Application of multiple analytical methods, leaching and geochemical modelling for waste classification

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APPLICATION OF MULTIPLE ANALYTICAL METHODS, LEACHING AND GEOCHEMICAL MODELLING FOR WASTE CLASSIFICATION

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SUMMARY: This study presents the application of tiered approach and worst case calculations for the assessment of potential hazard of residues from municipal solid waste incinerator (MSWI). The assessment was performed accordingly to the latest European regulations that are described in the document No 1272 of the European Parliament and of the Council of 16 December 2008 on classification, labelling and packaging of substances and mixtures (CLP). The novelty of this study lies in a combined use of total composition data, mineralogical data (e.g. XRD), characterisation leaching tests and geochemical modelling to perform mass balance calculations that allows to estimate how much of each relevant element is potentially available to be present in a hazardous form. Together with the tiered approach and worst cases analysis, the evaluation suggests that assessed MSWI residue presents no hazard.

1. INTRODUCTION

The classification of waste materials as non-hazardous or hazardous waste is an important subject for waste producers and receivers. Hazardous waste should be handled, stored and transported with potential additional care in comparison with non-hazardous waste, resulting in additional (societal) costs to comply with the regulatory requirements. Waste classification as hazardous or non-hazardous waste is performed based on Commission Decision 2000/532/EC (2000) on the List of Waste (LOW) and Annex III of the Waste Framework Directive (2008/98/EC) (2008a) and based upon the Regulation (EC) No 1272 (2008b) of the European Parliament and of the Council of 16 December 2008 on classification, labelling and packaging of substances and mixtures (CLP). In 2008, the CLP has replaced Directives 67/548/EC (1967) (Dangerous Substances Directive) and 1999/45/EC (1999) (Dangerous Preparations Directive). The CLP specifies 15 hazard properties (HP) and defines limit values for maximum concentrations of substances in the waste. The producer of the waste material needs to assess all HPs to see whether there is a hazard property that will render the material hazardous. The waste material is non-hazardous if the criteria for all HPs are fulfilled positively.

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The 15 HPs are divided into physical hazards (explosive, oxidizing and flammable), health hazards (irritant, single target organ toxicity/aspiration, acute toxicity, carcinogenic, corrosive, infectious, toxic for reproduction, mutagenic and sensitizing) and environmental hazards (ecotoxicity). The remaining two HPs (release of an acute toxic gas and yielding another substance) are additional hazard properties. The approach is relatively straightforward when the physical hazards need to be assessed because the criteria are clear and test methods are specified to assess the hazard properties. The other HPs are only straightforward for chemicals with a known composition of substances. The assessment becomes very challenging when these HPs are to be assessed for heterogeneous waste materials. The main reason for this is that analyses of the total content only reveals information regarding the elemental composition and it is largely unknown in which chemical forms the substances are present in these materials. Several analytical methods can be applied to increase the number of identified substances (although largely semi-quantitatively) but the vast majority of substances is likely to remain unknown. A schematic illustration of this difficulty is given in Figure 1. In addition, it should be realized that the mentioned substances in Table 3.1 (over 4000 substances) of the CLP do only specify the substances for which so-called harmonized hazard properties are derived. Waste classification is not limited to the list in Table 3.1 of the CLP and if other substances can be present, these should also be assessed. The latter point does increase the complexity and practicality even further.

To overcome part of these difficulties, we have applied a novel combination of analytical methods, leaching and geochemical modelling. Because it is impossible to assess every possible substance that might be present in waste materials, we have limited ourselves to the assessment of the 4000+ substances described in Table 3.1 of the CLP.

