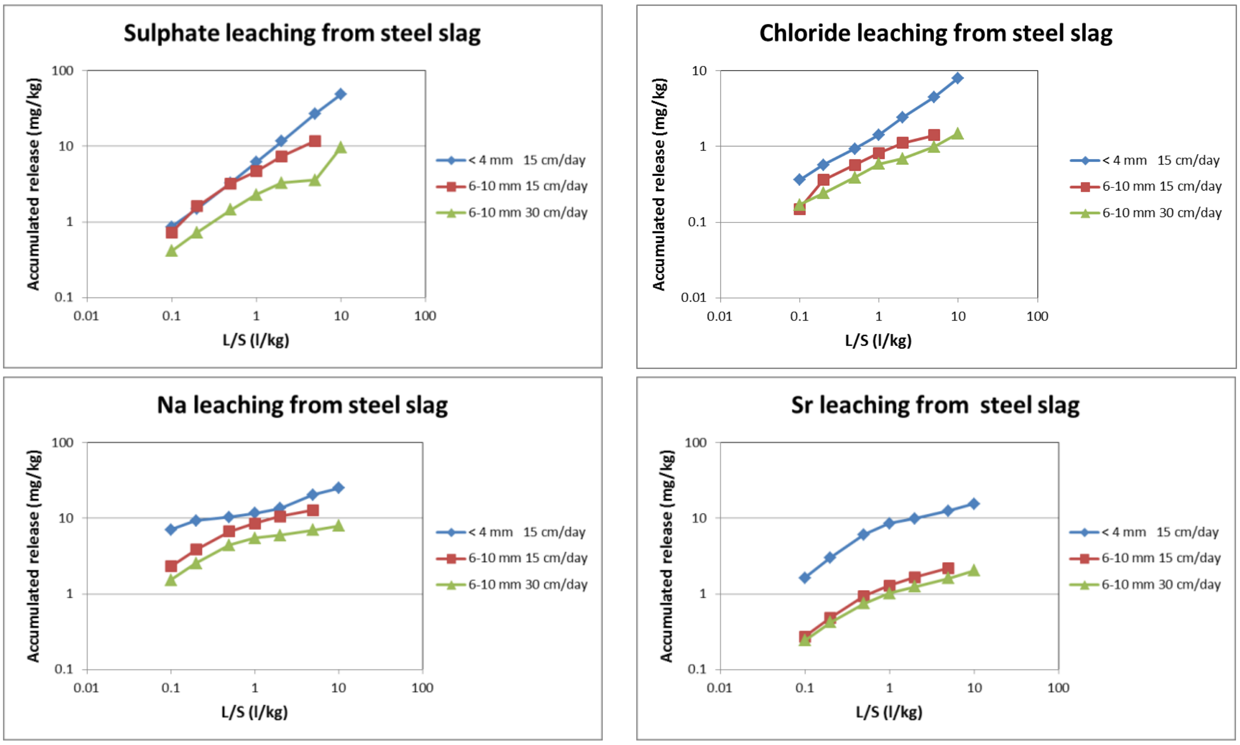


Figure 2a. Results of percolation leaching tests on BOF slag with varying particle size and flow rate.

