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Revised classification of MSWI bottom ash

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Abstract

MSWI bottom ash is currently considered to be a non-hazardous waste material. This was also supported by the conclusion of the study that DHI, ECN and Hans van der Sloot Consultancy conducted for CEWEP by Hjelmar et al [1].

Waste classification as hazardous or non-hazardous is performed based on Commission Decision 2000/532/EC on the List of Waste (LOW) and Annex III of the Waste Framework Directive 2008/98/EC (WFD), amended by regulation 1357/2014 (1 June 2015) due the implementation of the CLP regulation (1272/2008). In 2008, the CLP has replaced Directives 67/548/EC (Dangerous Substances Directive) and 1999/45/EC (Dangerous Preparations Directive). WFD, amended by regulation 1357/2014, specifies 15 hazard properties (HP) and defines limit values for maximum concentrations of substances in the waste.

After 2013, numerous discussions within the Commission and between Commission and stakeholders have taken place and some criteria were adjusted (e.g. HP 4 irritant/HP 8 corrosive). Moreover, attempts have been made to further specify the criteria for HP 14 (eco-toxic). In view of these new aspects, the aim of this work is to review the already existing classification of MSWI bottom ash described in the CEWEP report of 2013 by Hjelmar et al [1] and provide the arguments that are (or are not) in favour of the previous conclusions.

Since the CEWEP report [1] uses the total content data of a large set of European MSWI bottom ash samples, the same total content data will be used in the current assessment for twofold reasons: using the same data set will allow a comparison with the previous assessment, and also because using such an elaborated dataset becomes representative for the European bottom ash. At the same time, the report leaves the possibility to use the dataset of different installations of individual countries to evaluate the classification for the specific situation on local/national level.

Although classification is relatively straightforward for materials or products with a known composition, the application to heterogeneous waste materials is more challenging since it is largely unknown in which chemical forms chemical elements are present in wastes. Total content analyses only reveals information regarding the elemental composition but does not give information on the chemical binding form (speciation) of these elements in the waste, i.e. the substances.

Therefore, a tiered classification approach in combination with worst case scenario is followed in this work. A tiered approach has been already applied in [1] for European

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MSWI bottom ash classification. The novelty of this work lies in using a worst case scenario approach and assessment of the most hazardous substances (as introduced by Hennebert in 2015) in combination with a tiered approach.

In this work, Tier 1 is a screening judgement in which general assessment of the relevance of hazardous properties (HP 1 to HP 15) to bottom ash is carried out based on knowledge of the gross characteristics and composition of bottom ash. Tier 2 focuses on those hazardous properties that are not excluded in Tier 1. A worst case assessment and most hazardous substances analysis was applied in Tier 2 assuming that the total amount of each relevant element is bound in its most hazardous form. The worst case assessment safely rules out a number of hazard properties and/or hazardous substances while the potentially present remaining hazardous substances are taken to Tier 3. In Tier 3, expert judgement (knowledge on stabilities of the substances, information from geochemical modelling, information on leaching properties, literature data) is used to evaluate the remaining hazard properties.

As a result of Tier 1, HP 1 (explosive), HP 2 (oxidising), HP 3 (flammable), HP 9 (infectious) and HP 15 (yielding another substance) were excluded from the assessment. Assessment of Tier 2 involved a worst-case approach and excluded HP 5 (STOT/Aspiration), HP 6 (acute toxicity), HP 11 (mutagenic), HP 13 (sensitising). Tier 3 resulted in the elimination of HP 7 (carcinogenic), HP 4 (irritant) and HP 8 (corrosive). Note that current report only covers quenched bottom ash, and the conclusions (especially for HP 4 and HP 8) drawn in this report cannot be used in case of dry extracted bottom ash. For hazard property HP 10 (toxic for reproduction), the results showed that bottom ash samples with a total Pb concentration below 3500 mg/kg present no hazard. The 95 percentile concentration of Pb is 3969 mg/kg and part of the individual samples from this dataset are, therefore, critical towards the limit value. Possibly, the dataset contains outliers and/or individual samples that were not (or insufficiently) processed to remove (non-) ferrous metals before analyses. It is therefore recommended to review the original Pb data. It should be noted that the current assessment on HP 10 makes no distinction between the powder and massive (not considered hazardous) forms of metallic Pb (as shall apply from March 2018 according to ATP 9 to the CLP).

HP 14 (eco-toxic) assessment was performed using five different calculation methods. Four calculation methods were already proposed by the Commission. The fifth method includes a new proposal from the Commission that combines methods 1 and 2 (criteria as defined in method 1 with cut-off values from method 2). Since M-factors are not defined for all substances with the relevant eco-toxic hazard, but only for some of them, M-factors for all substances are assumed to be 1 for all five methods. With these assumptions, methods 1, 3 and 5 lead to an exceedance of at least one order of magnitude in comparison with the limit values. For methods 2 and 4, the limit values are exceeded to a much lesser extent, but nevertheless, all five methods concluded that HP 14 was a relevant hazard property for MSWI bottom ash (based on the total content of elements). Based on these results, it concluded that considerations on M-factors higher than 1 will not lead to different conclusions for HP 14.

An alternative assessment for HP 14 is also proposed in this report. This alternative approach takes the leached concentrations into account rather than the total content. . Eco-toxic effects that the organisms can be exposed to by the water phase, i.e., the substances should be in solution first in order to exert a potential effect. This pathway is also described in the ECHA guidance on the application of the CLP criteria (Part 4, Annex

IV, pp. 489 and 580). Therefore, exposure from eco toxic substances is limited by their solubility and availability in the water phase.

As a first example, leaching data was considered and two possible starting points were assessed: the maximum leachable concentrations at pH 2 was taken as a worst case starting point. In addition, the actual leached concentrations in the pH domain from 7 to 12 (generally much lower concentrations than observed at pH 2) were considered .

This assessment resulted in the following:

- MSWI bottom ash would be considered as non-hazardous with respect to HP 14 by method 2 and method 4, and hazardous by each of methods 1, 3 and 5, when availability data (pH 2) are taken as basis in the assessment.
- When the assessment takes leaching data in the pH domain from 7 to 12 as a basis for the assessment, MSWI bottom ash would be considered non-hazardous waste with respect to HP 14 by each of the 5 methods. All M-factors were considered to be 1 in this assessment. When leaching would be the basis for assessment of HP 14, additional discussion on the M-factors would also be of relevance for HP 14.

Finally, we want to stress that assessments based on total content or availability (maximum leached under extreme conditions, pH 2) are always a worst-case assessment. In other legislations that aim to protect ecosystems (e.g., EU landfill directive, Dutch soil quality decree, EU construction products regulation, etc.) actual leached concentrations at the native pH (i.e., using a percolation leaching tests) are used as a basis for the assessment of the true impact on ecosystems using impact assessment modelling (risk based approach). Hence, a risk based approach is preferred over a worst-case hazard based assessment, that may ultimately limit the reuse of waste materials in a circular economy.



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Introduction

1.1 Motivation and objectives of the study

The Waste Framework Directive (2008/98/EC) describes, among others, criteria for the classification of waste materials as either non-hazardous or hazardous. Hazard classification of waste materials is closely linked to storage, transportation, disposal, recycling and landfilling requirements and associated costs. Incorrect classification can lead to environmental and economic impacts.

MSWI bottom ash is currently considered to be a non-hazardous waste material and this was also supported by the conclusion of the study that DHI, ECN and Hans van der Sloot Consultancy conducted for CEWEP in Hjelm et al, 2013 [1]. Since 2013, numerous discussions within the Commission and between Commission and stakeholders have taken place and some criteria were adjusted (e.g. HP 4/HP 8). In addition, the state of the art on how to determine/model the speciation of elements in bottom ash has advanced. Moreover, attempts have been made to further specify the criteria for HP 14. A study of BIO by Deloitte and INERIS of 2015 [2] indicated four different methods to pragmatically assess HP 14 including limit values. In view of the introduction of new methods for HP 14 and, additionally, more strict criteria mentioned in the Guidance document from ECHA [3] for HP 4/ HP 8 (irritant/corrosive) hazard properties (an extreme pH of the MSWI bottom ash and its buffering capacity in combination with in vitro testing requirements) present a new aspect that has to be taken into account in the assessment. Besides the above mentioned arguments, a need for a revision of the former classification is related to the replacement of Directives 67/548/EEC (the Dangerous Substances Directive: DSD) and Directive 1999/45/EC (the Dangerous Preparations Directive: DPD) by the criteria of CLP(Regulation (EC) No 1272/2008 of the European Parliament and of the Council on Classification, labelling and packaging of substances and mixtures, amending and repealing Directives 67/548/EEC and 1999/45/EC and amending Regulation (EC) No 1907/2006) that

became in force starting from June 2015 for the classification of substances and mixtures.

Altogether, the above mentioned reasons and the new texts published at the end of 2014 (see 1.2 Legislative background) led to the question of Vereniging Afvalbedrijven (Dutch Waste Management Association), CEWEP (Confederation of European Waste-to-Energy Plants) and FIR (Fédération Internationale du Recyclage) whether the waste classification for MSWI bottom ash is still up to date and what is the potential impact of the proposed calculation methods for HP 14.

Therefore the aim of this work is to review the already existing classification of MSWI bottom ash described in the CEWEP report of 2013 by Hjelmar et al [1]. Subsequently, the objective of the work is to check whether the previous conclusion regarding consideration of the MSWI bottom ash as non-hazardous waste can be verified and provide the arguments that are (or are not) in favour of the previous conclusions. As a result of the project, all hazard properties will be reported that will lead to the conclusion whether the MSWI should be considered as hazardous or non-hazardous waste. Since the CEWEP report uses the total content data of a large set of European MSWI bottom ash samples, the same total content data will be used in the current assessment for twofold reasons: using the same data set will allow a comparison with the previous assessment, and also because using such an elaborated dataset becomes representative for the European bottom ash including the Dutch bottom ash (provided there are no principal differences, e.g. with respect to the national legislation or other important factors such as treatment).

1.2 Legislative background

Waste classification as hazardous or non-hazardous is performed based on Commission Decision 2000/532/EC on the List of Waste (LoW) amended by Commission Decision 2014/995/EU and Annex III of the Waste Framework Directive 2008/98/EC (WFD), amended by Commission Regulation (EU) No 1357/2014 (1 June 2015) due the implementation of the Regulation (EC) No 1272/2008 (CLP regulation).

LoW (former European Waste Catalogue) is established by the Commission Decision 2000/532/EC and amended by Commission Decision 2014/995/EU that applies from 1 June 2015. It introduces 20 waste categories with a specific entry (six-digit code) for a given waste. MSWI bottom ash falls into category 19 (waste from waste management facilities, off-site waste water treatment plants and the preparation of water intended for human consumption and water for industrial use), subcategory 19 01 (waste from incineration and pyrolysis of waste). There are two entries for bottom ash in the LoW: mirror hazardous 19 01 11* (bottom ash and slag containing hazardous substances) and mirror non-hazardous 19 01 12 (bottom ash and slag other than those mentioned in 19 01 11). Having mirror entries in the LoW indicates that MSWI bottom ash is not automatically hazardous or automatically non-hazardous and it can be allocated either to hazardous or non-hazardous entry depending on a specific case and on the composition of the waste. Therefore, a threshold assessment as outlined in Commission Regulation (EU) No 1357/2014 of MSWI bottom ash is needed. As a result of the

threshold assessment, MSWI bottom ash will be ascribed one of the two above mentioned codes, depending on the outcome of the threshold assessment.

The Waste Framework Directive (WFD) is the main legislative document for waste at the EU level. The WFD contains a general definition of a waste material, definitions of all properties that can make waste hazardous, basic principles and basic obligations when handling a waste. In our assessment, we will refer to Annex III of WFD, amended by Commission Regulation (EU) No 1357/2014 for definitions of 15 hazard properties (HP) and limit values for maximum allowed concentrations of substances in the waste. The hazard properties to consider and that can render waste hazardous are:

- HP 1. Explosive
- HP 2. Oxidizing
- HP 3. Flammable
- HP 4. Irritant
- HP 5. Single/Specific Target Organ Toxicity (STOT)/Aspiration
- HP 6. Acute toxicity
- HP 7. Carcinogenic
- HP 8. Corrosive
- HP 9. Infectious
- HP 10. Toxic for reproduction
- HP 11. Mutagenic
- HP 12. Release of an acute toxic gas cat. 1, 2 or 3
- HP 13. Sensitizing
- HP 14. Eco-toxic
- HP 15. Yielding another substance

Within every hazard property, different hazard statement codes are recognised in order to distinguish between different levels of hazard within the same hazard property. Hazard statement code is a code, starting with the letter H and followed by three digits. Statements which correspond to related hazards are grouped together by code number, Usually codes between H200-H299 are reserved for representing possible physical hazard and are related to HP 1, HP 2 or HP 3, codes H300-H399 are representing possible health hazard (HP 4 – HP 11 and HP 13), codes H400-H499 describe possible environmental hazard (HP 14). For HP 12 and HP 15 separate hazard statement codes are used that can be found in Regulation (EU) No 1357/2014. For convenience, hazard statement codes that are relevant for each hazard property will be listed in the sections where the definitions of hazard properties are given.

In 2008, Regulation (EC) 1272/2008 on classification, labelling and packaging of substances and mixtures (CLP) has replaced Directives 67/548/EC (Dangerous Substances Directive) and 1999/45/EC (Dangerous Preparations Directive) and since June 2015 became a key legislation for classification of substances and mixtures. Article 1(3) of the CLP regulation states that waste is not considered a substance, mixture or an article. However, Annex III to the WFD is based on the CLP regulation and most of the HP criteria in Annex III of the WFD (with a few exceptions as limit values for HP 13, set of criteria for HP 4, units for HP 6) are equal to the CLP criteria. In this report, Table 3.1 of Annex VI in the CLP is used as the basis for the list of potential hazardous substances in bottom ash. This list of substances contains harmonised classification of substances

and gives a good basis for the hazard assessment. The known or assumed potential presence of these substances is subjected to an expert judgement based on (geo)chemical knowledge of substances and processes in MSWI bottom ash.

In order to conclude if a material is hazardous or not with respect to HP 4, HP 6, HP 8 and HP 14, the sum of all relevant concentrations of identified (or assumed) substances have to be compared with concentration limits defined in Regulation 1357/2014. The so-called cut-off values are introduced in order to exclude substances that are present in very low concentrations and will not have significant contribution to the summation. Cut-off values are defined for hazard properties where the additivity criteria are applicable. When concentrations of individual substances are above the cut-off value, they have to be taken into account in the assessment of the summation of concentration of relevant substances. Consequently, concentrations of individual substances below the cut-off limit do not have to be considered in the summation. For instance, the cut-off value for HP 8 corrosive is 1% that means that the presence of substances with concentrations lower than 1% can be ignored.

Conclusions for HP 5, HP 7, HP 10, HP 11 and HP 13 can be done by comparing individual concentrations of relevant substances, with concentration limits defined in Commission Regulation (EU) No 1357/2014. When concentrations (in total or for an individual substance, depending on the hazard property) exceed the limit, one should assess the chemical speciation in order to find out whether the substance of interest is in a chemical form that is hazardous. Assessment of HP 1, HP 2, HP 3, HP 9 and HP 15 does not refer to concentration limits and is normally done by assessing possible physical hazard.

The next paragraph presents definitions, criteria for assessment and limit values (where defined), for every hazard property. In order to conclude whether a waste material under assessment is non-hazardous, it should fulfil all criteria as defined in the next chapter of this report and should not display any of the 15 hazard properties . In addition it must not exceed the limit values for Persistent Organic Pollutants (POPs) that are defined in Article 7(4) (a) of Regulation (EC)850/2004 on persistent organic pollutants.

1.3 Hazard properties definitions and limit values overview

Each of the next subparagraphs include definitions and the evaluation criteria as given in Annex III of the WFD (amended by Commission Regulation (EU) No 1357/2014) when a material can possess given hazard properties. These definitions are cited from Commission Regulation (EU) No 1357/2014 that is indicated by quotation marks in the next paragraphs. Relevant hazard statement codes (HSC) are also listed, as well as the corresponding concentration limits (where applicable)

1.3.1 HP 1: Explosive

Definition

“Waste which is capable by reaction or producing gas at such a temperature and pressure and at such a speed as to cause damage to the surroundings. Pyrotechnic waste, explosive organic peroxide waste and explosive self-reactive waste is included”.

Hazard categories and Hazard Statement Codes to address

H200, H201, H202, H203, H204, H240, H241

Table 1. Hazard categories and Hazard Statement Codes according to Commission Regulation (EU) No 1357/2014 for waste constituents for the classification of wastes as HP 1.

| HSC | Hazard Class and Category | H statement |
|------|------------------------------------|---|
| H200 | Unstable explosive | |
| H201 | Expl. 1.1 | Explosive; mass explosion hazard |
| H202 | Expl. 1.2 | Explosive; severe projection hazard |
| H203 | Expl. 1.3 | Explosive; fire, blast or projection hazard |
| H204 | Expl. 1.4 | Fire or projection hazard |
| H240 | Heating may cause an explosion | Self-reacting, type A |
| | | Organic peroxides, type A |
| H241 | Heating may cause a fire explosion | Self-reacting, type B |
| | | Organic peroxides, type B |

Criteria

When a waste contains one or more substances classified by one of the hazard class and category codes and hazard statement codes shown in Table 1, the waste shall be assessed for HP 1, where appropriate and proportionate, according to test methods. If the presence of a substance, a mixture or an article indicates that the waste is explosive, it shall be classified as hazardous by HP 1. Test methods are specified in Annex I to Regulation (EC) No 1272/2008 (CLP).

1.3.2 HP 2: Oxidising

Definition

“Waste which may, generally by providing oxygen, cause or contribute to the combustion of other materials”.

Hazard categories and Hazard Statement Codes to address

H270, H271, H272

Table 2: Hazard categories and Hazard Statement Codes according to Regulation (EU) No1357/2014 for waste constituents for the classification of wastes as HP 2

| HSC | Hazard Class and Category | H statement |
|------|---|--|
| H270 | Oxidizing gas 1 | May cause or intensify fire; oxidizer |
| H271 | Oxidizing liquid 1 Oxidizing solid 1 | May cause fire or explosion; strong oxidizer |
| H272 | Oxidizing liquid 2 | May intensify fire; oxidizer |
| | Oxidizing liquid 3 | |
| | Oxidizing solid 2 | |
| | Oxidizing solid 3 | |

Criteria

When a waste contains one or more substances classified by one of the hazard class and category codes and hazard statement codes shown in Table 2, the waste shall be assessed for HP 2, where appropriate and proportionate, according to test methods. If the presence of a substance indicates that the waste is oxidising, it shall be classified as hazardous by HP 2. Test methods are specified in Annex I to Regulation (EC) No 1272/2008 (CLP).

1.3.3 HP 3: Flammable

Definition

- flammable liquid wastes: liquid wastes having a flash point below 60°C or waste gas oil, diesel and light heating oils having a flash point > 50°C and ≤ 75°C;
- flammable pyrophoric liquid and solid wastes: solid or liquid wastes which, even in small quantities, are liable to ignite within five minutes after coming into contact with air;
- flammable solid wastes: solid wastes which are readily combustible or may cause or contribute to fire through friction;
- flammable gaseous wastes: gaseous wastes which are flammable in air at 20°C and a standard pressure of 101.3 kPa;
- water reactive wastes: wastes which, in contact with water, emit flammable gases in dangerous quantities;
- other flammable wastes: flammable aerosols, flammable self-heating wastes, flammable organic peroxides and flammable self-reactive wastes.