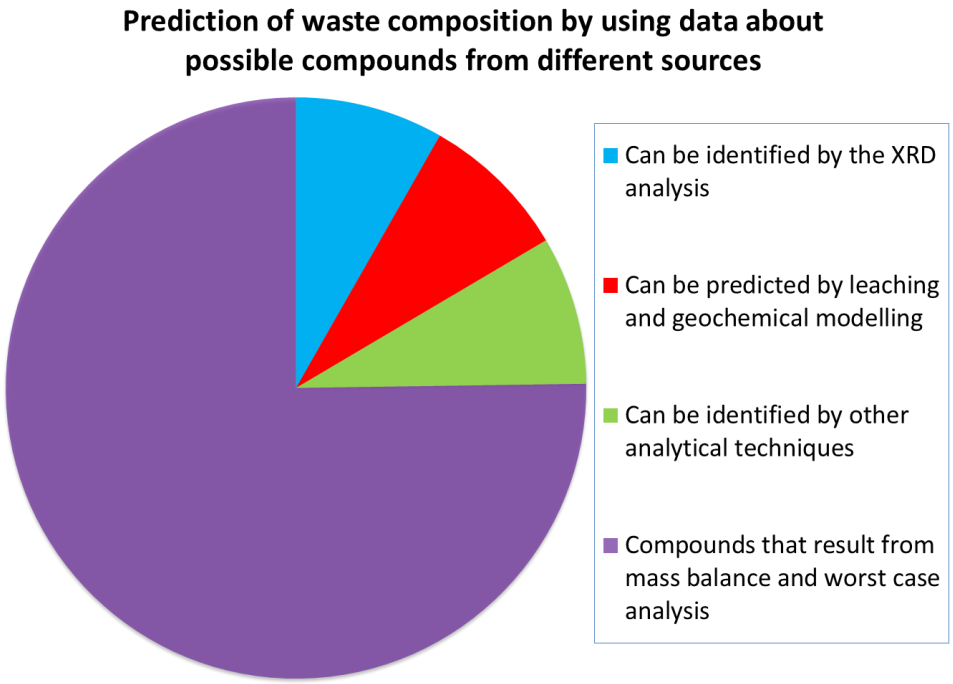

Figure 1. Schematic overview of substances that can be identified using various analytical methods. Most substances that can be present in waste materials are unknown and result from worst case assessment in combination with analysis of their stability and the likelihood to be present in the material.

The novelty of this study lies in a combined use of total composition data, mineralogical data (e.g. XRD), characterisation leaching tests and geochemical modelling to perform mass balance calculations that allows to estimate how much of each relevant element is potentially available to be present in a hazardous form. In addition, the possibility to base the waste classification on the leachable amounts will be discussed as an alternative to the approach based on total composition. The rationale for the alternative approach is that substances need to be in the water phase before they can pose an hazardous effect for most of the hazard properties. The paper further describes details of the approach and the potential implications of this work to the assessment of hazard properties in waste materials. An example for an MSWI residue was taken from a recent project. Due to confidentiality wishes of the client, the material name was kept general but this does not conflict with the scientific discussion on the approach and interpretation of the results.

2. ANALYTICAL METHODS

2.1 Total composition analyses

The total content of elements present in the residue was determined using the so-called aqua regia extraction and subsequent analyses using ICP-AES. Mercury was analysed using CV-AFS. Chloride, fluoride, bromide and sulphate were determined by ion chromatography after digestion. In total 11 samples from the production over three years were collected and analysed. A relatively high number of samples enhances the representativity of the assessment and balances out the extremes. In this study, the 95-percentile concentrations were calculated and taken for classification.

2.2 X-ray diffraction

Powder XRD was performed to identify cristalline mineral phases in the material. X-ray diffractograms were collected using a Siemens D500 X-ray diffractometer, with a diffraction angle range $2\Theta = 20–80°$ using Cu Kα radiation.

2.3 Leaching test methods

The pH static leach test (EN 14997, 2015) was applied on the MSWI residue sample. This test provides information on the pH dependent leaching of the material. The test consists of a number of parallel extractions of a material at an L/S 10 during 48 hours at a series of pre-set pH values. About 15 grams of sample (undried) was weighed and demineralised water was added (taken into account the initial water content of the sample) to obtain an L/S ratio of 10 L/kg. The pH of the suspension was automatically adjusted by the addition of 1 or 5 M HNO_3 and/or NaOH. The pH set points of the experiment were: pH 2, 4, 5.5, 7, 8, 9, 10 and 12. After 48 hours, the final pH was recorded and the suspensions were centrifuged and filtered over a 0.45 µm filter.

The leachates were analysed for major, minor and trace elements by ICP-AES (Al, As, B, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Mo, Na, Ni, P, Pb, S, Sb, Se, Si, Sn, Sr, Th, Ti, Tl, U, V, Zn. Chloride (Cl), bromide (Br) and sulphate (SO4) were analysed by ion-chromatography.

2.4 Geochemical modelling

Independent estimates of the amount of reactive surfaces present in the bottom ash matrix, which are required for sorption modelling, were made by selective chemical extractions. The solid and dissolved organic carbon in the samples was characterised quantitatively in terms of four fractions, i.e. HA, FA, hydrophilic acids (denoted by HY) and hydrophobic neutral acids (denoted by HON) by a batch procedure (van Zomeren and Comans, 2007) derived from the method currently recommended by the International Humic Substances Society (Swift, 1996; Thurman and Malcolm, 1981). The amount of amorphous and crystalline iron (hydr)oxides in the bottom ash matrix was estimated by a dithionite extraction described in Kostka and Luther III (1994), and will be referred to as Fe-DITH. The portion of amorphous iron (hydr)oxides was estimated by an ascorbate extraction (Kostka and Luther III, 1994), and will be referred to as Fe-ASC. The amount of amorphous aluminum (hydr)oxides was estimated by an oxalate extraction according to Blakemore et al. (1987) and will be referred to as Al-OX. The approach for geochemical modelling is described elsewhere (van der Sloot and van Zomeren, 2012).

