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PAPER

Background paper on the use of leaching tests for assessing the disposal and re-use of waste-derived materials

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Questions regarding this report should be directed to:
Department of Environment Regulation
Locked Bag 33 Cloisters Square
PERTH WA 6850
Phone: +61 8 6467 5000
Fax: +61 8 6467 5562
Email: info@der.wa.gov.au
Web: www.der.wa.gov.au

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Purpose

To provide context and background information to support the draft *Environmental Standard: Assessing leachates from waste-derived materials*.

Introduction

The Department of Environment Regulation (DER), in administering the *Environmental Protection Act 1986*, may need to determine whether the application of waste-derived materials to land may cause pollution or environmental harm. In order to do this, DER must be able to assess whether potentially harmful chemical constituents will be leached from the applied materials under the full range of chemical conditions that they are likely to be exposed to in a soil profile, in tailings storage facilities (TSF) or waste rock dumps at mine sites, or at licensed waste disposal sites.

Currently, DER uses the Australian Standard Leaching Procedure (ASLP) tests (Australian Standard AS4439) to determine the potential leaching hazards associated with solid wastes that are being sent to a landfill site. This is done to ensure that the concentrations of potentially harmful chemical constituents that are leached from the wastes will meet criteria set for particular categories of landfill sites that have been established to manage the environmental risks associated with different types of wastes. A number of similar leaching tests are also used by the mining industry to assess the potential for metals and other contaminants to be leached from mine wastes by rainwater.

However, these leaching tests generally have a very limited application as they only provide information about the leaching potential of solid materials under the specific chemical conditions that occur in a putrescible waste disposal site or at a particular location at a mine site. They do not indicate whether significant leaching would take place if these materials were transported and disposed of in soils with different chemical characteristics, or buried at depth within a soil profile or in a waste rock heap.

This knowledge gap is of concern as many wastes (or mixtures of waste materials) have the potential to be valuable soil amendment agents that could increase agricultural productivity in regions with impoverished soils. Such soil amendment agents have the potential to increase the water and nutrient holding capacity of soils and to prevent the export of phosphorus from agricultural land to estuaries where it could exacerbate existing environmental problems in many of these water bodies.

This paper provides background information on the factors that control the magnitude and rate of leaching of chemical constituents from solids, and provides information on the uses and limitations of various leaching assessment methods that are currently used in Western Australia. Finally, the document also recommends the implementation of four new leaching test procedures that will enable management decisions to be made about the re-use of waste materials with a much higher level of confidence than is possible using the ASLP test alone.

Characteristics of leaching

Leaching in an environmental context is the process of transferring chemical constituents from a solid particle to an aqueous solution (water containing dissolved salts and gases) in contact with the particle. The manner and rate at which chemical constituents are transferred from the solid to water in contact with the particle is governed by a combination of chemical processes and mass transfer processes that depend on:

- the chemical composition and physical properties of the solid material; and
- chemical conditions in the contacting aqueous solution including its pH, chemical composition, and oxidation-reduction potential.