Hazard categories and Hazard Statement Codes to address

H220, H221, H222, H223, H224, H225, H226, H228, H242, H250, H251, H252, H260, H261

Table 3: Hazard categories and Hazard Statement Codes according to Regulation (EU) No 1357/2014 for waste constituents for the classification of wastes as HP 3

| HSC | Hazard Class and Category | H statement |
|------|---|---|
| H220 | Flammable gas 1 | Extremely flammable gas |
| H221 | Flammable gas 2 | Flammable gas |
| H222 | Flammable aerosol 1 | Extremely flammable aerosol |
| H223 | Flammable aerosol 2 | Flammable aerosol |
| H224 | Flammable liquid 1 | Extremely flammable liquid and vapor |
| H225 | Flammable liquid 2 | Highly flammable liquid and vapor |
| H226 | Flammable liquid 3 | Flammable liquid and vapor |
| H228 | Flam. solid 1, Flam. Solid 2 | Flammable solid |
| H242 | Self-react. subst. and mix., type C, D | Heating may cause a fire |
| | Self-react. subst. and mix., type E, F | |
| | Organic peroxides, type C, D | |
| | Organic peroxides, type E, F | |
| H250 | Pyrophoric liq. 1 and pyrophoric solid 1 | Catches fire spontaneously if exp. to air |
| H251 | Self-heating subst. and mixtures, type 1 | Self-heating; may catch fire |
| H252 | Self-heating subst. and mixtures, type 2 | Self-heating in large quantities; may catch fire |
| H260 | Water-reactive subst. and mixt., type 1 | In contact with water releases flammable gases which may ignite spontaneously |
| H261 | Water-reactive subst. and mixt., type 2 and 3 | In contact with water releases flammable gases |

Criteria

When a waste contains one or more substances classified by one of the following hazard class and category codes and hazard statement codes shown in Table 3, the waste shall be assessed, where appropriate and proportionate, according to test methods. If the presence of a substance indicates that the waste is flammable, it shall be classified as hazardous by HP 3. Test methods are specified in Annex I to Regulation (EC) No 1272/2008 (CLP).

1.3.4 HP 4: Irritant – skin irritation and eye damage

Definition

“Waste which on application can cause skin irritation or damage to the eye”.

Hazard categories and Hazard Statement Codes to address

H314, H315, H318, H319

Table 4: Hazard categories and Hazard Statement Codes according to Regulation (EU) No 1357/2014 for waste constituents and the corresponding concentration limits for the classification of wastes as hazardous by HP 4

| HSC | Hazard Class and Category | H statement | Concentration limit |
|-----------|---------------------------|---|---------------------|
| H314 | Skin corrosion 1A | Causes severe skin burns and eye damage | 1% |
| H315 | Skin irritant 2 | Causes skin irritation | |
| H318 | Eye damage 1 | Causes eye damage | 10% |
| H319 | Eye damage 2 | Causes eye irritation | |
| H315+H319 | | | 20% |

Criteria

When a waste contains one or more substances in concentrations above the cut-off value, that are classified by one of the following hazard class and category codes and hazard statement codes and one or more of the following concentration limits is exceeded or equalled, the waste shall be classified as hazardous by HP 4.

The cut-off value for Skin corr. 1A (H314), Skin irrit. 2 (H315), Eye dam. 1 (H318) and Eye irrit. 2 (H319) is 1 % for any of these categories.

If the sum of the concentrations of all substances classified as Skin corr. 1A (H314) exceeds or equals 1 %, the waste shall be classified as hazardous according to HP 4.

If the sum of the concentrations of all substances classified as H318 exceeds or equals 10 %, the waste shall be classified as hazardous according to HP 4.

If the sum of the concentrations of all substances classified H315 and H319 exceeds or equals 20 %, the waste shall be classified as hazardous according to HP 4.

Note that wastes containing substances classified as H314 (Skin corr.1A, 1B or 1C) in amounts greater than or equal to 5 % will be classified as hazardous by HP 8. HP 4 will not apply if the waste is classified hazardous by HP 8.

All relevant ingredients or substances shall be assessed. Relevant ingredients are those that are present at concentrations of 1% or above (cut-off limit). However, if there is a presumption that an ingredient present at a concentration below 1% can also lead to corrosion or irritation, such ingredient shall also be taken into account.

Note that Commission Regulation (EU) No 1357/2014 that replaces Annex III to Directive 2008/98/EC (WFD), does not specify pH as a criterion for the assessment of irritant or corrosive (HP 8) hazard properties.

1.3.5 HP 5: Single/Specific Target Organ Toxicity (STOT) / Aspiration Toxicity

Definition

“Waste which can cause specific target organ toxicity either from a single or repeated exposure, or which cause severe acute toxic effects following aspiration”

Hazard categories and Hazard Statement Codes to address

H304, H370, H371, H372, H373, H375

Table 5: Hazard categories and Hazard statement Codes according to Regulation (EU) No 1357/2014 for waste constituents and the corresponding concentration limits for the classification of wastes as hazardous by HP 5.

| HSC | Hazard Class and Category | H statement | Concentration limit |
|------|---------------------------|--|---------------------|
| H370 | STOT SE1 | Causes damage to organs <or state all organs affected, if known><state route of exposure if it is conclusively proven that no other routes of exposure cause the hazard>. | 1% |
| H371 | STOT SE2 | May cause damage to organs <or state all organs affected, if known><state route of exposure if it is conclusively proven that no other routes of exposure cause the hazard>. | 10% |
| H335 | STOT SE3 | May cause respiratory irritation | 20% |
| H372 | STOT RE1 | Causes damage to organs <or state all organs affected, if known> through prolonged or repeated exposure <state route of exposure if it is conclusively proven that no other routes of exposure cause the hazard>. | 1% |
| H373 | STOT RE2 | May cause damage to organs <or state all organs affected, if known> through prolonged or repeated exposure <state route of exposure if it is conclusively proven that no other routes of exposure cause the hazard>. | 10% |
| H304 | Asp. Tox. 1 | May be fatal if swallowed and enters airways | 10% |

Criteria

When a waste contains one or more substances classified by one or more of the Hazard Class and Category Codes and Hazard statement Codes shown in Table 5, and one or more of the concentration limits in Table 5 are exceeded or equalled, the waste shall be classified as hazardous according to HP 5. When substances classified as STOT are present in a waste, an individual substance has to be present at or above the concentration limit for the waste to be classified as hazardous by HP 5.

When a waste contains one or more substances that have been classified as Asp. Tox. 1 and the sum of those substances exceeds or equals the concentration limit, the waste shall be classified as hazardous by HP 5 only where the overall kinematic viscosity (at 40°C) does not exceed 20.5mm²/s² (paragraph 3.10.3.3.1.1, page 128, CLP).

Note that Asp. Tox 1 H304 is only relevant for liquids.

1.3.6 HP 6: Acute toxicity

Definition

“Waste which can cause acute toxic effects following oral or dermal administration, or inhalation exposure”.

Hazard categories and Hazard Statement Codes to address

H300, H301, H302, H310, H311, H312, H331, H332

Table 6: Hazard categories and Hazard statement Codes according to Regulation (EU) No 1357/2014 for waste constituents and the corresponding concentration limits for the classification of wastes as hazardous by HP 6

| HSC | Hazard Class and Category | H statement | Concentration limit |
|------|-------------------------------|------------------------------|---------------------|
| H300 | Acute toxicity 1 (oral) | Fatal if swallowed | 0.1% |
| | Acute toxicity 2 (oral) | Fatal if swallowed | 0.25% |
| H301 | Acute toxicity 3 (oral) | Toxic if swallowed | 5% |
| H302 | Acute toxicity 4 (oral) | Harmful if swallowed | 25% |
| H310 | Acute toxicity 1 (dermal) | Fatal in contact with skin | 0.25% |
| | Acute toxicity 2 (dermal) | Fatal in contact with skin | 2.5% |
| H311 | Acute toxicity 3 (dermal) | Toxic in contact with skin | 15% |
| H312 | Acute toxicity 4 (dermal) | Harmful in contact with skin | 55% |
| H330 | Acute toxicity 1 (inhalation) | Fatal if inhaled | 0.1% |
| | Acute toxicity 2 (inhalation) | Fatal if inhaled | 0.5% |
| H331 | Acute toxicity 3 (inhalation) | Toxic if inhaled | 3.5% |
| H332 | Acute toxicity 4 (inhalation) | Harmful if inhaled | 22.5% |

Criteria

If the sum of the concentrations of all substances contained in a waste, classified with the acute toxic Hazard Class and Category Codes and Hazard statement Codes given in Table 6, exceeds or equals the thresholds given in Table 6, then the waste shall be

classified as hazardous according to HP 6. When more than one substance classified as acute toxic is present in a waste, the sum of the concentrations is required only for substances within the same hazard category.

Inhalation toxicity includes inhalation of gases, vapours and dust/mist as stated in the CLP. Since the lowest concentration limits among gases, vapours and dust/mist are for gases, they are mentioned as limiting/discriminating concentrations for H330, H331 and H332 and Table 6. The limiting concentrations for vapours and dust/mist are not mentioned in Table 6 but can be found Table 3.1.2 of the CLP.

The following cut-off values shall apply for consideration in an assessment:

For Acute Tox. Categories 1, 2 or 3 (H300, H310, H330, H301, H311, H331): 0.1%;

For Acute Tox. Category 4 (H302, H 312, H332): 1 %.

1.3.7 HP 7: Carcinogenic

Definition

“Waste which induces cancer or increases its incidence”

Hazard categories and Hazard Statement Codes to address

H350, H351

Table 7.: Hazard categories and Hazard statement Codes according to Regulation (EU) No 1357/2014 for waste constituents and the corresponding concentration limits for the classification of wastes as hazardous by HP 7.

| HSC | Hazard Class and Category | H statement | Concentration limit |
|------|---|--|---------------------|
| H350 | Carcinogenic 1A; known to have carcinogenic potential for humans | May cause cancer <state route of exposure if it is conclusively proven that no other routes of exposure cause the hazard> | 0.1% |
| | Carcinogenic 1B; presumed to have carcinogenic potential for humans | | 0.1% |
| H351 | Carcinogenic 2; Suspected human carcinogens | Suspected of causing cancer <state route of exposure if it is conclusively proven that no other routes of exposure cause the hazard> | 1.0% |

Criteria

When a waste contains a substance classified by one of the following Hazard Class and Category Codes and Hazard statement Codes and exceeds or equals one of the concentration limits, shown in Table 7, the waste shall be classified as hazardous by HP

7. When more than one substance classified as carcinogenic is present in a waste, an individual substance has to be present at or above the concentration limit.

1.3.8 HP 8: Corrosive

Definition

“waste which on application can cause skin corrosion”.

Hazard categories and Hazard Statement Codes to address

H314

Table 8: Hazard categories and Hazard statement Codes according to Commission Regulation (EU) No 1357/2014 for waste constituents and the corresponding concentration limits for the classification of wastes as hazardous by HP 8.

| Hazard Class and Category | H statement | Concentration limit |
|---------------------------|--|---------------------|
| Skin corrosion 1A | Causes severe skin burns and eye damage 1A: Exposure less than 3min, observation less than 1h 1B: 3min-1hour; 14days 1C: 1hour-4hours; 14days | 5% |
| Skin corrosion 1B | | 5% |
| Skin corrosion 1C | | 5% |

Criteria

If the sum of the concentrations of all substances classified as H314 Skin corrosion/irritation (Hazard Category 1A, 1B or 1C) exceeds or equals 5%, the waste shall be classified as hazardous by HP 8:

If $\sum c_{H314} \geq 5\%$, the waste shall be classified as hazardous by HP 8.

The cut-off value for consideration in an assessment for Skin corrosion 1A, 1B and 1C (H314) is 1.0 %.

1.3.9 HP 9: Infectious

Definition

“Waste containing viable micro-organisms or their toxins which are known or reliably believed to cause disease in man or other living organisms”.

A waste isn’t assessed for HP 9 with reference to limiting concentrations of chemical substances. The Commission Regulation (EU) No 1357/2014 states that “The attribution of HP 9 shall be assessed by the rules laid down in reference documents or legislation in the Member States.”

1.3.10HP 10: Toxic for reproduction

Definition

“Waste which has adverse effects on sexual function and fertility in adult males and females, as well as developmental toxicity in the offspring”.

Hazard categories and Hazard Statement Codes to address

H360, H361

Table 9: Hazard categories and Hazard statement Codes according to Regulation (EU) No 1357/2014 for waste constituents and the corresponding concentration limits for the classification of wastes as hazardous by HP 10.

| HSC | Hazard Class and Category | H statement | Concentration limit |
|------|--|--|---------------------|
| H360 | Reproductive 1A; known human reproductive toxicant | May damage fertility or the unborn child <state specific effect if known><state route of exposure if it is conclusively proven that no other routes of exposure cause the hazard> | 0.3% |
| | Reproductive 1B; presumed human reproductive toxicant | | 0.3% |
| H361 | Reproductive 2; suspected human reproductive toxicant | Suspected of damaging fertility or the unborn child <state specific effect if known><state route of exposure if it is conclusively proven that no other routes of exposure cause the hazard> | 3% |

Criteria

When a waste contains a substance classified by one of the following Hazard Class and Category Codes and Hazard statement Codes, and exceeds or equals one of the concentration limits shown in Table 9, then the waste shall be classified hazardous according to HP 10. When more than one substance classified as toxic for reproduction is present in a waste, an individual substance has to be present above the concentration limit for the waste to be classified as hazardous by HP 10.

1.3.11 HP 11: Mutagenic

Definition

“Waste which may cause a mutation, that is a permanent change in the amount or structure of the genetic material in a cell”.

Hazard categories and Hazard Statement Codes to address

H340, H341

Table 10: Hazard categories and Hazard statement Code(s) according to Regulation (EU) No 1357/2014 for waste constituents and the corresponding concentration limits for the classification of wastes as hazardous by HP 11

| HSC | Hazard Class and Category | H statement | Concentration limit |
|------|---|---|---------------------|
| H340 | Mutagenic 1A ; known to induce mutations in the germs cells of humans | May cause genetic defects <state route of exposure if it is conclusively proven that no other routes of exposure cause the hazard> | 0.1% |
| | Mutagenic 1B; regarded as if they induce mutations | | 0.1% |
| H341 | Mutagenic 2; substances which cause concern | Suspected of causing genetic defects <state route of exposure if it is conclusively proven that no other routes of exposure cause the hazard> | 1.0% |

Criteria

When a waste contains a substance that is classified by one of the following Hazard Class and Category Codes and Hazard statement Codes, and exceeds or equals one of the concentration limits shown in Table 10, then the waste shall be classified as hazardous accordingly to HP 11. When more than one substance classified as mutagenic is present in a waste, an individual substance has to be present at or above the concentration limit for the waste to be classified as hazardous by HP 11.

1.3.12 HP 12: Release of an acute toxic gas cat. 1,2 or 3

Definition

“Waste which releases acute toxic gases (Acute Tox. 1, 2 or 3) in contact with water or an acid”.

Hazard categories and Hazard Statement Codes to address

EUH029, EUH031, EUH032

Table 11: Hazard categories and Hazard statement Code(s) according to Regulation 1357/2014 for waste constituents and the corresponding concentration limits for the classification of wastes as hazardous by HP 12.

| | |
|--------|--|
| EUH029 | Contact with water liberates toxic gas |
| EUH031 | Contact with acid liberates toxic gas |
| EUH032 | Contact with acid liberates very toxic gas |

Criteria

When a waste contains a substance classified by one of the following Hazard Class and Category Codes EUH029, EUH031 and EUH032, it shall be classified as hazardous by HP 12 according to test methods or guidelines.

1.3.13 HP 13: Sensitizing

Definition

“Waste which contains one or more substances that are known to cause sensitizing effects to the skin or the respiratory organs”.

Hazard categories and Hazard Statement Codes to address

H317, H334

Table 12: Hazard categories and Hazard statement Code(s) according to Regulation 1357/2014 for waste constituents and the corresponding concentration limits for the classification of wastes as hazardous by HP 13.

| HSC | Hazard class and category | Concentration limit |
|------|---------------------------------------|---------------------|
| H317 | H317 Skin sensitization, cat.1 | 10% |
| H334 | H334 Respiratory sensitization, cat.1 | 10% |

Criteria to apply ^{1 2}

Commission Regulation (EU) No 1357/2014 states that “when a waste contains a substance classified as sensitizing and is assigned to one of the hazard statement codes H317 or H334, and one individual substance equals or exceeds the concentration limit of 10%, the waste shall be classified as hazardous by HP 13”.

¹ The limit value of 10% in the WFD differs substantially from the limit value in the CLP (1%).

² On page 142 the UK-EA WM3 guideline (2015) states that “A HP 13 assessment of a waste will be based on the identification of the individual substances in the waste, their classification, and reference to concentration limits. Where this is not possible, waste containing H317 and H334 substances should be assessed for sensitising properties in accordance with the section 3.4 of the European Chemical Agency’s guidance on the application of the CLP criteria”

1.3.14 HP 14: Eco-toxic

Definition

“waste which presents or may present immediate or delayed risks for one or more sectors of the environment”.

Hazard categories and Hazard Statement Codes to address

H400, H410, H411, H412, H413, H420

Table 13: Hazard categories and Hazard statement Code(s) that are relevant for HP 14 assessment of wastes [5]

| HSC | Hazard category and LC ₅₀ values |
|------|--|
| H400 | Aquatic acute 1; Very toxic to aquatic life LC ₅₀ < 1mg/l |
| H410 | Aquatic chronic 1; Very toxic to aquatic life with long lasting effects LC ₅₀ < 1mg/l |
| H411 | Aquatic chronic 2; Toxic to aquatic life with long lasting effects LC ₅₀ : 1mg/l to 10 mg/l |
| H412 | Aquatic chronic 3; Harmful to aquatic life with long lasting effects LC ₅₀ : 10mg/l to 100 mg/l |
| H413 | Aquatic chronic 4; May cause long lasting harmful effects to aquatic life |
| H420 | Hazardous to the ozone layer |

LC₅₀ (lethal concentration) is a standard measure of the toxicity of the surrounding medium toxicity and is defined as a concentration at which half of the sample population (50%) die from exposure via possible exposure ways. LC₅₀ is often expressed measurement in micrograms or milligrams of material per litre of water. The lower the LC₅₀ value, the more toxic the material.

Currently, there are 4 methods proposed to the European Commission for the assessment of HP 14 hazard property [2]:

METHOD 1

- When a waste contains a substance classified as ozone depleting and is assigned the hazard statement code(s) H420 according to the CLP rules and such individual substance equals or exceeds the concentration limit of 0.1%, the waste shall be classified as hazardous by HP 14.
- When a waste contains one or more substances classified as aquatic acute and is assigned to the hazard statement code(s) H400 according to the CLP rules and the sum substances equals or exceeds the concentration limit of 25% the waste shall be classified as hazardous by HP 14.

- When a waste contains one or more substances classified as aquatic chronic 1, 2 or 3 and is assigned to the hazard statement code(s) H410, H411 or H412 according to the CLP rules and the sum of all substances classified aquatic chronic 1 (H410) multiplied by 100 added to the sum of all substances classified aquatic chronic 2 (H411) multiplied by 10 added to the sum of all substances classified aquatic chronic 3 (H412) equals or exceeds the concentration limit of 25%, the waste shall be classified as hazardous by HP 14.
 $(100 \times \Sigma \text{ Aquatic Chronic 1}) + (10 \times \Sigma \text{ Aquatic Chronic 2}) + \Sigma \text{ Aquatic Chronic 3} \geq 25\%$
- When a waste contains one or more substances classified as aquatic chronic 1, 2, 3 or 4 and is assigned to the hazard statement code(s) H410, H411, H412 or 413 according to the CLP rules and the sum of all substances classified aquatic chronic equals or exceeds the concentration limit of 25%, the waste shall be classified as hazardous by HP 14.

Method 1 short version:

$$c(\text{H420}) \geq 0.1\%$$

$$\Sigma c \text{ H400} \geq 25\%$$

$$(100 \times \Sigma c \text{ H410}) + (10 \times \Sigma c \text{ H411}) + (\Sigma c \text{ H412}) \geq 25\%$$

$$\Sigma c \text{ H410} + \Sigma c \text{ H411} + \Sigma c \text{ H412} + \Sigma c \text{ H413} \geq 25\%$$

METHOD 2

- When a waste contains a substance classified as ozone depleting and is assigned the hazard statement code H420 and such an individual substance equals or exceeds the concentration limit of 0.1%, the waste shall be classified as hazardous by HP 14.
- When a waste contains one or more substances, at or above the cut-off value, that are classified as Short term (acute) Aquatic hazard and are assigned to the hazard statement code H400 and the sum of the concentrations of all substances multiplied by their respective multiplying factors (M-factors) equals or exceeds the concentration limit of 25%, the waste shall be classified as hazardous by HP 14.
- When a waste contains one or more substances, above the cut-off value, that are classified as Long term Aquatic hazard Chronic 1 or 2 and are assigned to the hazard statement codes H410 or H411 and the sum of the concentrations of all substances classified Long term Aquatic hazard Chronic 1 (H410) multiplied by 10, multiplied by their respective multiplying factors M, added to the sum of the concentrations of all substances classified Long term Aquatic hazard Chronic 2 (H411), equals or exceeds the concentration limit of 25%, the waste shall be classified as hazardous by HP 14.