3. WASTE CLASSIFICATION APPROACH

In order to classify waste materials, a novel tiered classification approach was followed in this work, based on the work of Hjelmar et al. (2013). The approach was applied to a municipal solid waste incineration residue. A schematic illustration of the tiered approach is given in Figure 2. The assessment at each tier was aimed to eliminate those hazard properties that cannot be displayed in the material. Each next tier considered only those hazard properties that were not ruled out at the previous level of assessment.

Thus, tier 1 is a screening judgement in which general assessment of the relevance of hazardous properties (HP1 to HP15) is carried out based on knowledge of the gross characteristics and composition of the material. Tier 2 focuses on those hazardous properties that are not excluded in Tier 1. A worst case assessment was applied in Tier 2 assuming that the total amount of each relevant element is bound in its most hazardous form. A similar approach has also been described and used by Hennebert and Rebischung (2013) and Hjelmar et al. (2013). The worst case assessment safely rules out a number of additional hazard properties and/or hazardous substances while the potentially present remaining hazardous substances are taken to Tier 3.

In Tier 3, a combined use of characterisation leaching tests, geochemical modelling, mineralogical characterisation data (e.g. XRD) and the total composition is used to perform mass balance calculations. The estimated amount of identified minerals from XRD analyses (detection limit was used as a safe starting point) and probable minerals identified from the leaching and geochemical modelling assessment (amounts estimated based on difference between total and leached amounts) are subtracted from the total amount. This approach allows to estimate how much of each relevant element is potentially available (mentioned as residual concentrations further in the paper) to be present in a hazardous form realising that part of the elemental composition is tightly bound in the identified mineral forms. Subsequently, the remaining list of potentially present hazardous substances is checked for the relevance in the material considering the nature of the process to produce this material. For example, the remaining list of substances can include substances that are unstable at higher temperatures and are therefore unlikely to be present in incineration ashes. Finally, an assessment was made to convert the worst case concentrations to more realistic concentrations of remaining hazardous substances to be checked against the limit values in the CLP.

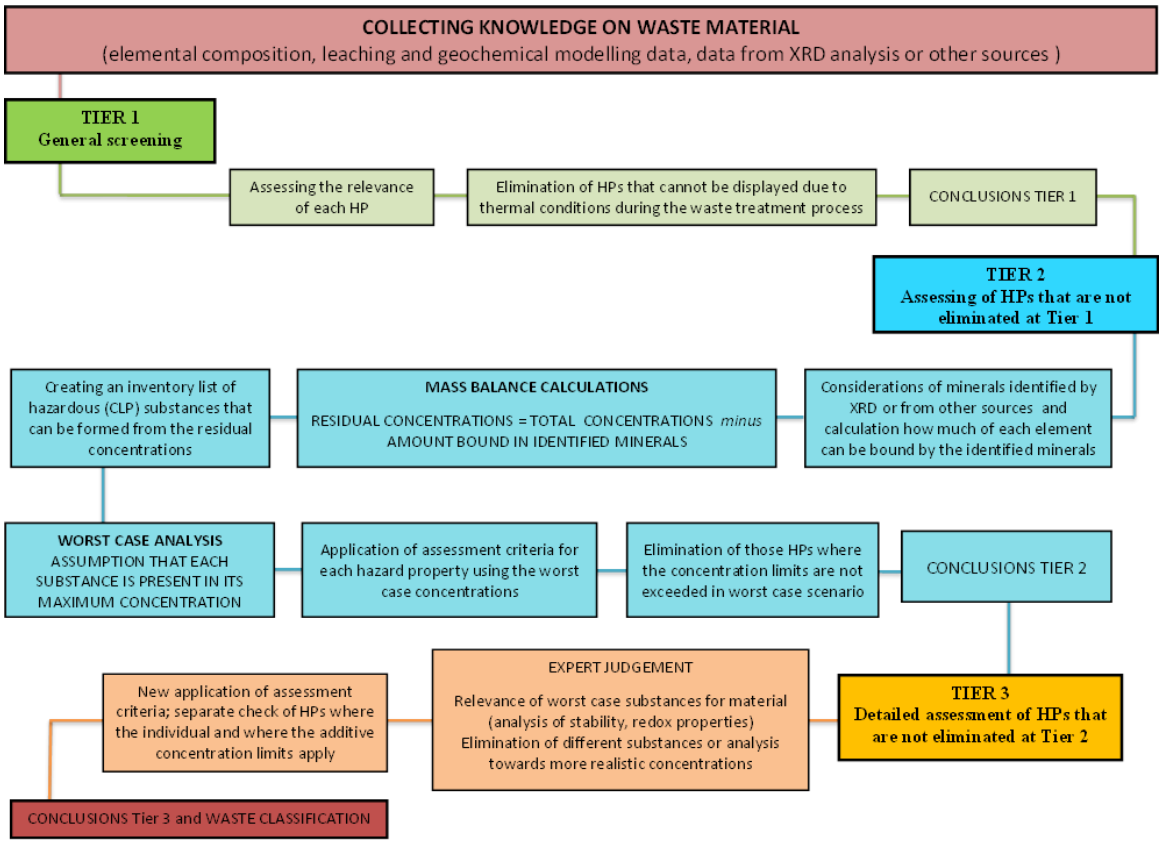

Figure 2. Schematic illustration of the applied tiered approach for waste classification.

