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HAZARD CLASSIFICATION OF WASTE: REVIEW OF AVAILABLE PRACTICAL METHODS AND TOOLS

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ABSTRACT

The different steps for the classification of waste as hazardous are the collection of information, the use of the European list of waste, the sampling, the analysis, the tests, the hypothesis of speciation of elements into mineral substances, the collection of hazard statement codes of substances, and finally, the comparison of weighted sum or maxima of concentrations or tests results with given concentration limits for each hazard property, or possible use of now available internet sites. Practical methods are suggested: tables for generic classification of elements, for "worst case with information" speciation hypothesis of elements into mineral substances, tests for hazardous property HP 1, HP 2, HP 3, HP 12, HP 14, methods for HP 9 and HP 15.

1. INTRODUCTION

The hazard classification of waste is useful for the sound management and the recycling of potential resources. According to the EU, the chemicals and waste policy areas are now converging, since the aim is to minimize the adverse effects on human health and the environment, by phasing out hazardous chemicals or reducing their release into the air, water and soil. An exhaustive analysis of elements and substances as well as some tests are required to prove that a waste is non-hazardous. This process can help to identify substances of concern not clearly evidenced by the waste management community. Many of these substances were legally used when the products were manufactured, but when those products become waste and are recovered, the now banned or restricted substances may still be contained in the recovered material. This classification can be used to improve the recycling of resources and to avoid dispersion of hazardous elements or substances during uncontrolled uses (avoiding loops of hazardous substances). Some notable examples are plastic products with low concentration of antimony and brominated flame retardants from recycled plastics, concrete blocks with granulate of lead activated glass from cathode ray tubes, or dike reinforcement by sand and gravel from copper and lead slags.

This paper will introduce practical methods and tests for waste classification. A novel approach for speciation of elements into substances based on "worst case with information" of the physico-chemical characteristics of the waste, as a first step for classification, will be proposed. This method makes it possible to immediately identify the elements that cannot classify the waste as hazardous and thus to concentrate the classifier's efforts on the elements that can be classified as hazardous. A special attention to HP 14 'Ecotoxic' will be paid, the most frequent hazard property (when the multiplying factors of the concentration are used for the most hazardous substances, as in products).

To fine-tune the classification of waste is not a routine job. Interactive sites like HazWasteOnline (https://www.hazwasteonline.com/ of OneTouch Data, UK) or ClassifyMyWaste (https://www.ecn.nl/classifymywaste/ of Energy Centre of the Netherlands, NL) are helpful in the speciation options, and provide reliable and up-to-date hazard statement codes, classification rules and classification reports. The first site mentioned, HazWasteOnline, has nice interfaces for uploading the data of composition. The speciation options are proposed to the user. The website documents all the choices in a very complete report. The ClassifyMyWaste website offers worst-case calculations for all the elements mentioned in the CLP. This first approach is useful to identify elements of concern.

The structure of this document follows the logical reasoning of waste classification: (i) Legal background, technical guidance, general assessment, (ii) Sampling, analyses and tests, (iii) Hazard statement codes of substances, (iv) Speciation of elements into mineral substances, (v) Hazard properties of waste (mixtures of substances).

The purpose of this paper is to help waste producers, waste managers and public authorities to use the classification of hazardous waste. In addition to the legal obliga-

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tions, this classification allows the management of hazardous waste by controlling the risk of their reuse or recycling for people, infrastructures, and the environment.

2. LEGAL BACKGROUND, TECHNICAL GUIDANCE, GENERAL ASSESSMENT

The 15 hazard properties of waste plus the POP rendering waste hazardous are presented in Table 1, that will be used all along the paper. They cover physical, health and environmental hazard. They can be assessed by expertise, by (bio)test, or by chemical composition and calculations (last column of Table 1).

Legal background can be found in the EU (2014a, b), the EU (2017a), and in national regulations. A European notice of technical guidance is available (EU 2018). UK and Nordic countries have proposed guidance documents (NRW et al. 2018, Norden 2015). To assess whether a waste is hazardous or not, the available data about the waste composition and properties must first be gathered, data such as:

- Knowledge of the waste and the process originating the waste;
- Literature data;
- Statistics of composition;
- Waste analysis (fractional composition analysis, physical and chemical characterization, bioassay, etc…).

The existing information on the waste can at best be enough to classify without performing complementary (analytical) work. Otherwise, it can guide the choices on the order and verification of the 15 hazard properties and the persistent organic pollutant (POP) content.

A tiered assessment is recommended:

- 1st tier: The classification by origin of the waste according to the European List of Waste (LoW) as “hazardous”, “non-hazardous”, or as “mirror entry”. In this latter case:
- 2nd tier: Some HP can be assessed as “hazardous” or “non-hazardous” by expert judgment;
- 3rd tier: The remaining HP can be assessed as “hazardous” or “non-hazardous” from organic substances content and simple “worst case with information” hypothesis (using the tables of this document) from total elemental content. If the “worst case with information” approach is unsatisfactory (unrealistic, not in accordance with what is known of the waste), perform 4th tier;
- 4th tier: For some HP, perform specialized total analysis, leachate analysis or speciation of mineral content (from elements to mineral substances), or tests.

If the waste exhibits at least one hazard property among the 15 HP or exceed some POP specific concentration, it is classified as hazardous. Conversely, to demonstrate that a waste is not hazardous, the 15 properties and POPs concentration must be checked as non-hazardous. For suspected hazardous waste, cascading work is typically performed in an order depending of the waste and is stopped as soon as one property is verified as hazardous. For suspected non-hazardous waste, a comprehensive study of the entire HP set is performed. It is important to remember that landfill acceptance criteria cannot replace the waste hazardousness assessment.

The European list of Waste (EU 2014a) has been refined with a more precise definition of “absolute” entries (hazardous or not) and “mirror” entries (waste that can be hazardous or not depending on the concentration of hazardous substances) in (EU 2018). If the waste fits in an “absolute entry”, the classification is done. Otherwise, further analyses (calculations or testing) are required.

3. SAMPLING, ANALYSES AND TESTS

The first step is the representative sampling. A precise sampling plan requires the previous knowledge of the elements or substances’ distribution, ideally for each range of particle size. Standards for sampling plan calculations and sampling techniques are available (EN 14899, CEN/TR 15310-1 to -5, EN 15002). Regarding waste of electrical and electronic equipment (WEEE), sampling plans are suggested for some fractions (CENELEC 2015). For solid waste, the key concept (from the binomial law) is the number of particles that must be in a portion of matter to be representative of a larger portion of matter. This number depends on the analytical precision achievable for the analyses of the smallest possible test portion, and the frequency of particles having the studied property. From data of analytical variability and experimental data, the resulting recommended number of particles that should constitute a sample at any scale from the waste stream (thousands of tons) to the test portion (frequently less than one gram) is estimated being 100 000 if some particles are rare (1 of 1000) (CEN TR/15310-1 to -5, EN 15002, Hennebert 2019). Sampling delivers one or more laboratory samples.

The second step is the analysis. The laboratory samples must be pre-treated according to EN 15002. A standard method to determine the elements and organic substances contained in waste (with an analytical mass balance > 90% for solid waste and > 70% for liquid waste - not considering water) is practiced in France (AFNOR XP X30-489, Hennebert et al. 2013) and discussed at the CEN level (TC 444 ‘Environmental analyses of solid matrices’). Specific laboratory methods are needed for some peculiar analyses:

- Petroleum cuts (gasoline – i.e. CAS No 8006-61-9, gas oils/diesel – i.e. CAS No 68334-30-5, mineral lubricating oil – i.e. CAS No 64742-54-7) and creosote (CAS No 90640-85-0) should be identified and quantified as such (and not molecule by molecule) by the laboratory, additionally to total petroleum hydrocarbons (C10-C40), since they have harmonized classification (i.e. diesel HP 7 ‘Carcinogenic’ H351 concentration limit of 1%). The concentration of the cut is, of course, much higher (and hence classifying) than the concentration of individual hydrocarbon molecule. The precise CAS No of the petroleum cut(s) should be attributed by the laboratory, by comparing the chromatographic response of the sample with standards. These specialized analyses should be performed by skilled laboratories;
- The transformation of congeners analysis to the con-

TABLE 1: The 15 hazard properties and POP property of waste and classification methods.

