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HAZARD PROPERTY CLASSIFICATION OF HIGH TEMPERATURE WASTE MATERIALS

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SUMMARY: A three-tiered approach to classification of incinerator bottom ash (IBA) from grate furnace installations incinerating non-hazardous waste under the proposed new EU regulations for hazard assessment of waste with reference to the new chemicals legislation has been established and applied to European IBA, based on 95 percentile values of composition data obtained for up to 1700 bottom ashes from 9 European countries. Tier 1 is a screening based on gross characteristics of the waste, Tier 2 is a conservative assessment based on total composition data, whereas Tier 3 is a more precise assessment of the hazardous properties and substances not eliminated in Tiers 1 and 2, based on leaching data and chemical speciation modelling. With a few reservations for properties for which no test methods currently exists, the results indicate that European IBA at 95 percentile level will be non-hazardous when applying this procedure to the proposed revised classification rules.

1. INTRODUCTION

The assessment of the hazardousness of wastes in relation to their classification as non-hazardous or hazardous is done based on Commission Decision 2000/532/EC on the List of Waste (LOW) and Annex III to Directive 2008/98/EC on waste (the revised Waste Framework Directive), which defines the properties that may render waste hazardous.

Both pieces of legislation are currently under review. The main purpose of the review is to adapt the legislation to technical and scientific progress aligning it with the new chemicals legislation, i.e. Regulation (EC) No. 1272/2008 (CLP regulation). Some of the rather significant challenges associated with classification of waste as hazardous or non-hazardous stem from the fact that the CLP regulation primarily addresses pure substances and mixtures of pure substances, not materials or wastes of complicated composition consisting of mixtures of numerous substances with properties that may change with the exposure conditions. Until now, the 15 hazardous properties in Annex III to Directive 2008/98/EC have been assessed with reference to risk phrases (R phrases) and limit values for individual substances in the Dangerous Substances Directive (67/548/EEC) and the rules in the Dangerous Preparations Directive (1999/45/EEC). New legislation is expected to enter into force on 1 June 2015.

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During a transitional period the old system can still be used, but from 2017 the R phrases will be fully withdrawn and replaced by the hazard statements (H statements and EUH statements) in Annex III to the CLP Regulation with reference to Table 3.1 (List of harmonised classification and labelling of hazardous substances) in Annex VI to the CLP. The “old” R phrases are also listed in Annex VI to the CLP.

Late in 2012 the EU Commission sent a proposal for amendments to Directive 2008/98/EC (unofficial draft of 7 November 2012) and Commission Decision 2000/532/EC (unofficial draft of 21 December 2012) to Member States. On 16 January 2013 (HP 14) the Commission proposed additional changes to Decision 2000/532/EC. The Commission plans to have the changes implemented into the legislation during 2013, following a vote by the Member States.

The consequences of the revision of the European waste classification legislation have not yet been assessed, and many stakeholders are concerned about whether or not specific waste types will be reclassified as compared to the classification under the existing legislation.

This paper presents an attempt at a hazardous property classification of European incinerator bottom ash (IBA) from grate furnace installations incinerating non-hazardous waste in accordance with the revised legislation as it is expected to appear. The paper describes a three-tiered methodology that can be applied also to other largely inorganic waste materials, in particular those produced at high temperatures. It should, however, be noted that following the meeting of the Technical Adaptation Committee in February 2013, the EU Commission changed the proposal to include the so-called M factors in the assessment of H14: Ecotoxicity. The methodology described here is based on the previous Commission proposal which did not apply M factors for H14 assessment, but it can easily be adjusted to include the M factors (although M factors for many relevant substances are not readily available). The EU Commission has proposed that at least during the transitional period M = 1 should be used when assessing H14 for substances for which no M factors have been established in the CLP (Burgués, 2013).

2. EUROPEAN INCINERATOR BOTTOM ASH (IBA)

In this context a general classification is carried out based on 95 percentile composition data on European IBAs, but the methodology described may also be used to classify sufficiently characterised IBA from specific incinerators.

Raw, untreated IBA as it appears at the incinerator after quenching or cooling, contains slag-like material, stones, soil, glass, concrete, tiles, porcelain, etc. in aggregate form as well as pieces of ferrous and non-ferrous (elemental) metals (aluminium, copper, lead, zinc) in various sizes. In most cases the ferrous metals and during later years also some of the non-ferrous metals are recovered on-site or at an off-site facility, regardless of the further fate of the IBA. If the IBA is landfilled, it is generally not subjected to further treatment. If the IBA is recovered for use e.g. as a road construction material, it will generally be crushed and sieved and then stored in heaps/rows in the open exposed to ambient conditions (ageing/carbonation) for one to six months or more (depending on conditions and regulatory requirements) prior to actual utilisation.