Method 2 short version:

$$c(\text{H420}) \geq 0.1\%$$

$$\Sigma (c \text{ H400} \times M) \geq 25\%$$

$$\Sigma (M \times 10 \times c \text{ H410}) + \Sigma c \text{ H411} \geq 25\%$$

The cut-off value for consideration in an assessment for Aquatic Acute 1 and Aquatic Chronic 1 is $0.1/M\%$; and for Aquatic Chronic 2 is 1% , M is the M-factor for a given substance

The M-factors will be determined as follows:

For substances for which M-factors have been established in Table 3.1, Annex VI of the CLP Regulation, those multiplying factors shall apply.

For substances for which no M-factors have been established in Annex VI, a multiplying factor $M = 1$ shall apply.

METHOD 3

This summation method does not include generic cut-off values and M-factors and allows only the summation of substances that belong to the same eco-toxic category. This method excludes aquatic acute hazard (H400) from the assessment.

- When a waste contains a substance classified as ozone depleting and is assigned the hazard statement code H420 and such an individual substance equals or exceeds the concentration limit of 0.1%, the waste shall be classified as hazardous by HP 14.
 $c(H420) \geq 0.1\%$
- The rest of criteria that need to be fulfilled are summarized as follows :

| Hazard Class and Category Code(s) | Hazard Statement Code(s) | Concentration limit |
|-----------------------------------|--------------------------|---------------------|
| Sum of Aquatic Chronic 1 | H410 | 0.1% |
| Sum of Aquatic chronic 2 | H411 | 2.5% |
| Sum of Aquatic chronic 3 | H412 | 25% |
| Sum of Aquatic chronic 4 | H413 | 25% |

METHOD 4

No generic cut-off values are considered. This method takes into account only aquatic chronic 1 (H410) and aquatic chronic 2 (H411) categories.

- When a waste contains a substance classified as ozone depleting and is assigned the hazard statement code H420 and such an individual substance equals or exceeds the concentration limit of 0.1%, the waste shall be classified as hazardous by HP 14.
 $c(H420) \geq 0.1\%$
- The rest of criteria that need to be fulfilled are summarized as follows :

| Hazard Class and Category Code(s) | Hazard Statement Code(s) | Concentration limit |
|-----------------------------------|--------------------------|---------------------|
| Sum of Aquatic Chronic 1 | H410 | 2.5/M% |
| Sum of Aquatic chronic 2 | H411 | 25% |

The M-factors will be determined as follows:

For substances for which M-factors have been established in Table 3.1, Annex VI CLP, those multiplying factors shall apply.

For substances for which no M-factors have been established in CLP, a multiplying factor $M = 1$ shall apply.

Method 1 is based on Regulation 1272/2008 (CLP) for classification of mixture based on summation of classified components. This calculation method allows for the consideration of each class/category of hazard previously mentioned.

The same criteria as those defined in the Regulation 1272/2008 for classification of mixture are applied, however, two differences could be observed. Firstly, this method does not take into account multiplying factors (M-factors) of highly toxic compounds for calculation. Secondly, no generic cut-off values that defined the relevant components that should be taken into account for the purpose of classification are considered in this calculation method. Therefore, all components are taken into account for calculation with Method 1 - see [2].

Method 2 is also based on Regulation 1272/2008 for classification of mixture based on summation of classified components. The generic cut-off values reported in the Regulation 1272/2008 are applied as well as the consideration of M-factor. The generic cut-off values of "0.1/M %" and "1 %" are respectively applied for hazard statements H410 and H411. However, contrary to Regulation 1272/2008, the chronic hazard category 3 and 4 are not considered in this calculation method.

In addition, another calculation rule of Regulation 1272/2008 that uses higher multiplying factor for category 1 and 2, and is then more strict, is not applied in method 2. The CLP rule not taken into account is the following one: $\Sigma (M \times 100 \times c \text{ H410}) + \Sigma (10 \times c \text{ H411}) + \Sigma (c \text{ H412}) \geq 25\%$.

It should be noted that the values "0.1/M %" and "1 %" are cut-off values that define the relevant components that should be taken into account for the purpose of classification. The other values correspond to the concentration limit values which are used for classification [2]

As mentioned in [2], Method 3 is adapted from the old classification system of mixtures: Directive 1999/45/EC (Dangerous Preparations Directive). This method did not allow the summation of components classified for different hazard categories. This is very different to the concept of classification criteria of Regulation 1272/2008 based on summation of classified components. Moreover, this calculation method does not take into account acute hazard category 1, multiplying factor (M-factor) of highly toxic components and generic cut-off values as reported in the Regulation 1272/2008.

The hazard classes/categories considered in Method 4 are very limited. The only hazards considered are the hazard to the ozone layer and the chronic hazard category 1 and 2. As in methods 1 and 3, this calculation method does not take into account generic cut-off values reported in the Regulation 1272/2008. However, M-factors are taken into account for calculation for chronic category 1 compounds [2].

Currently, according to a new proposal from the Commission [9], a new method is considered that combines Method 1 with cut-off values from Method 2. This method is referred to as Method 5 in the HP 14 paragraph of this report.

1.3.15 HP 15: Waste capable of exhibiting a hazardous property listed above not directly displayed by the original waste

Definition

“Waste capable of exhibiting a hazardous property listed above not directly displayed by the original waste”.

Hazard categories and Hazard Statement Codes to address

H205, EYH001, EUH019, EUH044

Table 14: Hazard categories and Hazard statement Code(s) according to Regulation (EU) No 1357/2014 for waste constituents and the corresponding concentration limits for the classification of wastes as hazardous by HP 15

| HSC | Hazard statement |
|--------|---|
| EUH001 | Explosive when dry |
| EUH019 | May form explosive peroxides |
| EUH044 | Risk of explosion if heated under confinement |
| H205 | May mass explode in fire |

Criteria

When a waste contains a substance classified by one of the Hazard Categories and Hazard statement Codes shown in Table 14, the waste shall be classified as hazardous by HP 15, unless the waste is in such a form that it will not under any circumstances exhibit explosive or potentially explosive properties. In addition, Member States may characterise a waste as hazardous by HP 15 based on other applicable criteria, such as an assessment of the leachate.

2

Assessment of hazard properties

Assessment of hazard properties and hazard classification is relatively straightforward for chemicals (products) with a known composition. However, its application to waste materials is far more challenging since it is often largely unknown which substances are present in wastes. For inorganic substances, total content analyses only reveal information regarding the elemental composition but do not give information on the chemical binding form (speciation) of these elements in the waste, i.e. the substances. To reduce the complexity of hazard classification for waste materials and to have a systematic assessment, a tiered approach is followed.

2.1 Approach and methodology

Due to complexity and the largely unknown presence of specific substances in waste materials, a tiered approach can be chosen for the assessment of hazard classification of wastes in general. This tiered approach has been applied in this report for the assessment of hazard properties of MSWI bottom ash using the elemental composition (at 95th percentile) as a starting point. The composition of MSWI bottom ash from several Member States was assessed in detail in [1] and is given in Table 15. Since there is no guideline at EU level on the method to “treat” the data base for an hazard assessment (median, mean, 95th percentile composition), the 95 percentile concentrations of elements is considered to be a starting point as this value covers as wide as possible range of elements concentrations observed in the total dataset.

The tiered approach implies subsequent elimination of hazard properties starting from the relevance or non-relevance of a given hazard property for the bottom ash (Tier 1) and moving towards more detailed assessment of hazard properties that could not be excluded based on general knowledge (Tier 2 and Tier 3).

In this work, **Tier 1** presents a screening process in which a high level assessment of the relevance of hazardous properties (HP 1 to HP 15) to bottom ash is carried out based on knowledge of the gross characteristics and composition of bottom ash.

Tier 2 consists of further investigation of hazardous properties not excluded in Tier 1, by using a worst case assessment approach. It is assumed that the total amount of an element is present in its most hazardous form (i.e. the most hazardous substance) using the stoichiometry of that substance. Using this worst case approach, a comprehensive list of substances can be identified that do not have to be assessed further, because their concentrations are below the cut-off limit, or because their maximum possible concentrations do not exceed the concentration limits defined for a corresponding hazard property. The remaining substances that cannot be excluded in the worst case scenario should be further assessed in Tier 3.

Tier 3 includes detailed investigation of any HPs and substances not eliminated in Tier 2. Tier 3 uses detailed knowledge on the geochemistry of MSWI bottom ash, consisting of scientific literature by ECN and other institutes on this topic, interpretation of available leaching data using the database/expert system LeachXS (<http://www.leachxs.com/lxsdll.html>), conducting realistic chemical speciation calculations, as well as assumptions on exposure conditions.

2.2 Tiered assessment of hazard properties

2.2.1 Tier 1 assessment: general screening

This paragraph presents the assessment of hazard properties HP 1-HP 15 on a first level (Tier 1) where general knowledge and information about the incineration process is used to conclude on the relevance of each of the 15 hazard properties for the MSWI bottom ash.

HP 1. Explosive. Tier 1 assessment according to criteria defined in 1.3.1 and conclusion

Any substance in the waste with properties as described in Table 1 will be destroyed during the incineration process. Therefore HP 1 classification of MSWI bottom ash is concluded as non-hazardous.

HP 2. Oxidizing. Tier 1 assessment according to criteria defined in 1.3.2 and conclusion

If any oxidising substances are present as an input to an incinerator, they would be destroyed during the incineration process. Thus none of the Hazard Statement Codes from Table 2 are relevant to MSWI bottom ash. Therefore we conclude that the MSWI bottom ash can be classified as non-hazardous with respect to HP 2.

HP 3. Flammable. Tier 1 assessment according to criteria defined in 1.3.3 and conclusion

The Hazard Statement that is relevant to the MSWI bottom ash is H261. Strongly alkaline MSWI bottom ash, that also contains elementary aluminium, may develop hydrogen gas in contact with water which can burn if it is ignited. The formation of small amounts of hydrogen gas has been observed in MSWI bottom ash in closed applications as construction material under isolated conditions, i.e., where hydrogen could not escape to the atmosphere [10]. However, due to the strong advancement of separation technologies of ferrous and non-ferrous metals of the past decade, it is unknown whether current MSWI bottom ash still contains sufficient amounts of elementary aluminium to form hydrogen gas.

The guidance document to the CLP (version 4.1, June 2015, [4]) does specify two test methods that can be used to determine the amount of released flammable gas (Table 2.12.6-a of the CLP). When the material is stored dry, the risk of hydrogen production is negligible. Assuming that the material is stored under dry conditions, the MSWI bottom ash is currently classified as non-hazardous with respect to HP 3. Under wet conditions and open to the atmosphere, the risk of formation and accumulation of hydrogen is negligible.

The effect of possible hydrogen formation can be eliminated when the material is first moistened in a controlled environment. The addition of moisture leads to hydrogen formation and after some time the reaction will stop. Then, the hazard of hydrogen formation is negligible. In addition, it is recommended to test the MSWI bottom ash for the hydrogen production capacity using a method described in literature [12]. This method has been used for MSWI fly ash and is probably also suitable for MSWI bottom ash. The results of those measurements would further substantiate the conclusion on HP 3. Current conclusion is that MSWI bottom ash displays no HP 3 hazard.

HP 4. Irritant. Tier 1 assessment according to criteria defined in 1.3.4 and conclusion

Classification of MSWI bottom ash as hazardous under HP 4 could be due to the presence of substances that might possess irritant and/or corrosive properties and this cannot be excluded at this point. Therefore HP 4 can be of relevance to MSWI bottom ash. Further evaluation should therefore be done at Tier 2 and/or Tier 3 level. HP 8 (corrosive) will also be assessed at this level – see paragraph 3.3.5 of this report. HP 4 assessment will not be continued if the waste is classified as HP 8.

It should be noted that a high pH of fresh MSWI bottom ash (>11.5; most bottom ashes have a pH lower than 11.5 but there are exceptions) does not necessarily lead to a classification as hazardous. For materials with extreme low (<2) or extreme high (>11.5) pH the acid-alkaline reserve test can be performed [21]. This is not required according to Regulation (EU) No 1357/2014, although it is recommended in a Guidance document [3] to the CLP. More considerations on pH and its relevance in the assessment will be given in Tier 2.

HP 5. Single/Specific Target Organ Toxicity (STOT)/Aspiration. Assessment according to criteria defined in 1.3.5 and conclusion

HP 5 is relevant to MSWI bottom ash as the bottom ash might contain substances which can cause specific target organ toxicity either from a single or repeated exposure, or which can cause severe acute toxic effects following aspiration. Assessment of the MSWI bottom ash in accordance with HP 5 should be carried out at Tier 2, and possibly

at Tier 3 if not eliminated after Tier 2. H304 only refers to liquids and therefore does not need further consideration.

HP 6. Acute toxicity. Tier 1 assessment according to criteria defined in 1.3.6 and conclusion

HP 6 can be of relevance to MSWI bottom ash since at Tier 1 we cannot conclude that MSWI bottom ash does not cause acute toxic (oral, dermal or inhalation) effects. Assessment at Tier 2 and at Tier 3 if not excluded at Tier 2.

HP 7. Carcinogenic. Tier 1 assessment according to criteria defined in 1.3.7 and conclusion

It is unknown whether substances in MSWI bottom ash can induce cancer or increase its incidence and, therefore, HP 7 hazardous property can be relevant to MSWI bottom ash. This conclusion implies that we cannot exclude HP 7 at Tier 1 assessment. Further assessment will be performed at Tier 2 and at Tier 3 if not excluded at Tier 2.

HP 8. Corrosive. Tier 1 assessment according to criteria defined in 1.3.8 and conclusion

It is unknown whether substances in MSWI bottom ash can induce corrosive effects. Therefore, at this stage we cannot exclude that substances in MSWI bottom ash can cause skin corrosion. Therefore, HP 8 is potentially relevant to MSWI bottom ash. Further assessment will be performed at Tier 2 and at Tier 3 if not excluded at Tier 2.

HP 9. Infectious. Tier 1 assessment according to criteria defined in 1.3.9 and conclusion

Since MSWI bottom ash is 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 HP 9 is considered to be not relevant to MSWI bottom ash.

HP 10. Toxic for reproduction. Tier 1 assessment according to criteria defined in 1.3.10 and conclusion

At this stage we cannot exclude that substances in MSWI bottom ash have no adverse effects on sexual function and fertility in adult males and females, as well as developmental toxicity in the offspring. Therefore, HP 10 may be relevant to MSWI bottom ash and shall be addressed during the assessment of the MSWI bottom ash at Tier 2 and/or Tier 3 level.

HP 11. Mutagenic. Tier 1 assessment according to criteria defined in 1.3.11 and conclusion

It cannot be excluded that substances in MSWI bottom ash may cause a mutation, that is permanent change in the amount or structure of the genetic material in a cell. Therefore, HP 11 may be of relevance to MSWI bottom ash and shall be assessed at Tier 2 and if necessary at Tier 3 level.

HP 12. Release of an acute toxic gas cat. 1, 2 or 3. Tier 1 assessment according to criteria defined in 1.3.12 and conclusions

No release of toxic gases such as HF or H₂S has been observed by producers of MSWI bottom ash in contact with water or a strong acid. Due to the content of carbonates, MSWI bottom ash may liberate CO₂ in contact with acid, but CO₂ is not a toxic gas.

Some of the free metals (e.g. elementary aluminium) that are present, can cause production of H₂ if brought into contact with water at high pH, but H₂ is not a toxic gas. As mentioned in [1], certain acids as HF and HCl could develop toxic gases in contact with IBA, but in such cases the toxic gases would generate from these acids and not from the bottom ash, and therefore are outside the scope of HP 12. It should be noted, that development of phosphine gas in the IBA management systems at some incinerators has been observed (mentioned in [1]), presumably caused by high phosphorous contents in the bottom ash. Testing on MSWI bottom ash and flue gas treatment residue has found negligible phosphine emissions values. Therefore, typical MSWI bottom ash can be considered non-hazardous with respect to HP 12.

HP 13. Sensitizing. Tier 1 assessment according to criteria defined in 1.3.13 and conclusion

The presence of one or more substances that are known to cause sensitizing effects to the skin or the respiratory organs cannot be excluded for MSWI bottom ash. Therefore, we cannot conclude that HP 13 is not relevant to MSWI bottom ash and this property should be further assessed in Tier 2.

HP 14. Eco-toxic. Tier 1 assessment according to criteria defined in 1.3.14 and conclusion

It cannot be excluded that substances in MSWI bottom ash may present immediate or delayed risks for one or more sectors of the environment and, therefore, HP 14 is of potential relevance for MSWI bottom ash. However, since MSWI bottom ash is not a gas and is unlikely to emit ozone layer depleting gases, H420 is not relevant to MSWI bottom ash. Following the general tiered approach, further assessment on HP 14 should be performed accordingly to the criteria defined in 1.3.14 at Tier 2 and/or Tier 3 levels.

It should be noted that decision 2000/532/EC (in its current version) does not provide specific indications on how to perform the assessment of HP 14 in practice. In Directive 2008/98/EC, a note included in Annex III states that "Attribution of the hazardous properties (...) 'eco-toxic' shall be made on the basis of the criteria laid down by Annex VI, to Council Directive 67/548/EEC". In practice, this instruction has been interpreted in different ways in the MS. In some MS eco-toxicity is assessed mainly by performing tests, but the test methods are not harmonized. The Commission launched the study in 2014 and steer the debate with the MS and stakeholders. Involvement of stakeholders shall ensure that viable solutions are proposed. As a result, 5 methods (including the proposal made by the Commission) for the HP 14 assessment are presently proposed. Currently, no official method is selected among these 5 methods. Therefore all 5 methods described in 1.3.14 need to be applied. The establishment of the preferable method shall be done by the Commission and will not be commented in this report.

HP 15. Yielding another substance. Tier 1 assessment according to criteria defined in 1.3.15 and conclusion

Tier 1 assessment concludes that none of the hazard statements in Table 14 are relevant to MSWI bottom ash since all of the incidents described would have occurred during or will have been prevented by the incineration process. Criteria for HP 15 (paragraph 1.3.15) say that Member States may characterise a waste as hazardous by HP 15 based on other applicable criteria, such as an assessment of the leachate. To our

knowledge such criteria have not been developed and currently the assessment is based on the relevance of the hazard statements from Table 14.

The conclusion is therefore that MSWI bottom ash can be considered non-hazardous with respect to HP 15.

Assessment of Persistent Organic Pollutants (POPs)

For the composition of organic substances in IBA from Germany, Italy, the Netherlands and the UK one is referred to [1], Part 1, Table 3.2. POPs assessment is done according to Regulation (EC) No 1195/2006 amending Annex IV to Regulation (EC) No 850/2004 of the European Parliament and of the Council on persistent organic pollutants [20].

It is likely that not all organic substances that are present in waste will be destroyed or irreversibly transformed at high temperatures during the incineration process. Up to a few percent of organic carbon has been measured in MSWI bottom ash, mainly present as natural organic matter [16],[17],[22]. There is no data on POPs other than those mentioned in Table 3.2 , Part 1 of [1]. According to these data, limit values of 50mg TEQ /kg defined for PCBs (polychlorinated biphenyls) and 15µg TEQ /kg defined for PCDD/PCDFs (polychlorinated dibenzo-p-dioxines and dibenzofuranes) are not exceeded.

Other POPS that could be present but are not specifically mentioned in Table 3.2 , Part 1 of [1], are implicitly considered to be present in concentrations below the threshold values mentioned in the POPs regulation.

2.2.2 Summary Tier 1

Based on the general screening of hazard properties and their relevance to MSWI bottom ash, hazard properties HP 1, HP 2, HP 3, HP 9, HP 12 and HP 15 are excluded from further assessment based on the considerations presented in the above paragraph. Hazard properties HP 4, HP 5, HP 6, HP 7, HP 8, HP 10, HP 11, HP 13 and HP 14 require further investigations at Tier 2.

2.2.3 Tier 2 assessment: worst case analysis

In Tier 2, the composition of the waste is taken into account for the assessment of the potentially relevant HPs. Table 15 presents the median, average and the 95-percentile composition of the European MSWI bottom ash dataset. Since the CEWEP report [1] uses the total content data of a large set of European MSWI bottom ash samples, the same total content data will be used in the current assessment since it will allow a comparison with the previous assessment, and also because using such an elaborated dataset becomes representative for the composition of European bottom ash. Further calculations in the report are done based on the 95-percentile composition, unless otherwise specified. The decision to follow the 95-percentile composition is made in order to include most of the samples. Table 15 also includes “the average” pH for

European MSWI bottom ash. The main part of this paragraph is devoted to worst case analysis, but prior to this, considerations on pH are given.

