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EU WASTE HAZARDOUSNESS ASSESSMENT - PROPOSITION OF METHODS

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SUMMARY: The European waste hazardousness classification is currently under revision by the DG ENV of the European Commission and the Member States. This paper proposes some methods for measuring or calculating some Hazard Properties (HP). Laboratory test batteries for assessing HP 1 ‘Explosive’, HP 2 ‘Oxidising’, HP 3 ‘Flammable’ and HP 14 ‘Ecotoxic’ are proposed. For calculations of HP 3 to 8, 10, 11 and 13 to 14, a general analytical protocol for the determination of elements and substances in waste has been developed in France and is submitted to CEN TC292 “Characterisation of waste” for standardization. All the organic substances, mineral elements and main anions are identified and quantified if their concentration is greater than > 0.1% or a lower threshold. For mineral elements, a stepwise approach for the difficult speciation of elements in mineral substances in waste is proposed. In a first “worst case” approach, for the different HPs, tables with concentration limits triggering the classification control are presented. For HP 14, two additional “worst case” methods are proposed, as well as an approach based on leachate concentration, taking into account the aquatic bioavailability of potential pollutants of waste. Detailed proposition of methods with tables of EC_{50}, NOEC and M factors for hundreds of organic and mineral substances for calculation of HP 14 are provided in a full technical document (soon available at http://www.ineris.fr/taxonomy/term/1591).

1. INTRODUCTION

The European Waste Framework Directive (2008/98/EC) and the List of Wastes Decision (2000/532/EC) are under revision. The DG Environment of the EU has proposed new definitions for the waste hazardousness assessment (DG ENV 2012a and b). This paper proposes methods to apply the classification rules where no methods are available or defined yet.

A tiered approach is recommended for waste assessment:

- 1st tier: Classification 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 content and "worst case" hypothesis from total elemental content. If the "worst case" 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, or tests.

An example of tiered approach can be found in Lewin *et al* (2012).

It is remembered that landfill acceptance criteria cannot replace the waste hazardousness assessment.

The classification approach and the propositions of this paper are summarized in Figure 1.