4. RESULTS AND DISCUSSION

4.1 Tier 1 assessment

After the general screening of the HPs, the following hazard properties were considered to be not relevant for the example material: HP1, HP2, HP3, HP9, HP12 and HP 15. The reasons for excluding these HPs are given below.

HP1, explosive: any possible explosive substance will be destroyed during the combustion process. Therefore HP1 classification of the incineration residue is concluded as non-hazardous.

HP2, oxidizing: oxidising substances would be destroyed during the incineration process. Therefore, we conclude that the incineration residue can be classified as non-hazardous with respect to HP2.

HP3, flammable: The Hazard Statement that is relevant to incineration residues is H261. Strongly alkaline residues containing elementary aluminium may develop hydrogen gas in contact with water which can burn if it is ignited. It is unknown whether the studied material can contain elementary aluminum and there is also no method specified in Annex I of the CLP for testing of the potential hydrogen gas production in relation to classification under HP3. When the material is stored dry, the risk of hydrogen production is negligible. Assuming that the material is stored under dry conditions and considering that no test method is available, the incineration residue is currently classified as non-hazardous with respect to HP3 until an appropriate test method is developed.

HP9, infectious: Since incineration residues are produced at high temperatures, any micro-organisms or toxins originating from micro-organisms present in the input waste will be destroyed in the incineration process. Therefore HP9 is considered to be not relevant to

incineration residues.
HP12, release of an acute toxic gas category 1,2, or 3: The incineration residue is unlikely to emit toxic gasses. Due to the current lack of methods of measurement and limit values, the material is considered non-hazardous with respect to HP12
HP15, yielding another substance: Tier 1 assessment recommends that none of the hazard statements are relevant to the incineration residue since all of the incidents described with the hazard statements would have occurred during or will have been prevented by the incineration process. The conclusion is therefore that the material can be considered non-hazardous with respect to HP15.

4.2 Tier 2 assessment

The elemental composition of the MSWI residue is summarized in column (2) of **Fout! Verwijzingsbron niet gevonden.**. This column provides an overview only of the elements that were detected at concentrations ≥0.1%. The rest of elements that are present in concentrations less than 0.1% are regarded as trace elements. Their speciations are not included in the assessement due to their negligible contribution except the cases where the specific concentration limits, if defined in the CLP, can apply (f.e for Ni and Cr substances).

XRD analysis resulted in a number of minerals that were identified and assumed to be present: calcium oxide phosphate $Ca_4O(PO_4)_2$, match = 87%; calcium silicate chloride $Ca_2SiO_3Cl_2$, match = 85%; anhydrite, syn $CaSO_4$, match = 43%; nepheline, syn. $NaAlSiO_4$, match = 95%; armalcolite, ferrian $(MgFe)(Ti_3Fe)O_{10}$,match = 65%; magnesium phosphate MgP_4O_{11}, match = 74%; magnesium phosphate alpha MgP_2O_7, match = 65%.
Minerals revealed from geochemical modelling are: calcite ($CaCO_3$); tobermorite (calcium silicate hydrate, $Ca_5Si_6O_{16}(OH)_2 \cdot 4H_2O$); $2CaO \cdot Al_2O_3 * SiO_2 \cdot 8H_2O$; alpha-TCP; gypsum ($CaSO_4 \cdot 2H_2O$); willemite ($Zn_2SiO_4$).

Elemental composition together with data from XRD analysis and analysis of the geochemical modelling data are used to perform mass balance calculations (see Table 1). These calculations aim to estimate residual concentrations, i.e to calculate how much of each element is left to form possible CLP compounds, knowing that each of the substances identified by XRD and those that are predicted by geochemical modelling, are already present in the system and bound some amount of available elements. Resulting residual concentrations are presented in column (4) of

Table 1.

For the evaluation, columns (4) and (5) of

Table 1 have to be compared. As it can be seen, all P and Ti that are present in the ash residue are bound in the identified XRD compounds, or by the substances predicted by geochemical modelling. Therefore, none of possible CLP substances that involve any of Ti and P elements, can be formed. The rest of the elements from

Table 1 demand further worst-case assessment.