Category and HP	Hazard	Hazard Class and Category codes Hazard Statement Codes	Cut-off values	Methods, classification rules and Concentration Limits
Physical				
HP 1	Explosive	H200, H201, H202, H203, H204, H240, H241	/	Presence or tests (mainly EC A14) or expertise
HP 2	Oxidising	H270, H271, H272	/	Presence or tests (mainly UN 01) or expertise
HP 3	Flammable	H220 à H226, H228, H242, H251, H252, H260, H260	/	Presence or tests (mainly UN N1) or expertise
Health				
HP 4	Irritant (Skin irritation and eye damage)	H314 Skin corr. 1A H318 Eye dam. 1 H315 Skin irrit. 2, H319 Eye irrit. 2	1%	A: ∑ H314 1A ≥ 1% B: ∑ H318 ≥ 10% C: ∑ (H315 et H319) ≥ 20%
HP 5	Specific target organ toxicity/Aspiration Toxicity	H370 STOT SE 1 H371 STOT SE 2 H335 STOT SE 3 H372 STOT RE 1 H373 STOT RE 2 H304 Asp. Tox. 1	/	A: max (H370) ≥ 1% B: max (H371) ≥ 10% C: max (H335) ≥ 20% D: max (H372) ≥ 1% E: max (H373) ≥ 10% F: max (H304) ≥ 10% G: ∑ H304 ≥ 10% and global cinematic viscosity of the waste at 40°C < 20.5 mm^2/s
HP 6	Acute Toxicity	H300 Acute Tox.1 (Oral) H300 Acute Tox. 2 (Oral H301 Acute Tox. 3 (Oral) H302 Acute Tox 4 (Oral) H310 Acute Tox.1 (Dermal) H310 Acute Tox.2 (Dermal) H311 Acute Tox. 3 (Dermal) H312 Acute Tox 4 (Dermal) H330 Acute Tox 1 (Inhal.) H330 Acute Tox.2 (Inhal.) H331 Acute Tox. 3 (Inhal.) H332 Acute Tox. 4 (Inhal.)	Cat. 1, 2 or 3: 0.1% Cat. 4: 1%	A: ∑ H300 1 ≥ 0.1% B: ∑ H300 2 ≥ 0.25% C: ∑ H301 ≥ 5% D: ∑ H302 ≥ 25% E: ∑ H310 1 ≥ 0.25% F: ∑ H310 2 ≥ 2.5% G: ∑ H311 ≥ 15% H: ∑ H312 ≥ 55% I: ∑ H330 1 ≥ 0.1% J: ∑ H330 2 ≥ 0.5% K: ∑ H331 ≥ 3.5% L: ∑ H332 ≥ 22.5%
HP 7	Carcinogenic	H350 Carc. 1A et 1B H351 Carc. 2	/	A: max (H350) ≥ 0.1% B: max (H351) ≥ 1%
HP 8	Corrosive	H314 Skin Corr. 1A, 1B et 1C	1%	A: ∑ H314 ≥ 5%
HP 9	Infectious	/	/	Presence of infectious germs code UN 2814 or 2900 or by origin or by expertise
HP 10	Toxic for reproduction	H360 Repr. 1A et 1B H361 Repr. 2	/	A: max (H360) ≥ 0.3% B: max (H361) ≥ 3%
HP 11	Mutagenic	H340 Muta. 1A et 1B H341 Muta. 2	/	A: max (H340) ≥ 0.1% B: max (H341) ≥ 1%
HP 12	Toxic gas	Presence of substances with HSC EUH029, EUH031, EUH032	/	Presence of these substances by detection of specific gases PH_3, HCN, HF, H_2S, SO_2, HCl et Cl_2 emitted during a test
HP 13	Sensitizing	H317 Skin Sens. 1 H334 Resp. Sens. 1	/	A: max (H317) ≥ 10% B: max (H334) ≥ 10%
Environment				
HP 14	Ecotoxic	H400 Aquatic Acute 1 H410 Aquatic Chronic 1 H411 Aquatic Chronic 2 H412 Aquatic Chronic 3 H413 Aquatic Chronic 4 H420	H400, H410: 0.1% H411, H412, H413: 1%	A: ∑ H400 ≥ 25% B: ∑ [(100*H410) + (10*H411) + (H412)] ≥ 25% C: ∑ (H410 + H411 + H412 + H413) ≥ 25% D: max (H420) ≥ 0.1% Or tests
Physical, Health and Environment (Evolutive)				
HP 15	Capable of exhibiting a hazardous property not displayed by the original waste	Presence of substances with HSC H205, EUH001, EUH019, EUH044 (explodes if heated or dried or confined)		A property HP 1 to HP 14 may appears by evolution of the waste Or presence of substances with HSC in the third column Or expertise
Health and Environment				
POP	Waste containing one or more POP substances with a concentration > CL	Polychlorinated dibenzo-p-dioxins et dibenzofurans (PCDD/PCDF), DDT, chlordane, hexachlorocyclohexanes (including lindane), dieldrin, endrin, heptachlor, hexachlorobenzene, chlordecone, aldrin, pentachlorobenzene, PCB, mirex, toxaphene, hexabromobiphenyl.		PCDD/PCDF: ≥ 15 µg TEQ/kg Others: ≥ 50 mg/kg

centration of (total) polychlorobiphenyls (PCB) should be done according to EN 12766-1 and EN 12766-2 (petroleum products and used oils) as explained in (EU 2018): the total PCB content is calculated as five times the sum of the concentrations of 6 selected congeners 28, 52, 101, 138, 153 and 180 (method B). These congeners represent in fact about 20% of the mass of all the congeners in the commercial mixtures (with variations according to the rate of chlorination thereof);
- Some POP substances require specific laboratory methods;
- The extraction yield of additives in plastics (brominated flame retardants in fire-protected plastics, pesticides in packaging), must be checked with reference material. The analysis of brominated flame retardants in plastics should be done according to EN 62321-6, and in the other waste material according to EN 16377. These analyses are best conducted in industrial (product control) laboratories rather than environmental laboratories.

For HP 1 ‘Explosive’, HP 2 ‘Oxidising’, HP 3 ‘Flammable’, HP 12 ‘Release of an acute toxic gas’ and HP 14 ‘Ecotoxic’, laboratory tests complement the laboratory analyses, or are the preferred methods. These tests will be presented with these HPs.

4. HAZARD STATEMENT CODES OF SUBSTANCES

A third step is to gather the hazard statement codes of substances (HSC) found or assessed in the waste. The EU “harmonized” classification of Table 3.1 of Annex VI of the CLP Regulation (CLP 2008) and its different adaptations to technical progress (ATP) should first be used (spreadsheet file: https://echa.europa.eu/information-on-chemicals/annex-vi-to-clp). The ECHA's Classification and Labeling (C & L Inventory) database (with the information of Table 3.1 (blue-headed tables), and the classification by the notifiers (yellow-headed tables)) (http://echa.europa.eu/web/guest/information-on-chemicals/cl-inventory-database) are not validated by ECHA but can be used in the absence of harmonized classification. In France, the portal of chemicals of INERIS (http://www.ineris.fr/substances/fr/) is also taken as a reference (bilingual English/French).

5. SPECIATION OF ELEMENTS INTO MINERAL SUBSTANCES

The laboratory delivers a total elemental concentration for each element, and a substance concentration for organic substances. The elements have no hazard statement codes (HSC), except for 11 elements with “generic” classification (Table 2). So, the fourth step is speciation of elemental concentrations into mineral substances concentrations.

Some forms or substances have specific methods:

- Calcium oxide or hydroxide (important for HP 4/ HP 8 in thermal process residues like slags, bottom ashes, ashes) and limed waste (sludges from WWTP) or containing lime (concretes and mortars and construction and demolition waste) should be measured according to EN 1744-1 (aggregates, not suitable for low concentrations) or EN 451-1 (fly ash). The EN 459-2 (building lime) and the EN 196-2 (cement) should not be used for another waste/material. Quicklime CaO and hydrated lime $Ca(OH)_2$ can be differentiated by thermogravimetry (quantification of the loss of water during heating). These analyses are carried out by laboratories specialized in studies and research on building materials;
- Chromium (VI), also called chromate, is measured by EN 15192.

Specialized laboratory methods are available for speciation: X-ray diffraction (limit of quantification 5%-1%), thermogravimetry (0.5%), specific extraction and analysis (as calcium oxide and chromate), and extraction at different pH with geomodelling (10 mg/kg). These methods are not practiced in routine characterization of waste, excepted Cr (VI). A synthesis can be found in AFNOR FD X30-494:2015.

A first simple approach is to calculate “worst case with information” substances concentrations (Table 3), using among other information of leaching concentrations. If the waste is calculated not hazardous, the assessment can be stopped. In Table 3, the elements are presented in the following order: major elements (of the earth's crust), major anions, 12 "heavy metals", and various minor, rare or little sought-after elements. A summary for teh 12 "hevy metals" is presented in Table 4.