Table 15: European MSWI bottom ash composition (data taken from Hjelm et al., 2013).

| Element | Average | Median | Min | Max | 95 percentile | 95 percentile | N |
|------------|---------|--------|-------|--------|---------------|---------------|------|
| | mg/kg | mg/kg | mg/kg | mg/kg | mg/kg | % | |
| Ca | 130833 | 125586 | 50825 | 198289 | 190442 | 19.0 | 322 |
| CO3 | 61073 | 59100 | 26160 | 103800 | 103404 | 10.3 | 38 |
| Fe | 58714 | 56703 | 34216 | 118220 | 103299 | 10.3 | 259 |
| Si | 82713 | 84180 | 61060 | 96078 | 93898 | 9.4 | 129 |
| Al | 47232 | 44627 | 30527 | 75089 | 71620 | 7.2 | 311 |
| Cl | 9211 | 5943 | 3644 | 37633 | 37188 | 3.7 | 136 |
| Na | 21379 | 22270 | 12308 | 34791 | 32121 | 3.2 | 234 |
| TOC | 10092 | 9340 | 1350 | 42760 | 24664 | 2.5 | 1382 |
| Mg | 12429 | 11242 | 6377 | 34372 | 21025 | 2.1 | 287 |
| K | 7748 | 7595 | 4854 | 12722 | 11857 | 1.2 | 260 |
| P | 5633 | 5049 | 2531 | 12556 | 11773 | 1.2 | 220 |
| Cu | 3275 | 2510 | 738 | 17620 | 8863 | 0.89 | 1699 |
| S | 3862 | 3475 | 1310 | 16808 | 7873 | 0.79 | 455 |
| Ti | 4244 | 4112 | 2873 | 7479 | 6636 | 0.66 | 262 |
| Zn | 3241 | 2871 | 1142 | 9370 | 6250 | 0.63 | 1697 |
| C | 3171 | 2919 | 1119 | 5702 | 5383 | 0.54 | 69 |
| Pb | 1309 | 1058 | 197 | 6441 | 3969 | 0.40 | 1706 |
| Ba | 1102 | 958 | 760 | 2970 | 2207 | 0.22 | 288 |
| Mn | 1173 | 1104 | 644 | 2248 | 1965.3 | 0.20 | 313 |
| PO4 | 248 | 10 | 10 | 1360 | 1311 | 0.13 | 38 |
| F | 148 | 71 | 13 | 1779 | 1219.5 | 0.12 | 78 |
| Cr | 353 | 315 | 115 | 852 | 754 | 0.075 | 1701 |
| NO3 | 172 | 100 | 5 | 875 | 732 | 0.073 | 38 |
| Ni | 185 | 153 | 38 | 850 | 531 | 0.053 | 1696 |
| Sn | 181 | 154 | 52 | 737 | 519 | 0.052 | 335 |
| B | 198 | 183 | 30 | 532 | 401 | 0.040 | 191 |
| Sr | 271 | 270 | 267 | 369 | 356 | 0.036 | 136 |
| Sb | 73 | 63 | 18 | 250 | 159 | 0.016 | 612 |
| NH4 | 53.3 | 46.5 | 5 | 131 | 128 | 0.013 | 43 |
| NO2- | 13 | 1 | <1 | 100 | 100 | 0.010 | 38 |
| Co | 31.8 | 23 | 11 | 103 | 91.1 | 0.0091 | 376 |
| Br | 44.7 | 42 | 23 | 95 | 80.6 | 0.0081 | 50 |
| Mo | 30.1 | 28 | 5 | 84 | 80.6 | 0.0081 | 533 |
| V | 41.2 | 36 | 19 | 248 | 76.3 | 0.0076 | 349 |
| As | 17.3 | 14.7 | 4.4 | 73.2 | 46.5 | 0.0047 | 1615 |
| Ag | 15.2 | 14.3 | 2.3 | 47.1 | 37.5 | 0.0038 | 127 |
| Tl | 6.7 | 3.8 | 3.4 | 27.5 | 28.6 | 0.0029 | 137 |
| Li | 14 | 14 | 2 | 29 | 23 | 0.0023 | 92 |
| Te | 10 | 9.8 | 5.3 | 24.8 | 22 | 0.0022 | 49 |
| Cd | 4.8 | 4.3 | 1.1 | 117 | 13.9 | 0.0014 | 1661 |
| Se | 5.2 | 4.7 | 2.3 | 12.2 | 12.7 | 0.0013 | 145 |
| Bi | 2.1 | 0.05 | 0.05 | 11.3 | 7.4 | 0.00074 | 34 |
| Hg | 2.3 | 1.53 | 1.39 | 9.69 | 7.3 | 0.00073 | 316 |
| Be | 1.2 | 0.83 | 0.46 | 6.6 | 2.3 | 0.00023 | 162 |
| CN | 0.7 | 0.64 | 0.5 | 0.94 | 0.9 | 0.00009 | 50 |
| Cr VI | 0.5 | 0.5 | 0.3 | 0.8 | 0.8 | 0.00008 | 82 |
| Sol frac % | 2.5 | 2.6 | 1.4 | 4.2 | 4.1 | | 31 |
| LOI % | 4.2 | 4.6 | 2.6 | 6 | 5.9 | | 81 |
| pH | 10.86 | 10.78 | 9.28 | 12.13 | 11.74 | | 1639 |

- **pH considerations**

Following the ECHA Guidance document on the application of the CLP criteria (version 4.1, 2015, [3]), extreme pH values ≤ 2 or pH values ≥ 11.5 may indicate the potential to cause skin corrosive (HP 8) or skin irritant (HP 4) effects. In case of such high or low pH values, the guidance document recommends acid/alkali reserve test to prove that a material is not corrosive or irritant despite its high pH value. This recommendation also applies if the summation rules (defined in 1.3.4 of this report) show that there is no additive hazard as a result of added effects of individual substances present in the material. Requirements of the acid/alkali reserve test and in vitro test are defined in the CLP for substances and mixtures (see also [21] – Young test), however, they are not defined in the WFD that is followed in the assessment of wastes: Commission Regulation (EU) No 1357/2014 that replaces Annex III to Directive 2008/98/EC (WFD), does not specify pH as a criterion for the assessment of irritant or corrosive (HP 4 and HP 8) hazard properties.

Therefore the pH value of European MSWI bottom ash will not be considered as a criterion for the irritant or corrosive potential. As a remark the alkali reserve method has been tested in [13]. It has been found that the method can be applied but the performance conditions are not well defined. It was found that the same information can be obtained from a pH dependence test, therefore the use of EN 14997 (with continuous pH control) was recommended there.

As remark, from data presented in Table 15, the average pH is 10.86, its median value 10.78, minimal 9.28 with its maximum 12.13 and the 95 percentile value 11.74. These values are obtained from large set of 1639 samples and result in the median and average values that are close to each other and the 95percentile value that is more close to the maximum value. The acid/alkali test for MSWI bottom ash would be needed only for samples with $\text{pH} \geq 11.5$. If the decision is made to do the acid/alkali reserve test [22] to obtain extra information on irritant or corrosive potential of MSWI bottom ash, then our recommendation is to distinguish between the samples with $\text{pH} < 11.5$ and $\text{pH} \geq 11.5$ and to perform the test only for samples with $\text{pH} \geq 11.5$. From our experience, when performing the Young test and applying the corresponding criteria for material with pH 12.5 (much higher than for the bottom ash), there was only very small exceedance of the limit value when checking the criterion on irritant properties: $[\text{pH} + (\text{alkali reserve}/6)]$ was equal to $13.24 \geq 13$ that indicated possible irritant potential of the material. The criterion to check the corrosive potential $[\text{pH} + (\text{alkali reserve}/12) \geq 14.5]$ was met. Therefore, having lower pH than 12.5, MSWI bottom ash is expected to fulfil these criteria too. However, to have a strict conclusion for the bottom ash samples with $\text{pH} > 11.5$, a proper testing on these samples would be needed.

- **Worst case analysis based on composition**

As it was already mentioned, Tier 2 assessment of waste materials foresees the so-called worst case analysis. In general, the worst case scenario presumes that:

- 1: either any substance that can be present in waste, is present in its maximum possible concentration consuming all of the total amount of a limiting element that is necessary to form the substance (see Example 1);
- 2: or any element that is present in waste forms the most hazardous substance from Table 3.1, Annex III of the CLP. The most hazardous substance is determined as the substance that needs the lowest amount of an element to exceed the limit value for the

hazard property considered (see Example 2). This case will be followed for the assessment of hazard properties that were taken to Tier 2 (except HP 14 (eco-toxic) assessment, for which the 1st case is decided to follow. The motivation of the choice for the HP 14 approach is explained in the HP 14 paragraph of this report).

EXAMPLE 1. Calculation of the maximum possible concentration of CuCl. The total content of Cu is 0.89%, for the Cl the total content is 3.7% (all data based on the 95-percentile composition, Table 15). Since the total content of Cu is lower than the total content of Cl (recalculated in moles), Cu will be the limiting element that will define what is the maximum of CuCl that can be formed: assuming that all total Cu (64g/mol) is bound in CuCl (99g/mol), one will get $0.89 \cdot 99 / 64 = 1.4\%$ as maximum theoretically possible concentration of CuCl.

EXAMPLE 2. Determination of the most hazardous substance of Pb among several Pb substances. For the purpose of this example, it is assumed that among possible forms of Pb, the following Pb substances are present in the waste: PbCrO_4 , PbSO_4 and Pb(OH)_2 . Assuming that these substances have the same hazard - toxic for reproduction with the hazard statement code H360, the corresponding limit value is 0.3%. If any of these substances is present in a concentration $\geq 0.3\%$, the waste shall be considered as toxic for reproduction.

In order to determine which of these three substances is most hazardous, one needs to determine how much Pb is needed individually for each of these substances to be formed in the concentration of 0.3%. The substance that will need the lowest amount of Pb to reach the 0.3% limit will be referred to as the most hazardous (most toxic for reproduction) among these three substances. Thus among PbCrO_4 , PbSO_4 and Pb(OH)_2 , in order to be present on the amount of 0.3%, PbCrO_4 would need 0.192% of Pb (assuming there is enough of Cr to form this substance), 0.205% of Pb would be needed to form PbSO_4 at concentration of 0.3%, and 0.258% of Pb would be required to have Pb(OH)_2 at 0.3% level. Since in order to be at the 0.3% concentration, PbCrO_4 requires less Pb compared to the other two speciations, PbCrO_4 will be referred to as the most hazardous for reproduction among these three considered speciations. The amount of Pb 0.192% is then referred to as a **critical amount or critical concentration**. In case there are more speciations of the same element that have the same HSC, similar analysis is necessary for every individual speciation.

2.2.3.1 Hazard assessment method

In order to establish the most hazardous substance for every element that is relevant for a given hazard property (HP) and a given hazard statement code (HSC), the next algorithm has been followed:

1. For a selected element, all substances of that element, that are relevant for a given HP and HSC, are collected. Typically a HSC defines a limit value, exceedance of this value will lead to classification as hazardous (for instance, all Zn substances that belong to HP 8 (corrosive) have HSC H314 and a limit value of 5%). For the collection of the substances one can use Table 3.1 of the CLP that contains more than 5000 substances with known and harmonised hazard information. If there is evidence that substances other than mentioned in Table 3.1, are also present in the waste and can display a hazard relevant for the HP that is under assessment, such substances have to be taken into account as well. Since there is no guideline at the EU level which information sources should be taken into account, in this report, the CLP substances and the INERIS collection of substances (hereafter: INERIS database) is used (<http://www.ineris.fr/substances/fr/>). Note, that in general it is not necessary to have information on the speciation of the elements that have a “generic entry” in the list of substances in Table 3.1 of the CLP regulation.
2. Next step is to refer to the Commission Regulation (EU) No 1357/2014 for the concentration limit of the hazard property and related HSC .
3. From the list of possible substances for a given element, one has to determine what is the most hazardous substance for this specific element (as explained in Example 2 of this report) and what is the critical concentration of this element. A **critical concentration of an element** is defined as the amount of that element that is required for a given substance to reach its concentration limit (defined in the CLP for that substance). Among several substances that are relevant for the same HP and HSC, the one that requires the lowest critical concentration, is the most hazardous substance.
4. Determined in the previous step critical amount for a given element is subsequently compared to the total content of this element in the waste (95-percentile). The so-called hazard index (HI) is then calculated as a ratio between the element total concentration (95-percentile) and the critical amount of that element for a given HP and HSC (see Example 3). A hazard index <1 indicates that the limit value cannot be exceeded under this worst-case calculation.
5. In order to conclude about the hazard potential of the waste in Tier 2, hazard indices have to be determined for all the hazard properties that are not excluded after Tier 1 assessment.
 - For hazard properties **HP 5 (STOT/Aspiration), HP 7 (carcinogenic), HP 10(toxic for reproduction), HP 11 (mutagenic) and HP 13 (sensitising)**, the hazard index for every individual substance of relevance needs to be <1 to conclude that no corresponding hazard will be displayed by the waste. This is applicable only for HP 5, HP 7, HP 10, HP 11 and HP 13 where the hazard assessment can be done on the individual basis. It implies that in order to have no hazard effect, the amount of every individual substance should not exceed a corresponding limit value defined for each of these hazard properties.
 - For hazard properties **HP 4 (irritant), HP 6 (acute toxic), HP 8 (corrosive) and HP 14 (eco-toxic), the additive hazard has to be taken into account and the resulting (total) hazard index needs to be calculated.** This is done by the summation of all hazard indices that are relevant for the same hazard property. If for one of these hazard properties a sum of all

the hazard indices is <1 , it is concluded that this hazard property will not be displayed by the waste.

- Hazard properties that are not excluded after this worst case analysis, shall be considered at Tier 3, where a more detailed assessment is performed for those substances that in Tier 2 could render the waste hazardous.

REMARK: because of its complexity, the assessment of HP 14 (eco-toxic) will be done in a separate paragraph beyond the tiered approach

EXAMPLE 3. Hazard index calculation. Assume that the total content of Pb is 0.15% and that PbCrO_4 is the most hazardous Pb substance for HP 10 (H360, toxic for reproduction with 0.3% concentration limit). It can be calculated that 0.3% of PbCrO_4 needs 0.19% of Pb (Example 2).

The hazard index is then equal to $0.15\%/0.19\% = 0.78$ and this value is <1 .

Therefore, it can be concluded that this Pb substance will not exceed the limit value of 0.3%.

In general, in order to conclude that HP 10 will not be displayed by a waste material, it is necessary to repeat the same calculations for other substances (of other elements, not only Pb) relevant for HP 10 H360 hazard. If for each of the relevant substances the HI is less than 1, it is concluded that the waste is non-hazardous with respect to HP 10. If HI exceeds 1 for one or more elements, the waste material is concluded to be hazardous with respect to HP 10.

The above described approach has been introduced by Hennebert [14] and is followed and further extended in the assessment of European MSWI bottom ash considered in this report.

2.2.3.2 Lists of most hazardous substances for every hazard property

The application of the above described algorithm resulted in a list of the most hazardous substances for every hazard property. With reference to [14], this paragraph presents the most hazardous speciation of each element and the corresponding critical amount of each element per hazard property. The elements that are considered are: Ag, Al, As, B, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, Hg, K, Li, Mg, Mn, Mo, Na, Ni, P, Pb, S, Sb, Se, Si, Sn, Sr, Tl, U, V and Zn. If an element is not listed in Tables 16-23, it indicates that this element and its substances do not display a corresponding hazard property. The elements Cl, S or P, for some hazard properties are not mentioned because they are already bound in other substances (e.g. ZnCl_2 or PbSO_4).

Table 16: Most hazardous substances by element and corresponding critical amounts of elements for HP 4 (irritant – skin irritation and eye damage)

| Element | Concentration limit | Worst case substance | Formula | CAS No | Critical amount of an element |
|---------|---------------------|---|--|------------|-------------------------------|
| B | 10% | Sodium perborate tetrahydrate | Na ₃ BO ₃ ·7H ₂ O | 10486-00-7 | 0.43% |
| Be | 20% | Be(OH) ₂ | Be(OH) ₂ | 13327-32-7 | 4.19% |
| Ca | 20% | Calcium chloride | CaCl ₂ | 10043-52-4 | 7.22% |
| Cr VI | 1% | Sodium chromate | Na ₂ CrO ₄ | 7775-11-3 | 0.32% |
| Cu | 20% | CuSO ₄ ·5H ₂ O | CuSO ₄ ·5H ₂ O | 7758-98-7 | 5.09% |
| Fe | 20% | Ferrous sulfate heptahydrate | FeSO ₄ ·7H ₂ O | 7782-63-0 | 4.02% |
| Hg | 20% | Mercury (I) chloride | Hg ₂ Cl ₂ | 10112-91-1 | 16.99% |
| K | 20% | Potassium chromate | K ₂ CrO ₄ | 7789-00-6 | 8.05% |
| Na | 10% | Sodium bifluoride; sodium hydrogen difluoride | NaHF ₂ | 1333-83-1 | 3.71% |
| Ni | 10% | Nickel dinitrate | Ni(NO ₃) ₂ | 13138-45-9 | 3.21% |
| S | 1% | Sulphuric acid ... % | H ₂ SO ₄ | 7664-93-9 | 0.33% |
| Se | 20% | BeSeO ₄ ·4H ₂ O | BeSeO ₄ ·4H ₂ O | | 7.05% |
| Tl | 20% | Dithallium sulphate; thallic sulphate | Tl ₂ SO ₄ | 7446-18-6 | 16.19% |
| Zn | 10% | ZnSO ₄ ·H ₂ O | ZnSO ₄ ·H ₂ O | 7446-19-7 | 3.64% |

Table 17: Most hazardous substances by element and corresponding critical amounts of elements for HP 5 (STOT/Aspiration Toxicity)

| Element | Concentration limit | Worst case substance | Formula | CAS No | Critical amount of an element |
|---------|---------------------|---------------------------------------|---|------------|-------------------------------|
| Be | 1% | Be(OH) ₂ | Be(OH) ₂ | 13327-32-7 | 0.21% |
| Cd | 1% | Cadmium sulfate | CdSO ₄ | 10124-36-4 | 0.54% |
| Cr VI | 1% | Sodium chromate | Na ₂ CrO ₄ | 7775-11-3 | 0.32% |
| Hg | 1% | Mercuric chloride | HgCl ₂ | 7487-94-7 | 0.74% |
| Mn | 10% | MnSO ₄ | MnSO ₄ | 7785-87-7 | 3.64% |
| Ni | 1% | Nickelous sulfate | NiSO ₄ | 7786-81-4 | 0.38% |
| Pb | 10% | Minium | Pb ₃ O ₄ | 1314-41-6 | 3.02% |
| Se | 1% | BeSeO ₄ ·4H ₂ O | BeSeO ₄ ·4H ₂ O | | 0.35% |
| Tl | 1% | Dithallium sulphate; thallic sulphate | Tl ₂ SO ₄ | 7446-18-6 | 0.81% |
| U | 10% | Ningyosite | CaU(PO ₄) ₂ ·2H ₂ O | | 4.72% |
| V | 1% | V ₂ O ₅ | V ₂ O ₅ | 1314-62-1 | 0.56% |