Most bottom ashes are strongly alkaline when they leave the quencher, and the uptake of carbon dioxide (which requires moist conditions) during storage will normally lower the pH of the IBA to 7.5 to 9.5. This has a strong influence on the leachability of several substances but does not generally not alter the gross composition of the IBA significantly. Due to the drastic changes in chemical conditions, some mineral changes may occur which in turn may lead to changes in speciation of some substances.

Table 1 shows data on the content of inorganic substances in European IBA obtained by combining information several countries (Belgium, Denmark, France, Ireland, Italy, The Netherlands, Sweden and UK, (Hjelmar et al., 2013)). Some information was also available on the content of organic substances in European IBA, but due to the high temperature at which IBA is produced, organic compounds and organo-metallic compounds covered by hazard statement codes are not expected to be present in concentrations that will render the IBA hazardous, and they have therefore been excluded from further assessment in this context.

Table 1. Content* of inorganic substances and a few other properties of European IBAs from grate furnace installations incinerating non-hazardous waste. N = no. of samples. Data on both processed and unprocessed IBA are included.

Substance	*Average*	*Median*	*Min*	*Max*	*Min 95% CL-*	*Max 95% CL+*	*95 Percentile*		*N*
	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	%	
Ca	130833	125586	50825	198289	58600	370130	190442	19.0	322
CO3	61073	59100	26160	103800	52660	69486	103404	10.3	38
Fe	58714	56703	34216	118220	38424	106400	103299	10.3	259
Si	82713	84180	61060	96078	10	115292	93898	9.4	129
Al	47232	44627	30527	75089	28020	112621	71620	7.2	311
Cl	9211	5943	3644	37633	2278	19252	37188	3.7	136
Na	21379	22270	12308	34791	6172	40841	32121	3.2	234
TOC	10092	9340	1350	42760	4330	21230	24664	2.5	1382
Mg	12429	11242	6377	34372	9141	33816	21025	2.1	287
K	7748	7595	4854	12722	3156	12919	11857	1.2	260
P	5633	5049	2531	12556	3302	10635	11773	1.2	220
Cu	3275	2510	738	17620	1494	6562	8863	0.89	1699
S	3862	3475	1310	16808	158	8159	7873	0.79	455
Ti	4244	4112	2873	7479	1174	7111	6636	0.66	262
Zn	3241	2871	1142	9370	1415	6158	6250	0.63	1697
C	3171	2919	1119	5702	1200	7147	5383	0.54	69
Pb	1309	1058	197	6441	530	3262	3969	0.40	1706
Ba	1102	958	760	2970	311	2529	2207	0.22	288
Mn	1173	1104	644	2248	547	2620	1965.3	0.20	313
PO4	248	10	10	1360	95	400	1311	0.13	38
F	148	71	13	1779	20	692	1219.5	0.12	78
Cr	353	315	115	852	73	883	754	0.075	1701
NO3	172	100	5	875	94	249	732	0.073	38
Ni	185	153	38	850	29	482	531	0.053	1696
Sn	181	154	52	737	36	339	519	0.052	335
B	198	183	30	532	271	370	401	0.040	191
Sr	271	270	267	369	283	377	356	0.036	136
Sb	73	63	18	250	5	164	159	0.016	612
NH4	53.3	46.5	5	131	72.5	133.8	128	0.013	43
NO2-	13	1	< 1	100			100	0.010	38
Co	31.8	23	11	103	10	116	91.1	0.0091	376
Br	44.7	42	23	95	18	117	80.6	0.0081	50
Mo	30.1	28	5	84	6	220	80.6	0.0081	533
V	41.2	36	19	248	4	105	76.3	0.0076	349
As	17.3	14.7	4.4	73.2	2.6	49.7	46.5	0.0047	1615
Ag	15.2	14.3	2.3	47.1	0.6	83	37.5	0.0038	127

