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Influence of leaching conditions for ecotoxicological classification of ash

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ABSTRACT

The Waste Framework Directive (WFD; 2008/98/EC) states that classification of hazardous ecotoxicological properties of wastes (i.e. criteria H-14), should be based on the Community legislation on chemicals (i.e. CLP Regulation 1272/2008). However, harmonizing the waste and chemical classification may involve drastic changes related to choice of leaching tests as compared to e.g. the current European standard for ecotoxic characterization of waste (CEN 14735). The primary aim of the present study was therefore to evaluate the influence of leaching conditions, i.e. pH (inherent pH (~10), and 7), liquid to solid (L/S) ratio (10 and 1000 L/kg) and particle size (<4 mm, <1 mm, and <0.125 mm), for subsequent chemical analysis and ecotoxicity testing in relation to classification of municipal waste incineration bottom ash. The hazard potential, based on either comparisons between element levels in leachate and literature toxicity data or ecotoxicity testing of the leachates, was overall significantly higher at low particle size (<0.125 mm) as compared to particle fractions <1 mm and <4 mm, at pH 10 as compared to pH 7, and at L/S 10 as compared to L/S 1000. These results show that the choice of leaching conditions is crucial for H-14 classification of ash and must be carefully considered in deciding on future guidance procedures in Europe.

1. Introduction

According to the Waste Framework Directive (WFD; 2008/98/EC), waste and hazardous waste should be classified in accordance with the List of waste (European Commission, 2000), in which so-called mirror entries concern waste types with the potential to be either hazardous or non-hazardous depending on their composition and concentrations of hazardous substances. Furthermore, Annex III of the WFD lists 15 properties (i.e. H-criteria) of waste that may render it hazardous. Of these, ecotoxicological properties of waste should be classified based on its inherent hazardous effects under criterion H-14 (“Ecotoxic”: *substances and preparations which present or may present immediate or delayed risks for one or more sectors of the environment*, European Commission, 2008a). Also, the WFD states that “classification of waste as hazardous waste should be based, *inter alia*, on the Community legislation on chemicals, in particular concerning the classification of preparations as hazardous…”. In this context, the Regulation on the Classification, Labelling and Packaging of substances and mixtures (CLP Regulation 1272/2008, European Commission, 2008b) implements globally harmonized criteria for the classification of substances and mixtures according to their physical, health and environmental hazards. In order to harmonize the legislations, the Committee for the Adaptation to Scientific and Technical Progress and Implementation is reviewing both the List of waste and Annex III in the WFD (European Commission, 2012).

Hazard classification is mandatory for bottom ash from municipal and industrial waste incineration (MSIWI). This is a waste stream that has steadily increased, since the energy recovery from waste is promoted (Blumenthal, 2011). Finding ways to utilize ash material in an environmental and economically efficient manner is an important goal throughout Europe. Previously, the CEN guideline 14735 (Characterization of waste – Preparation of waste samples for ecotoxicity tests) has been proposed to provide guidance for classification on waste and has also been used in a major European intercalibration on the subject (Moser and Rombke, 2009). This guidance document proposes a batch leaching test method designed to be conducted without pH adjustments, at an liquid to solid (L/S) ratio of 10 L/kg, on a material with a particle size <4 mm. However, these leaching conditions are inappropriate for hazard classification since they deviate significantly from the requirements stated in the CLP Regulation. MSIWI bottom ash consists mainly of a complex mixture of metal compounds and other inorganic substances (Donatello et al., 2010; Williams, 2005). For complex metal containing materials, guidance on the application of the CLP criteria (ECHA, 2012) refers to the UN GHS protocol Guidance on transformation/dissolution of metals and metal compounds in aqueous media (UN, 2007) for testing. In contrast to CEN 14735, the UN GHS protocol proposes that particle size should be the same

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as for the product on the market or, if unknown, <1 mm. Moreover, three different L/S ratios should be used, i.e. L/S 10,000, 100,000 and 1,000,000, and the leaching should be conducted at a pH where a maximum leaching potential can be reached, yet within a range which is commonly found in the environment (i.e. 5.5–8.5). Given that it is well-known that the toxic response in ecotoxicity tests on ash leachates is dependent on the extent of leached toxic compounds (Engelsen et al., 2009; Stiernström et al., 2011) that in turn is dependent on the characteristics of the material as well as the design of the leaching procedure (Dijkstra et al., 2008; Postma et al., 2009; van der Sloot and Zomeren, 2009; Quina et al., 2009, 2011), it is important to evaluate whether these differences in leaching conditions impact on the classification of ash.