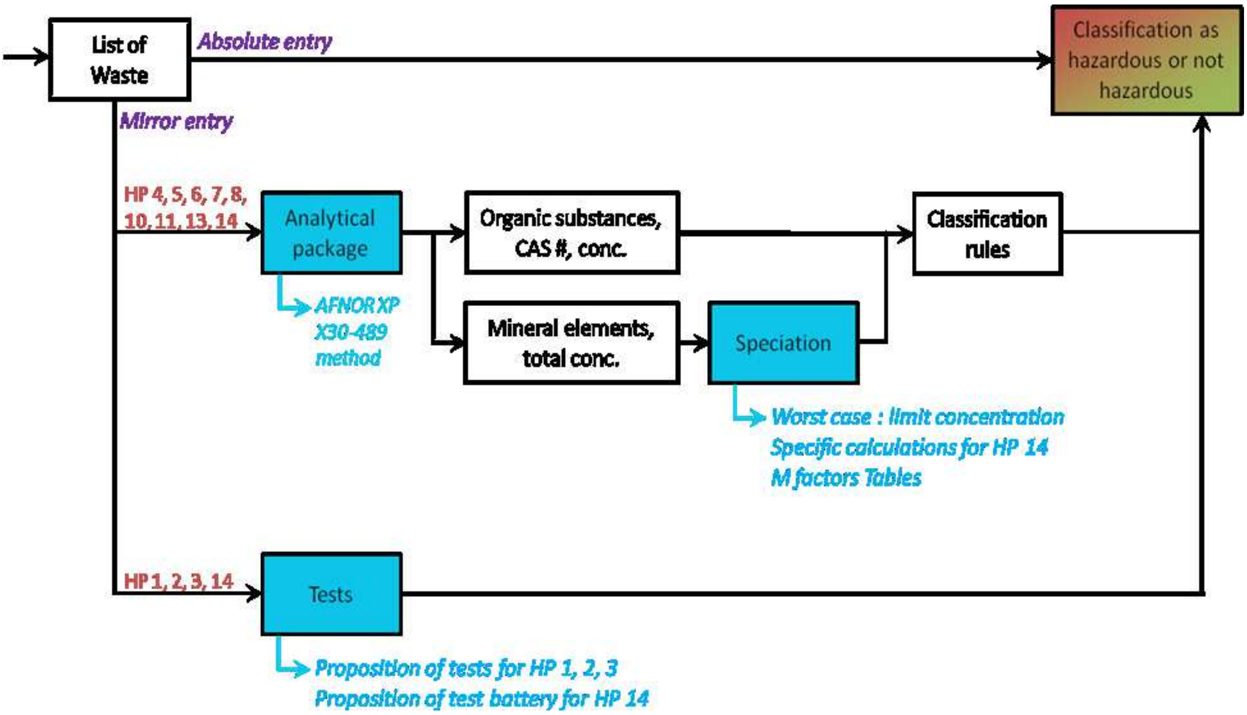

Figure 1: Method for classification of waste from chemical composition and tests

An **analytical package** allows the detection and the semi-quantification of all the organic substances and all the mineral elements present in a liquid or solid waste sample. New parameters are defined and a mass balance is used as quality control. Results can be used for calculations of HP 3 to 8, 10, 11 and 13 to 14.

Stepwise surrogates methods are proposed for the **speciation of the elements in mineral substances**, from the "worst case" approach: if the element concentration, expressed in substance, is below the concentration limit of the most hazardous substance of that element for that HP, the waste is not hazardous by that element. This rule is refined when sum of substances are to be accounted for.

Battery of laboratory tests are proposed for HP 1 'Explosive', HP 2 'Oxidising' and HP 3 'Flammable'. They are more convenient than the detection of substances with corresponding hazard statement codes (R or H), as it is proposed by DG ENV. A battery of ecotoxicological test is proposed for HP 14 ‘Ecotoxic’.

A useful concept is the hazard index. A hazard index of a rule of a hazard property is the ratio of the relevant concentrations (for some HPs the sum or the weighted sum) by the concentration limit of this rule of this HP. If it is ≥ 1 [the (sum of) (weighted) concentration(s) is/are above the concentration limit(s)], the waste is hazardous for this HP. If it is <1, the waste is considered as non-hazardous.

Those methods are explained in detail in a guide (Hennebert and Rebischung, 2013).

2. PROPOSITION OF ANALYTICAL PACKAGE

A method for the exhaustive determination of elements and substances in liquid and solid waste has been developed in France (AFNOR 2013). It is proposed for standardization at European level to CEN TC 292 « Characterization of waste ».

New parameters taking into account unresolved chromatographically mass of volatile extracts, semi-volatile extracts, and non extractible pool, are proposed. This latter is assumed to be high molecular weight insoluble compounds –polymers, cellulose, lignin, etc…), without hazard. An analytical mass balance between 90% and 110% is reached for most waste. The analytical laboratory will provide tabular mass balance, the list of elements and substances, CAS number, concentrations, and limits of quantification. Concentrations in solid waste are expressed in mg/kg dry matter at 105 °C (some analyses are performed on raw waste or pretreated at 40 °C, the water content of raw and pretreated are measured on a separate aliquot and the results are expressed on a dry matter at 105 °C) and in mg/kg of raw material. Concentrations of liquid waste are expressed in mg/kg of raw material. The method and results with 32 waste can be found in Hennebert *et al*, 2013.

3. PROPOSITION OF ELEMENT SPECIATION SURROGATES

The elemental analyses performed in the laboratory do not speciate the chemical form of minerals present in the waste. Since classification rules are based on substances, it is necessary to reconstruct a mineralogical set from available information, or to bypass the problem. Different methods are presented below. A tiered approach is proposed.

3.1 Cases for which speciation is not neseccary: “worst case calculations”, generic entries

3.1.1”Worst case” calculation

For each HP (and for some HP for each different rule), a hypothetical mineralogical set can be developed from stoichiometric calculation focusing on the most toxic substances (i.e. classifying substances with lowest limit concentration). This method is called "worst case". This approach is used in the document of the German Federal Ministry of the Environment (BAM 2002) and by the consulting firm POLDEN in 2004 (Abdelghafour *et al*, 2002).

It can be used for HP 4 'Irritant – Skin irritation and eye damage', HP 5 'Specific Target Organ Toxicity (STOT)/Aspiration', HP 6 'Acute Toxicity', HP 7 'Carcinogenic', HP 8 'Corrosive', HP 10 'Toxic for reproduction', HP 11 'Mutagenic', HP 13 'Sensitising'. Tables are available for each HP in Hennebert and Rebischung 2013. An example is given for HP 4 in Table 1.

The method is the following:

- calculate for each element the ratio between the element concentration in the waste and the calculated element concentration limit supplied in the Table
- compare the sum or the maximum of these ratios to 1:
    - Sum for HP 4, HP 6, HP 8 and HP 14. This sum should also include the ratios for organic substances detected in the waste, between the measured concentration and the corresponding concentration limit;
    - Maximum for HP 5, HP 7, HP 10, HP 11 and HP 13.