Table 18: Most hazardous substances by element and corresponding critical amounts of elements for HP 6 (acute toxicity)

| Element | Concentration limit | Worst case substance | Formula | CAS No | Critical amount of an element |
|---------|---------------------|--|--|------------|-------------------------------|
| As | 0.25% | Diarsenic trioxide; arsenic trioxide | As ₂ O ₃ | 1327-53-3 | 0.19% |
| B | 22.50% | Sodium perborate tetrahydrate | Na ₃ BO ₃ ·7H ₂ O | 10486-00-7 | 0.96% |
| Ba | 5.00% | Barium chloride | BaCl ₂ | 10361-37-2 | 3.30% |
| Be | 5.00% | Be(OH) ₂ | Be(OH) ₂ | 13327-32-7 | 1.05% |
| Cd | 0.10% | Cadmium sulfate | CdSO ₄ | 10124-36-4 | 0.05% |
| Co | 2.50% | Cobalt sulfate | CoSO ₄ | 10124-43-3 | 0.95% |
| Cr VI | 0.25% | Sodium chromate | Na ₂ CrO ₄ | 7775-11-3 | 0.08% |
| Cu | 25% | CuSO ₄ ·5H ₂ O | CuSO ₄ ·5H ₂ O | 7758-98-7 | 6.36% |
| Hg | 0.10% | HgSO ₄ | HgSO ₄ | | 0.07% |
| Mn | 25% | Potassium permanganate | KMnO ₄ | 7722-64-7 | 8.69% |
| Ni | 3.50% | Nickel dichloride | NiCl ₂ | 7718-54-9 | 1.59% |
| Pb | 22.50% | Lead sulfate | PbSO ₄ | 7446-14-2 | 15.37% |
| Sb | 5.00% | Antimony trifluoride | SbF ₃ | 7783-56-4 | 13.62% |
| Se | 0.10% | Sodium selenite | Na ₂ O ₃ Se | 10102-18-8 | 0.05% |
| Tl | 0.10% | Dithallium sulphate; thallic sulphate | Tl ₂ SO ₄ | 7446-18-6 | 0.04% |
| U | 0.10% | UO ₂ | UO ₂ | | 0.09% |
| V | 25% | V ₂ O ₅ | V ₂ O ₅ | 1314-62-1 | 7.00% |
| Zn | 25% | Zinc sulfate | ZnSO ₄ | 7733-02-0 | 10.12% |

Table 19: Most hazardous substances by element and corresponding critical concentrations of elements for HP 7(carcinogenic)

| Element | Concentration limit | Worst case substance | Formula | CAS No | Critical amount of an element |
|---------|---------------------|--|--|------------|-------------------------------|
| As | 0.1% | Arsenic acid and its salts with the exception of those specified elsewhere in this Annex | H ₃ AsO ₄ | 7778-39-4 | 0.05% |
| Be | 0.1% | Be(OH) ₂ | Be(OH) ₂ | 13327-32-7 | 0.02% |
| Cd | 0.1% | Cadmium sulfate | CdSO ₄ | 10124-36-4 | 0.05% |
| Co | 0.01%(1) | Cobalt sulfate | CoSO ₄ | 10124-43-3 | 0.01%(2) |
| Cr VI | 0.1% | Sodium chromate | Na ₂ CrO ₄ | 7775-11-3 | 0.03% |
| Mo | 1.0% | MoO ₃ | MoO ₃ | 1313-27-5 | 0.67% |
| Ni | 0.1% | Nickelous sulfate | NiSO ₄ | 7786-81-4 | 0.04% |
| Pb | 0.1% | Lead sulfochromate yellow; C.I. Pigment Yellow 34; [This substance is identified in the Colour Index by Colour Index Constitution Number, C.I. 77603.] | PbCrO ₄ + PbSO ₄ | 1344-37-2 | 0.10%(2) |
| Sb | 1.0% | Valentinite | Sb ₂ O ₃ | 1317-98-2 | 0.84% |

Table 20: Most hazardous substances by element and corresponding critical amounts of elements for HP 8(corrosive)

| Element | Concentration limit | Worst case substance | Formula | CAS No | Critical amount of an element |
|---------|---------------------|---|----------------------------------|-----------|-------------------------------|
| Ag | 5% | AgNO ₃ | AgNO ₃ | 7761-88-8 | 3.18% |
| As | 5% | Diarsenic trioxide; arsenic trioxide | As ₂ O ₃ | 1327-53-3 | 3.79% |
| Cr VI | 5% | Sodium chromate | Na ₂ CrO ₄ | 7775-11-3 | 1.61% |
| Hg | 5% | Mercuric chloride | HgCl ₂ | 7487-94-7 | 3.69% |
| K | 5% | Potassium bifluoride; potassium hydrogen difluoride | F ₂ HK | 7789-29-9 | 2.50% |
| Li | 5% | Lithium | Li | 7439-93-2 | 5.00% |
| Na | 5% | Disodium sulfide; sodium sulfide | Na ₂ S | 1313-82-2 | 2.95% |
| S | 5% | Sulphuric acid ... % | H ₂ SO ₄ | 7664-93-9 | 1.63% |
| Sb | 5% | Antimony pentachloride | SbCl ₅ | 7647-18-9 | 2.04% |
| Sn | 5% | SnCl ₄ | SnCl ₄ | 7646-78-8 | 2.28% |
| Zn | 5% | Zinc chloride | ZnCl ₂ | 7646-85-7 | 2.40% |

Table 21: Most hazardous substances by element and corresponding critical amounts of elements for HP 10(toxic for reproduction)

| Element | Concentration limit | Worst case substance | Formula | CAS No | Critical amount of an element |
|---------|---------------------|--|--|------------|-------------------------------|
| As | 0.3% | Pb ₃ (AsO ₄) ₂ | Pb ₃ (AsO ₄) ₂ | 3687-31-8 | 0.05% |
| B | 0.3% | Sodium perborate tetrahydrate | Na ₃ BO ₃ ·7H ₂ O | 10486-00-7 | 0.01% |
| Cd | 0.3% | Cadmium sulfate | CdSO ₄ | 10124-36-4 | 0.16% |
| Co | 0.3% | Cobalt dinitrate | Co(NO ₃) ₂ | 10141-05-6 | 0.10% |
| Cr VI | 0.3% | Sodium chromate | Na ₂ CrO ₄ | 7775-11-3 | 0.10% |
| Hg | 0.3% | Mercury | Hg | 7439-97-6 | 0.30% |
| Ni | 0.3% | Nickelous sulfate | NiSO ₄ | 7786-81-4 | 0.11% |
| Pb | 0.3% | Lead sulfate | PbSO ₄ | 7446-14-2 | 0.21% |
| V | 3.0% | V ₂ O ₅ | V ₂ O ₅ | 1314-62-1 | 1.68% |

Table 22: Most hazardous substances by element and corresponding critical amounts of element for HP 11(mutagenic)

| Element | Concentration limit | Worst case substance | Formula | CAS No | Critical amount of an element |
|---------|---------------------|-------------------------------|----------------------------------|------------|-------------------------------|
| Cd | 0.1% | Cadmium sulfate | CdSO ₄ | 10124-36-4 | 0.05% |
| Co | 1.0% | Cobalt sulfate | CoSO ₄ | 10124-43-3 | 0.38% |
| Cr VI | 0.1% | Sodium chromate | Na ₂ CrO ₄ | 7775-11-3 | 0.03% |
| Hg | 1.0% | Mercuric chloride | HgCl ₂ | 7487-94-7 | 0.74% |
| Ni | 1.0% | Nickelous sulfate | NiSO ₄ | 7786-81-4 | 0.38% |
| V | 1.0% | V ₂ O ₅ | V ₂ O ₅ | 1314-62-1 | 0.56% |

Table 23: Most hazardous substances by element and corresponding critical amounts of elements for HP 13(sensitising)

| Element | Concentration limit | Worst case substance | Formula | CAS No | Critical amount of an element |
|---------|---------------------|----------------------|-----------------------------------|------------|-------------------------------|
| Be | 10% | Be(OH) ₂ | Be(OH) ₂ | 13327-32-7 | 2.09% |
| Co | 10% | Cobalt sulfate | CoSO ₄ | 10124-43-3 | 3.80% |
| Cr VI | 10% | Sodium chromate | Na ₂ CrO ₄ | 7775-11-3 | 3.21% |
| Ni | 10% | Nickelous sulfate | NiSO ₄ | 7786-81-4 | 3.79% |
| Se | 10% | Sodium selenite | Na ₂ O ₃ Se | 10102-18-8 | 4.57% |

2.2.3.3 Results of Tier 2 assessment

Tier 2 assessment consists of two parts:

Part 1 - assessment of hazard properties for which the individual concentration limits are defined and, therefore, the individual hazard indices have to be calculated. The relevant HPs are: HP 5(STOT/Aspiration), HP 7(carcinogenic), HP 10(toxic for reproduction), HP 11(mutagenic) and HP 13(sensitising).

Part 2 – assessment of hazard properties with additive hazard where the summation rules are defined. Therefore, the resulting hazard index for these hazard properties is calculated as the sum of individual contributions from all relevant elements. The summation rules are applicable for HP 4(irritant), HP 6(acute toxic), HP 8(corrosive) and HP 14(eco-toxic). Because of the complexity in the assessment of HP 14(eco-toxic), this hazard property will be considered as a separate paragraph beyond the tiered approach.

The hazard index (individual or after summation) was calculated for every element as a ratio (sum of ratios) between the total content (Table 15) and the corresponding critical amount of each element for the specific hazard property (tables 16-23 are referred to for critical amounts of elements for every hazard property).

Part 1. Tier 2 assessment of individual hazard properties

HP 5(STOT/Aspiration)

Table 24 shows that Ni and Pb compounds contribute most to HP 5(STOT/Aspiration), as indicated by their hazard indices, however do not exceed 1 thus presenting no hazard. Note that in Table 3.1 of Annex VI of the CLP, Pb has “a generic entry” with specific concentration limit 0.5% for STOT RE 2, H373. The total amount of Pb present in the MSWI bottom ash is 0.4% (the 95 percentile). Assuming that all Pb is in this unknown form that has H373 hazard (entry 082-001-00-6 “lead compound with the exception of those specified elsewhere in this Annex”), the specific concentration limit of 0.5% will be not exceeded.

Table 24: Hazard indices for the most hazardous substance per element for HP 5.

| Element | Total content based on 95percentile, % | The most hazardous substance, Table 17 | Critical amount of an element for HP 5, % | Hazard index for the most hazardous substance for HP 5 |
|---------|--|--|---|--|
| Be | 0.00023 | Be(OH) ₂ | 0.21 | 0.0011 |
| Cd | 0.0014 | CdSO ₄ | 0.54 | 0.0026 |
| Cr VI | 0.00008 | Na ₂ CrO ₄ | 0.32 | 0.0002 |
| Hg | 0.00073 | HgCl ₂ | 0.74 | 0.0010 |
| Mn | 0.2 | MnSO ₄ | 3.64 | 0.0550 |

| Element | Total content based on 95percentile, % | The most hazardous substance, Table 17 | Critical amount of an element for HP 5, % | Hazard index for the most hazardous substance for HP 5 |
|---------|--|---|---|--|
| Ni | 0.053 | NiSO ₄ | 0.38 | 0.1397 |
| Pb | 0.40 | Pb ₃ O ₄ | 3.02 | 0.1324 |
| Se | 0.0013 | BeSeO ₄ ·4H ₂ O | 0.35 | 0.0037 |
| Tl | 0.0029 | Tl ₂ SO ₄ | 0.81 | 0.0036 |
| U | not measured | CaU(PO ₄) ₂ ·2H ₂ O | 4.72 | 0.0000 |
| V | 0.0076 | V ₂ O ₅ | 0.56 | 0.0136 |

All individual hazard indices calculated for most hazardous substances for HP 5 are lower than 1 (last column, Table 24), indicating that there is not enough of these elements to exceed the limit value assuming the most hazardous substance. It means that any other substances that might be assumed to be present will require higher amounts before the limit value is exceeded (the hazard index will be lower). Therefore, it can be concluded that HP 5 will not be displayed by MSWI bottom ash. HP 5 assessment is finished at this point.

HP 7 (carcinogenic)

Table 25: Hazard indices for the most hazardous substance per element for HP 7.

| Element | Total content based on 95percentile, % | The most hazardous substance, Table 19 | Critical amount of an element for HP 7, % | Hazard index for the most hazardous substance for HP 7 |
|---------|--|--|---|--|
| As | 0.0047 | H ₃ AsO ₄ | 0.05 | 0.09 |
| Be | 0.00023 | Be(OH) ₂ | 0.02 | 0.01 |
| Cd | 0.0014 | CdSO ₄ | 0.05 | 0.03 |
| Co | 0.0091 | CoSO ₄ | 0.01 | 0.91 |
| Cr VI | 0.00008 | Na ₂ CrO ₄ | 0.03 | 0.002 |
| Mo | 0.0081 | MoO ₃ | 0.67 | 0.01 |
| Ni | 0.053 | NiSO ₄ | 0.04 | 1.33 |
| Pb | 0.40 | PbCrO ₄ + PbSO ₄ | 0.10 | 4.00 |
| Sb | 0.016 | Sb ₂ O ₃ | 0.84 | 0.02 |

Hazard indices determined for most hazardous substances with respect to possible carcinogenic effects are less than 1, with the exception for Ni and Pb (NiSO₄ and lead sulphochromate yellow complex PbCrO₄+PbSO₄ as the most hazardous). These substances will be the subject for more detailed assessment at Tier 3. Therefore hazard property HP 7 carcinogenic cannot be excluded from the assessment at Tier 2.

HP 10(toxic for reproduction)

Table 26: Hazard indices for the most hazardous substance per element for HP 10.

| Element | Total content based on 95percentile, % | The most hazardous substance, Table 21 | Critical amount of an element for HP 10, % | Hazard index for the most hazardous substance for HP 10 |
|---------|--|--|--|---|
| As | 0.0047 | Pb ₃ (AsO ₄) ₂ | 0.05 | 0.094 |
| B | 0.04 | Na ₃ BO ₃ ·7H ₂ O | 0.01 | 4.00 |
| Cd | 0.0014 | CdSO ₄ | 0.16 | 0.009 |
| Co | 0.0091 | Co(NO ₃) ₂ | 0.10 | 0.094 |
| Cr VI | 0.00008 | Na ₂ CrO ₄ | 0.10 | 0.0008 |
| Hg | 0.0007 | Hg | 0.30 | 0.002 |
| Ni | 0.053 | NiSO ₄ | 0.11 | 0.47 |
| Pb | 0.4 | PbSO ₄ | 0.21 | 2.00 |
| V | 0.0076 | V ₂ O ₅ | 1.68 | 0.005 |

Hazard indices determined for substances listed in Table 21 are less than 1 with the exception for B and Pb (Na₃BO₃·7H₂O and PbSO₄ as the most hazardous forms of B and Pb – see also Table 21). These substances will be the subject for more detailed assessment at Tier 3. Therefore hazard property HP 10 toxic for reproduction cannot be excluded from the assessment at Tier 2.

HP 11(mutagenic)

Table 27: Hazard indices for the most hazardous substance per element for HP 11.

| Element | Total content based on 95percentile, % | The most hazardous substance, Table 22 | Critical amount of an element for HP 11, % | Hazard index for the most hazardous substance for HP 11 |
|---------|--|--|--|---|
| Cd | 0.0014 | CdSO ₄ | 0.05 | 0.03 |
| Co | 0.0091 | CoSO ₄ | 0.38 | 0.24 |
| Cr VI | 0.00008 | Na ₂ CrO ₄ | 0.03 | 0.002 |
| Hg | 0.00073 | HgCl ₂ | 0.74 | 0.001 |
| Ni | 0.053 | NiSO ₄ | 0.38 | 0.14 |
| V | 0.0076 | V ₂ O ₅ | 0.56 | 0.01 |

As it can be seen from Table 27, Co contributes most to HP 11 (mutagenic), as indicated by the highest hazard index 0.24 for CoSO₄ as the most hazardous form of Co. Since 0.24 is less than one and all the remaining individual hazard indices in Table 17 are lower than 1, it indicates that there is not enough of these elements to exceed the limit value assuming the most hazardous substance. Any other substances that might be assumed to be present will require higher amounts before the limit value is exceeded

(the hazard index will be lower). Therefore, it is concluded that HP 11 presents no hazard. HP 11 assessment is finished at this point.

HP 13(sensitising)

Table 28: Hazard indices for the most hazardous substance per element for HP 13.

| Element | Total content based on 95percentile, % | Most hazardous substance, Table 23 | Critical amount of an element for HP 13, % | Hazard index for the most hazardous substance for HP 13 |
|---------|--|------------------------------------|--|---|
| Be | 0.00023 | Be(OH) ₂ | 2.09 | 0.0001 |
| Co | 0.0091 | CoSO ₄ | 3.80 | 0.0023 |
| Cr VI | 0.00008 | Na ₂ CrO ₄ | 3.21 | 0.00002 |
| Ni | 0.053 | NiSO ₄ | 3.79 | 0.0140 |
| Se | 0.0013 | Na ₂ O ₃ Se | 4.57 | 0.0003 |

All individual hazard indices are lower than 1, indicating that there is not enough of these elements to exceed the limit value assuming the most hazardous substance. Any other substances that might be assumed to be present will require higher amounts before the limit value is exceeded (the hazard index will be lower). Therefore, it is concluded that HP 13 sensitising presents no hazard.

Part 2. Tier 2 assessment of additive hazard properties

In the assessment of the additive hazard properties, the sum of all relevant individual hazard indices needs to be calculated (this sum is referred to as resulting or total hazard index). In case the resulting hazard index is less than 1, the limit for a corresponding hazard property is not exceeded. In the opposite case Tier 3 assessment is performed with the focus on the compounds that are most contributing to the resulting hazard index. As a remark, since the approach that is followed in this report is based on the determination of most hazardous substance, the cut-off values can be omitted when assessing the hazard properties with additive hazard. Otherwise, if the concentrations of all relevant substances would have to be added together, only the substances with concentrations above the cut-off values would be needed to consider.

HP 6 (acute toxicity)

Table 29: Hazard indices for the most hazardous substance per element for HP 6.

| Element | Total content based on 95percentile, % | Most hazardous substance, Table 18 | Critical amount of an element for HP 6, % | Hazard index for the most hazardous substance for HP 6 |
|---------|--|--|---|--|
| As | 0.0047 | As ₂ O ₃ | 0.19 | 0.0248 |
| B | 0.04 | Na ₃ BO ₃ .7H ₂ O | 0.96 | 0.0417 |
| Ba | 0.22 | BaCl ₂ | 3.30 | 0.0667 |
| Be | 0.00023 | Be(OH) ₂ | 1.05 | 0.0002 |

| | | | | |
|--------------|---------|--------------------------------------|-------|--------------|
| Cd | 0.0014 | CdSO ₄ | 0.05 | 0.0260 |
| Co | 0.0091 | CoSO ₄ | 0.95 | 0.0096 |
| Cr VI | 0.00008 | Na ₂ CrO ₄ | 0.08 | 0.0010 |
| Cu | 0.89 | CuSO ₄ ·5H ₂ O | 6.36 | 0.1399 |
| Hg | 0.00073 | HgSO ₄ | 0.07 | 0.0108 |
| Mn | 0.2 | KMnO ₄ | 8.69 | 0.0230 |
| Ni | 0.053 | NiCl ₂ | 1.59 | 0.0330 |
| Pb | 0.4 | PbSO ₄ | 15.37 | 0.026 |
| Sb | 0.016 | SbF ₃ | 13.62 | 0.0011 |
| Se | 0.0013 | Na ₂ O ₃ Se | 0.05 | 0.0284 |
| Tl | 0.0029 | Tl ₂ SO ₄ | 0.04 | 0.0716 |
| U | | UO ₂ | 0.09 | not measured |
| V | 0.0076 | V ₂ O ₅ | 7.00 | 0.0011 |
| Zn | 0.63 | ZnSO ₄ | 10.12 | 0.062 |
| TOTAL | | | | 0.57 |

After summation of all individual hazard indices assuming the most hazardous substance to be present, the total hazard index for HP 6 is equal to 0.57. This indicates that the limit value of all added substances for HP 6 (acute toxicity) will not be exceeded. It can be seen that Cu with hazard index (0.14) contributes most to the resulting hazard index, but is still much lower than 1 and in combination with contributions from other elements does not exceed 1 as well. It is therefore concluded that HP 6 presents no hazard. Therefore HP 6 assessment is finished at Tier 2.