As a remark, for every element in

Table 1, the XRD concentrations of the minerals are calculated assuming that the minerals were present at concentrations of 5% (detection limit) and under the worst-case assumption that the same amount of a given element is present to form all relevant substances. In fact, if for instance, some amount of P is taken by one compound, there is less phosphorus left to form another P-containing compound. Negative values in column (4) shall be understood as there is zero amount of that element to form something else that was already identified by the XRD analysis or predicted by geochemical modelling.

Table 1. Mass balance: comparison of the elemental composition and the residual concentrations (available to form possible CLP compounds) and concentrations that are needed to form the CLP compounds at their corresponding concentration limits.

	Elemental composition based on 95percentile, %	Total identified at DL from XRD, and modelling, %	Residual concentrations available to make the CLP compounds, %	Concentrations needed to make CLP compounds at concentration limit, %
(1)	(2)	(3)	(4)*	(5)
Al	5.19	2.65	2.54	2.63
Ca	21.88	19.43	2.45	1.51
K	3.48	1.60	1.88	10.76
Na	2.72	0.81	1.91	3.98
Cl	4.33	2.98	1.35	30.65
S	3.86	1.92	1.94	10.65
P	1.24	4.33	***-3.09***	***3.01***
Mg	1.49	1.25	0.24	0.05
Mn	0.16	0	0.16	0.03
Ti	0.94	1.64	***-0.70***	***0.25***
Zn	1.05	0.39	0.66	0.60
Pb	0.13	0	0.13	0.06
Si	4.63	4.32	0.31	0.07
Fe	3.3	1.27	2.03	

*The calculated concentrations in column (4) are derived by subtracting the concentration in column (3) from the concentration in column (2).

As it follows from the mass balance calculations described above, all P- and Ti- involving substances can be eliminated from further assessment. Compounds that can be formed by Al, Ca, K, Na, Fe, Cl, S, Si, Mg, Mn, Pb and Zn need further considerations.

To assess further, residual concentrations (column 4 of Table 1) of Al, Ca, K, Na, Cl, S, Si, Mg, Mn, Pb, Fe and Zn are considered. These are the amounts of each of listed elements that are potentially left to form possible CLP compounds. Residual concentrations are used to perform worst case calculations: it is assumed that each of the possible compounds bound maximum of the needed elements. Then calculated worst case concentrations are compared to the corresponding concentration limits.

As result of worst case calculations, a list of critical compounds and relevant hazard properties was established. The list included SCl_4 (HP4, HP8, HP14), SCl_2O_2(HP4, HP5, HP8), SCl_2H_4 (HP4, HP6, HP8, HP14), $Ca(ClO)_2$ (HP4, HP6, HP8, HP14), $KClO_3$ (HP6, HP14), $KHSO_4$ (HP4, HP5, HP8) , $KMnO_4$ (HP6, HP14), NaN_3 (HP6, HP14), $NaNO_2$ (HP6, HP14), $NaClO_3$ (HP4, HP6, HP8), $PbCrO_4$ (HP7). Each of these compounds can lead to hazardous classification even without applying the summation criteria. Therefore, each of these compounds needed an individual assessment before the summation criteria could be applied for HP4, HP6, HP8 and HP14. Individual assessment of each of these compounds was a starting point for Tier 3.

4.3 Tier 3 assessment

Tier 3 assessment started from detail assessment of all substances that were regarded as critical in Tier 2 and are listed in Table 2. Conditions and processes at which MSWI residues are formed, their stabilities and likelihood to be present in waste were addressed for each substance individually. Such detailed investigation resulted in elimination of all critical compounds that resulted from Tier 2 as they are unlikely to be present because of stability reasons. See Table 2 for more details on the reasoning of elimination.

Table 2. List of critical substances from worst case assessment in Tier 3 and investigations of their stabilities.

Compound	Hazard property	Reason of elimination
SCl_4	HP4 (H314), HP8 (H314), HP14 (H400)	unstable at T > -30°C
SCl_2O_2	HP4 (H314), HP5 (H335), HP8 (H314)	decomposes at around 100°C
SCl_2H_4	HP4 (H314), HP6 (H301, H332), HP8 (H314) HP14 (H400)	decomposes at high temperatures
$Ca(ClO)_2$	HP4(H314), HP6 (H302), HP8 (H314), HP14 (H400)	highly unlikely, unstable and decomposes: http://fscimage.fishersci.com/msds/03990.htm
$KClO_3$	HP6 (H302, H332), HP14 (H411)	decomposes to KCl and oxygen; with MnO_2 as catalyst; http://en.wikipedia.org/wiki/Potassium_chlorate
$KHSO_4$	HP4 (H314), HP5 (H335), HP8 (H314)	decomposes at 200°C, http://www.inchem.org/documents/icsc/icsc/eics1585.htm
$KMnO_4$	HP6 (H300,H302), HP14 (H400, H410)	highly unlikely, forms other potassium and manganese containing compounds at temperatures above 250°C (see other tab). Too oxidizing for the formation conditions in incinerator.
NaN_3	HP6(H300), HP14(H400, H410)	highly unlikely, decomposes at around 300°C: http://www.ehs.neu.edu/hazardous_waste/fact_sheets/sodium_azide/. Too reducing for the formation conditions in incinerator.
$NaNO_2$	HP6 (H301), HP14 (H400)	highly unlikely, decomposes at around 330°C: http://en.wikipedia.org/wiki/Sodium_nitrite
$NaClO_3$	HP4 (H314), HP6 (H302), HP8 (H314)	highly unlikely, decomposes at 300°C. Too oxidizing for the formation conditions in incinerator.
$PbCrO_4$	HP7 (H350)	after assessment it was concluded that $PbCrO_4$ cannot be present in critical concentration due to the limited amount of Cr in the system.