5.1 Choice of substances "worst case with information" of Tables 3 and 4

1. Generic hazard statements are used primarily because they avoid hypotheses of speciation in substances. It is necessary to check in the Harmonized Table the hazard statements for substances (Annex VI of CLP) that the "other substances" of the same element (most often chemical industry intermediates, or highly reactive substances not found in common waste) are not in the waste. Substances with only one hazardous element are preferred (i.e. lead sulfate rather than lead arsenate);
2. Soluble forms if they have the relevant hazard statement codes (mainly sulphate - higher molar mass - for most properties, and chloride in some cases) are then used because they are often biologically more active, and their presence and concentration may be verified by leachable concentrations (EN 12457-2);
3. The most hydrated forms of substances are chosen because the concentration of element is lower for a given substance concentration;
4. In the absence of soluble forms, simple oxides (and among families of oxides, the most present form in the natural environment) have been chosen;
5. Of the major elements, only those forming acids and strong bases with hazard statements were used. Elementary forms (metal, oxidation stage 0) and very reactive forms, especially with water (hydrides, ...) were not retained, with one exception: elemental lithium, present in some rechargeable cells and batteries at a concentration of about 2%. The case of glass wool (index No.

650-016-00-2, H351), refractory ceramic fibers (index No. 650-017-00-8, H350), glass microfibers (fiber optic index No.° 014-046-00-4 H350 and glass fiber index no. 014-047-00-X H351) (see file Annex VI of the CLP mentioned above) has not been considered here. If the presence of such fibers is suspected (for instance in the ceramic of some models of catalytic converters), specialized laboratory analyses have to be performed;
6. Finally, when only one substance in the element has the relevant hazard statement, it is chosen, even if it is rare. For example: the only lead substance with the hazard statement H350 for the property HP 7 'Carcinogenic' is a sulfo-chromic pigment, with a lead concentration limit of 0.1%.

The conversion of the substance concentration into the elemental concentration is obtained by multiplying the mass percentage of the element in the substance (ratio of the atomic mass of the element multiplied by its stoichiometric coefficient, and the molar mass of the substance).

5.2 Indications of presence of these forms "worst case with information" in the waste

The presence and concentration of the chosen soluble forms (sulfate for most properties and chloride in some cases) can be verified by leachable concentrations (EN 12457-2). The pH and buffering capacity indicate whether acids (Cl, F, S, P, N) or bases (Na, Ca) are present and at which concentration (XP CEN/TS 15364). The redox potential and the redox capacity indicate whether oxidants [Cr (VI), Mn (VII), Cl_2] or reductants [Fe (II), sulphide, sulphite] are present and at which concentration (XP CEN/TS 16660). Calcium oxide and total chromate have specific analytical methods (see Analysis section).

5.3 Using the table

For properties defined by concentration maxima (denoted Max HP 5, Max HP 7, Max HP 10, Max HP 11, Max HP 13), if the total concentration of the element in the waste is less than the concentration limit of the "worst case with information" expressed in the element, the waste is not hazardous for this property by this element.

For the properties defined by sums of concentration (denoted Σ HP 4, Σ HP 6, Σ HP 8, Σ HP 14), the concentrations of the substances of all the elements plus the concentrations of relevant organic substances must be added according to the hazard statements in accordance with the rules of the Table 1. CLP "Note 1" of generic entries means that the concentration limit applies to the element and not to the substances. These cases are reported in Table 3.

The HP 14 property is presented for the three hazard statements codes (HSC) H400, H410 and H411, given that 50% of the hazardous waste is, in addition to the other properties, ecotoxic (according to our observations with the M factor system, explained below). Virtually all acute ecotoxic substances H400 are also ecotoxic chronic H410. Manganese and selenium may have one form with HSC H410 and another with HSC H411, which justifies two different lines for chronic HP14. Substances with hazard statements H412 and H413 are less numerous. Mineral substances ("worst case with information" approach) with the hazard statement H412 are SnCl4 (CAS No. 7646-78-8) and powdered nickel <1 mm (CAS No. 7440-02-0). Mineral substances ("worst case with information" approach) with the hazard statement H413 are cadmium sulphide (CAS No. 1306-23-6), various nickel oxides (i.e. CAS No. 11099-02-8), and the elements Co, Se, Th and U (at the zero-oxidation stage), but the concentration limit is 25% (Table 3). Waste with concentrations of 25% of these elements are resources.

6. HAZARD PROPERTIES OF WASTE (MIXTURE OF SUBSTANCE)

During the fifth step, the hazard properties can be assessed by applying classification rules (Table 1). Concentrations of substances lower than the cut-off values must not be considered. Waste can also be hazardous by some POP substances (EU 2014a) with specific concentration limits. The full list of these POPs and their specific concentration limits are presented in Table 5. Note that there are other POP substances that do not classify the waste as hazardous by their POP characteristics but can classify waste as hazardous for some HPs by their specific hazard statement codes and concentrations, like non-POP substances. These substances and their HSC are included in the spreadsheet file presented in Chapter 4 and are presented in the second part of Table 5 (without “x” in the 4th column).

Most POP substances also have hazard statement codes (not shown in Table 5), and hence concentration limits for HP, but they are always higher than by their POP content. Only short chain chlorinated paraffins (SCCPs) have a CL by HP lower than CL by POP regulation.

6.1 Physical hazard

6.1.1 By tests: HP 1 ‘explosive’, HP 2 ‘Oxidising’, HP 3 ‘Flammable’

These HPs are defined by the presence of substances with relevant HSC. They are in practice assessed by expert judgment and the origin of the waste, or by tests (Table 6). It has been recently suggested to calculate them if the chemical composition is known in detail (EU 2018). The website HazWasteOnline (see below) assesses HP 3 with total petroleum hydrocarbon analysis. The most commonly used methods are EC A9 (flash point for liquid waste) and UN N1 (speed of flame progression in a row of solid waste).

6.2 (Human) Toxicity

6.2.1 By analysis and calculation: HP 4 ‘Irritant — skin irritation and eye damage’, HP 6 ‘Acute Toxicity”, HP 8 ‘Corrosive’ (sums of concentrations for these HPs); HP 5 ‘Specific target organ toxicity (STOT)/Aspiration Toxicity’, HP 7 ‘Carcinogenic’, HP 10 ‘Toxic for reproduction, HP 11 ‘Mutagenic’, HP 13 ‘Sensitising’, HP ‘POP’ (maxima of concentrations for these HPs)

These HPs are typically calculated from chemical composition (Table 1). Biological tests have been evoked (EU 2018), without further clarification.

TABLE 2: Generic entry classification (hazard class and category, and hazard statement code) of 11 elements (CLP, 2008).