The primary aim of the present study was therefore to evaluate the influence of the three above-mentioned leaching conditions, i.e. L/S ratio, pH and particle size, for subsequent chemical analysis and ecotoxicity testing in relation to classification of MISWI bottom ash. For a number of reasons it is not possible to fully follow the UN GHS protocol on transformation/dissolution of metals. First, it is problematic to sample small yet representative amounts (i.e. <0.2–0.5 g solid material) of a heterogeneous waste material such as ash (Gy, 1998; CEN/TR 15310-1) and generating sufficiently large volumes of leachate at an L/S ratio >1000 could be difficult. An L/S ratio of 1000 was considered the highest practical ratio to handle in our laboratory (compared to the three different L/S ratios recommended in UN GHS (2007): 10,000, 100,000 and 1,000,000). This ratio was therefore tested together with L/S 10, proposed by the CEN guideline (14735). Second, UN GHS (2007) proposes that the particle size should be the same as for the product on the market or, if unknown, <1 mm. This particle size was therefore chosen in addition to the <4 mm fraction, normally used for classification of ash (CEN 14735; Stiernström et al., 2011; Moser and Rombke, 2009). However, we also chose a particle size of <0.125 mm since the uncertainty contribution that is attached to sampling and sample handling decreases radically with particle size (Gy, 1998; CEN/TR 15310-1). Third, ECHA (2012, p. 518) further proposes that hazard classification should be based on leaching at a pH where a maximum solubility can be reached, yet within a range which is commonly found in the environment (i.e. 5.5–8.5). Although aquatic test organisms may fairly well tolerate pH values in this range, in this study we chose pH 7 as a representative value to use alongside the inherent pH of the ash (recommended by the CEN 14735). A final modification to the UN GHS recommendations was that for the pH adjustments we used titration with 0.1–1 M HCl instead of buffer solutions to enable subsequent ecotoxicological testing.

Standard leaching tests performed at L/S 10 (e.g. CEN 14735) are designed and validated to represent equilibrium conditions. Test methods performed at high L/S ratios, such as 10,000 and above, may not reach equilibrium condition within the time frame of the test. The rate to which soluble available ionic and other metal-bearing species are produced is a relevant topic related to hazard classification (UN, 2007). The UN GHS protocol (2007) on transformation/dissolution tests includes both screening tests performed at high loads (L/S 10,000) in 24 h and full-tests (7 or 28-days of testing) at low loads (>L/S 10,000) for assessment of transformation and dissolution rates. In the present study we have used the screening test set-up for the screening of hazardous properties. A relevant ash material (age 3–6 months) from a Swedish incineration plant (Uppsala) was selected and extracted water leachates were prepared either with the batch method described in CEN 14735 or a modified pH static method (based on CEN/TS 14997). The impact of these conditions where mainly evaluated based on calculations of the Toxic Index (TI) for Ca, K, Zn, Cu, Al and Pb. These elements have previously been identified as responsible for the observed toxicity of a range of ash materials from Swedish incineration plants (Stiernström et al., 2011, 2013a). For validation of the calculated TI values, two of the generated leachates were also tested with acute and (sub)chronic ecotoxicological test methods with the crustacean *Nitocra spinipes*. Finally, both the solid ash material and generated leachates were analyzed for determination of levels of inorganic components as well as other important parameters (e.g. pH, DOC, SO_4).

2. Materials and methods

2.1. Ash material

The MSIWI bottom ash evaluated in the present study was sampled from a moving grate incineration plant in Uppsala, Sweden. Magnetic and non-magnetic metals were separated from the ash. The ash was aged outdoors for 3–6 months and thereafter stored in airtight sampling bags at 4 ± 2 °C for 1–6 months prior to the leaching and subsequent chemical analysis and ecotoxicity testing.

2.2. Sample preparation

The following particle fractions were evaluated in the present study: <4 mm, <1 mm and <0.125 mm. The ash was sieved <4 mm and particle fractions >4 mm were crushed until >95% of the material was <4 mm. These two fractions were then mixed and a sub-sample was once again sieved and crushed <1 mm according to above. Another sub-sample was grinded to < 0.125 mm. All subsampling of the material (for further preparation or leaching) was done using either a riffle box or a rotary sample divider. No non-crushable fractions were present in the ash. The water content of the ash was determined according to ISO 11465: 1.8–2.2% (<4 mm fraction), 1.7% (<1 mm fraction) and 1.3–1.4% (<0.125 mm fraction).

2.3. Leaching methods

Table 1 summarizes the different leaching tests and conditions used to evaluate the effect of pH, particle size and L/S ratio. Each leachate was prepared in triplicate samples. The two leaching methods used are presented in detail below.

2.3.1. Batch method

This method was performed according to the standard procedures described in EN 14735:2005/AC:2006. According to this procedure, the sample (90 g dry weight) is mixed with a leachant (deionized water, 900 g), shaken for 24 h at a L/S ratio of 10 and filtrated (pressure filtration through a 0.45 μm cellulose nitrate filter (Millipore). The pH was not adjusted during the batch leaching, but

Table 1
Summary of leaching tests for evaluating the effect of; Liquid/Solid (L/S) ratio, pH and particle size fraction on the ash leachate composition.

Leaching method	L/S ratio	pH	Particle fraction	Replicates
Batch	10	Inherent	<4 (mm)	3[a,b]
Batch	10	Inherent	<1 (mm)	3
Batch	10	Inherent	<0.125 (mm)	3
pH-stat	10	Inherent	<1 (mm)	3
pH-stat	10	7	<1 (mm)	3
pH-stat	10	Inherent	<0.125 (mm)	3
pH-stat	10	7	<0.125 (mm)	3
pH-stat	1000	Inherent	<0.125 (mm)	3
pH-stat	1000	7	<0.125 (mm)	3[a,b]
Blank	10	7	–	1
Blank	1000	7	–	1

[a] Duplicate sample generated at one occasion and another replicate sample generated about 6 months later.
[b] Leachate tested using acute and (sub)chronic ecotoxicity tests with *N. spinipes*.