Next, after all critical substances mentioned in Table 2 were ruled out from the assessment, the revision of all hazard properties can be performed.

To start, the hazard properties with individual concentration limits were addressed, i.e HP5 (single/specific target organ toxicity), HP7(carcinogenic), HP10(toxic for reproduction), HP11(mutagenic) and HP13(sensitizing). Worst case concentrations of all compounds that are

relevant for these hazard properties were compared with the proper concentrations limits defined in the CLP for each of those hazard properties **The assessment resulted in elimination of HP5, HP7, HP10, HP11 and HP13, as in worst case assessment there were no compounds that would individually exceed the concentration limits that are defined in the CLP for these HPs.**

Next, HP4 (irritant), HP6 (acute toxicity), HP8 (corrosive) and HP14 (eco-toxic) were assessed. For these hazard properties the additivity criteria for each relevant HSC need to be applied as defined in the CLP: corresponding summation criteria have to be applied for all relevant sunstances of Al, Ca, K, Na, Cl, S, Mg, Mn, Cr, Fe, Zn and Pb that can display one or more of mentioned HPs. Note that Ti- and P- containing substances will not contribute to the possible additive hazard anymore, since the mass balance calculations described above (Table 1) indicated that there is no residual amount of Ti or P to form hazardous substances that could involve these elements.

Subsequent application of summation criteria for HP4, HP6 and HP8 using the worst case concentrations resulted again in a number of substances that could render classification of the MSWI residue as hazardous. In order to avoid an overestimation of additive hazard when additing together worst case concentrations, further analysis of stability conditions and likelyhood of these substances to be present was done individually for each substance that was suspected to render hazardous classification. The updated list of critical substances and the results of detailed analysis on their stability is given in Table 3.

4.3.1 Assessment of Zn-containing compounds

Total amount of Zn in the MSWI residue was 1.05% based on the 95% composition. As follows from leaching and geochemical modeling data for Zn, Zn behavior in a wide range of pH is controlled by willemite phase (Zn_2SiO_4). Willemite is not a CLP compound. Geochemical modeling data for Zn suggest that 0.39% Zn (max available from pH dependence graph) will be bound in willemite phase. This leaves 0.66% (1.05 – 0.39) of Zn to form possible CLP compounds. Therefore Zn worst case assessment was done using 0.66% as available Zn to form possible CLP compounds. The assessment leads to several Zn compounds as compounds of possible concern in worst case scenario. However, as it was previously mentioned in Table 1, none of phosphorus compounds that are listed in the CLP compounds can be formed in the MSWI residue, since all available P in the system is already bound in compounds identified by XRD. Thus, it can be concluded that $Zn_3(PO_4)_2$ and Zn_3P_2 will not contribute to the classification of theMSWI residue. This leaves $ZnCl_2$, ZnS, ZnO and $ZnSO_3$ as compounds that will contribute to the summation for HP4, HP6, HP8 and HP14.

Further evaluation of HP4, HP6 and HP8 and application of the summation criteria as defined in the CLP led to the conclusion that for none of these hazard properties the concentration limits will be exceeded when considering the total contribution from all relevant substances in the worst case scenario. **Therefore, the apllication of the summation criteria to HP4, HP6 and HP8 does not trigger the classification of the MSWI residue as hazardous.**

However, it must be underlined here, that unlike other hazard properties, the assessment of possible corrosivity or irritancy of the MSWI residue shall be also done analyzing the pH and the buffering capacity of the material, as accordingly to paragraph 3.2.3.1.2 of the CLP, high or low pH (pH<2 or pH>11.5) suggests that a mixture is suspected to produce significant irritant or corrosive effects. Therefore materials with a high pH should be further assessed by measuring the buffering capacity (Young *et al.*, 1988) in order to investigate its corrosive or irritant potential that is due to the alkalinity of the material. This assessment, complementary to the summation of the concentrations of individual substances that are relevant for HP4 /HP8, would give an additional insigt into possible corrosive or irritant characteristics of the material.