Element	Index number	Chemical international identification	Number of substances with a specific entry (« specified elsewhere »)	Hazard class and category	Hazard Statement Code
As	033-002-00-5	arsenic compounds, with the exception of those specified elsewhere in this Annex. Note 1	4	Acute Tox. 3 * Acute Tox. 3 * Aquatic Acute 1 Aquatic Chronic 1	H331 H301 H400 H410
	033-005-00-1	arsenic acid and its salts with the exception of those specified elsewhere in this Annex.	6	Carc. 1A Acute Tox. 3 * Acute Tox. 3 * Aquatic Acute 1 Aquatic Chronic 1	H350 H331 H301 H400 H410
Ba	056-002-00-7	barium salts, with the exception of barium sulphate, salts of 1-azo-2-hydroxynaphthalenyl aryl sulphonic acid, and of salts specified elsewhere in this Annex	9	Acute Tox. 4 * Acute Tox. 4 *	H332 H302
Be	004-002-00-2	beryllium compounds with the exception of aluminium beryllium silicates, and with those specified elsewhere in this Annex	2	Carc. 1B Acute Tox. 2 * Acute Tox. 3 * STOT RE 1 Eye Irrit. 2 STOT SE 3 Skin Irrit. 2 Skin Sens. 1 Aquatic Chronic 2	H350i H330 Cat2 H301 H372 ** H319 H335 H315 H317 H411
Cd	048-001-00-5	cadmium compounds, with the exception of cadmium sulphoselenide (xCdS.yCdSe), reaction mass of cadmium sulphide with zinc sulphide (xCdS.yZnS), reaction mass of cadmium sulphide with mercury sulphide (xCdS.yHgS), and those specified elsewhere in this Annex. Note 1	15	Acute Tox. 4 * Acute Tox. 4 * Acute Tox. 4 * Aquatic Acute 1 Aquatic Chronic 1	H332 H312 H302 H400 H410
Cr(VI)	024-017-00-8	chromium (VI) compounds, with the exception of barium chromate and of compounds specified elsewhere in this Annex	19	Carc. 1B Skin Sens. 1 Aquatic Acute 1 Aquatic Chronic 1	H350i H317 H400 H410
Hg	080-002-00-6	inorganic compounds of mercury with the exception of mercuric sulphide and those specified elsewhere in this Annex. Note 1	6	Acute Tox. 2 * Acute Tox. 1 Acute Tox. 2 * STOT RE 2 * Aquatic Acute 1 Aquatic Chronic 1	H330 Cat2 H310 H300 Cat2 H373 ** H400 H410
	080-004-00-7	organic compounds of mercury with the exception of those specified elsewhere in this Annex. Note 1	7		
Pb	082-001-00-6	lead compounds with the exception of those specified elsewhere in this Annex. Note 1	17	Repr. 1A Acute Tox. 4 * Acute Tox. 4 * STOT RE 2 * Aquatic Acute 1 Aquatic Chronic 1	H360Df H332 H302 H373 ** H400 H410
Sb	051-003-00-9	antimony compounds, with the exception of the tetroxide (Sb2O4), pentoxide (Sb2O5), trisulphide (Sb2S3), pentasulphide (Sb2S5) and those specified elsewhere in this Annex. Note 1	7	Acute Tox. 4 * Acute Tox. 4 * Aquatic Chronic 2	H332 H302 H411
Se	034-002-00-8	selenium compounds with the exception of cadmium sulphoselenide and those specified elsewhere in this Annex	5	Acute Tox. 3 * Acute Tox. 3 * STOT RE 2 Aquatic Acute 1 Aquatic Chronic 1	H331 H301 H373** H400 H410
Tl	081-002-00-9	thallium compounds, with the exception of those specified elsewhere in this Annex	3	Acute Tox. 2 * Acute Tox. 2 * STOT RE 2 * Aquatic Chronic 2	H330 Cat2 H300 Cat2 H373 ** H411
U	092-002-00-3	uranium compounds with the exception of those specified elsewhere in this Annex	2	Acute Tox. 2 * Acute Tox. 2 * STOT RE 2 Aquatic Chronic 2	H330 Cat2 H300 Cat2 H373** H411

HP 4/HP 8

A European document (EU 2018) proposes, in line with the CLP, for classification according to HP 4 and HP 8 to consider the pH (≤ 2 and ≥ 11.5) and the buffer capacity (neutralization capacity of acids and bases, expressed in H^+ or OH^- equivalent per kg of material), especially in the case where not all substances in the composition of the waste are known. There is no buffer value indicated

TABLE 3: Concentration limits (CL) expressed in substance and in element concentrations by "worst case with information" approach for 36 elements and 9 hazard properties by calculation (NH: not hazardous for these 9 HP; "Note 1": the concentration limit applies to the element; CL by element percentage with four digits to have direct conversion to mg/kg; the lowest CL by element is colored).

Element	HP	Hazard Statement Code	CL by substance	«worst case with information» substance	Formula	CAS No	CL by element
Majors elements (cations)							
Si	NH						
Al	NH						
Fe	HP 4 (sum)	H315 H319	20%	Ferrous sulfate heptahydrate	$FeSO_4.7H_2O$	7782-63-0	4.0176
Mn	HP 5 (max)	H373	10%	Manganese sulphate	$MnSO_4$	7785-87-7	3.6384%
	HP 6 (sum)	H302	25%	Potassium permanganate	$KMnO_4$	7722-64-7	8.6910%
	HP 14 (sum) H400	H400	25.00%	Potassium permanganate	$KMnO_4$	7722-64-7	8.6910%
	HP 14 (sum) H410 H411 H412	H410	0.25%	Potassium permanganate	$KMnO_4$	7722-64-7	0.0896%
	HP 14 (sum) H410 H411 H412	H411	2.50%	Si pas KMnO4 (H400, H410) : MnSO4	$MnSO_4$	7785-87-7	0.9096%
Ca	HP 4 (sum)	H319	20%	Calcium chloride	$CaCl_2$	10043-52-4	7.2232%
	HP 4 (sum)	H315 H318	10%	Calcium oxide	CaO	1305-78-8	7.1470%
	HP 5 (max)	H335	20%	Calcium oxide	CaO	1305-78-8	14.2939%
Mg	NH						
Na	HP 4 (sum)	H314 1A	1%	Sodium hydroxide; caustic soda	NaOH	1310-73-2	0.5748%
	HP 8 (sum)	H314 1A	5%	Sodium hydroxide; caustic soda	NaOH	1310-73-2	2.8740%
K	HP 4 (sum)	H315 H319	20%	Potassium chromate	$K2CrO_4$	7789-00-6	8.0537%
	HP 8 (sum)	H314 1B	5%	potassium hydrogensulphate	$KHSO_4$	7646-93-7	1.4357%
Cr III	NH						
V	HP 5 (max)	H372	1%	Divanadium pentaoxide; vanadium pentoxide	V_2O_5	1314-62-1	0.5602%
	HP 6 (sum)	H302	25%	Divanadium pentaoxide; vanadium pentoxide	V_2O_5	1314-62-1	14.0044%
	HP 10 (max)	H361	3.00%	Divanadium pentaoxide; vanadium pentoxide	V_2O_5	1314-62-1	1.6805%
	HP 11 (max)	H341	1.00%	Divanadium pentaoxide; vanadium pentoxide	V_2O_5	1314-62-1	0.5602%
	HP 14 (sum) H410 H411 H412	H411	2.50%	Divanadium pentaoxide; vanadium pentoxide	V_2O_5	1314-62-1	1.4004%
Major elements (anions)							
B	HP 4 (sum)	H318	10%	Perboric acid, sodium salt, tetrahydrate = sodium perborate tetrahydrate	$NaBO_3.4H_2O$	10486-00-7	0.7024%
	HP 10 (max)	H360	0.30%	Disodium tetraborate decahydrate; borax decahydrate	$Na2B_4O7.10H_2O$	1303-96-4	0.0340%
Cl	HP 8 (sum)	H314 1B	5%	Hydrochloric acid ... % (concentration >5%)	HCl	7647-01-0	4.8619%
F	HP 4 (sum)	H314 1A	1%	Hydrofluoric acid ... % (concentration > 1%)	HF	7664-39-3	0.9497%
	HP 6 (sum)	H300 Cat 2	0.25%	Hydrofluoric acid ... % (concentration > 0.25%)	HF	7664-39-3	0.2374%
	HP 8 (sum)	H314 1A	5%	Hydrofluoric acid ... % (concentration >5%)	HF	7664-39-3	4.7483%
N	HP 4 (sum)	H314 1A	1%	Nitric acid ... % (concentration > 1%)	HNO_3	7697-37-2	0.2223%
	HP 8 (sum)	H314 1A	5%	Nitric acid ... % (concentration > 5%)	HNO_3	7697-37-2	1.1114%