Substance	*Average*	*Median*	*Min*	*Max*	*Min 95% CL-*	*Max 95% CL+*	*95 Percentile*		*N*
	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	%	
Tl	6.7	3.8	3.4	27.5	2	18	28.6	0.0029	137
Li	14	14	2	29	2	23	23	0.0023	92
Te	10	9.8	5.3	24.8	0.7	21	22	0.0022	49
Cd	4.8	4.3	1.1	117	2	32.9	13.9	0.0014	1661
Se	5.2	4.7	2.3	12.2	2	30	12.7	0.0013	145
Bi	2.1	0.05	0.05	11.3	0.1	9.3	7.4	0.00074	34
Hg	2.3	1.53	1.39	9.69	0.5	11	7.3	0.00073	316
Be	1.2	0.83	0.46	6.6	0.5	3.7	2.3	0.00023	162
CN	0.7	0.64	0.5	0.94	0.49	0.9	0.9	0.00009	50
Cr VI	0.5	0.5	0.3	0.8	0.3	0.8	0.8	0.00008	82
Sol frac %	2.5	2.6	1.4	4.2	2.3	2.8	4.1		31
LOI %	4.2	4.6	2.6	6	5.9	7	5.9		81
pH	10.86	10.78	9.28	12.13	9.37	12.6	11.74		1639

*: The chemical analytical data have been collected from many sources, and in most cases the analysis of several inorganic elements have been based on partial digestion using e.g. aqua regia or nitric acid rather than total digestion using e.g. HF+HNO_3+HCl. The former is often prescribed by legislation but does not completely dissolve silicates and elements embedded in silicates. A few of the results in the table, particularly those for silicate, while perfectly in line with legislation, including the CLP, will therefore not necessarily represent true totals.

2. HAZARDOUS PROPERTIES

Directive 2008/98/EC defines hazardous waste as waste which displays one or more of the hazardous properties listed in Table 2. The definitions in Table 2 have, however, not been taken from Annex III in the current version of Directive 2008/98/EC but rather from the Commission's proposal for amendments to Directive 2008/98/EC from November 2012 (unofficial draft of 7 November 2012).

Table 2. List of properties that render a waste hazardous.

HP code	*Hazardous property*
HP 1	Explosive: Wastes which are 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 wastes, explosive organic peroxide wastes and explosive self-reactive wastes are included.
HP 2	Oxidising: Wastes which may, generally by providing oxygen, cause or contribute to the combustion of other materials.
HP 3	Flammable: - flammable liquid wastes: liquid wastes having a flash point below 60℃ or waste gas oil, diesel and light heating oils having a flash point > 50℃ and ≤ 75℃; - 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℃ 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.
HP 4	Irritant: Skin irritant and eye damage: Wastes which on application can cause skin irritation or damage to the eye.
HP 5	Single target organ toxicity (STOT)/Aspiration:

HP code	*Hazardous property*
	Specific target organ toxicity (STOT)/Aspiration: Wastes which can cause specific target organ toxicity either from a single or repeated exposure, or which cause severe acute toxic effects following aspiration.
HP 6	Acute toxicity: Wastes that can cause acute toxic effects following oral or dermal administration or inhalation exposure.
HP 7	Carcinogenic: Wastes which induce cancer or increases its incidence.
HP 8	Corrosive: Wastes which on application can cause skin corrosion.
HP 9	Infectious: Waste containing viable micro-organisms or their toxins which are known or reliably believed to cause disease in man or other living organisms.
HP 10	Toxic for reproduction: Wastes which have adverse effects on sexual function and fertility in adult males and females, as well as developmental toxicity in the offspring..
HP 11	Mutagenic: Wastes which may cause a mutation, that is a permanent change in the amount or structure of genetic material in a cell.
HP 12	Release of an acute toxic gas cat. 1, 2 or 3: Wastes which release toxic gases cat. 1, 2 or 3 in contact with water or an acid.
HP 13	Sensitising: Wastes which contain one or more substances known to cause sensitising effects to the skin or the respiratory organs.
HP 14	Ecotoxic: Wastes which present or may present immediate or delayed risks for one or more sectors of the environment.
HP 15	Yielding another substance: Waste capable of exhibiting a hazardous property listed above not directly displayed by the original waste.

In the CLP, each of the HPs (H1 to H15) is associated with a number of Hazard Categories, each corresponding to a Hazard Statement Code. The properties of the waste, in this case IBA, should be considered under each of the HPs and each of the relevant Hazard Statement Codes (HSCs). In the Commission's proposal for amendments to Decision 2000/532/EC from 21 December 2012 (and January 2013), the relevant Hazard Categories and Hazard Statement Codes are listed for each HP. In the CLP, all substances to be considered under each HSC are listed.