If the sum / maximum of these ratios is lower than 1, the waste is not classified as hazardous for this property, and no other actions are necessary, especially speciation.

Conversely, if the sum / maximum of these ratios is greater than 1, the waste could be classified as hazardous by this element, and further speciation should be performed.

Note: Concentration of element or concentration of substance?

The important point in the calculation is to compare similar concentrations in the ratios:

- either element concentration in the waste and a calculated element concentration limit, as previously described worst case approach,
- or a (sometimes hypothetical) substance is attributed to the element, and this substance concentration is compared to the concentration limit provided by the regulation.

Table 1 : Most hazardous substances by element (worst case approach) and corresponding concentration limit of element for HP 4

Element	HP 4 Min. Concentration limit / substance	Worst case substance	Formula	CAS#	Worst case Concentration limit /element in this substance
Ag					
Al	1%	Aluminium lithium hydride	$LiAlH_4$	16853-85-3	0.71%
As					
B	1%	Boron tribromide	BBr_3	10294-33-4	0.043%
Ba	20%	BaS / Barium polysulphides	BaS	21109-95-5	16.21%
Be	20%	BeSeO4:4H2O	$BeSeO_4$:4H2O		0.80%
Ca	10%	Calcium cyanamide	$CCaN_2$	156-62-7	5.00%
Cd					
Co					
Cr III					
Cr VI	1%	Chromyl dichloride; chromic oxychloride	Cl_2CrO_2	14977-61-8	0.34%

Element	HP 4 Min. Concentration limit / substance	Worst case substance	Formula	CAS#	Worst case Concentration limit /element in this substance
Cu	10%	Copper(II) methanesulfonate	$C_2H_6CuO_6S_2$	54253-62-2	2.50%
Fe	20%	Ferrous sulfate heptahydrate	$FeSO_4.7H2O$	7782-63-0	4.02%
Hg	20%	Mercury (I) chloride	Hg_2Cl_2	10112-91-1	17.00%
K	1%	Potassium hydroxide; caustic potash	KOH	1310-58-3	0.70%
Li	1%	n-hexyllithium	$C_6H_{13}Li$	21369-64-2	0.075%
Mg					
Mn					
Mo	20%	BeMoO4	$BeMoO_4$		11.36%
Na	1%	Sodium hydroxide; caustic soda	NaOH	1310-73-2	0.57%
Ni	1%	Nickel(II) octanoate	$C_{16}H_{30}NiO_4$	4995-91-9	0.17%
P	1%	Phosphoryl trichloride	Cl_3OP	10025-87-3	0.20%
Pb	10%	Lead(II) methanesulphonate	$C_2H_6O_6PbS_2$	17570-76-2	5.21%
S	1%	Thionyl dichloride; thionyl chloride	Cl_2OS	7719-09-7	0.27%
Sb					
Se	20%	BeSeO4:4H2O	$BeSeO_4$:4H2O		7.05%
Si	1%	Trichlorosilane	HCl_3Si	10025-78-2	0.21%
Sn					
Sr					
Tl	20%	Dithallium sulphate; thallic sulphate	Tl_2SO4	7446-18-6	16.19%
U					
V	10%	Divanadyl pyrophosphate	$H_5O_{30}P_5V_6$	65232-89-5	3.23%
Zn	10%	ZnSO4:1H2O	$ZnSO_4$:1H2O	7446-19-7	3.64%

3.1.2 Generic entries

No speciation is necessary for the elements having a « generic entry » in the list of harmonized classification and labeling of hazardous substances (CLP Regulation 2008), subject to prove those elements are not under one of the other forms specified in the CLP Regulation annex.

The “generic” entries are presented in Table 2 (extract from CLP Regulation Table 3.1 of Annex VI). They have no CAS number.

Table 2: Generic entries of elements in the CLP

Element	Index No	International Chemical Identification	Hazard Class and Category Code(s)	Hazard Statement Code(s)
As	033-002-00-5	**arsenic** compounds, with the exception of those specified elsewhere in this Annex	Acute Tox. 3 * Acute Tox. 3 * Aquatic Acute 1 Aquatic Chronic 1	H331 H301 H400 H410
Ba	056-002-00-7	**barium** salts, with the exception of barium	Acute Tox. 4 *	H332