P	HP 8 (sum)	H314 1B	5.00%	Phosphoric acid ... %, orthophosphoric acid ... %	H_3PO_4	7664-38-2	1.5804%
S	HP 4 (sum)	H314 1A	1%	Sulphuric acid ... % (concentration > 1%)	H_2SO_4	7664-93-9	0.2543%
	HP 8 (sum)	H314 1A	5%	Sulphuric acid ... % (concentration > 5%)	H_2SO_4	7664-93-9	1.2714%
« Heavy metals »							
As	HP 6 (sum)	H300 Cat 2	0.25%	Diarsenic trioxide; arsenic trioxide	As_2O_3	1327-53-3	0.1893%
	HP 7 (max)	H350	0.10%	Arsenic acid and its salts with the exception of those specified elsewhere in this Annex	$H3AsO_4$	7778-39-4	0.0528%
	HP 8 (sum)	H314	5%	Diarsenic trioxide; arsenic trioxide	As_2O_3	1327-53-3	3.7870%
	HP 10 (max)	H360	0.30%	Lead hydrogen arsenate	$PbHAsO_4$	7784-40-9	0.0648%
	HP 14 (sum) H400	H400	25.00%	Generic classification (substance not defined). Note 1	As		25.00%
	HP 14 (sum) H410 H411 H412	H410	0.25%	Generic classification (substance not defined). Note 1	As		0.25%
Ba	HP 6 (sum)	H301 H332	5.00%	Barium chloride	$BaCl_2$	10361-37-2	3.2975%
Cd	HP 5 (max)	H372	1%	Cadmium sulfate	$CdSO_4$	10124-36-4	0.5392%
	HP 6 (sum)	H301 H330 Cat 2	0.50%	Cadmium sulfate	$CdSO_4$	10124-36-4	0.2696%
	HP 7 (max)	H350	0.10%	Cadmium sulfate	$CdSO_4$	10124-36-4	0.0539%
	HP 10 (max)	H360	0.30%	Cadmium sulfate	$CdSO_4$	10124-36-4	0.1618%
	HP 11 (max)	H340	0.10%	Cadmium sulfate	$CdSO_4$	10124-36-4	0.05%
	HP 14 (sum) H400	H400	25.00%	Generic classification (substance not defined). Note 1	Cd	10124-36-4	25.00%
	HP 14 (sum) H410 H411 H412	H410	0.25%	Generic classification (substance not defined). Note 1	Cd	10124-36-4	0.25%
Cr VI	HP 5 (max)	H372	1%	Sodium chromate	Na_2CrO_4	10588-01-9	0.3210%
	HP 6 (sum)	H301 H312 H330 Cat 2	0.50%	Sodium chromate	Na_2CrO_4	10588-01-9	0.1606%
	HP 7 (max)	H350	0.10%	Sodium chromate or Generic classification	Na_2CrO_4	10588-01-9	0.0321%
	HP 8 (sum)	H314	5%	Sodium chromate	Na_2CrO_4	10588-01-9	1.6051%
	HP 10 (max)	H360	0.30%	Sodium chromate	Na_2CrO_4	10588-01-9	0.0963%
	HP 11 (max)	H340	0.10%	Sodium chromate	Na_2CrO_4	10588-01-9	0.0321%
	Max HP 13	H317 H334	10%	Sodium chromate	Na_2CrO_4	10588-01-9	3.2102%
	HP 14 (sum) H400	H400	25.00%	Sodium chromate or Generic classification	Na_2CrO_4	10588-01-9	8.0250%
	HP 14 (sum) H410 H411 H412	H410	0.25%	Sodium chromate or Generic classification	Na_2CrO_4	10588-01-9	0.0803%
Cu	HP 4 (sum)	H315 H319	20%	Copper sulfate	$CuSO_4.5H_20$	7758-98-7	5.0905%
	HP 6 (sum)	H302	25%	Copper sulfate	$CuSO_4.5H_20$	7758-98-7	6.3631%
	HP 14 (sum) H400	H400	25.00%	Copper sulfate	$CuSO_4.5H_20$	7758-98-7	6.3631%
	HP 14 (sum) H410 H411 H412	H410	0.25%	Copper sulfate	$CuSO_4.5H_20$	7758-98-7	0.0636%
Hg	HP 4 (sum)	H315 H319	20%	Mercury (I) chloride	Hg_2Cl_2	10112-91-1	17.2440%
	HP 5 (max)	H372	1%	Mercuric chloride	$HgCl_2$	7487-94-7	0.7578%
	HP 6 (sum)	H300 Cat 2	0.25%	Generic classification (substance not defined). Note 1	Hg	7783-35-9	0.2500%
	HP 8 (sum)	H314	5%	Mercuric chloride	$HgCl_2$	7487-94-7	3.7889%

	HP 10 (max)	H360	0.30%	Mercury	Hg	7439-97-6	0.3000%
	HP 11 (max)	H341	1.00%	Mercuric chloride	$HgCl_2$	7487-94-7	0.7578%
	HP 14 (sum) H400	H400	25.00%	Generic classification (substance not defined). Note 1	Hg	7783-35-9	25.0000%
	HP 14 (sum) H410 H411 H412	H410	0.25%	Generic classification (substance not defined). Note 1	Hg	7783-35-9	0.2500%
Mo	HP 7 (max)	H351	1.00%	Molybdenum trioxide	MoO_3	1313-27-5	0.6665%
Ni	HP 4 (sum)	H318	10%	Nickel dinitrate	$Ni(NO_3)_2$	13138-45-9	3.2126%
	HP 5 (max)	H372	1%	Nickelous sulfate	$NiSO_4$	7786-81-4	0.3793%
	HP 6 (sum)	H331	3.50%	Nickel dichloride	$NiCl_2$	7718-54-9	1.5853%
	HP 7 (max)	H350	0.10%	Nickelous sulfate	$NiSO_4$	7786-81-4	0.0379%
	HP 10 (max)	H360	0.30%	Nickelous sulfate	$NiSO_4$	7786-81-4	0.1137%
	HP 11 (max)	H341	1.00%	Nickelous sulfate	$NiSO_4$	7786-81-4	0.3793%
	Max HP 13	H317 H334	10%	Nickelous sulfate	$NiSO_4$	7786-81-4	3.7934%
	HP 14 (sum) H400	H400	25.00%	Nickelous sulfate	$NiSO_4$	7786-81-4	9.4807%
	HP 14 (sum) H410 H411 H412	H410	0.25%	Nickelous sulfate	$NiSO_4$	7786-81-4	0.0948%
Pb	HP 5 (max)	H373	10%	Generic classification (substance not defined). Note 1	Pb		10.0000%
	HP 6 (sum)	H332	22.50%	Generic classification (substance not defined). Note 1	Pb		22.5000%
	HP 7 (max)	H350	0.10%	Only: Lead sulfochromate yellow; C.I. Pigment Yellow 34; [This substance is identified in the Colour Index by Colour Index Constitution Number, C.I. 77603.]. Note 1	Pb	1344-37-2	0.1000%
	HP 10 (max)	H360	0.30%	Generic classification (substance not defined). Note 1	Pb		0.3000%
	HP 14 (sum) H400	H400	25.00%	Generic classification (substance not defined). Note 1	Pb		25.0000%
	HP 14 (sum) H410 H411 H412	H410	0.25%	Generic classification (substance not defined). Note 1	Pb		0.2500%
Sb	HP 6 (sum)	H301	5.00%	Antimony trifluoride	SbF_3	7783-56-4	3.4058%
	HP 7 (max)	H351	1.00%	Antimony trioxide	Sb_2O_3	1309-64-4	0.8354%
	HP 8 (sum)	H314	5%	Antimony pentachloride	$SbCl_5$	7647-18-9	2.0360%
	HP 14 (sum) H410 H411 H412	H411	2.50%	Generic classification (substance not defined). Note 1	Sb	-	25.0000%
Se	HP 5 (max)	H373	10%	Generic classification (substance not defined) / Hyp. selenium dioxide	SeO_2	7446-08-4	7.1165%
	HP 6 (sum)	H300 Cat 2	0.25%	Sodium selenite	Na_2SeO_3	10102-18-8	0.1142%
	Max HP 13	H317	10%	Sodium selenite	Na_2SeO_3	10102-18-8	4.5662%
	SeO2	H400	25.00%	Generic classification (substance not defined) / Hyp. selenium dioxide	SeO_2	7446-08-4	17.7912%
	HP 14 (sum) H410 H411 H412	H410	0.25%	Generic classification (substance not defined) / Hyp. selenium dioxide	SeO_2	7446-08-4	0.1779%
	HP 14 (sum) H410 H411 H412	H411	2.50%	Sodium selenite	Na_2SeO_3	10102-18-8	1.1416%