3. HAZARDOUS PROPERTY ASSESSMENT OF IBA

3.1 General

The CLP was developed for assessment of products (pure chemicals or well-defined mixtures of chemicals) and is less suited for assessment of complex mixtures (e.g. mixtures of many substances like IBA). The total content as such of a substance in IBA is often a poor indicator of its hazardous nature. A tiered classification approach, that takes this into account is proposed and presented below. The tiered approach has been partly adopted from WRc (2012), where it was used under the existing waste classification legislation.

- Tier 1 is a screening process in which a high level assessment of the relevance of hazardous properties (HP1 to HP15) to IBA is carried out based on knowledge of the gross characteristics and composition of IBA.
- Tier 2 consists of further investigation of those hazardous properties not excluded in Tier 1 using a worst case assessment approach (e.g. assuming that the total amount of a substance is present in its most hazardous form of speciation).
- Tier 3 includes detailed investigation of any HPs and substances not eliminated in Tier 1 and 2 based on leaching data and chemical speciation calculations as well as assumptions on exposure conditions, leading to a final conclusion concerning the classification of (an) IBA as hazardous or non-hazardous.

3.2 Tier 1 assessment

At tier 1, screening HP 1 through HP 15, the following HPs are considered not to render IBA hazardous and hence not require further assessment:

- HP 1 (explosive)
- HP 2 (oxidising)
- HP 3 (flammable)
- HP 9 (infectious)
- HP 12 (release of an acute toxic gas)
- HP 13 (sensitising)
- HP 15 (yielding another substance)

In addition, H 304 (Asp. Tox. 1) under HP 5 does not need further consideration because it applies to liquids (IBA is not a liquid), and H 420 (Hazardous to the ozone layer) under HP 14 does not need further consideration because it applies to gases (and IBA is not a gas).

In relation to HP 3, Hazard Statement Code H 261: "In contact with water releases flammable gases", it is noted that strongly alkaline IBA containing elementary aluminium in contact with water may some-times develop hydrogen gas which can burn if it is ignited. There exists, however, no method for testing of the potential hydrogen gas production in relation to classification under HP 3 nor are there any limit values (it is expected that the EU Commission will ask CEN/TC 292 to develop an appropriate test method). Since treatment of IBA normally removes the aluminium and/or reduces the pH, treated IBA will not produce hydrogen. In addition, storing bottom ash moist in a confined space is undesirable. In view of the limited gas evolution, it is recommended to classify IBA as non-hazardous with respect to HP 3 at least until an appropriate test method and associated limit values are available. Practical guidance in handling IBA should encompass storage open to the atmosphere.

In relation to HP 12, Release of an acute toxic gas, it should be noted, that development of phosphine gas in the IBA management systems at some incinerators has been reported. It seems to be associated with the incineration of phosphorous-rich waste such as e.g. bone meal. However, in view of the current lack of prescribed methods of measurement and limit values, IBA is for the time being considered non-hazardous with respect to HP 12 with a strong recommendation to look further into and if possible prevent the development of phosphine.

3.3 Tier 2 assessment

3.3.1 Methodology

The remaining hazardous properties to be assessed at Tier 2 level are shown in Table 3 together with the associated Hazard Class and Category Codes and Hazardous statement codes (HSCs). Each of the HSCs has a cut-off value for single substances (i.e. if the concentration of a single substance listed under that HSC does not exceed the cut-off value, that substance does not have to be considered any further under that HSC) and/or one or more limit values for sums of the substances listed under that HSC or a combination of HSCs associated with a given HP. Cut-off values exist for all the HSCs shown in Table 3 except H 304 (HP 5) and the HSCs associated with HP 14 (H 400, H 410, H 411, H 412, H 413). Some of the concentration sums under HP 14 are further to be multiplied by 100 or 10 prior to comparison to the limit values which are given in the proposed amendment of Decision 2000/532/EC. The lowest cut-off value for any substance and any HSC is 0.1%.

The HPs considered relevant for IBA after Tier 1 (see Table 3) are evaluated further by substance and Hazard statement Codes by taking into account the concentration of the substance in the chemical formulations and assuming that the total concentration of a given substance/element is present as the compound described by the chemical formulation. The assessment is based on the 95 percentile of the content of substances in the dataset on European IBA shown in Table 1. For comparison, the (inorganic) substances associated with each of the HSCs are identified in the CLP and listed.

Subsequently, a number of substances on that list are excluded, either because they are not consistent with IBA, considering the combustion process and the redox and pH conditions under which the IBA is produced, or because they are present in concentrations that are low compared to the relevant cut-off values and single substance limit values for the various HSCs for the compounds in which they occur.