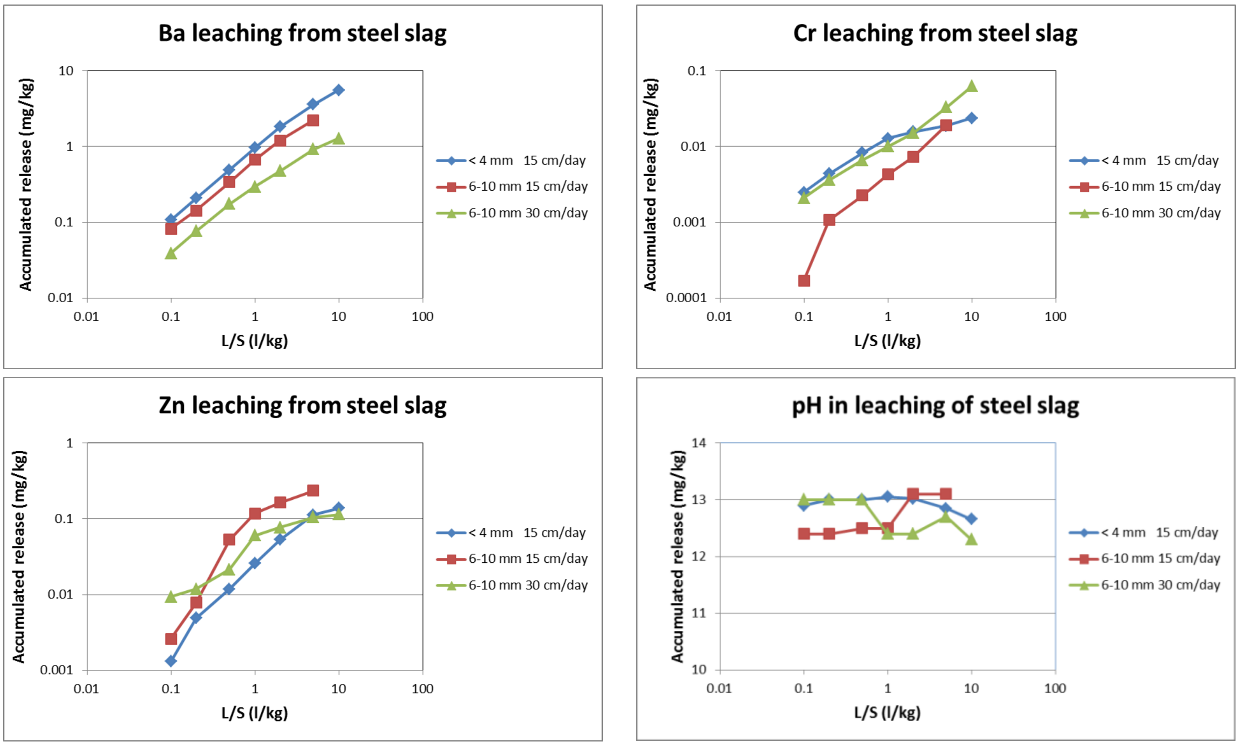


Figure 2b. Results of percolation leaching tests on BOF slag with varying particle size and flow rate.

Even though the relative standard deviations for some of the substances shown in Figures 2a and 2b are fairly high (27 % for sulphate, 30 % for chloride, 30 % for Na, 5 % for Sr, 7 % for Ba, 5 % for Cr and 56 % for Zn) based on performance of the test under standard conditions in triplo, the results for the five non-sensitive substances are quite consistent with the pattern that would be expected in the case of non-equilibrium in the two tests on the coarser material. The relatively high standard deviations for some of the substances are most likely caused by the relatively low concentration levels measured in the eluates from the BOF slag.

A series of robustness testing has been planned within the framework of CEN/TC 351 to assess the minimum proportion of particles < 4 mm required to ensure (near) local equilibrium conditions in the percolation test under standard flow conditions 15 cm/day and at increased flow rates for critical materials such as BOF steel slag. Results are expected at the end of 2013.

4. CHANGES IN CONDITIONS IMPOSED BY TESTING

In principle, coarse granular materials could be subjected to a percolation test without size reduction under local equilibrium conditions if the contact time is sufficiently long. A rough estimate shows, however, that this would require a contact time of more than 100 hours for a sample with a maximum particle size of e.g. 32 mm, which means that running the test to the end point of L/S = 10 l/kg would take approximately 8 months (Dijkstra and van Zomeren, 2012). This is very impractical and clearly unacceptable. In addition, ensuring a reasonably representative sample in the column would require a test portion of at least 10 kg and hence a larger column which experience shows is impractical, time consuming and inefficient with respect to the amount of resources required. The solution is therefore size reduction to ensure that a sufficiently large portion of the material has a particle size lower than 4 mm, and preferably an upper limit for the largest particle size of 10 mm.