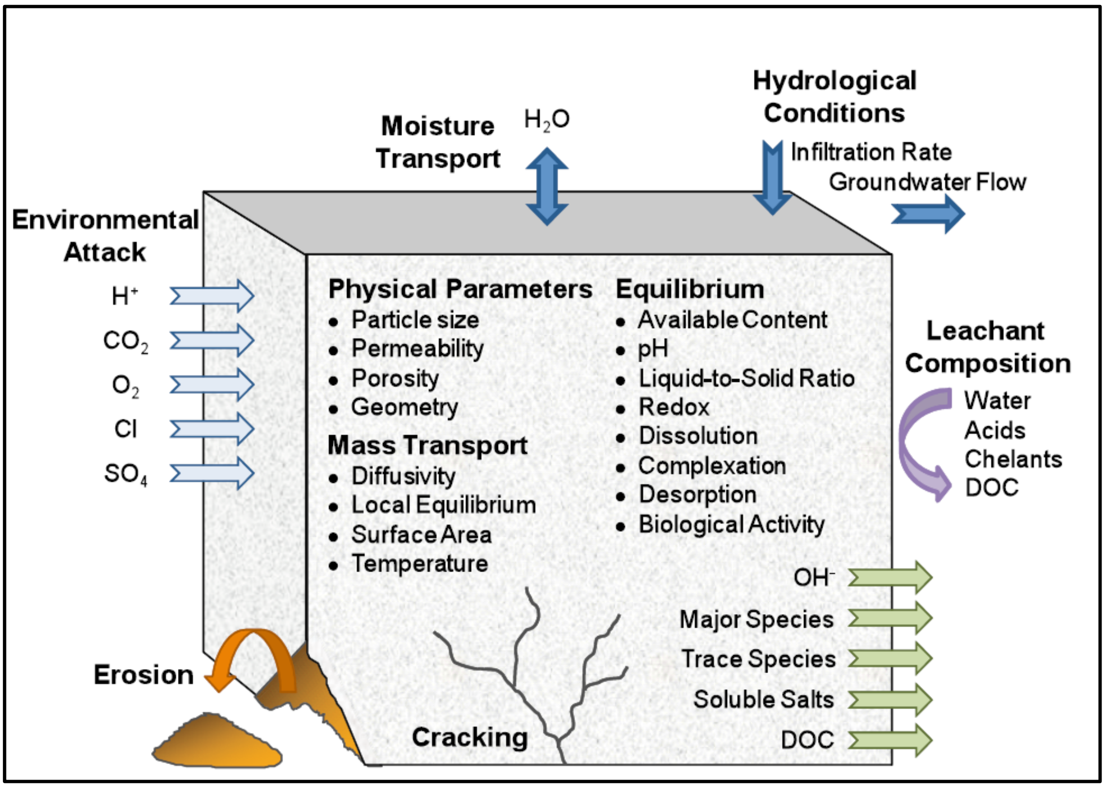

Figure 1 Internal and external factors that influence the extent and rate of leaching of a chemical constituent from a solid particle into a contacting aqueous solution (from Garrabrants *et al.*, 2010)

Figure 1 shows some of the physical and chemical factors (both within and external to a solid particle) that influence the magnitude and rate of leaching. The transport of gaseous and aqueous phases within a solid particle is controlled by the physical characteristics of the solid (particularly the porosity and permeability of the solid), and the characteristics of chemical processes that enable mass transfer of a specific chemical constituent between the surface of a solid particle and the aqueous phase that is in contact with the surface of the particle. In many cases, both the chemical reaction and mass transport rates within a solid particle are sufficiently fast that quantitative information about leaching can be determined within a few hours or days in test procedures.

This may not be the case when solid particles are either partially or wholly comprised of sulfide minerals. Under these circumstances, it may take several months for microbes on the surface of the particles to trigger significant sulfide oxidation and the release of acidity and metals into solution. Consequently, leaching tests for sulfidic materials are usually undertaken under alternating wetting and drying conditions over periods of several months to determine the long-term leaching behavior of these materials. These ‘kinetic tests’ are utilised by the mining sector to assess the potential for sulfidic mine wastes to produce acid or metalliferous drainage (AMD).

In general, the total concentration of a chemical constituent in a solid only has a limited influence on the extent to which that constituent will be leached from the solid (van der Sloot and Kosson, 2010). Therefore, practitioners should be cautious about making assumptions about the magnitude of a leaching risk posed by a solid based only on its chemical analysis, unless the material is known to contain large amounts of non-reactive soluble salts (such as NaCl) which are known to be readily leachable. This is an important consideration when undertaking assessments of the leaching potential of non-sulfidic mine wastes where the concentration of elements in the waste is often compared to average levels in the crust (the ‘Global Abundance Index’) to indicate the potential leaching risks associated with these materials.

Apart from particle size, a material’s pH and surrounding environment are often the most important factors that control the extent to which various chemical constituents are leached from a solid. Metal cations (i.e. metal ions that are positively charged) are most readily leached from a solid particle under acidic conditions (Figure 2), whereas elements that form stable anions in solution (negatively charged ions, including metals such as molybdenum and chromium, and metalloids like arsenic) are most readily leached from a solid particle under neutral to alkaline conditions (Figure 2). Highly soluble inorganic salts often leach readily over a wide range of pH conditions.