Table 3. Overview of remaining HPs and associated remaining HSCs to be assessed at Tier 2.

HP	Hazard Class and Category	HSC	HP	Hazard Class and Category	HSC
HP 4	Irritant (skin and eye)		HP 8	Corrosive	
	Skin corrosion 1A, 1B, 1C	H 314		Skin corrosive 1A	H 314
	Skin irritant 2	H 315		Skin corrosive 1B	H 314
	Eye damage 1	H 318		Skin corrosive 1C	H 314
	Eye damage 2	H 319			
HP 5	STOT/aspiration		HP 10	Toxic for reproduction	
	STOT SE 1	H 370		Repr. 1A	H 360
	STOT SE 2	H 371		Repr. 1B	H 360
	STOT SE 3	H 335		Repr. 2	H 361
	STOT RE 1	H 372			
	STOT RE 2	H 373			
HP 6	Acute toxicity		HP 11	Mutagenic	
	Acute Tox. 1 (Oral)	H 300		Mutagenic 1A	H 340
	Acute Tox. 2 (Oral)	H 300		Mutagenic 1B	H 340
	Acute Tox. 3 (Oral)	H 301		Mutagenic 2	H 341
	Acute Tox. 4 (Oral)	H 302			
	Acute Tox. 1 (Dermal)	H 310			
	Acute Tox. 2 (Dermal)	H 310			
	Acute Tox. 3 (Dermal)	H 311			
	Acute Tox. 4 (Dermal)	H 312			
	Acute Tox. 1 (Inhal.)	H 330			
	Acute Tox. 2 (Inhal.)	H 330			
	Acute Tox. 3 (Inhal.)	H 331			
	Acute Tox. 4 (Inhal.)	H 332			
HP 7	Carcinogenic		HP 14	Ecotoxic	
	Carcinogenic 1A	H 350		Aquatic acute 1	H 400
	Carcinogenic 1B	H 350		Aquatic chronic 1	H 410
	Carcinogenic 2	H 351		Aquatic chronic 2	H 411
				Aquatic chronic 3	H 412
				Aquatic chronic 4	H 413

STOT: Single/Specific Target Organ Toxicity   SE: Single exposure   RE: Repeated exposure

In this way a large number of the substances listed in Table 1 are eliminated as not being critical with respect to classification of IBA as hazardous. Only a few substances cannot be eliminated at this stage and have to be assessed in more detail for each of the remaining HPs. They are: Cu, Ni, Pb, Sn and Zn. These substances are therefore assessed for each remaining HP and the associated lists of substances for each HSC in the CLP.

3.3.2 Assessment of individual HPs

Tier 2 assessment for HP 4 (irritant): If the substances identified in the HSCs for HP4 would be assumed to be present as the critical compounds, then Zn as ZnCl2 would result in a classification as hazardous under HP4. Further assessment of HP 4 should therefore be carried out at Tier 3.

Tier 2 assessment for HP 5 (STOT/Aspiration): Since none of the substances exceed any of the limits specified under H370 – H373 and H335, HP 5 is not likely to render IBA hazardous. HP 5 will therefore not be considered further.

Tier 2 assessment for HP 6 (acute toxicity): HS codes H 300, H301, H302, H 310, H332, H312, H311 and H331 do not lead to classification of IBA under HP 6. Under H 330 $Li_2[Ni_{0.5}Co_{0.5}]_2O_2$ was identified as a possible critical compound associated with Ni, but due to the relatively low concentration of Li (0.0023%), this substance cannot exceed the limit value of 0.1% and hence no further evaluation of HP 6 is needed.

Tier 2 assessment for HP 7 (carcinogenic): HP 7 is of relevance to IBA when the compounds listed in HSCs are assumed to be present in IBA. Assessment of the classification of IBA in accordance with HP 7 needs to be taken forward to Tier 3 level.

Tier 2 assessment for HP 8 (corrosive): If all Zn in IBA is present as ZnCl2 this will render IBA hazardous with respect to HP 8. Assessment of the classification of IBA in accordance with HP 8 should be carried out at Tier 3 level to address the chemical form of Zn in IBA.

Tier 2 assessment for HP 10 (toxic for reproduction): Under HP 10 trilead bis(orthophosphate) is identified as a critical compound for Pb, which renders IBA hazardous, if all Pb is present as either of these compounds. Therefore a Tier 3 evaluation taking speciation into account is necessary.