Size reduction of a granular material, e.g. by crushing in a jaw crusher may, however, change the leaching characteristics of the material by opening new surfaces. This could, for example, give rise to changes in the pH of the eluate and hence changes in the solubility of pH-sensitive substances. This is particularly important for strongly alkaline waste materials which have formed a surface layer of carbonate due to uptake of atmospheric carbon dioxide. Such a layer would react neutrally or slightly alkaline upon contact with water, but when the material is crushed, new, strongly alkaline surfaces would be exposed and produce a high pH in contact with water and in the percolation test. This would generally not affect soluble salts (although the release of Ca may be solubility controlled at a low level, which may cause an increase in the release of sulphate), but several regulated trace elements are sensitive to changes in pH.

Under such conditions, the effect of the changes in pH should be taken into account when the results of the percolation test are interpreted. The results of a pH dependence leaching test such as CEN/TS 14997 or CEN/TS 14429 can provide strong support to such assessments. Another option could be not to test the freshly size reduced material immediately but to allow uptake of carbon dioxide and let a new surface of carbonate form prior to testing.

An argument which is often heard from certain stakeholders is that even a rather coarse granular material should be tested “as it is” and, for example, not be size reduced since “this is not the way it will be applied e.g. in a road construction project”. However, the same stakeholders already accept a certain degree of size reduction of large particles and they also accept up-flow percolation under saturated conditions in the test (but suggest tripling the flow rate) although this is also in most cases a significant deviation from “as it is” conditions. For coarse granular materials both size reduction, moderate flow rates and up-flow percolation are necessary to ensure local equilibrium conditions and appropriate robustness in the testing.

In general, simulation of various scenario-specific conditions in the laboratory test should be avoided. The optimum situation has proven to be a robust percolation leaching test which is insensitive to moderate variations in the test conditions (i.e. a test performed under local equilibrium conditions). The results can then be related to specific scenario conditions by means of modelling which takes these issues into account, and used in waste management to set regulatory limit values, to test compliance with such criteria or to estimate the source term in an environmental impact assessment.

5. CONCLUSIONS

The conditions under which the percolation leaching test, CEN/TS 14405, is carried out are intended to ensure that the local equilibrium assumption is fulfilled throughout the duration of the test. With the chosen standard flow rate of 15 cm/day this requires that a substantial proportion of the particles in a granular material to be tested are smaller than 4 mm, without or with size reduction. For more coarse granular materials that are not crushed local equilibrium for several substances can generally only be achieved by using rather long contact times or flow rates which lead to an impractically long duration of the test. Local equilibrium is important for the applicability of CEN/TS 14405 within a regulatory waste management framework. By carrying out the percolation test under (near) local equilibrium conditions, conditionality is avoided, i.e. the test results become independent of the specific test conditions and more generally applicable, and lab results can be up-scaled to field conditions. At the same time local equilibrium facilitates robustness and provides the best repeatability and reproducibility of the test results. Finally, results produced under local equilibrium conditions provide good references that can be used as a source term in environmental impact assessments to derive limit values. Simulation of various scenario-specific conditions in the laboratory test should be avoided. The optimum situation has proven to be a robust percolation leaching test which is insensitive to moderate variations in the test conditions (i.e. a test performed under local equilibrium conditions). The results can then be related to specific scenario conditions by means of modelling which takes these issues into account, and used in waste management to set regulatory limit values, to test compliance with such criteria or to estimate the source term in an environmental impact assessment. The need to fulfil the local equilibrium assumption by placing appropriate requirements on particle size and flow rate when performing a percolation leaching test on a granular material is clearly illustrated by test results for fairly dense BOF steel slag: Tests that are not complying with the local equilibrium requirement due to large particle sizes and/or high flow rates lead to other results than tests performed under local equilibrium conditions. A test programme is in progress to assess the proportion of fine particles (< 4 mm) required in a sample of granular materials required to ensure fulfilment of the (near) local equilibrium assumption at the existing standard flow rate of 15 cm/day and possibly at faster flow rates.

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