HP 8 (corrosive)

Table 30: Hazard indices for the most hazardous substance per element for HP 8.

| Element | Total content based on 95percentile, % | Most hazardous substance, Table 20 | Critical amount of an element for HP 8, % | Hazard index for the most hazardous substance for HP 8 |
|--------------|--|------------------------------------|---|--|
| Ag | 0.0038 | AgNO ₃ | 3.18 | 0.0012 |
| As | 0.0047 | As ₂ O ₃ | 3.79 | 0.0012 |
| Cr VI | 0.00008 | Na ₂ CrO ₄ | 1.61 | 0.00005 |
| Hg | 0.00073 | HgCl ₂ | 3.69 | 0.0002 |
| K | 1.2 | F ₂ HK | 2.50 | 0.48 |
| Li | 0.0023 | Li | 5.00 | 0.0005 |
| Na | 3.2 | Na ₂ S | 2.95 | 1.08 |
| S | 0.79 | H ₂ SO ₄ | 1.63 | 0.48 |
| Sb | 0.016 | SbCl ₅ | 2.04 | 0.0077 |
| Sn | 0.052 | SnCl ₄ | 2.28 | 0.0228 |
| Zn | 0.63 | ZnCl ₂ | 2.40 | 0.26 |
| TOTAL | | | | 2.24 |

In the worst case assessment, the total hazard index for HP 8 equals to 2.24 that exceeds 1. Furthermore, the individual hazard index for Na (Na₂S is the most hazardous

form, Table 20) is equal to 1.08 that is already larger than 1. Additionally, K, S and Zn (correspondingly K_2S , H_2SO_4 and $ZnCl_2$ as the most hazardous forms) are most contributing to the total hazard index. Using the worst-case assessment in Tier 2, it cannot be excluded that bottom ash can display HP 8 (corrosive) hazard. Therefore, assessment of HP 8 will be continued in Tier 3, with a focus on the potentially realistic presence/existence and the speciation of substances that are most contributing to the total hazard index.

HP 4 (irritant)

As already mentioned in paragraph 1.3.4, HP 4 assessment does not apply if the waste is classified hazardous by HP 8. Since HP 8 (corrosive) assessment was not excluded in Tier 2, HP 4 (irritant) assessment automatically goes to Tier 3. However, it is helpful to already know what the main focus in Tier 3 assessment of HP 4 should be. Therefore, the hazard indices of the most hazardous substances were calculated and shown in Table 31.

Table 31: Hazard indices for the most hazardous substance per element for HP 4.

| Element | Total content based on 95percentile, % | Most hazardous substance, Table 16 | Critical amount of an element for HP 4, % | Hazard index for the most hazardous substance for HP 4 |
|--------------|--|------------------------------------|---|--|
| B | 0.04 | $Na_3BO_3 \cdot 7H_2O$ | 0.43 | 0.0939 |
| Be | 0.00023 | $Be(OH)_2$ | 4.19 | 0.000055 |
| Ca | 19 | $CaCl_2$ | 7.22 | 2.63 |
| Cr VI | 0.00008 | Na_2CrO_4 | 0.32 | 0.0002 |
| Cu | 0.89 | $CuSO_4 \cdot 5H_2O$ | 5.09 | 0.17 |
| Fe | 10.3 | $FeSO_4 \cdot 7H_2O$ | 4.02 | 2.56 |
| Hg | 0.00073 | Hg_2Cl_2 | 16.99 | 0.00004 |
| K | 1.2 | K_2CrO_4 | 8.05 | 0.15 |
| Na | 3.2 | $NaHF_2$ | 3.71 | 0.86 |
| Ni | 0.053 | $Ni(NO_3)_2$ | 3.21 | 0.0165 |
| S | 0.79 | H_2SO_4 | 0.33 | 2.42 |
| Se | 0.0013 | $BeSeO_4 \cdot 4H_2O$ | 7.05 | 0.0002 |
| Tl | 0.0029 | Tl_2SO_4 | 16.19 | 0.0002 |
| Zn | 0.63 | $ZnSO_4 \cdot H_2O$ | 3.64 | 0.17 |
| TOTAL | | | | 9.08 |

Table 31 shows that the total hazard index, assuming that all relevant substances are present in their most hazardous form (Table 16), is much higher than 1. The largest contributions to the total hazard index come from Ca, Fe and S ($CaCl_2$, $FeSO_4 \cdot 7H_2O$ and H_2SO_4 as most hazardous forms of Ca, Fe and S respectively). These elements have a hazard index that individually already exceeds 1. Therefore, assessment of HP 4 will be continued in Tier 3, with a focus on the potentially realistic presence/existence and the speciation of substances that are most contributing to the total hazard index.

HP 14 (eco-toxic)

As it was already mentioned above, because of its complexity, the assessment of HP 14 (eco-toxic) will be done in a separate paragraph beyond the tiered approach.

2.2.3.4 Summary Tier 2

Based on the above described assessment of individual (HP 5, HP 7, HP 10, HP 11, H 13) and additive (HP 4, HP 6, HP 8 and HP 14) hazard properties, Tier 2 eliminates the following hazard properties from further assessment: HP 5 (STOT/Aspiration), HP 6 (), HP 11 (mutagenic), HP 13 (sensitising).

Hazard properties HP 4 (irritant), HP 7 (carcinogenic), HP 8 (corrosive) and HP 10 (toxic for reproduction) could not be excluded after Tier 2 and will be assessed in Tier 3. HP 14 (eco-toxic) was not addressed in Tier 2 because of its complexity.

The assessment of HP 14 will be done in a separate paragraph beyond the tiered approach.

2.2.4 Tier 3 assessment: beyond worst case analysis

Tier 3 assessment focuses only on the hazard properties that were not excluded after the worst case analysis performed in Tier 2:

HP 7 – carcinogenic

HP 10 – toxic for reproduction

HP 8 – corrosive

HP 4 – irritant

The assessment in Tier 3 focusses mainly on the possible presence and existence of the worst case substances that were identified as potentially problematic in Tier 2. In addition, (geo)chemical knowledge about substances and mineral formation/stability in bottom ash is used to conclude the hazard assessment.

HP 7. Carcinogenic. Tier 3 assessment

The hazard indices listed in Table 25 are less than 1 for all relevant elements with the exception of two elements: Ni with $HI(Ni \text{ as } NiSO_4)=1.33$ and Pb with $HI(Pb \text{ as } PbCrO_4+PbSO_4)=4.00$. These compounds are the subject for more detailed assessment at Tier 3.

$NiSO_4$ is a soluble salt that decomposes at temperatures higher than $840^\circ C$ (https://pubchem.ncbi.nlm.nih.gov/compound/nickel_sulfate#). Because $NiSO_4$ is a soluble salt it will readily dissolve in water, such as in the quench tank of an MSWI incinerator. The resulting dissolved Ni at the high pH in the quench tank will be oversaturated with respect to more stable Ni oxides and -hydroxides, of which $Ni(OH)_2$ (or a very similar species) precipitates, as has been demonstrated with leaching data in combination with geochemical modelling [15]. Therefore, it is concluded that $NiSO_4$ will not be present in MSWI bottom ash. The most likely dominant form of Ni in bottom ash is $Ni(OH)_2$ and it is considered realistic to base the assessment on this substance. The hazard index of $Ni(OH)_2$ is 0.82 (0.053%/0.064%) and this implies that Ni substances will not exceed the limit value for HP 7.

Table 32 shows the calculated maximum concentrations (taking the stoichiometry of the elements into account) for all possible Pb substances relevant for HP 7. The

substance PbHAsO_4 (H350) has a limit value of 0.1% (this limit value was assumed in the worst case assessment for all Pb substances), while other Pb substances have a limit value of 1% (H351).

The As concentration in MSWI bottom ash was 47mg/kg and assuming that all As will be bound in PbHAsO_4 , the maximum theoretical amount of PbHAsO_4 is 0.02%. This concentration is far below the limit of 0.1%.

The rest of Pb substances listed in Table 32 (H351) have a limit value of 1% and this limit value will not be exceeded (most of organic lead substances that are listed in the CLP are omitted). The presence of the specific organic metal substances listed in the CLP can be considered as not likely to be present in MSWI bottom ash. It is known that only a small fraction of the total organic carbon in MSWI bottom ash is capable of forming metal complexes (in the order of 9% of total organic carbon), and these organic substances are identified as natural humic and fulvic substances [16], [17]. Table 32 shows that none of the relevant Pb substances with H351 will exceed the 1% limit and that the substance with H350 (PbHAsO_4) does not exceed the 0.1% limit. Therefore, it is concluded that MSWI bottom ash will not be hazardous with respect to HP 7 carcinogenic.

Table 32: Pb substances relevant for HP 7 assessment

| Cat 1, H350 | Cat 2, H351 | Substance | REMARKS |
|-------------------|-----------------|---|--|
| 0.1% limit | 1% limit | | |
| | 0.47% <1% | PbCrO_4 | CrVI 0.8mg/kg ; Cr total 754mg/kg, if all Cr=CrIII, 1% limit is not exceeded |
| 0.02%<0.1% | | HPbAsO_4 | As a limiting element (47mg/kg), total Pb - 3989mg/kg |
| | 0.08% | $\text{PbCrO}_4+\text{PbMoO}_4+\text{PbSO}_4$ | PbSO_4 too soluble to form this complex, also will not exceed 1% limit when Mo(81mg/kg) is the limiting element |
| | 0.84% | $\text{PbSO}_4+\text{PbCrO}_4$ | PbSO_4 too soluble to form this complex, also will not exceed 1% limit when all Cr is CrIII and taken as the limiting element |

HP 10. Toxic for reproduction. Tier 3 assessment

From Tier 2, hazard indices for B and Pb exceeded 1: $\text{HI}(\text{B as Na}_3\text{BO}_3 \cdot 7\text{H}_2\text{O}) = 4.0$ and $\text{HI}(\text{Pb as PbSO}_4) = 2.0$. These forms of B and Pb were considered as the most hazardous substances of these two elements (see Table 21). Therefore, these substances will be discussed in more detail.

$\text{Na}_3\text{BO}_3 \cdot 7\text{H}_2\text{O}$ was mentioned in Table 21 as the most hazardous form of B since it required the lowest amount of B in order to obtain a concentration 0.1% (limit value) of the substance $\text{Na}_3\text{BO}_3 \cdot 7\text{H}_2\text{O}$. However, it is known that $\text{Na}_3\text{BO}_3 \cdot 7\text{H}_2\text{O}$ decomposes at

temperatures higher than 150 °C (Lide, D. R., CRC Handbook of Chemistry and Physics, 2005, (86th edition ISBN 0-8493-0486-5), p.88) and, therefore, B is not believed to be present in MSWI bottom ash in the form of Na₃BO₃·7H₂O. Instead, even though not much is known about the speciation of B in MSWI bottom ash, B₂O₃ is the most stable form, and therefore is considered as the most probable speciation of B. In order to be present in a concentration of 0.3%, B₂O₃ will require 0.095% of B which is higher than the total content of 0.04%. Subsequently, the hazard index for B will become 0.04/0.095=0.42. This indicates that the presence of B in its most stable form of B₂O₃ will not render bottom ash as toxic for reproduction.

The relevant substances of Pb are listed in Table 33. All substances possess toxic for reproduction effect of category 1 (H360, known to have effects toxic for reproduction) with the lower limit value of 0.3%. There are no relevant Pb substances with H361 (reproductive 2; suspected of damaging fertility of the unborn child; 3% concentration limit for an individual substance with H361). The maximum amount and the stability of these substances is assessed (Table 33). It was found that for some substances the maximum concentration of these substances was limited by the concentration of another element (e.g. a relatively low F concentration limits the amount of PbSiF₆ that can be formed). Other substances were not stable under the conditions in the incinerator (e.g. PbN₆ and all organic lead substances). PbSO₄ is very soluble and will immediately precipitate at a high pH as Pb(OH)₂ (or a very similar substance) in the quench tank. The calculations indicate that only Pb₃(PO₄)₂ cannot be excluded based on the stability and limiting concentrations of Pb (marked red in Table 33).

Table 33: Pb substances relevant for HP 10 assessment

| Cat 1, H360 | Cat 2, H361 | | REMARKS |
|-------------|-------------|---|--|
| 0.3% limit | 3% limit | | |
| 0.024 | | PbSiF ₆ | F (78mg/kg) as a limiting element |
| 0.558 | | PbN ₆ | decomposes at 190C: https://pubchem.ncbi.nlm.nih.gov/compound/Lead_diazide#section |
| 0.001 | | PbCrVIO ₄ | CrVI 0.8mg/kg, Cr total 754mg/kg; CrVI as a limiting element |
| 0.518 | | Pb ₃ (PO ₄) ₂ | Pb as limiting element |
| 0.022 | | HPbAsO ₄ | Arsenic as a limiting element (47mg/kg), total Pb - 3989mg/kg |
| 0.084 | | PbCrO ₄ + PbMoO ₄ +PbSO ₄ | PbSO ₄ too soluble to form this complex, also will not exceed 0.3% limit when Mo(81mg/kg) is the limiting element |
| 0.835 | | PbSO ₄ +PbCrO ₄ | PbSO ₄ too soluble to form this complex |

The theoretical maximum concentration of Pb₃(PO₄)₂ is 0.52% and this concentration would exceed the limit value of 0.3% if all Pb is bound in this substance. Pb₃(PO₄)₂

present in amount of 0.52% exceeds 0.3% and therefore would render classification of MSWI bottom ash as toxic for reproduction.

However, there could also be other forms of Pb that are likely to be present in MSWI bottom ash and cannot be excluded without having an evidence for this. The most probable Pb substances in bottom ash are: Pb(OH)_2 , PbCO_3 , PbO , metallic Pb (e.g., See Dijkstra et al., 2008), and possibly small amounts of $\text{Pb}_3(\text{PO}_4)_2$, PbHAsO_4 and PbCrO_4 (a Cr(VI) containing substance). The latter two substances can only be present in a very low amounts due to limiting amounts of Cr(VI) (0.8mg/kg) and As (47mg/kg) in the MSWI bottom ash.

The distribution of Pb among the possible substances as Pb(OH)_2 , PbO , PbCO_3 , $\text{Pb}_3(\text{PO}_4)_2$ and metallic Pb is not known and cannot be predicted or quantified for such a complex material as MSWI bottom ash with the current scientific means. Geochemical modelling to predict leached concentrations can be used to identify the minerals that control leaching, but determination of the amounts of minerals is complicated (with exceptions e.g., as discussed in [15] and elsewhere in this report (Figure 1)). This is because of the following reasons:

(1) In case the leaching of a certain element (e.g. Pb) is in equilibrium with a mineral (e.g., Pb(OH)_2), the concentrations in solution are independent on the amount of that mineral. In practice, this means that in most cases it is not possible to quantitatively determine the amount of a mineral based on the leached concentration in a leaching test.

(2) Geochemical models assume chemical equilibrium. Chemical equilibrium implies that only the most stable (insoluble) mineral is able to exist, while MSWI bottom ash is a thermodynamic unstable mixture of minerals that have a different stability, such as Pb(OH)_2 , PbO , and PbCO_3 . This limits the possibility to draw quantitative conclusions on the distribution of an element over different mineral forms, that may in reality be present in MSWI bottom ash.

Spectroscopic techniques are in principle suitable to determine the speciation of an element over different mineral forms, however, the sensitivity of these techniques is too low to quantify the often low amounts in MSWI bottom ash. Therefore worst case analysis remains the only mean to quantify the amount of relevant substances. Worst case analysis for these Pb substances (Pb(OH)_2 , PbO , PbCO_3 , $\text{Pb}_3(\text{PO}_4)_2$ and metallic Pb) results in a hazard that is substantially overestimated (cells that are marked in red in Table 34). There are no arguments that could prove equal distribution of total Pb among Pb speciations listed in Table 34 and therefore cannot be considered as part of the analysis, however it can illustrate that in such case for all speciations 0.3% limit would not be exceeded.

Table 34: Analysis of Pb substances

| | | g/mol | Pb total 95%, % | Max concentration in worst case % | Pb <u>assumed</u> equal distribution, % | Max concentration at assumed equal distribution, % |
|--------------------|---|-------|--------------------|--|--|--|
| 0.3% limit | PbCO ₃ | 267 | 0.40 | 0.52 | 0.08 | 0.10 |
| 0.3% limit | PbO | 223 | 0.40 | 0.43 | 0.08 | 0.09 |
| 0.3% limit | Pb(OH) ₂ | 241 | 0.40 | 0.47 | 0.08 | 0.09 |
| CLP, 0.3% limit | Pb metallic | 207 | 0.40 | 0.40 | 0.08 | 0.08 |
| CLP, 0.3% limit | Pb ₃ (PO ₄) ₂ | 812 | 0.40 | 0.52 | 0.08 | 0.11 |

In order to have a deeper look into the behaviour of Pb and its substances in the MSWI bottom ash, solubilities of the above mentioned Pb substances were modelled as a function of the pH and are presented in Figure 1. Horizontal lines in the figure indicate the total content of Pb in the samples of several different MSWI bottom ashes. Leaching data from 5 UK and NL bottom ashes shows that the leached concentrations at L/S=10 l/kg, including those at pH 2 (extremely acidic), are much lower than the total content of Pb in the sample (factor 10-100 difference). The black/grey solid and dashed lines represent the calculated (using the geochemical speciation code Orchestra) solubility of different Pb substances (Pb₃(PO₄)₂, PbCO₃, Pb(OH)₂, PbO and metallic Pb) as a function of the pH. The colored data points represent the measured solubility of Pb (measured as total dissolved Pb) as a function of pH. The modelling results of the five assumed Pb substances show that each of these minerals will be completely dissolved at pH=2. However, the measurements on bottom ash show that not all Pb is dissolved at pH 2. This means that these five Pb substances are not present at concentrations that explain the total Pb content. The results in Figure 1 imply that the amount of Pb that is present in Pb₃(PO₄)₂, PbCO₃, Pb(OH)₂, PbO or metallic Pb (individually or as a sum) is very unlikely to be higher than the leached concentration at pH=2. The difference between the total content of Pb and the leached amount at pH=2 can be ascribed then to an “unknown” form, such as trapped into glassy phases for instance.

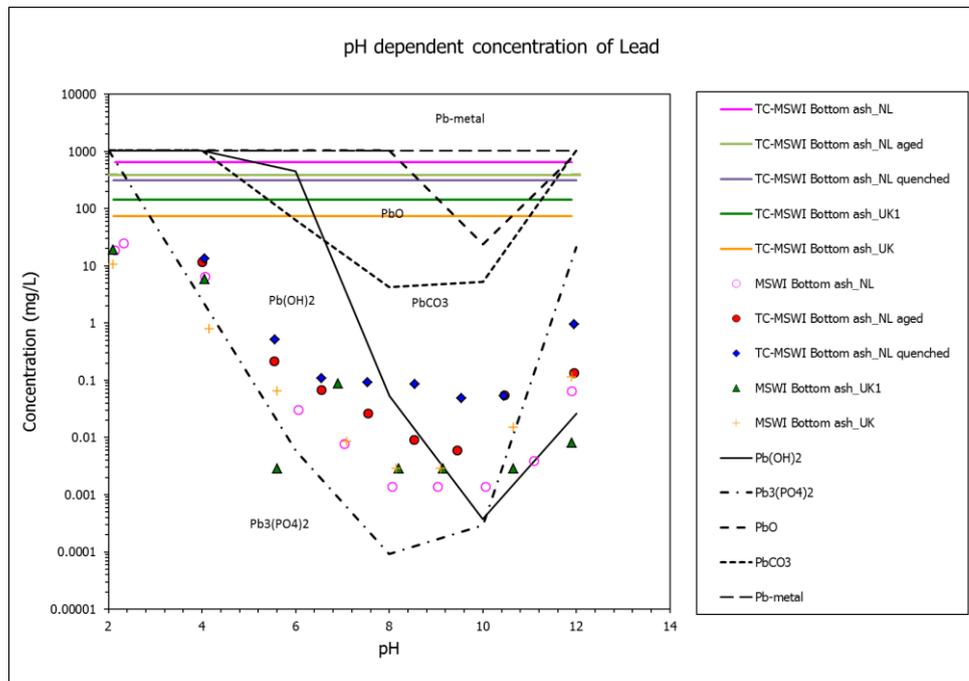


Figure 1: pH dependent concentration of Pb. Horizontal lines in the figure indicate the total content of Pb in the samples of several different MSWI bottom ashes. The black/grey solid and dashed lines represent the calculated (using the geochemical speciation code Orchestra) solubility of different Pb substances ($Pb_3(PO_4)_2$, $PbCO_3$, $Pb(OH)_2$, PbO and metallic Pb) as a function of the pH. The coloured data points represent the measured solubility of Pb (measured as total dissolved Pb) as a function of pH.

Using the data from Figure 1, our calculations show that $PbCO_3$, PbO , $Pb(OH)_2$, metallic Pb, and $Pb_3(PO_4)_2$ consume together at maximum 14.5% of the total amount of Pb present in the sample thus leaving 85.5% of total Pb in the sample in “unknown” form. This is also summarized in Table 35. Assuming that each of the minerals $PbCO_3$, PbO , $Pb(OH)_2$, metallic Pb, and $Pb_3(PO_4)_2$ will consume 14.5% of total Pb, it will result in 0.07% as maximum for $PbCO_3$, 0.06% as maximum for PbO , 0.06% as maximum for Pb metallic, 0.07% as maximum for $Pb(OH)_2$ and 0,08% as maximum for $Pb_3(PO_4)_2$. Thus any of these forms of Pb would not render the waste as toxic for reproduction Category 1 (0.3% limit) or Category 2 (3% limit).