Tier 2 assessment for HP 11 (mutagenic): Under H 340, none of compounds listed exceed the 0.1 limit. Under H 341, none of the compounds identified as containing Cu, Ni, Pb, Sn and Zn exceed the 1.0% limit, even if the total contents of the elements are present as these substances. Therefore, IBA can be considered non-hazardous with respect to HP 11, which is not considered any further.

Tier 2 assessment for HP 14 (ecotoxic): Under H 400 (aquatic acute), the sum of the concentrations of the relevant substances (which are $CuSO_4$, Cu_2O, $Ni(OH)_2$ and $ZnCl_2$) assuming all Cu, Ni and Zn is present as these compounds, comes to 15.4 %, which is less than the limit value of 25%. IBA is therefore not hazardous in relation to H 400. Based on the first Aquatic Chronic criterion with HS codes H 410, H 411 and H 412 covering Aquatic Chronic 1, 2 and 3, the mass to be compared with the limit value by combining the lowest and the highest values (depending on which of the copper, nickel and Zn compounds relevant for these HSCs are chosen, assuming all Cu, Ni and Zn is present as these compounds) ranges from 187 % to 417%, clearly exceeding the first Aquatic Chronic criterion (100 x sum c H410 + 10 x sum c H411 + c H 412) of 25 % and thereby rendering IBA hazardous under these assumptions. This implies that evaluation based on the second Aquatic chronic criterion based on Aquatic Chronic 1, 2, 3 and 4 is not needed at this stage. Further assessment of the classification of IBA with respect to HP 14 for Cu, Ni and Zn compounds should be carried out at Tier 3 level.

3.3.3 Summary of Tier 2 assessment

European IBAs are not likely to be rendered hazardous at the 95 percentile level by the following Hazardous Properties (which will not be further assessed):

- HP 5 (single target organ toxicity/aspiration)
- HP 6 (acute toxicity)
- HP 11 (mutagenic)

The IBA should be further assessed for the following HPs at Tier 3 level (critical chemical compounds listed):

- HP 4 (irritant): $ZnCl_2$
- HP 7 (carcinogenic): $NiSO_4$, $NiCO_3$, $NiCl_2$, $Ni(NO_3)_2$, $NiHPO_4$, $NiSiO_3$
- HP 8 (corrosive): $ZnCl_2$
- HP 10 (toxic for reproduction): $Pb_3(PO_4)_2$
- HP 14 (ecotoxic): various Cu, Ni, and Zn compounds

Since Sn is only appearing as organo-metallic substances in the H codes, it is not considered a critical substance for IBA hazard assessment.

3.4 Tier 3 assessment

3.4.1 Methodology

The main problem of applying the CLP to complex mixtures such as IBA is that IBA consists of a multitude of different substances and minerals, and although the composition of IBA is largely known in terms of elements (see Table 1), it is very difficult to determine whether or not the many specific compounds/formulations listed under the HSCs in the CLP are actually present in the waste.

Assuming that all the content of e.g. Zn is present as one of the specific compounds on the relevant lists, as was done at Tier 2, is obviously a gross exaggeration that does not reflect the actual hazard properties of IBA. It is therefore necessary to obtain a better assessment of whether or not the relevant compounds are present in significant amounts, and if they are, also a better estimate of the con-centration level at which they occur.

This can be achieved by subjecting the IBA (or other wastes) to multi-elemental chemical speciation modelling which is based on and verified by leaching data showing the leaching of numerous elements as a function of pH (e.g. CEN/TS 14997 or CEN/TS 14429). The speciation modelling can determine which mineral phases are present in the waste and control the leaching/release of relevant substances at various pH values (and under various redox conditions), and when using e.g. the speciation model LeachXS/Orchestra, it can also account for the effect of TOC in the IBA (largely consisting of humic, fulvic and hydrophilic substances). In the context of classification of IBA, speciation modelling provides two main results, namely:

- Information on the presence or non-presence of specific minerals/substances;
- For the substances shown to be present, the solubility/release can be determined at selected pH values.

3.4.2 Assessment of individual HPs

Speciation modelling was performed on a variety of IBA samples from different countries and several samples from different incinerators in one country.