Zn	HP 4 (sum)	H318	10%	Zinc sulphate (hydrous) (mono-, hexa- and hepta hydrate)	$ZnSO_4{:}7H_2O$	7446-19-7	2.2741%
	HP 6 (sum)	H302	25%	Zinc sulphate (hydrous) (mono-, hexa- and hepta hydrate)	$ZnSO_4{:}7H_2O$	7446-19-7	5.6851%
	HP 8 (sum)	H314	5%	Zinc chloride	$ZnCl_2$	7646-85-7	2.43986%
	HP 14 (sum) H400	H400	25.00%	Zinc sulphate (hydrous) (mono-, hexa- and hepta hydrate)	$ZnSO_4{:}7H_2O$	7446-19-7	5.6851%
	HP 14 (sum) H410 H411 H412	H410	0.25%	Zinc sulphate (hydrous) (mono-, hexa- and hepta hydrate)	$ZnSO_4{:}7H_2O$	7446-19-7	0.0569%
Minor and rare elements							
Ag	HP 8 (sum)	H314	5%	Silver nitrate	$AgNO_3$	7761-88-8	3.1750%
	HP 14 (sum) H400	H400	25.00%	Silver nitrate	$AgNO_3$	7761-88-8	15.8750%
	HP 14 (sum) H410 H411 H412	H410	0.25%	Silver nitrate	$AgNO_3$	7761-88-8	0.1588%
Be	HP 4 (sum)	H315 H319	10%	Generic classification (substance not defined) / Hyp. beryllium hydroxide	$Be(OH)_2$	13327-32-7	2.0946%
	HP 5 (max)	H372	1%	Generic classification (substance not defined) / Hyp. beryllium hydroxide	$Be(OH)_2$	13327-32-7	0.2095%
	HP 6 (sum)	H301	5.00%	Generic classification (substance not defined) / Hyp. beryllium hydroxide	$Be(OH)_2$	13327-32-7	1.0473%
	HP 7 (max)	H350	0.10%	Generic classification (substance not defined) / Hyp. beryllium hydroxide	$Be(OH)_2$	13327-32-7	0.0209%
	Max HP 13	H317	10%	Generic classification (substance not defined) / Hyp. beryllium hydroxide	$Be(OH)_2$	13327-32-7	2.0946%
	HP 14 (sum) H410 H411 H412	H411	2.50%	Generic classification (substance not defined) / Hyp. beryllium hydroxide	$Be(OH)_2$	13327-32-7	0.5237%
	HP 6 (sum)	H302	25.00%	Cobalt sulfate. Note 1	$CoSO_4$	10124-43-3	25.0000%
Co	HP 7 (max)	H350	0.10%	Cobalt sulfate. Note 1	$CoSO_4$	10124-43-3	0.1000%
	HP 10 (max)	H360	0.30%	Cobalt sulfate. Note 1	$CoSO_4$	10124-43-3	0.3000%
	HP 11 (max)	H341	1.00%	Cobalt sulfate. Note 1	$CoSO_4$	10124-43-3	1.0000%
	Max HP 13	H317 H334	10%	Cobalt sulfate. Note 1	$CoSO_4$	10124-43-3	10.0000%
	HP 14 (sum) H400	H400	25.00%	Cobalt sulfate. Note 1	$CoSO_4$	10124-43-3	25.0000%
	HP 14 (sum) H410 H411 H412	H410	0.25%	Cobalt sulfate. Note 1	$CoSO_4$	10124-43-3	0.2500%
Li	HP 8 (sum)	H314	5%	Lithium (element)	Li	7439-93-2	5.0000%
Sn	HP 8 (sum)	H314	5%	Tin tetrachloride; stannic chloride	$SnCl_4$	7646-78-8	2.2781%
	HP 14 (sum) H410 H411 H412	H412	25%	Tin tetrachloride; stannic chloride	$SnCl_4$	7646-78-8	11.39%
Tl	HP 4 (sum)	H315	20%	Dithallium sulphate; thallic sulphate	Tl_2SO_4	7446-18-6	16.1944%
	HP 5 (max)	H372	1%	Dithallium sulphate; thallic sulphate	Tl_2SO_4	7446-18-6	0.8097%
	HP 5 (max)	H373	10%	Generic classification (substance not defined) / Hyp. thallium(III) oxide	Tl_2O_3	7446-18-6	8.9492%
	HP 6 (sum)	H300 Cat2	0.25%	Dithallium sulphate; thallic sulphate	Tl_2SO_4	7446-18-6	0.2024%
	HP 14 (sum) H410 H411 H412	H411	2.50%	Generic classification (substance not defined) / Hyp. thallium(III) oxide	Tl_2O_3	-	2.2373%

U	HP 5 (max)	H373	10%	Generic classification (substance not defined) / Hyp. uranium oxide	UO_2		8.8150%
	HP 6 (sum)	H300 Cat2	0.25%	Generic classification (substance not defined) / Hyp. uranium oxide	UO_2		0.2204%
	HP 14 (sum) H410 H411 H412	H411	2.50%	Generic classification (substance not defined) / Hyp. uranium oxide	UO_2	-	2.2038%

TABLE 4: Synthesis of Concentration limits (CL) expressed in element for 12 heavy metals and metalloids by "worst case with information" approach (blank : not hazardous for this HP; "Note 1": the concentration limit applies to the element; the lowest CL by element is colored): if the total concentration of the element is lower than CL min (penultimate column), the waste is not hazardous by that element.

CL min (%) / Elts	HP 4	HP 5	HP 6	HP 7	HP 8	HP 10	HP 11	HP 13	HP 14 ΣH400	HP 14 Σ100*H410+ 10*411+ 412	HP 14 Σ100*H410+ 10*411+ 412	CL min (%)	Corresponding substance
	Sum	Max	Sum	Max	Sum	Max	Max	Max	Sum	Sum	Sum		
Cut-off value (%)	**1**		**0.1/1**		**1**				**0.1**	**0.1 (H410)**	**1 (H411)**		
As			0.1893	0.0528	3.7870	0.0648			25.0000	0.2500		0.0528	Generic. Note 1
Ba			3.2975									3.2975	$BaCl_2$
Cd		0.5392	0.2696	0.0539		0.1618	0.0539		25.0000	0.2500		0.0539	$CdSO_4$
Cr VI	5.3552	0.3970	0.1985	0.0268	1.9848	0.1191	0.0268	2.6776	6.6940	0.0669		0.0268	Na_2CrO_4
Cu	5.0905		6.3631						6.3631	0.0636 → 0.1		→ 0.1000	$CuSO_4.5H_20$
Hg	17.2440	0.7578	0.2500		3.7889	0.3000	0.7578		25.0000	0.2500		0.2500	Generic. Note 1
Mo				0.6665								0.6665	MoO_3
Ni	3.2126	0.3793	1.5853	0.0379		0.1138	0.3793	3.7934	9.4807	0.0948 → 0.1		0.0379	$NiSO_4$
Pb		10.0000	22.5000	0.3000		0.3000			25.0000	0.2500		0.3000	Generic. Note 1
Sb			3.4058	0.8354	2.0360						2.5000	0.8354	Sb_2O_3
Se		7.1165	0.1142					4.5662	17.7912	0.1779	1.1416	0.1142	Na_2SeO_3
Zn	2.2741		5.6851		2.3986				5.6851	0.0569 → 0.1		→ 0.1000	$ZnSO_4.7H_2O$

in the European document. For alkaline waste, the most frequently relevant substances are NaOH (H314-1A in the CLP, cut-off value 1%, HP 4 if sum ≥ 1% and HP 8 if sum ≥ 5%) and $CaO/Ca(OH)_2$ (H315 in the ECHA declaration system, cut-off value 1%, HP 4 if sum ≥ 20%). Practically, the concentration of (totally soluble) NaOH in the waste can be assessed by the concentration of leachable Na and the pH of the leachate. The concentration of $CaO/Ca(OH)_2$ must be measured by a dedicated analysis (see Chapter 5 Speciation). If the pH of the leachate is ≥ 11.5, these analyses should be used to correctly assess HP 4. Speciation of Ni and Zn in substances should also be performed for HP 4 and HP 8. If either Ni or Zn is the only element with HSC H314 1A, 1B and 1C, H315, H318 and H319 in the waste, concentration of Table 3 can be used. Otherwise, the sum of concentrations of substances must be used (Table 1).

6.2.2 By list: HP 9 'Infectious'

It is suggested to use the UN ADR list of infectious organisms, or the origin of the waste, or an expert judgment (ADR 2014). A technical report is available (Hennebert 2017).

6.2.3 By test: HP 12 'Release of an acute toxic gas"

The definition of HP 12 is that waste contains substances with HSC EUH029, EUH031 and EUH032. These (very) reactive substances are not analyzed in routine environmental laboratories. Therefrom, the following method is proposed (Hennebert et al. 2016a):

1. Measure the volume of gases emitted into contact with water or an acid (automated calcimeter in 5 min, solid/liquid ratio of 10 l/kg, acid 2.5 M HNO_3). The limit of quantification has been found at INERIS to be 0.1 liter of gas per kg of raw waste in 5 minutes;
2. If gas is emitted beyond that limit, check if one of the following gases is emitted: HCN, HF, PH_3, H_2S, SO_2, HCl and Cl_2 with detection probes or simple qualitative colorimetric methods;
3. If one of these gases is detected, specify the emitting substances (either by direct method if they are in high concentration or by calculation by the "worst case" method if they are in low concentrations, or by specific methods) and check whether they have a hazard statement code EUH029, EUH031 or EUH032, or alternatively check if the waste is likely to contain substances with these HSC (list in the publication).

6.3 Ecotoxicity

6.3.1 By calculation: HP 14 'Ecotoxic'

The calculation formulas are presented in Table 1.

TABLE 5: Hazard property by POP substances (EC 2008 and updates).