Table 35: Pb substances and estimated distribution of Pb

| Pb substances | Estimated amount, % from total amount of Pb |
|---|---|
| $PbCO_3$, PbO , $Pb(OH)_2$, metallic Pb, and $Pb_3(PO_4)_2$ | Together consume maximum 14.5% of total Pb |
| Unknown forms of Pb | Remaining 85.5% of total Pb |

Extrapolating the results from this dataset to the “general” MSWI bottom ash implies that $0.4\% \times 0.855 = 0.34\%$ of Pb is in unknown substances with unknown hazard. Pb in

unknown form can potentially be toxic for reproduction Category 1, under the CLP reference Table 3.1, entry 082-001-00-6 “lead compound with the exception of those specified elsewhere in this Annex” with H360-Df reproduction category 1 hazard (limit value is 0.3%). This would mean that the unknown Pb substances could be just above the limit value for this entry formally leading to classification of MSWI bottom ash as toxic for reproduction. To verify whether this conclusion is valid and reasonable for the majority of bottom ash samples, the statistical parameters (as the choice of the 95 percentile) can be checked for Pb. The decision of choosing of the 95% composition for the European MSWI bottom ash in the assessment was made in order to cover the maximally wide range of Pb concentration in different samples. However, in the particular case of Pb for the assessment of possible unknown substances with H360 (referring to the generic entry for Pb substances in the CLP), the choice of the 95percentile level of Pb is suspected to be overestimated for the majority of the samples and is recommended for reviewing.

Considering that it is only the unknown forms of Pb (85.5% of the total Pb) that can lead to the exceedance of the 0.3% limit, in order to fulfil the 0.3% criteria, total Pb content should not exceed 0.35% ($0.3\% / 0.855 = 0.35\%$ as total Pb content).

Therefore for the time being it can be concluded that all sample with total Pb content that is lower than 0.35% (3500mg/kg) will not render hazardous classification of MSWI bottom ash. For samples with Pb content higher than 0.35% (3500mg/kg), it is recommended to review Pb content and to explain the origin of high Pb levels.

As a remark, information on the distribution for Pb over different possible Pb phases is not necessary due to its generic entry. In that case, the conclusion will be that MSWI bottom ash with Pb amounts lower than 3000mg/kg will present no HP10 hazard. Our assessment is done based on the 95 percentile value for Pb (3969mg/kg) in order to cover a range as wide as possible. With such a Pb level, the general conclusion would be that MSWI bottom ash displays HP10 hazard. However, the present report takes the approach one step further using leaching data and geochemical modelling and increased the critical level for Pb to 3500mg/kg. But even in that case, we cannot make a general positive conclusion on IBA with the composition from the CEWEP report. Currently, we do not have the individual data needed to state how many of the 1706 samples (on which the 95percentile 3969 mg/kg in the CEWEP report is based) are below 3000 or 3500 mg/kg. As a consequence, currently we conclude that MSWI bottom ash with Pb amounts lower than 3500mg/kg will present no HP10 hazard.

Note that according to Commission regulation (EU) 2019/1179 published on 19 July 2016 (shall apply from 1 March 2018) regarding to Pb substance, “in view of the lack of certainty regarding the bioavailability of lead in the massive form, a distinction needs to be made between the massive form (particle size more than or equal to 1 mm) and the powder form (particle size of less than 1 mm). It is therefore appropriate to introduce a specific concentration limit (SCL) of $\geq 0.03\%$ for the powder form and a generic concentration limit (GCL) of $\geq 0.3\%$ for the massive form.” It implies that for Pb (CAS No 7439-92-1), a distinction needs to be made between lead powder (particle diameter <1mm) and lead massive (particle diameter > 1mm).

The new commission proposal implies that data is needed on the metallic lead content as well as on the particle size distribution of the metallic lead (<1mm and > 1mm). Such data are currently unavailable and most probably very challenging to obtain. Current assessment on HP 10 makes no distinction between the powder and the massive form of Pb. The assessment was done using 0.3% limit for HP 10 H360 (not 0.03% as it will be required for the assessment of the powder forms of Pb).

HP 8. Corrosive. Tier 3 assessment

- The additive hazard of all relevant substances for HP 8 has to be considered. In Tier 2, the total hazard index for HP 8 was calculated to be 2.24 with dominant contributions from Na (1.08), K(0.48), S(0.48) and Zn(0.26), see Table 30 for the individual hazard indices and most hazardous substances of these elements are Na₂S, KHF₂, H₂SO₄ and ZnCl₂. Analysis of Na₂S stability shows that this substance auto-ignites at temperatures higher than 480 °C and, therefore, Na will not be present in this substance in MSWI bottom ash (<https://pubchem.ncbi.nlm.nih.gov/compound/237873#>). As additional argument, literature data [18], [19] were used to calculate how much sulfur and other elements can be bound by minerals (calcite, quartz, ettringite, hematite, weddellite, gibbsite, goethite=lepidocrocite, halotrichite, coquimbite, melanterite, rostitite and gypsum) that were reported to be present in several waste materials. Concentrations of these minerals were also quantified in these references. Based on the data from this selected literature, our calculations show that all S that is present in bottom ash and all Si that is present in bottom ash will be bound by these minerals. Therefore there will be no additional S or additional Si left to form any possible hazardous forms that would need S or Si (calculations shown in Annex I). Thus H₂SO₄ can be eliminated from the HP 8 assessment too, also because it cannot exist at the pH range met in the MSWI bottom ash.
- NaCl is considered to be the only stable substance of Na in bottom ash that is relevant for HP 8. Leaching data for Na for the 5 UK and NL bottom ashes (Figure 2) show that in worst case, maximum 15% of the total Na in the bottom ash can be present in NaCl. For the remaining 85% of Na, there is no substance that is ascribed corrosive properties in the CLP. Therefore it can be concluded that the remaining 85% of total Na (27000mg/kg) will not contribute to possible corrosive hazard.

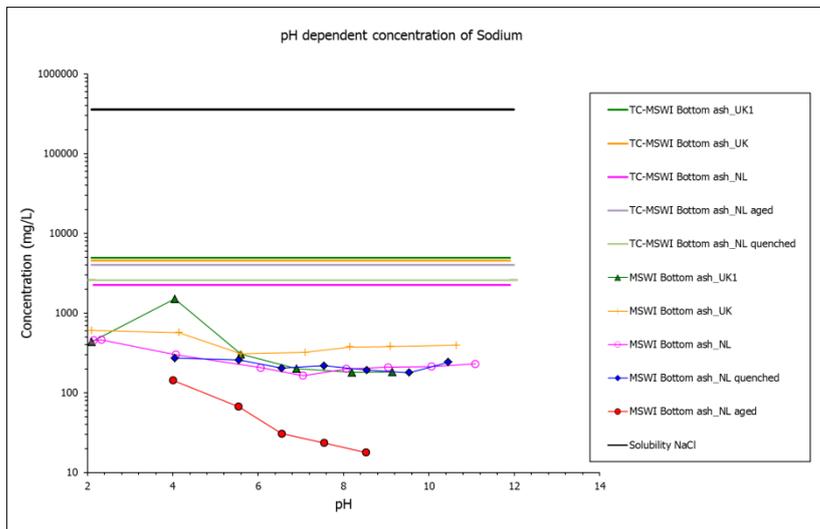


Figure 2: pH dependent concentration of Na. Coloured horizontal lines in the figure indicate the total content of Na in the samples of several different MSWI bottom ashes. The black solid horizontal line represents NaCl solubility as a function of the pH. The coloured data points represent the measured solubility of Na as a function of pH.

- $ZnCl_2$ is known to be very soluble in water, and any $ZnCl_2$ present will be readily dissolved when the MSWI bottom ash is quenched in the MSWI facility. Subsequently, the dissolved Zn will precipitate in Zn (hydr)oxides, of which $Zn(OH)_2$ or a very similar form is most likely to precipitate (Dijkstra et al., 2009). Therefore, $ZnCl_2$ cannot be considered as the most probable substance of Zn and will be replaced by $Zn(OH)_2$ to recalculate the total hazard index.

All above considerations reduce the total hazard index for HP 8 from 2.24 to 0.94 with most contributions from, K as KHF_2 (HI=0.48), Na as NaCl (HI=0.24) and Zn as $Zn(OH)_2$ (HI=0.19). In total these individual hazard indices results in 0.94 as the resulting hazard index for HP 8 than is already less than 1 still assuming the worst case compound for K as KHF_2 . Similar analysis as for Na, can be done also for K. However, since the total hazard index is already less than 1 indicating that HP 8 presents no hazard, HP 8 assessment can be stopped without further analysis. Further analysis of K or other compounds would result in even lower hazard index for HP 8.

HP 4. Irritant. Tier 3 assessment

Since MSWI bottom ash presents no HP 8 corrosive hazard, the assessment of HP 4 irritant can continue. The additive hazard of all relevant substances for HP 4 has to be considered. In Tier 2, the total hazard index for HP 4 was calculated to be 9.08 (from all different types of hazard together) with dominant contributions from Ca (2.63), Fe(2.56) and S(2.42) each of them already exceeding 1. For more detailed assessment, next considerations can be taken into account:

- Mass balance calculations (described in HP 8 assessment, also Annex I), that shows that no S is available to form any possible hazardous substances of S. Therefore no S substances will contribute to possible irritant hazard.

- Geochemical modelling and literature data show that ettringite consumes 11% of total Ca, calcite – bounds 26% of total Ca and laumontite that bounds 23% of total Ca that are not known for their irritant properties according to the CLP. The remaining 40% of total Ca are in unknown. Therefore contributions of Ca to the possible irritant hazard will be calculated using only 40% of the total Ca. [15], [18], [19]

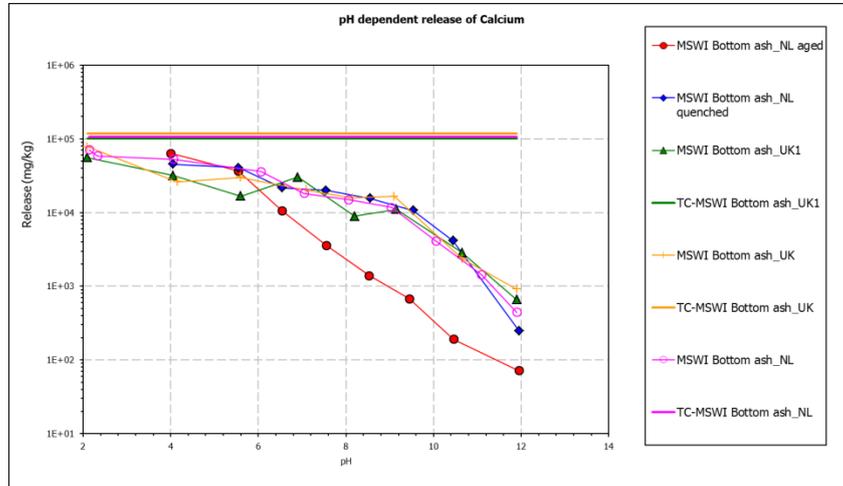


Figure 3: pH dependent release of Ca. Coloured horizontal lines in the figure indicate the total content of Ca in the samples of several different MSWI bottom ashes. The coloured data points represent the measured solubility of Ca as a function of pH.

- Leaching data of iron shown that at pH=2 about 10% of the total Fe is dissolved (Figure 4). The remaining 90% of total iron is in unknown substances, but most probably present as metallic iron [15]. Since metallic Fe is not among CLP substances with HP 4 hazard, it can be concluded that it gives no contribution to possible irritant hazard and can be ignored when calculating the total hazard index for HP 4. To have more general picture on the metallic Fe content in European MSWI bottom ash, it is recommended to gather more data on this.

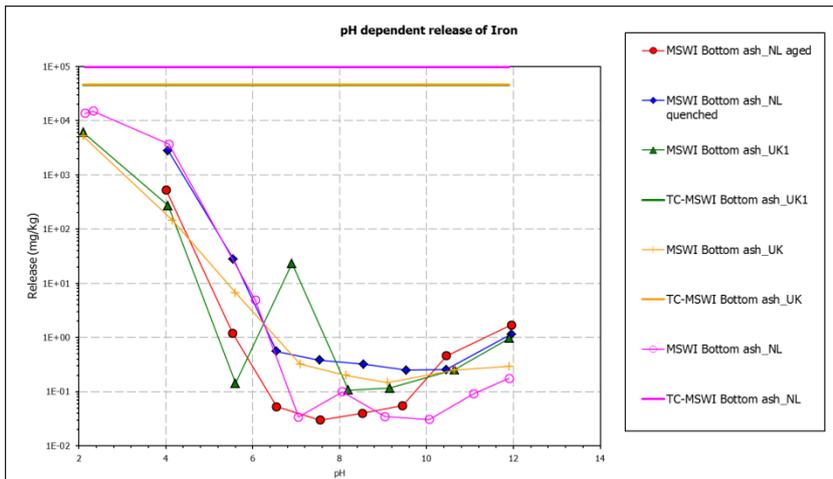


Figure 4: pH dependent release of Fe. Coloured horizontal lines in the figure indicate the total content of Fe in the samples of several different MSWI bottom ashes. The coloured data points represent the measured solubility of Fe as a function of pH.

With these considerations, the recalculated total hazard indices become equal to:

0.33 < 1 for H318 (eye damage, 10% total limit)

0.91 < 1 for H315+H319 (skin irritant and eye irritant, 20% total limit)

negligible contribution from H314 1A (skin corrosion, 1% limit) with 0.0002 as hazard index for $\text{Na}_2\text{Cr}_2\text{O}_7$, CrVI present in amount 0.8mg/kg

Since the total hazard indices are each less than 1 for every hazard type defined under HP 4, based on the above arguments it can be concluded that MSWI bottom ash will not be classified as hazardous by HP 4.

2.2.5 Summary Tier 3

Detailed analysis of HP 7 (carcinogenic), HP 8 (corrosive), HP 4 (irritant) reveals that MSWI bottom ash can be classified as non-hazardous with respect to each of these HPs. For the time being no general conclusion is made on HP 10 (toxic for reproduction), however it can be concluded that samples with Pb content below 3500mg/kg present no toxic for reproduction hazard.

2.2.6 Conclusions and recommendations from tiered approach

Conclusions

In Tier 1, general screening of relevant hazard properties was performed. As a result HP 1 (explosive), HP 2 (oxidising), HP 3 (flammable), HP 9 (infectious) and HP 15 (yielding another substance) were excluded from the assessment.

Tier 2 excluded HP 5 (STOT/Aspiration), HP 6 (acute toxicity), HP 11 (mutagenic), HP 13 (sensitising).

Tier 3 resulted in the elimination of HP 7 (carcinogenic), HP 4 (irritant), HP 8 (corrosive). No general conclusion is made with respect to HP (10 toxic for reproduction), however it is concluded that samples with Pb content below 3500mg/kg present no toxic for reproduction hazard.

HP 14 (eco-toxic) assessment will be performed separately (paragraph 2.2.7).

Recommendations

In relevance to HP 10 (toxic for reproduction) assessment, for samples with high Pb levels (higher than 3500mg/kg) it is recommended to review and to explain the origin of high Pb levels. It is also recommended to find more information on possible Pb speciations in MSWI bottom ash. In relevance to HP 4(irritant) assessment, it is recommended to gather more data on metallic Fe content in MSWI bottom ash.

2.2.7 HP 14 (eco-toxic) assessment

Eco-toxic assessment focuses on the assessment of substances with the following hazard statement codes:

H400 – aquatic acute effects, very toxic to aquatic life, LC₅₀ <1mg/l (lethal concentration, at which half of the population is killed)

H410 – aquatic chronic effects category 1 - very toxic to aquatic life with long lasting effects, LC₅₀<1mg/l

H411 - aquatic chronic effects category 2 - toxic to aquatic life with long lasting effects, LC₅₀ in the range from 1 to 10 mg/l

H412 - aquatic chronic effects category 3 - harmful to aquatic life with long lasting effects, LC₅₀ in the range from 10 to 100 mg/l

H413 – aquatic chronic category 4 – may cause long lasting harmful effects to aquatic life

H420 – hazardous to the ozone layer.

The limit values and the corresponding criteria are mentioned in paragraph 1.3.14.

Since MSWI bottom ash is not a gas and also does not emit ozone layer depleting gases, H420 hazard is therefore not relevant for MSWI bottom ash. The assessment of HP 14 is thus based on assessing the possible hazard that could result from the presence of substances with H400, H410, H411, H412 and H413 hazard statement codes. The

analysis consists of two parts: part 1 - assessment based on total content, and part 2 – assessment based on leaching.

2.2.7.1 HP 14 (eco-toxic) assessment based on total content

In the assessment of HP 14 it is assumed that any substance that can be present in waste and that has hazard statement codes relevant for HP 14 (H400, H410, H411, H412) is present in its maximally possible concentration. This means that a substance consumes the entire amount of a limiting element to form this substance (see text in paragraph 2.2.3 before Example 1). Subsequently, the stability of all relevant substances is checked and the 4 methods that are referred to in 1.3.14 for HP 14 assessment are applied for the same set of substances. In a view of recent discussions on eco-toxicity assessment methods, a separate method 5, that combines methods 1 and 2 from paragraph 3.14 (criteria as defined in method 1 with cut-off values from method 2), is considered as well [9]. In the current assessment, since M-factors are not defined for all substances with the relevant eco-toxic hazard, but only for some of them, M-factors for all substances are assumed to be 1 for all 5 methods. It is considered as a first simple hypothesis that represents the “best case” for M-factors as any M-factors greater than 1 will only increase the exceedance of limit values. In addition, assuming all M=1 allows us to rank the substances based purely on their worst case concentrations, from highest concentration to lowest. This in turn allows us to focus on the eco-toxic contributions from the substances that, being present at highest concentrations, contribute most to the summation. A disadvantage of setting all M-factor to 1 is that the impact from M-factors is omitted.

Based on the worst-case analysis of approximately 200 substances that have eco-toxic hazards (extracted from the INERIS database), Cu as CuCl, Zn as ZnO, Pb as $Pb_3(PO_4)_2$ and Ni as $Ni_3(PO_4)_2$ are the most critical substances, i.e. substances that can be present in the highest amounts for each of these metals. Therefore, they mostly determine the conclusions on eco-toxicity for each of applied methods. In order to keep mass balance it is assumed that all Cu, Zn, Pb and Ni form only the substances that are present in the highest amounts: all total Cu, Zn, Pb and Ni are only present as CuCl, ZnO, $Pb_3(PO_4)_2$ and $Ni_3(PO_4)_2$. These substances are not (and cannot be) proven to be present in the bottom ash but since it can also not be proven that they are not present, the worst-case approach is the only way to assess HP 14. In reality, Cu, Zn, Pb and Ni are most probably distributed over more than one substance in the bottom ash. Based on the current insights as explained in the HP10 section, speciation calculations are not sufficiently discriminative to draw conclusions on the amounts, actual presence and distribution of the different (combination of) minerals in MSWI bottom ash.

Application of methods 1-5 as defined in paragraph 3.14 shows that the criteria defined by each of these methods are not met even considering the “best case” for M-factors (all equal to 1) for methods 2 and 4.

All of the proposed methods fail on the criterion that involves substances with H410 statement code (aquatic chronic 1).

Methods 1, 3 and 5 lead to an exceedance of at least one order of magnitude in comparison with the limit values (25% or 0.1%). It will be very difficult to meet the limit value for these methods by further assessing the relevant substances and the potential distribution of elements over different substances because the exceedance is mainly determined by the factors 100 and 10 in the corresponding criteria for H410 substances. Comparison of methods 1 and 5 shows that the introduction of cut-off values to method 1 did not have a substantial effect (319% versus 25% limit from method 1 and 284% versus 25% limit in method 5, see Table 36). However, the introduction of cut-off values helps to narrow down the potential list of substances that should be considered for classification.

For methods 2 and 4, the limit values are exceeded to a much lesser extent: concentration of worst-case substances is 28% for method 2 (limit value is 25%) and 3.1% for method 4 (limit value is 2.5%). If either method 2 or 4 will be chosen eventually (with M-factors all equal to 1), further assessment to identify the quantitative speciation of elements is recommended to obtain a more realistic assessment for HP 14.