Based on the speciation modelling (identification of mineral phases), the following conclusions can be drawn:

- None of the various compounds identified under Tier 2 above as critical for HP 4, HP 7, HP 8, HP 10 or HP 11 match with compounds identified as solubility controlling phases (linked to actual measurements through pH dependence test results). Hence these compounds can be safely assumed not to be present in the IBA. This implies that based on this Tier 3 evaluation, IBA is not likely to be rendered hazardous by HP 4 (irritant), HP 7 (carcinogenic), HP 8 (corrosive), HP 10 (toxic for reproduction) or HP 11 (mutagenic).
- In evaluating the compounds identified as potentially Aquatic Chronic 1, 2, 3 and 4 under HP 14 in Tier 2, none of the various Cu, Ni and Zn compounds with the exception of Ni(OH)2

and possibly Zn3(PO4) remain as possible critical mineral phases in the IBA that could potentially render it hazardous. Further assessment of these two substances is therefore required for HP 14 at Tier 3 level.

Ecotoxicological effects are generally determined on dissolved substances in an aqueous phase. As pointed out in Annex IV to ECHA's Guidance on the application of the CLP criteria, issued in November 2012 (ECHA, 2012), a substance (metal) must be dissolved (in water) in order to be available for an ecotoxicological responses or to migrate into the environment, and the solubility is therefore a key parameter in determining the potential ecotoxicity of a given substance. The maximum solubility of a substance in the relevant pH range (7 to 12, which includes practically all production, handling, transport, beneficial use and landfilling scenarios from freshly produced to fully carbonated IBA) therefore represents a worst case situation with respect to exposure of any organism to the substance. The speciation modelling on IBA has provided the solubilities of Ni(OH)2 and several Zn species on the Aquatic Chronic List in the CLP, including those remaining for consideration under HP 14.

In Table 4 the highest solubilities in the pH range of 7 to 12 of several Zn and Ni compounds shown to be present in IBA are shown as a result of the speciation modelling. To make the results comparable to the limit values, the solubilities are recalculated to solid content, assuming a liquid to solid (L/S) ratio of 10 l/kg, corresponding to the L/S used in the pH dependence leaching tests (48 hours contact time).

Table 4. Solubilities of Zn and Ni minerals identified in IBA by geochemical speciation modelling and the highest solubilities in the pH range 7 to 12, calculated by the modelling. The solubilities are recalculated to solid content in mg/kg and per cent (w/w), assuming an L/S ratio of 10 l/kg.

Zn compounds	*Highest solubility IBA in pH range 7 – 12 (mg/l)*	*Corresponding solid content* mg/kg*	*Corresponding solid content %*
$ZnCl_2$	28	280	0.028
$Ca_4Zn(PO_4)_3(OH)$	1.1	11	0.0011
$Zn_3(PO_4)_2$	1.7	17	0.0017
$CaZn_2(OH)_6.2H_2O$	28	280	0.028
$ZnSiO_4$)	4.5	45	0.0045
$ZnSiO_3$	0.06	0.6	0.00006
Ni compounds	*Highest solubility IBA in pH range 7 – 12 (mg/l)*	*Corresponding solid content mg/kg*	*Corresponding solid content %*
$Ni(OH)_2$	4.28	43	0.0043

*: Assuming L/S = 10 l/kg (as in the pH dependence leaching tests)

In the case of Zn, the compound identified through the Hazard statement code H 410 (Aquatic Chronic 1), $Zn_3(PO_4)$, has a low solubility (recalculated to a content of 0.0017%), while the most likely solubility controlling minerals identified by the geochemical modelling indicate even less solubility ($ZnSiO_3$ and $Ca_4Zn(PO_4)_3(OH)$).

For Ni, the solubility of $Ni(OH)_2$ is 0.0043%, which is close to the availability of Ni for leaching at low pH determined in pH dependence leaching tests on IBA.

When summarised and multiplied as required by rules for assessment of HP 14, the result is < 1% as compared to the limit value of 25%. IBA is therefore not likely to be rendered hazardous by HP 14.

3.4.3 Summary of Tier 3 assessment

At Tier 3 level, the assessment is based on geochemical speciation modelling, which shows that the substances that could potentially render IBA hazardous according to HP 4, HP 7, HP 8 and HP 10 are not present in significant amounts in IBA or at least not controlling solubility. This leaves HP 14 to be assessed for Ni and Zn compounds on the list of potentially hazardous substances for H 410 (Aquatic Chronic 1). Taking into account that a substance must become dissolved in an aqueous phase to exhibit an ecotoxicological effect or to become a threat to the environment, and that the pH range 7 to 12 covers all realistic fate scenarios for IBA, the speciation modelling shows that, based on maximum solubility of the potentially critical compounds, IBA will not be rendered hazardous under HP 14.