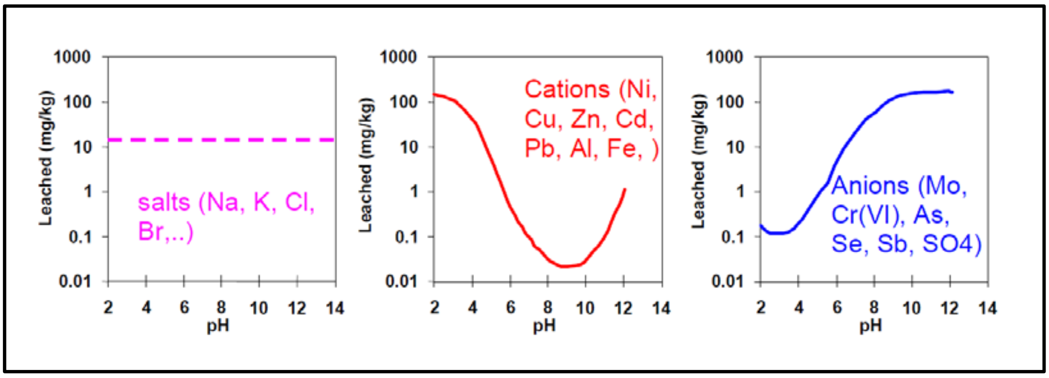

Figure 2 Leaching behavior of various types of inorganic chemical constituents (from van der Sloot and Kosson, 2010)

Another factor that is likely to have a significant effect on leaching in some parts of Western Australia is the salinity of the soil or water that waste materials may come into contact with. Leaching is often increased under conditions of high salinity as metals can form soluble complexes with ions present in highly saline soil pore water or groundwater. This is an important consideration at mine sites where wastes are disposed of below the watertable in mine pits and where groundwater is hypersaline. DER is currently working with the Chemistry Centre of WA to develop test methods that will be appropriate for assessing the leaching risks associated with the contact of mine wastes with hypersaline water.

The role of leaching tests in supporting risk assessments

Leaching tests have an important role in providing information to support the assessment of potential environmental risks associated with the use of waste materials as soil amendment agents. This is because these tests will help determine the concentrations of chemical constituents in soil pore water that are in direct contact with amended soil which is bioavailable and capable of being taken up by plant roots and soil fauna and entering local food webs.

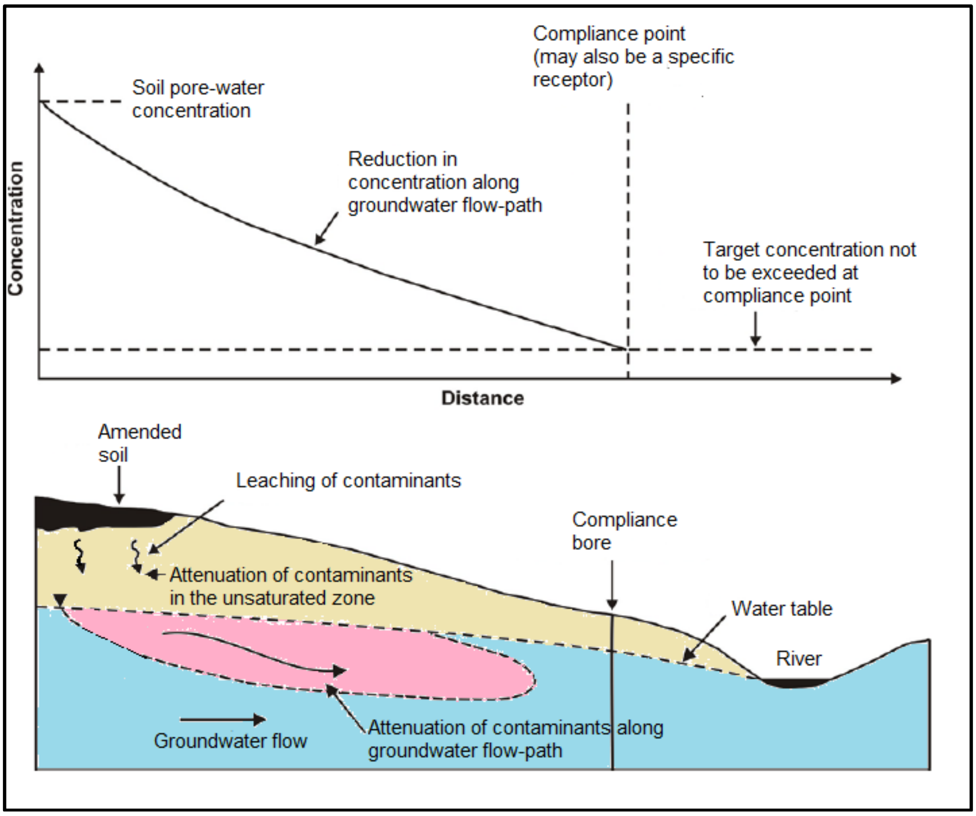

Figure 3 Components of a risk assessment for assessing the potential impacts of a waste-amended soil on environmental receptors via a groundwater pathway (adapted from UKEA, 2006)