Substance	CAS No	EC No	Waste hazardous if concentration > CL (2014/ 955/ UE)	Concentration limit of the POP regulation
Polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/PCDF)			X	15 µg/kg (= 0.0000015%) (Toxicity Equivalent Factors for congeners in the POP regulation)
DDT (1,1,1-trichloro-2-2-bis(4-chlorophenyl)ethane)	50-29-3	200-024-3	X	50 mg/kg (= 0.005%)
Chlordane	57-74-9	200-349-0	X	50 mg/kg (= 0.005%)
Hexachlorocyclohexanes, including lindane	58-89-9 319-84-6 319-85-7 608-73-1	210-168-9 200-401-2 206-270-8 206-271-3	X	50 mg/kg (= 0.005%)
Dieldrine	60-57-1	200-484-5	X	50 mg/kg (= 0.005%)
Endrine	72-20-8	200-775-7	X	50 mg/kg (= 0.005%)
Heptachlore	76-44-8	200-962-3	X	50 mg/kg (= 0.005%)
Hexachlorobenzene	118-74-1	200-273-9	X	50 mg/kg (= 0.005%)
Chlordecone	143-50-0	205-601-3	X	50 mg/kg (= 0.005%)
Aldrine	309-00-2	206-215-8	X	50 mg/kg (= 0.005%)
Pentachlorobenzene	608-93-5	210-172-5	X	50 mg/kg (= 0.005%)
Polychlorobiphenyles (PCB)	1336-36-3 and others	215-648-1	X	50 mg/kg (= 0.005%)
Mirex	2385-85-5	219-196-6	X	50 mg/kg (= 0.005%)
Toxaphene	8001-35-2	232-283-3	X	50 mg/kg (= 0.005%)
Hexabromobiphenyle	36355-01-8	252-994-2	X	50 mg/kg (= 0.005%)
Endosulfan	115-29-7 959-98-8 33213-65-9	204-079-4		50 mg/kg (= 0.005%)
Hexachlorobutadiene	87-68-3	201-765-5		100 mg/kg (= 0.01%)
Naphtalenes polychlores				10 mg/kg (= 0.001%)
Alkanes C10-C13, chloro (short-chain chlorinated paraffins) (SCCPs)	85535-84-8	287-476-5	Lower CL by HP14 H410: 0.25%	10 000 mg/kg (= 1%)
Tetrabromodiphenylether $C_{12}H_6Br_4O$				Σ tetra-. penta-. hexa- et hepta-BDE: 1 000 mg/kg (= 0.1%)
Pentabromodiphenylether $C_{12}H_5Br_5O$				
Hexabromodiphenylether $C_{12}H_4Br_6O$				
Heptabromodiphenylether $C_{12}H_3Br_7O$				
Decabromodiphenylether - Bis(pentabromophenyl) ether	1163-19-5	214-604-9	Decision in 2019	1 000 mg/kg for products (EU 2017b)
Perfluorooctane sulfonic acid and its derivatives (PFOS) $C_8F_{17}SO_2X$ (X = OH, Metal salt (O-M +), halide, amide, and other derivatives including polymers)	1763-23-1 [1] 2795-39-3 [2] 70225-14-8 [3] 29081-56-9 [4] 29457-72-5 [5]	217-179-8 [1] 220-527-1 [2] 274-460-8 [3] 249-415-0 [4] 249-644-6 [5]		50 mg/kg (= 0.005%)
Hexabromocyclododecane (HBCDD) 'Hexabromocyclododecane' means: HBCDD, 1,2,5,6,9,10-HBCDD and its main diastereoisomers: alpha- HBCDD; beta-HBCDD; and gamma- HBCDD	25637-99-4 3194-55-6 134237-50-6 134237-51-7 134237-52-8	247-148-4 221-695-9		1 000 mg/kg (= 0.1%). Subject to review by the Commission by 20.4.2019
Candidate POP: Dicofol	115-32-2	204-082-0		
Candidate POP: Pentadecafluoroctanoic acid (perfluorooctanoic) (PFOA), its salts and derivatives	335-67-1	206-397-9		
Candidate POP: Perfluorohexane sulfonic acid (PFHxS), its salts and derivatives	355-46-4	206-587-1		

TABLE 6: Tests for HP 1, HP 2, HP 3.

H properties	Definition of "product"	Methods
H1 Explosive	Substances and preparations which may explode under the effect of flame or which are more sensitive to shocks or friction than dinitrobenzene	EC Method A14: thermal and mechanical sensitivities (impact and friction)
H2 Oxidizing	Substances and preparations which, in contact with other substances, particularly flammable substances, present a highly exothermic reaction	Gas: Method ISO 10156 (paragraph 5) Liquids: UN O2 test (liquid oxidizers) Solids: UN test O1 (oxidizing solids)
H3-A Highly flammable	Substances and preparations: in liquid form, with a flash point below 21°C, or	EC method A9
	which may become hot and finally catch fire in air at ambient temperature without any input of energy, or	Test UN N2 (pyrophoric solids) or UN N3 (pyrophoric liquids) and UN N4 (solid, self-heating)
	In the solid state, which may readily catch fire after brief contact with a source of ignition and which continue to burn or to be consumed after removal of the source of ignition, or	Test UN N1 (flammable solids)
	in the gaseous state, which are flammable in air at normal pressure, or	A11 EC method or a method of ISO 10156 (paragraph 4) standard
	which, in contact with water or damp air, evolve highly flammable gases in hazardous quantities.	Test UN N5 (substances which, in contact with water, emit flammable gases)
H3-B Flammable	Liquid substances and preparations having a flash point equal to or greater than 21°C and less than or equal to 55°C	EC method A9

Discussion on calculation methods

The method does not include the multiplier of concentration of substances with H400 and H410 hazard statement codes of the CLP (M factors), developed by classificators of products to fine tune the calculated ecotoxicity of mixtures with the most ecotoxic substances (CLP 2008). This multiplier (10, 100, 1000…) depends on the ecotoxicological effects of pure substances observed in ecotoxicological laboratory tests for substance classification. The method with M factors (CLP method limited to the level 1 and 2 of chronic ecotoxicity) has the best correspondence (80%) with the European List of Waste (Hennebert et al. 2014, 2016b, MEEM 2015). The list of harmonized M-factors is continuously completed (for instance 10 M-factors for copper in ATP9 of CLP (EU 2016)). Some classification of waste with the two methods are presented in Table 7. This point is raised because discrepancies occur when some waste become products in the circular economy and vice-versa (examples in Table 7). Without M factors, the sum of acute ecotoxic substances H400 must reach 25% of the waste, and the waste will almost never be ecotoxic acute. The rule that classifies waste is that of chronic ecotoxicity.

Attribution of an ecotoxicity hazard statement code H400 and H410 to H413 to an element

To avoid speciation hypothesis and to attribute an HSC to an element in a waste (whatever is/are the substance(s) of the element), a simple method is to compare the leachable fraction of this element to the lowest published EC_{50} (concentration producing 50% of biological effect in acute/short term tests) or NOEC (no-observed effect concentration in chronic/longer term tests) of that element. The ECHA Guidance document states that: “IV.2.3 Comparison of aquatic toxicity data and solubility data - A decision on whether or not the substance is classified will be made by comparing aquatic toxicity data and solubility data.” (page 586 of ECHA 2017). The measured solubility of an element from a substance is compared with published ecotoxicological data of the same (dissolved) element (USEPA data base, INERIS portal, list for common elements and corresponding HSC in Hennebert et al. 2014). If the soluble concentration of the element from the unknown substance(s) is lower than the classifying EC_{50} or NOEC of that dissolved element, that substance is not ecotoxic. If it is higher, the element is ecotoxic, and an HSC can be attributed to the unknown substance(s) of this element, according to the CLP rules (see Table 4.1.0 of the CLP, not presented here). The total concentration of the element (and not only the leachable concentration! See for instance CEWEP 2017) must be used in the HP 14 calculation. This approach has been proven to be consistent for a large set of waste with the European List of Waste classification and the calculation method with M-factors (Hennebert et al. 2016b). Tables of lowest EC_{50} and NOEC are supplied in this later paper.

Bioavailability

The assessment of waste should consider the bioavailability of the substances (EU 2017, 2018). According to ECHA guideline: “In general, there are no specific environmental test methods developed to measure biological availability of substances or mixtures.” (ECHA 2017). Bioavailability of elements and substances of waste is not limited to the leachable fraction: ingestion, inhalation, dermal contact are significant routes of exposure. The bioavailable fraction is not measurable. It seems today that the best method to assess bioavailability is to use a battery of biotests (Table 8).

Classification by calculation with leachable concentrations instead of total concentrations

The principle is to calculate the sum of ecotoxic substances using leachable concentrations, rather than total concentrations. Leachable concentrations of metals are

TABLE 7: Waste less severely and more severely classified without multiplying factors of concentration of substances with H400 and H410 hazard statement codes for HP 14 'Ecotoxic' chronic by calculation.