Table 3. List of critical substances for HP4, HP6, HP8 and HP14.

Compound	Relevant HP and HSC	Assessment
NaOH	HP4, H314	Generally likely to be present because it is a common substance and usually MSWI residues are alkaline materials containing a substantial concentration of sodium. However, NaOH was mentioned as non-matching compound, based on the results of the XRD analysis
Na_2S	HP4, H314	Not likely to be present because the oxidizing conditions in the furnace are not favorable to form this compound. Organoleptic tests (adding water to the sample and smell any H_2S formation) can be performed to obtain more information. The test was performed and no H_2S formation was detected at native pH of the material.
KOH	HP4, H314	Likely to be present, was mentioned as "best match" compound in the XRD analysis
K_2SH	HP4, H314	Not likely to be present because the oxidizing conditions in the furnace are not favorable to form this compound
$NaClO_4$	HP6, H302	Not likely to be present because this compound decomposes at temperatures >130°C
$AlCl_3$	HP4, H314	In general, $AlCl_3$ can be present in MSWI residue because of substantial amounts of both Al and Cl in the matrix. However, it was mentioned as non-matching compound from XRD data on the MSWI residue. Therefore $AlCl_3$ will be excluded from the summation
Zn compounds	HP4, HP8, HP14	See below

4.3.2 Eco-toxicity assessment

Contrarily to HP4, HP6 and HP8 where the summation criteria can be applied as defined in the CLP, hazard property HP14 (eco-toxicity) was assessed in another manner: using not the residual concentrations but the leached concentrations (at the natural pH of the material) based on data from leaching experiments; and accordingly to criteria defined by the UK as described in WM2 (Appendix C14, page C39). The decision not to follow the CLP when assesing HP14 was made for two reasons:

1. There is no harmonised view in the EU on M-factors which makes the application of the CLP criteria for HP14 not straightforward. The UK criteria in WM2 currently represents the most complete and straightforward set of equations for the assessment of HP14.

2. ECHA document of 2012 "Guidance on the application of the CLP criteria. Guidance to Regulation (EC) No 1272/2008 on classification, labelling and packaging (CLP) of substances and mixtures" Version 3.0, issued in November 2012, Annex IV, states that the eco-toxic substances need to be first in the water phase before their eco-toxic effect will become apparent. Exposure to these substances is limited by the solubility of the substances in water and the associated bioavailability of the substance to organisms in the aquatic environment. Therefore, in our view, leaching data for the substances that are relevant for the eco-toxicity assessment can

provide more insight regarding possible eco-toxic hazard then using their elemental composition or residual concentrations using the mass-balance approach.

Accordingly to WM2, hazard property H14 eco-toxic involves the assessment of substances that can belong to one or more of the next risk phrases: R50 (very toxic to aquatic organisms), R51(toxic to aquatic organisms), R52(harmful to aquatic organisms), R53(may cause long-term adverse effects in the aquatic environment), R50-53(very toxic to aquatic organisms, may cause long-term adverse effects in the aquatic environment); R51-53(toxic to aquatic organisms, may cause long-term adverse effects in the aquatic environment) and R52-53(harmful to aquatic organisms, may cause long-term adverse effects in the aquatic environment). Generic cut-off values are 0.1% for for R50, R50-53, R51-53 and 1% for R52, R52-53, R53.

Table 14.2 of WM2 specifies Eqs.1-4 that have to be applied in a subsequent manner in order to determine if a waste is hazardous or not with respect to eco-toxicity. Below we list the equations that have to be referred to: one has to start from Eq.1. If criteria defined by Eq.1 are not met, than the waste is defined to be hazardous for the environment. If criteria defined by Eq.1 are fulfilled, one can proceed with Eq.2. In order to be non-hazardous with respect to eco-toxicity, the criteria that are defined by all four equations have to be fulfilled. To apply the formulas, the derived concentrations (above cut-off values) for all substances with the mentioned R symbols need to be taken into account.

Eq. 1: (R50-53)/0.25 + (R51-53)/2.5 + (R52-53 R50-53)/0.25 + (R51-53)/2.5 + (R52-53)/25 > = 1%
Eq. 2: R50 + R50-53 >= 25%
Eq. 3: R52 >= 25%
Eq. 4: R53 + R50-53 + R51-53 + R52-53 >= 25%

Since only compounds that belong to R50 and R50-53 risk phases were potentially present (based on the analysis of the relevant substances), the criteria defined by Eqs.1-4 transform to the next set of the requirements:

Eq. 1 → Eq. 1.1: (R50-53)/0.25 > = 1%
Eq. 2 → Eq. 2.1: R50 + R50-53 >= 25%
Eq. 3 → not applicable since there are no substances with R52 risk phrases
Eq. 4 → Eq. 4.1: R50-53 >= 25%

Formal application of Eqs.1.1-4.1 to the substances that are relevant for eco-toxic assessment (see Table 4) shows that criteria defined by Eq.1.1 will not be met based on a worst-case approach.