4. CONCLUSION

A three-tiered approach to classification of incinerator bottom ash (IBA) from grate furnace installations incinerating non-hazardous waste been established and applied to European IBA, based on 95 percentile values of composition data obtained for up to 1700 bottom ashes from 9 European countries. The hazardous property assessment has followed the new procedure proposed by the EU Commission, including the latest changes received on 16 January 2013. The proposed legislation requires the use of the CLP which was developed for pure chemicals and mixtures of pure chemicals, and its application to highly complex mixtures of many substances such as IBA presents significant challenges in identifying specific substances present in the mixture.

In the screening process of Tier 1, it was determined that European IBA at the 95 percentile level is not likely to be rendered hazardous by the hazardous properties HP 1 (explosive), HP 2 (oxidising), HP 3 (flammable), HP 9 (infectious), HP 12 (release of an acute toxic gas), HP 13 (sensitising) and HP 15 (yielding another substance).

At Tier 2 level the assessment is carried out assuming that the total content of a given element is pre-sent as the potentially hazardous substances identified in the CLP as associated with the various HPs and Hazard statement codes. In this way it was determined that European IBA at the 95 percentile level is not likely to be rendered hazardous by the hazardous properties HP5 (single target organ toxicity/aspiration), HP 6 (acute toxicity) and HP 11 (mutagenic). In addition the number of substances to be considered at Tier 3 was reduced.

At Tier 3 level geochemical speciation modelling was applied, first to determine if the relevant hazardous substances identified in the CLP as associated with the remaining Hazard statement codes and HPs, were actually present in the IBA. Many of them were found not to be present or solubility controlling. In this way it was determined that European IBA at the 95 percentile level is not likely to be rendered hazardous by the hazardous properties HP 4 (irritant), HP 7 (carcinogenic), HP 8 (corrosive) or HP 10 (toxic for reproduction). Geochemical speciation modelling was subsequently used to determine the maximum solubility in the pH range of 7 to 12 of the remaining relevant substances that could potentially render the IBA hazardous in accordance with HP 14 (ecotoxic), listed under H 410 (Aquatic Chronic 1).

Taking into account that a substance must become dissolved in an aqueous phase to exhibit an ecotoxicological effect or to become a threat to the environment (pointed out in Annex IV to the ECHA guidance issued in November 2012), and that the pH range 7 to 12 covers all realistic fate scenarios for IBA, the speciation modelling shows that, based on maximum solubility of the potentially critical compounds, European IBA at the 95 percentile level is not likely to be rendered hazardous by HP 14.

In conclusion, based on the three-tiered hazard classification procedure described, European

IBA appears to be non-hazardous at the 95 percentile level according the amendments to Directive 2008/98/EC (unofficial draft of 7 November 2012) and Commission Decision 2000/532/EC (unofficial draft of 21 December 2012, including changes to H 14 of 16 January 2013). The methodology is equally applicable to H14 when M factors are introduced and will, at least under the currently suggested transition rules, in all likelihood reach the same results for IBA as shown in this paper.

The procedure can also be used to assess IBA from individual incinerators and other high temperature waste materials, provided that the waste materials are sufficiently well characterised.

It should be noted that while the IBA is not considered hazardous according to HP 3 or HP 12, prescribed methods for measurement of the potential development of hydrogen from highly alkaline IBA containing elementary aluminium (HP 3) and for measurement of the potential development of phosphine from IBA from incineration of phosphorous-rich waste (HP 12) as well as associated limit values are missing. Production of hydrogen is generally low and unproblematic if it occurs, and production of phosphine can only be expected from rare, specifically phosphorous-rich IBAs such as those resulting from incineration of bone and meat meal.

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REFERENCES

Burgués, J.G. (2013): Amendment of the waste classification system. Presentation made in Brussels on 21 March 2013. European Commission, DG Environment, Brussels.

ECHA (2012): Guidance on the application of the CLP criteria. Guidance to Regualtion (EC) No 1272/2008 on classification, labelling and packaging (CLP) of substances and mixtures. Version 3.0, issued in November 2012.

Hjelmar, O., van der Sloot, H.A. and van Zomeren, A. (2013): HP classification of European incinerator bottom ash (IBA). Assessment of hazardous properties of IBA. Executive Summary of report produced for CEWEP.

WRc (2012): Assessment of Hazard Classification of UK IBA. Report for the January-June 2011 IBA dataset. Report for Environmental Services Association. WRc reference: UC8540.06.

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