Chronic ecotoxicity	Concentration limits		Hazard HP14 vs CLP	Example of elements (« worst case with information ») or substance
M-factor	HP14: hazardous if ∑ [(100 * H410) + (10 * H411) + (H412)] ≥ 25%	CLP chronic 2: hazardous if ∑ [(10 * M * H410) + (H411)] ≥ 25%		
1 or no M	0.25% = 2 500 mg/kg	2.5% = 25 000 mg/kg	Overestimated by factor 10	Waste with Ag, Mn, Ni Plastics with brominated flame retardants
10	0.25% = 2 500 mg/kg	0.25% = 2 500 mg/kg	Equal	Waste with As, Co, Cr(VI), Cu, Pb, Se, Zn Waste with some PAH: anthracene, benzo(k) fluoranthene, fluoranthene, pyrene
100	0.25% = 2 500 mg/kg	0.025% = 250 mg/kg	Underestimated by factor 10	Waste with Cd, Hg Waste with PAH benzo(g,h,i)perylene Packaging and plastics with pesticide
1000 - 1000000	0.25% = 2 500 mg/kg	0.0025% = 25 mg/kg	Underestimated by factor 100…100000	Packaging and plastic with pesticide (i.e. chlorpyrifos M = 1 000 000)

TABLE 8: Proposed Biotest battery for HP 14 with validated concentration limits (CL) based on a set of non-hazardous and hazardous waste according to the European List of Waste (sample preparation EN 15002, EN 14735 without pH neutralization of the leachate).

Test	Standard	Expression of results of the test: Concentration of waste generating 50% effect (EC_{50})	Duration	CL (in fraction of waste in the respective dilution medium): The waste is hazardous if measured EC_{50} < CL
Aquatic tests (liquid waste or leachate of solid waste)				
Inhibition of the light emission of *Vibrio fischeri* (Luminescent bacteria test)	EN ISO 11348-3 (2007)	Eluate concentration which results in 50% inhibition of light emission (EC_{50})	30 min	EC_{50} < 15.8% rounded 15%
Freshwater algal growth inhibition test with *Pseudokirchneriella subcapitata*	EN ISO 8692 (2012)	Eluate concentration which results in 50% inhibition of population growth (EC_{50})	72 hours	EC_{50} < 7.03% rounded 10%
Inhibition of the mobility of *Daphnia magna*	EN ISO 6341 (2012)	Eluate concentration which results in 50% inhibition of mobility (EC_{50})	48 hours	EC_{50} < 7.95% rounded 10%
Terrestrial tests (solid waste)				
Soil contact test with *Arthrobacter globiformis*	ISO 18187 (2014)	Waste concentration which results in 50% inhibition of enzyme activity (EC_{50})	6 hours	EC_{50} < 2.25% rounded 5%
Effects of chemicals on the emergence and growth of higher plants (*Brassica rapa*)	EN ISO 11269-2 (2012)	Waste concentration which results in 50% inhibition of growth (EC_{50})	14 days	EC_{50} < 13.7% rounded 15%
Avoidance test with earthworms (*Eisenia fetida*)	ISO 17512-1 (2007)	Waste concentration which affects behavior by 50% (EC_{50})	48 hours	EC_{50} < 3.75% rounded 5%

typically 1/100 to 1/1000 of the total concentrations. This method classified 0 sample hazardous from 19 different waste, while the method with M factors classified 12 samples hazardous (Hennebert et al. 2014). A similar result has been found by ECN for incinerator bottom ashes (CEWEP 2017): the 95th percentile of a set of bottom ashes was found not ecotoxic based on the leaching concentration, and ecotoxic based on the total content. Furthermore, the leaching concentrations were lower than the cut-off values (CEWEP 2017).

6.3.2 By tests: HP 14 'Ecotoxic'

It is recognized that test results prevail on calculation results (EU 2017a, EU 2018), due to not-enough-detailed chemical analysis, unknown antagonist or synergic effects, unknown speciation, unknown bioavailability, and so on. An additional reason is that the current calculation formula for waste do not use the M factors. No harmonized test battery is available at EU level. Building on a very large interlaboratory trial in 2006 (Moser and Römbke 2009, Moser and Kessler 2009, Moser et al. 2010), French and German experts have suggested a test battery (Pandard and Römbke 2013), now without options and with validated concentration limits (Hennebert 2018) (Table 8). Concentration limits are based on a reference: it is not possible to assess "ex nihilo" the hazardousness or not of a given biological effect. Educated guess by experts has not produced a consensus on that topic since the '90s (Hennebert 2018). The proposed concentrations limits are simply the highest ecotoxic effect observed in a set of 10 waste non-hazardous by the European list of waste (taken as the reference) and well-studied from Belgium, France and Germany. They have correctly classified 13 hazardous waste by list as ecotoxic. Hence, these limits are validated by 23 waste from 3 countries. They can be improved, as more data of H or non-H by list (in particular from the Member States of the EU) are available.

Discussion on neutralization of leachate of acid or alkaline waste before dilution and testing, or for some dilutions

EN 14735:2006 "Characterization of waste - Preparation of waste samples for ecotoxicity tests" states at section 10.5 pH: "Tests shall be carried out without pH adjustment of the test portion. pH of all test mixtures is measured at the beginning and at the end of the test and reported." And in a note (non-normative): "If toxic effects are observed in the dilutions where pH is not compatible with the survival of the organisms, the test(s) can be repeated with pH adjustment of the test portion." As most elements (in particular in equilibrium with a solid phase) are more soluble in acid and alkaline pH domains (for instance CEWEP 2017), the pH neutralization (for some dilutions of the test portion or for the whole test portion) precipitates a significant part of the elements (for instance Nilsson et al. 2016) and reduce ecotoxicity beyond the effect of $[H^+]$ or $[OH^-]$ concentrations. The classification of waste for the hazard property HP 14 'Ecotoxic' is weakened: experimental data show that neutralization of the leachate before dilution deletes ecotoxicity, even when the final pH of the different mixtures of culture medium and waste leachate is the same. The effects are less if only the ecotoxic dilutions are neutralized (and not the original leachate). Additional neutralization of leachates removes ecotoxicity, beyond the ecotoxicity of H^+ and OH^-. It should be noted that the culture media that is mixed with the waste leachate at different dilutions for the test (the result of the test is a dose/response relationship) is buffered for acid/base concentrations. The test battery has been developed since 2006 without pH neutralization of the leachate.

To reduce ecotoxicity for beneficial use, prior to reuse or storage in contact with natural environment, the waste flow (and not the laboratory waste leachate) should be pre-treated. For acidic waste (like waste containing sulphide that oxidize to sulfuric acid in contact with air), input of alkalinity (eventually with waste like concrete) is necessary. For alkaline waste, a simple solution is to let them freely evolve by natural carbonation with atmospheric CO_2, to reach the desired pH, like the "maturation" of the municipal solid waste incinerator bottom ashes. If the soluble alkalinity in the waste is sodic or potassic, soluble calcium (like synthetic gypsum from desulfurization of fumes of coal power plants) must be added. The soluble alkalinity will precipitate as calcium carbonate, and the pH of the liquid phase will be about 8.5 when the reaction is completed.

6.4 Capable of exhibiting a hazardous property not displayed by the original waste

Aside the presence of some very specific heating or explosive substances in confined environments with specific HSC (EU 2018), this HP needs a specific study. Waste with reduced substances that can oxidize with detrimental environmental effects (sulphidic ores unbalanced by alkalinity, producing sulfuric acid and dissolving mined elements, acid mine drainage), substances that can be liberated by anaerobic biodegradation of organic matter (decay of marine algae producing toxic H_2S) or on the long term by weathering of minerals, should be considered. The presence of sulphide and alkalinity can be assessed by EN 15875. It should be noted that "acid-generating tailings from processing of sulphide ore" are a hazardous entry in the European List of Waste (01 03 04*; "*" means hazardous in the list).

7. CONCLUSIONS

A complete set of practical methods is now available for a proper classification of waste, becoming more important as loops of material are increasingly created in the circular economy. Experience has shown that unexpected substances can be detected by the methods expounded here, allowing a better management of matters and materials.

A novel approach for speciation of elements into substances based on "worst case with information" of the physico-chemical characteristics of the waste, as a first step for classification, has been suggested. This method makes it possible to immediately identify the elements that cannot classify the waste as hazardous and thus to concentrate the classifier's efforts on the elements that can classify as hazardous.

Finally, the identification of the hazard helps waste producers, waste managers and public authorities to manage hazardous waste by controlling the risk of their reuse or recycling for people, infrastructures, and the environment.

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