For all of the methods, the knowledge of the metallic (free) content of Cu, Ni, Zn and Pb would improve the basis HP 14 classification and is relatively straightforward to include (in comparison with investigations on the detailed quantitative analyses of substances in the bottom ash). Once the amount of metallic Cu, Ni, Zn and Pb is known, this amount can be subtracted from the total content that is currently used to assess HP 14. The amount of metallic Pb will need to be assessed against the generic entry in the CLP. Therefore, it is recommended to perform measurements on the metallic content of Cu, Ni, Pb and Zn in MSWI bottom ash. Such assessment may change the conclusions for methods 2 and 4, but most probably not for the other methods (if the factors 100 and 10 remain relevant).

Table 36: Assessment of HP 14 based on total content

| Method 1 | H400 | H410 | H411 | H412 | H413 | H420 | Concentration limit, % | Result worst case, % | Remark |
|-----------------|------|------|------|------|------|------|------------------------|----------------------|---|
| no Σ | | | | | | 1 | 0.1 | - | No M factors |
| Σ | 1 | | | | | | 25 | 8.2 | |
| Σ | | 100 | 10 | 1 | | | 25 | 318.7 | |
| Σ | | 1 | 1 | 1 | 1 | | 25 | 7.0 | No cut-off values |
| Method 2 M=1 | H400 | H410 | H411 | H412 | H413 | H420 | Limit, % | Result worst case | |
| no Σ | | | | | | 1 | 0.1 | - | H400, H410: cut-off 0.1% H411, H412: cut-off value 1% M=1 |
| no Σ | 1 | | | | | | 0.1/M | | |
| Σ | M | | | | | | 25 | 8.2 | |
| no Σ | | 1 | | | | | 0.1/M | | |
| no Σ | | | 1 | | | | 1 | | |
| Σ | | 10M | 1 | | | | 25 | 28.0 | |
| Method 3 | H400 | H410 | H411 | H412 | H413 | H420 | Limit, % | Result worst case | |
| no Σ | | | | | | 1 | 0.1 | - | No M factors |
| Σ | | 1 | | | | | 0.1 | 3.1 | |
| Σ | | | 1 | | | | 2.5 | 0.4 | |
| Σ | | | | 1 | | | 25 | 3.3 | No cut-off values |
| Σ | | | | | 1 | | 25 | 0.2 | |
| Method 4 M=1 | H400 | H410 | H411 | H412 | H413 | H420 | Limit, % | Result worst case | |
| no Σ | | | | | | 1 | 0.1 | - | M=1 No cut-off values |
| Σ | | M | | | | | 2.5 | 3.1 | |
| Σ | | | 1 | | | | 25 | 0.4 | |
| Method 5 | H400 | H410 | H411 | H412 | H413 | H420 | Limit, % | Result worst case | |
| no Σ | | | | | | 1 | 0.1 | - | M 1 with cut-offs from M 2 |
| Σ | 1 | | | | | | 25 | 8.2 | |
| Σ | | 100 | 10 | 1 | | | 25 | 283.5 | |
| Σ | | 1 | 1 | 1 | 1 | | 25 | 6.0 | |

2.2.7.2 Alternative HP 14 (eco-toxic) assessment based on leaching

The assessment of HP 14 based on the total content is a substantial overestimation of the perceived eco-toxic risks that a material as MSWI bottom ash exhibits. As an alternative approach, according to the view of ECN and Danish Waste Solutions, the eco-toxicity of substances is only of relevance for substances that can be present in the water phase because then they are potentially bio-available and able to pose eco-toxic hazards. In addition, the ECHA document of 2015 "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 4.1, issued in June 2015, Part 4 (environmental hazards), discusses 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, two cases were checked and presented below: 1) when the HP 14 assessment is based on leaching data at pH=2 (maximum amount that can leach out and 2) using leaching data in the pH range 7-12 (in the range of native pH).

The results of the assessment based on the leached amounts at pH=2 are given in Table 37. Availability data at pH=2 (data from Table 3.3 in CEWEP report of 2013 [1]) were used to perform an alternative HP 14 assessment based on the leached amount of relevant elements (replacing the total content of these elements by their concentration from leaching data at pH=2).

Table 37: Assessment of HP 14 based on data from leaching tests at pH=2.

| Method 1 | H400 | H410 | H411 | H412 | H413 | H420 | Concentration limit, % | Result worst case, % | Remark |
|-----------------|------|------|------|------|------|------|------------------------|----------------------|--|
| no Σ | | | | | | 1 | 0.1 | - | No M factors No cut-off values |
| Σ | 1 | | | | | | 25 | 1.2 | |
| Σ | | 100 | 10 | 1 | | | 25 | 100.0 | |
| Σ | | 1 | 1 | 1 | 1 | | 25 | 2.3 | |
| Method 2 M=1 | H400 | H410 | H411 | H412 | H413 | H420 | Limit, % | Result worst case | |
| no Σ | | | | | | 1 | 0.1 | - | H400, H410: cut-off 0.1% H411, H412: cut-off value 1% |
| no Σ | 1 | | | | | | 0.1/M | | |
| Σ | M | | | | | | 25 | 1.2 | |
| no Σ | | 1 | | | | | 0.1/M | | |
| no Σ | | | 1 | | | | 1 | | |
| Σ | | 10M | 1 | | | | 25 | 9.6 | |
| Method 3 | H400 | H410 | H411 | H412 | H413 | H420 | Limit, % | Result worst case | |
| no Σ | | | | | | 1 | 0.1 | - | No M factors No cut-off values |
| Σ | | 1 | | | | | 0.1 | 1.0 | |
| Σ | | | 1 | | | | 2.5 | 0.0 | |
| Σ | | | | 1 | | | 25 | 1.3 | |
| Σ | | | | | 1 | | 25 | 0.0 | |
| Method 4 M=1 | H400 | H410 | H411 | H412 | H413 | H420 | Limit, % | Result worst case | |
| no Σ | | | | | | 1 | 0.1 | - | No cut-off values |
| Σ | | M | | | | | 2.5 | 1.0 | |
| Σ | | | 1 | | | | 25 | 0.0 | |
| Method 5 | H400 | H410 | H411 | H412 | H413 | H420 | Limit, % | Result worst case | |
| no Σ | | | | | | 1 | 0.1 | - | M 1 with cut-offs from M 2 |
| Σ | 1 | | | | | | 25 | 1.2 | |
| Σ | | 100 | 10 | 1 | | | 25 | 97.5 | |
| Σ | | 1 | 1 | 1 | 1 | | 25 | 2.3 | |

As one can see from Table 37, when HP 14 assessment takes availability data as a basis in the assessment, this resulted in different conclusion when Methods 2 and 4 (non-hazardous) and Methods 1, 3 and 5 (hazardous) are applied. As in the previous step, methods 1, 3 and 5 fail on the criterion that involves substances with H410 statement code (aquatic chronic 1).

Table 38 presents the results of the assessment when it is done taking the leached amount at the pH range 7-12 as a basis.

Table 38: Assessment of HP 14 based on data from leaching tests at pH range 7-12.

| Method 1 No M factors | H400 | H410 | H411 | H412 | H413 | H420 | Concentration limit, % | Result worst case, % | Remark |
|--------------------------------------|------|------|------|------|------|------|------------------------|----------------------|--|
| no Σ | | | | | | 1 | 0.1 | - | No M factors No cut-off values |
| Σ | 1 | | | | | | 25 | 1.2 | |
| Σ | | 100 | 10 | 1 | | | 25 | 4.5 | |
| Σ | | 1 | 1 | 1 | 1 | | 25 | 1.3 | |
| Method 2 M=1 | H400 | H410 | H411 | H412 | H413 | H420 | Limit, % | Result worst case | |
| no Σ | | | | | | 1 | 0.1 | - | H400, H410: cut-off 0.1% H411, H412: cut-off value 1% |
| no Σ | 1 | | | | | | 0.1/M | | |
| Σ | M | | | | | | 25 | 1.2 | |
| no Σ | | 1 | | | | | 0.1/M | | |
| no Σ | | | 1 | | | | 1 | | |
| Σ | | 10M | 1 | | | | 25 | 0.0 | |
| Method 3 No M factors | H400 | H410 | H411 | H412 | H413 | H420 | Limit, % | Result worst case | |
| no Σ | | | | | | 1 | 0.1 | - | No cut-off values |
| Σ | | 1 | | | | | 0.1 | 0.0 | |
| Σ | | | 1 | | | | 2.5 | 0.0 | |
| Σ | | | | 1 | | | 25 | 1.3 | |
| Σ | | | | | 1 | | 25 | 0.0 | |
| Method 4 M=1 | H400 | H410 | H411 | H412 | H413 | H420 | Limit, % | Result worst case | |
| no Σ | | | | | | 1 | 0.1 | - | No cut-off values |
| Σ | | M | | | | | 2.5 | 0.0 | |
| Σ | | | 1 | | | | 25 | 0.0 | |
| M5: M 1 with cut-offs from M 2 | H400 | H410 | H411 | H412 | H413 | H420 | Limit, % | Result worst case | |
| no Σ | | | | | | 1 | 0.1 | - | H400, H410: cut-off 0.1% H411, H412: cut-off value 1% |
| Σ | 1 | | | | | | 25 | 1.2 | |
| Σ | | 100 | 10 | 1 | | | 25 | 1.3 | |
| Σ | | 1 | 1 | 1 | 1 | | 25 | 1.3 | |

The results show that when leaching data at pH range 7-12 is considered for the evaluation of eco-toxicity, the assessment reveals that MSWI bottom ash presents no eco-toxicity hazard.

In summary, comparing the outcome of three cases where the HP 14 assessment is done based on the total content, based on the availability data and based on the leached amounts at pH 7-12 (M factors assumed to be 1 in all three cases), the HP 14 assessment reveals:

- MSWI bottom ash as hazardous by HP 14 by each of 5 methods when the assessment is done based on the total content;
- MSWI bottom ash as non-hazardous with respect to HP 14 by method 2 and method 4, and hazardous by each of methods 1, 3 and 5, when availability data (pH=2) are taken as basis in the assessment
- MSWI bottom ash as non-hazardous with respect to HP 14 by each of 5 methods when the assessment takes leaching data at (close to) native pH (range 7-12) as a basis in the assessment.

A point for discussion here is the influence of M-factors for all the relevant substances on the HP14 assessment. This will be worthwhile only when the leached content is taken as a basis for the HP 14 assessment. Since using the leached content in the pH range 7-12, the limit values are not exceeded for all relevant substances with all M=1, it is a logical step to see how the result of the assessment will change when M-factors others than 1 will be taken into account. Preliminary assessment using M-factors 10 for all relevant substances showed that the methods involving M-factors (method 2 and method 4) indicate no eco-toxic hazard. Assuming the M-factors for all the substances to be 100 (overestimation, that however allows one to see the effect), the results indicated an eco-toxic hazard by methods 2 and 4. These assumptions assign equal "averaged" eco-toxic hazardousness for all relevant substances that allows us to see how the outcome of the summation methods will change. However, in order to have a realistic picture, the knowledge of the LC₅₀ values and proper M-factors for the individual substances are needed.

3

Conclusions and recommendations

MSWI bottom ash is currently regarded as a non-hazardous material by most Member States. The material is recycled in different construction works in several Member States for decades. As such, this practice helps to replace virgin materials and is in line with the circular economy strategy of Europe. Hazard classification of MSWI bottom ash is closely linked to storage, transportation, disposal, recycling, landfilling requirements and associated costs. Incorrect classification can lead to environmental and economic impacts. Because of ongoing developments in criteria for hazard classification, the European bottom ash industry requested ECN to revise the existing classification of MSWI bottom ash.

A tiered approach was applied to perform a revised hazard classification of European MSWI bottom ash. The 95 percentile concentration of a substantial dataset containing information from several Member States was taken as a basis for classification. The choice of the 95percentile concentration was made to cover the majority of element concentrations in different samples across Europe.

In Tier 1, a general screening of relevant hazard properties was performed. As a result HP 1 (explosive), HP 2 (oxidising), HP 3 (flammable), HP 9 (infectious) and HP 15 (yielding another substance) were excluded from the assessment. Assessment of Tier 2 involved a worst-case approach and excluded HP 5 (STOT/Aspiration), HP 6 (acute toxicity), HP 11 (mutagenic), HP 13 (sensitising).

Tier 3 resulted in the elimination of HP 7 (carcinogenic), HP 4 (irritant) and HP 8 (corrosive). The results showed that bottom ash samples with a total Pb concentration below 3500 mg/kg present no HP 10 (toxic for reproduction) hazard. The 95 percentile concentration of Pb is 3969 mg/kg and part of the individual samples from this dataset are, therefore, critical towards the limit value. Possibly, the dataset contains outliers

and/or individual samples that were not (or insufficiently) processed to remove (non-) ferrous metals before analyses.

It should be noted that the current assessment on HP 10 makes no distinction between the powder and massive (not considered hazardous) form of metallic Pb, as shall apply from March 2018 according to ATP 9 to the CLP.

HP 14 (eco-toxic) assessment was performed using five different calculation methods. Four calculation methods were already proposed by the Commission. The fifth method includes a new proposal from the Commission that combines methods 1 and 2 (criteria as defined in method 1 with cut-off values from method 2). Since M-factors are not defined for all substances with the relevant eco-toxic hazard, but only for some of them, M-factors for all substances are assumed to be 1 for all five methods. It was considered as a first simple hypothesis that represented the “best case” for M-factors as any M-factors greater than 1 would only increase the exceedance of limit values. With these assumptions, methods 1, 3 and 5 lead to an exceedance of at least one order of magnitude in comparison with the limit values. For methods 2 and 4, the limit values are exceeded to a much lesser extent, but nevertheless, all five methods concluded that HP14 was a relevant HP for MSWI bottom ash (based on the total content of elements). Based on these results, it is also concluded that considerations on M-factors higher than 1 will not lead to different conclusions for HP 14.

An alternative assessment for HP 14 was proposed in this report. This alternative approach takes the leached concentrations into account rather than the total content. Exposure to the eco-toxic effects (aquatic acute and chronic) can only be in the water phase, i.e., the substances should be in solution first in order to exert a potential effect. This pathway is also described in the ECHA guidance on the application of the CLP criteria (Part 4, Annex IV, pp. 489 and 580). Therefore, exposure from eco toxic substances is limited by their solubility and availability in the water phase.

As a first example, leaching data was considered and two possible starting points were assessed: the maximum leachable concentrations at pH 2 was taken as a worst case starting point. In addition, the actual leached concentrations in the pH domain from 7 to 12 (generally much lower concentrations than observed at pH 2) was considered.

This assessment resulted in the following:

- MSWI bottom ash would be considered as non-hazardous with respect to HP 14 by method 2 and method 4, and hazardous by each of methods 1, 3 and 5, when availability data (pH 2) are taken as basis in the assessment.
- When the assessment takes leaching data in the pH domain from 7 to 12 as a basis for the assessment, MSWI bottom ash would be considered non-hazardous waste with respect to HP 14 by each of the 5 methods. All M-factors were considered to be 1 in this assessment. When leaching would be the basis for assessment of HP 14, additional discussion on the M-factors would also be of relevance for HP 14.

In relation to this, it should be stressed that assessments based on total content or availability (maximum leached under extreme conditions, pH 2) are always a worst-case assessment. In other legislations that aim to protect ecosystems (e.g., EU landfill directive, Dutch soil quality decree, EU construction products regulation, etc.) actual leached concentrations at the native pH (i.e., using a percolation leaching tests) are used as a basis for the assessment of the true impact on ecosystems using impact

assessment modelling (risk based approach). **Hence, a risk based approach is preferred over a worst-case hazard based assessment, that may ultimately limit the reuse of waste materials in a circular economy.**

Recommendations to the Commission

- Consider next to the proposed methods for HP14 also a risk based approach (leaching data) for classification. At least give Member states the opportunity to implement this in their state.

Recommendations to EfW

- With respect to HP 10 (toxic for reproduction), it is recommended to review and to explain the origin of the high Pb concentrations in part of the dataset. The main reason for this is the substantial difference between the average (1309mg/kg), median (1058mg/kg) and the 95 percentile (3969mg/kg) data for Pb, The aim of that work would be to check whether a more general conclusion on HP10 for MSWI bottom can be made.
- ATP 9 to the CLP (applicable from 1 March 2018) suggest that *“in view of the lack of certainty regarding the bioavailability of lead in the massive form, a distinction needs to be made between the massive form (particle size more than or equal to 1 mm) and the powder form (particle size of less than 1 mm). It is therefore appropriate to introduce a specific concentration limit (SCL) of $\geq 0,03$ % for the powder form and a generic concentration limit (GCL) of $\geq 0,3$ % for the massive form”*. In order to apply these requirements, additional measurements on the metallic Pb content and the particle size distribution of this Pb fraction is needed.
- It is recommended to discuss the proposed leaching based approach for HP14 with the Commission and other stakeholders to check whether they see a basis for further discussion on this topic.
- For HP 4 (irritant), the metallic Fe content was estimated based on a few samples. Therefore, it is recommended to gather more data on the metallic Fe content in MSWI bottom ash.
- If there are bottom ash samples available with a pH higher than 11.5 (relevant for HP4 and HP8), it is recommended (although not strictly required by the WFD) to apply the buffering capacity test (“Young test”) for these samples. All pH and buffering capacity data at ECN involves bottom ash samples that already have a pH value of <11.5.

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Annex I. Mass balance calculations

Literature data [15],[18], [19] on concentrations of some minerals that are present in bottom ash are used for mass balance calculations. Mass balance calculations aim to estimate how much of each element can be bound in these minerals. The remaining amount (not bound in minerals) is thus available to form possible hazardous substances of these elements. As it can be seen from the calculations (Table A1), all Si and S that are present in the bottom ash, are already bound by the minerals listed in Table A1: negative values in the last column of Table A1 shall be understood as there is zero amount of this element left to form any possible hazardous substances involving this element. Thus based on the mass balance calculations none of possible hazardous substances that involve Si or S elements, can be formed.

Table A1. Mass balance calculations

| Minerals [18], decreasing frequency, that are observed often then 1% | Mineral | webmineral.com g/mol | Concentration fresh BA, % from [19] and adjusted with data from [15] | % of an element bound in each mineral | Element | Total bound in all minerals, % | MASS BALANCE: total minus bound in minerals |
|--|--------------------------|----------------------|--|---------------------------------------|---------|--------------------------------|---|
| Calcite (20%) | CaCO3 | 100 | 3 | 1.20 | Ca | 5.06 | 8.02 |
| Quartz (18%) | SiO2 | 60 | 31.4 | 14.70 | Si | 14.70 | -5.31 |
| Ettringite (10%) | Ca6Al2(SO4)3(OH)12*26H2O | 1255 | 1 | 0.08 | S | 0.04 | 7.12 |
| | | | | 0.04 | Al | 1.02 | -0.23 |
| | | | | 0.19 | Ca | 0.63 | 5.24 |
| Anhydrite (6%) | CaSO4 | 136 | 3.2 | 0.94 | Ca | | |
| | | | | 0.75 | S | | |
| Hematite (6%) | Fe2O3 | 160 | 1.9 | 1.33 | Fe | | |
| Weddellite (5%) | CaC2O4*2H2O | 165 | | | | | |
| Gibbsite (4%) | Al(OH)3 | 81 | | | | | |
| Goethite (4%) = lepidocrocite | FeO(OH) | 89 | 1 | 0.63 | Fe | | |
| Halotrichite (3%) | FeAl2(SO4)4*2H2O | 890 | | | | | |
| Coquimbite (2%) | Fe2(SO4)3*9H2O | 562 | | | | | |
| Melanterite (2%) | FeSO4*7H2O | 314 | | | | | |
| Rostite (2%) | Al(SO4)(OH)0.8*5(H2O) | 231 | | | | | |
| Gypsum (2%) | CaSO4*2H2O | 172 | 1 | 0.23 | Ca | | |
| | | | | 0.19 | S | | |
| Zeolites (2%) | | | | | | | |
| gismondine | Ca2Al4Si4O16*9H2O | 719 | | | | | |
| laumontite | CaAl2Si4O12*4H2O | 470 | From [15] | 2.50 | Ca | | |
| boggsite | Ca8Na3(Si)96O192*70H2O | 1846 | | | | | |

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