The principal sub-surface pathways for the movement of soluble chemical constituents that are leached from the amended soil are shown in Figure 3. As the leached chemical constituents move firstly through the unsaturated zone above the watertable and then in groundwater flow below the watertable, they are subjected to a variety of chemical, physical and biological processes that will progressively reduce their concentrations. Depending on the setting where waste products are being used as soil amendment agent, there are a number of potential ‘environmental receptors’ that should be considered when undertaking a risk assessment of the use of these materials. These include:

- the pore water at shallow depth in the soil profile which can be accessed by plant roots and soil fauna;
- groundwater immediately beneath the amended soil area; and
- offsite groundwater users, surface water bodies and deep-rooted vegetation that may be affected by the quality of groundwater that flows from the area where waste materials have been applied to soils.

The potential impacts on receptors are managed by ensuring that concentrations of potentially harmful chemical constituents remain below levels of environmental concern in soil pore water or in groundwater at the receptor, and a ‘compliance point’ (Figure 3) may be established between the amended soil and the receptor to ensure that concentrations of the chemical constituent remain below levels of environmental concern. If the maximum concentration of the chemical constituent that can be tolerated to protect a receptor at the point of compliance is known, geochemical modelling can be used to determine the acceptable pore water concentration of the constituent within the amended soil. The relationship between solid and leachate concentrations developed from the leaching test results can then be used to determine the maximum permissible concentration of the chemical constituent within the soil that could be tolerated (with an appropriate safety factor) to protect the selected receptor.

Similar risk assessments should be considered when waste rock or tailings are deposited on the surface or below the watertable at mine sites. Mine operators need to consider whether leachate from these materials could affect nearby environmental receptors, including vegetation or soil fauna, or whether particulates could be transported from these repositories by wind action or rainfall erosion and deposited on soils or in a water body elsewhere where leaching may take place. Additionally, solid particles may be ingested by animals and be exposed to highly acidic conditions in their stomachs.

It is often assumed that mine wastes will remain *in situ* over long periods of time, and leaching tests are regularly used to simulate conditions at the surface of a waste rock or tailings repository. This assumption may not be valid at some mine sites, and consequently leaching assessments of mine waste materials should consider a wide range of geochemical conditions that these materials could be exposed to.

Limitations of the current leaching test methods

The ASLP leaching tests that are currently required by DER were originally based on the Toxicity Characteristic Leaching Procedure (TCLP) developed by the United States Environmental Protection Agency (US EPA, 1992), a procedure designed to simulate leaching of industrial wastes under acidic conditions within a putrescible landfill. The leaching agents used in the TCLP tests and the initial version of the ASLP tests were an acetic acid solution and a buffered acetic acid/sodium hydroxide solution, which are used to measure leaching at an initial pH of 2.88 or 4.93 respectively. As this testing regime is likely to give misleadingly high concentrations of metals in leachate under more moderate pH conditions, water was later added as a leaching agent within the ASLP test methods. Deionised water is also generally used as a leaching agent in test procedures that are utilised for assessing the leaching potential of waste rocks and tailings at mine sites.

The main limitation of the procedures that are currently used is that they only provide representative leaching data for the two or three pH values under which the tests are carried out, and therefore may not provide information on the long-term leaching behavior of the material being tested under a range of conditions (van der Sloot, 1996). Additionally, the tests are biased for acidic conditions which may give conservative values of leaching potential for chemical constituents present as cations in solution, but which also may greatly underestimate the concentrations of anionic substances under neutral to alkaline pH conditions (see Figure 2). Leaching tests need to be undertaken under the full range of pH conditions that waste materials may be exposed to in the environment to provide a much higher level of confidence in predicting the likely concentrations of contaminants in leachate from these materials in various settings.

Another limitation of the current leaching test procedures is that they do not consider how the concentrations of chemical constituents in leachate will vary as the liquid to solid ratio changes. Additionally, the current test procedures provide no information about the release rate of chemical constituents of concern from solid wastes. This information may be required to determine the mass flux of contaminants that could be leached from solid waste materials into the environment.