However, ECHA document of 2012 “Guidance on the application of the CLP criteria. Guidance to Regulation (EC) No 1272/2008 on classification, labelling and packaging (CLP) of substances and mixtures” Version 3.0, issued in November 2012, Annex IV, has stated that the eco-toxic substances need to be first in the water phase before their eco-toxic effect will become apparent. Exposure to these substances is limited by the solubility of the substances in water and the associated bioavailability of the substance to organisms in the aquatic environment. Therefore, leaching data for the substances that are relevant for the eco-toxicity assessment were used. The use of leaching data for Zn, Pb, Cu and Ba at the natural pH of the material (12.5) at L/S=10 l/kg has been made in order to perform the HP14 assessment.

Table 4. HP14 assessment – final summation when taking account the residual concentrations of relevant elements in comparison with the assessment done based on data at pH=12.5 from leaching experiments (worst case concentrations in wt%).

Element	**Relevant CLP compounds**	cut-off 0.1%	cut-off 0.1%	cut-off 0.1%	cut-off 0.1%
		R50	R50-53	R50	R50-53
		Based on residual concentrations (content)		**Based on data from leaching**	
Ba	BaS (R31, R20-22, ***R50***)	0.15		0.0002	
Cu	CuSO4 (R22, R36-38, ***R50-53***)		0.15		0.0000
	CuCl2 (R22, ***R50-53***)		0.13		0.0000
Pb	Pb2CrO5 (R40, R61, R62, ***R50-53***)		0.21		0.0084
	Pb(N3)4 (R3, R61, R62, R20-22, ***R50-53***)		0.24		0.0115
Zn	ZnS (***R50-53***)		0.98		0.0048
	ZnSO4*7H2O (R22, R41, ***R50-53***)		2.90		0.0141
	ZnO (***R50-53***)		0.82		0.0040
	SUM	0.15	5.43	0.0002	0.0239
Criteria		**Application of criteria**			
	Eq 1.1				
	(R50-53)/0.25 >= 1%		**21.72 > 1**		**0.096 < 1**
	Eq 2.1				
	R50 + R50-53 >= 25%		**5.58 < 25**		**0.024 < 25**
	Eq 4.1				
	R50-53 >= 25%		**5.43 < 25**		**0.024 < 25**

The result of the eco-toxicity assessment when using data from leaching at pH = 12.5 is also presented in Table 4 with the applications of criteria defined by Eqs.1.1 – 4.1 for all relevant substances. As one can see, **when leaching data are considered for the evaluation of eco-toxicity, the assessment reveals that the MSWI residue presents no eco-toxicity hazard.** Note, that the concentrations mentioned in Table 4 are still worst case concentrations (assuming, for instance, that the same maximum amount of Cu (or Zn, or Pb, or Ba) that can leach at pH = 12.5 will be bound by each of compounds listed in Table 4). Additionally, the check of stability suggest that BaS may be not relevant in view of non-existent reducing conditionsduring the incineration process. $PbCrO_5$ is too oxidizing and $Pb(N_3)_4$ is too reducing.

Therefore, based on this assessment using leaching data instead of total or residual concentrations for the MSWI residue, **it can be concluded that hazard property HP14 will not render the material hazardous.**

5. CONCLUSIONS

In this study, an example was given to classify waste materials using the CLP and how to coop with some of difficulties that were encountered for heterogeneous waste materials. The approach is relatively straightforward when the physical hazards need to be assessed because the criteria are clear and test methods are specified to assess the hazard properties. The other HPs are only straightforward for chemicals with a known composition of substances. The assessment becomes very challenging when these HPs are to be assessed for heterogeneous waste materials. The main reason for this is that analyses of the total content only reveals information regarding the elemental composition and it is largely unknown in which chemical forms the substances are present in these materials. In addition, it should be realized that the mentioned substances in Table 3.1 (about 4000 substances) of the CLP do only specify the substances for which so-called harmonized hazard properties are derived. Waste classification is not limited to the list in Table 3.1 of the CLP and if other substances can be present, these should also be assessed. The latter point does increase the complexity and practicality even further.

To overcome part of these difficulties, we have applied a novel combination of analytical methods, leaching and geochemical modelling. The novelty of this study lies in a combined use of total composition data, mineralogical data (e.g. XRD), characterisation leaching tests and geochemical modelling to perform mass balance calculations that allows to estimate how much of each relevant element is potentially available to be present in a hazardous form.

Due to the ongoing discussions with regard to HP14, it is still unclear wheteher the applied equations would hold in a final assessment. However, the approach to assess hazard classification should be applied to other waste materials to validate the general applicability.

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