Development of a new leaching assessment framework

Recently, jurisdictions in the European Union (EU) and the United States of America have recognised the limitations of single-condition leaching tests like the Australian ASLP test method, and have progressively replaced these tests with a number of inter-linked test methods that provide additional information about how leaching takes place from a solid material under a range of environmental conditions. New tests to determine how leaching varied with pH and the liquid-to-solid ratio were developed as in the EU as part of a process of harmonisation of test methods across member countries, and in 2012, these tests were adopted and updated by the US EPA to form part of a new leaching environmental assessment framework (LEAF).

LEAF consists of four separate leaching test procedures that can be used individually or as a combination of tests. These are:
- ***Test Method 1313***, which determines how liquid-solid partitioning varies with the pH of the leaching solution using a parallel batch extraction procedure;
- ***Test Method 1314***, which determines how liquid-solid portioning varies with varying liquid to solid ratios using an up-flow percolation column procedure;
- ***Test Method 1315***, which determines mass transfer rates of chemical constituents in leachate from monolithic and compacted granular materials (e.g. construction materials) using a semi-dynamic tank leaching procedure; and
- ***Test Method 1316***, which determines how liquid-solid partitioning varies with the liquid to solid ratio using a parallel batch extraction procedure.

Detailed information on these test methods is provided in Garrabrants *et al*. (2010) and at www.vanderbilt.edu/leaching/leaching-tests/.

Extensive laboratory work and field trials have been undertaken to validate test methods 1313, 1314, 1315 and 1316. These methods have been incorporated into the US EPA manual ‘*Test Methods for Evaluating Solid Waste: Physical/Chemical Methods*’ (SW-846), available at www.epa.gov/epawaste/hazard/testmethods/sw846/new_meth.htm.

The US EPA-approved test methods 1313, 1314, 1315 and 1316 are considered to be the most appropriate leaching tests for assessing the surface application of wastes as soil amendment agents, particularly the variable-pH Test Method 1313. Plots of leachate concentration as a function of pH for specific chemical constituents of environmental concern (Figure 4) can provide information about the potential for leaching under different environmental and human health exposure scenarios.

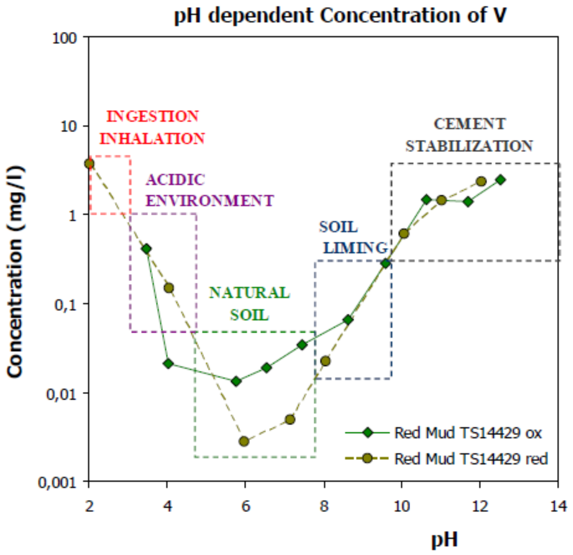

Figure 4 Results of a variable pH leaching test to assess the potential for vanadium to be leached from bauxite residues used as a soil amendment agent under different environmental conditions (from van der Sloot and Kosson, 2010)

Results from variable pH leaching tests can be examined using geochemical models such as ORCHESTRA to determine how specific chemical constituents are likely to be bound up in a solid particle, and when results from Test Method 1313 are combined with Test Method 1314, information about the processes responsible for leaching can be determined.

The LEAF test methods can also be utilised for assessing the leaching potential of non-sulfidic mine wastes. Currently, large amounts of waste materials are classified as being ‘environmentally benign’ on the basis of the absence of sulfide minerals and limited short-term leaching tests using deionised water to simulate rainfall leaching. These short-term leaching tests may not provide sufficient information to adequately characterise the environmental risks posed by some mine waste materials, whereas data from LEAF test methods 1313 and 1314 can enable a more holistic assessment of the risks to environmental receptors to be determined for these materials (van der Sloot and Kosson, 2010).

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