Element	Index No	International Chemical Identification	Hazard Class and Category Code(s)	Hazard Statement Code(s)
		sulphate, salts of 1-azo-2-hydroxynaphthalenyl aryl sulphonic acid, and of salts specified elsewhere in this Annex	Acute Tox. 4 *	H302
Be	004-002-00-2	**beryllium** compounds with the exception of aluminium beryllium silicates, and with those specified elsewhere in this Annex	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 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	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	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	Acute Tox. 2 * Acute Tox. 1 Acute Tox. 2 * STOT RE 2 * Aquatic Acute 1 Aquatic Chronic 1	H330 H310 H300 H373 ** H400 H410
Pb	082-001-00-6	**lead** compounds with the exception of those specified elsewhere in this Annex	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 (Sb_2O_4), pentoxide (Sb_2O_5), trisulphide (Sb_2S_3), pentasulphide (Sb_2S_5) and those specified elsewhere in this Annex	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	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	Acute Tox. 2 * Acute Tox. 2 * STOT RE 2 *	H330 H300 H373 **

Element	Index No	International Chemical Identification	Hazard Class and Category Code(s)	Hazard Statement Code(s)
			Aquatic Chronic 2	H411
U	092-002-00-3	**uranium** compounds with the exception of those specified elsewhere in this Annex	Acute Tox. 2 * Acute Tox. 2 * STOT RE 2 Aquatic Chronic 2	H330 H300 H373** H411

In practice, speciation is therefore important for **copper, zinc** and **nickel,** which have no generic entries:

- Some **copper** substances have toxic and ecotoxic properties of level 1 and 2 due to the accompanying anions (CN, Se, SeO_3, CrO_4). Copper sulphate has toxic properties of level 2 or 4 and acute and chronic ecotoxicity of level 1. Copper with oxidation level of one Cu(I) (i.e. Cu(I)Cl, $Cu(I)_2O$) is considered as not present in oxidized waste;
- **Zinc** sulphate and chloride have some toxic properties. Sulphate, chloride and oxide have acute and chronic exotoxicity code H400 and H410;
- **Nickel** substances have ± 40 entries in the CLP. Some substances have hazard statement codes classifying for HP 4, 5, 6, 7, 10, 11 and 15. For HP 14, all M factors are set to 1 when the substances have a hazard statement code H400 or H410.

3.2 “Worst case with information” calculation

The method is identical to the previous one, but some substances are not taken into account on the basis of available information on waste: pH, redox potential, rare or highly reactive substances, anions, production process, knowledge of similar waste, etc... Expertise plays an important role. This method is called "worst case with information".

If the calculated mineralogical set does not trigger the classification as hazardous, the waste is considered to be non-hazardous for this classification rule. Otherwise, or if an element is not likely to be in the form of some hazardous substance, but data is lacking to be sure, the evaluation can be deepened by true speciation of only the element(s) identified as presenting issue of classification.

3.3 Speciation

In this case, there are several ways to determine the mineralogical set in the waste:

- via the literature for waste from processes with composition known as constant, with statistical approach to mineral composition, or;
- using different analytical methods (electron microscopy, XRD ... with LOQ of 5 – 2 %w/w), or;
- via a calculation from geochemical solubility measurements at different pH. **This method is in practice the sole that can be used for trace elements**. From solubility at 8 different pH from 2 to 12 (CEN/TS 14429, CEN 2005), mineralogy is derived by saturation index (matching between observed and calculated concentrations at different pH) taking into account all the the species in solution and particular reactive solid phases. A useful tool is the database and databrowser LeachXS and the associated (editable)

geochemical code Orchestra (van der Sloot et al, 2008). Un example can be foind in Turrel et al (2012).

Unfortunately, hazard statement code will most of the time not be available for the minerals that have been found.

3. 4. The specific case of HP 14

HP 14 is the most frequent hazardous properties (Hennebert *et al*, 2013). The proposition of DG ENV (2012a) is that a waste is hazardous if

$$\text{If } \sum(\text{cc Aquatic Acute 1 H400} \times M_{acute}) \geq 25\ \%, \text{ or}$$

$$\text{If } (M_{chronic} \times 10 \times \sum \text{cc Aquatic Chronic 1 H410}) + \sum(\text{cc Aquatic Chronic 2 H411}) \geq 25\%$$

M factor is a multiplicative substance factor used to adapt the concentration limits to information available on aquatic ecotoxicity of substances H400 and H410 (and to avoid multiple concentration limits). It is calculated from the lowest data available of EC_{50} (concentration with 50% of biological effect) and NOEC (no observed effect concentration) of a substance among different organisms. If a substance has an EC_{50} or a NOEC < 0.1 mg/l and 0.01 mg/l respectively, but has not a hazard statement code H400 or H410, M factors do not apply.

Table 3 : Multiplying factors for highly toxic components or mixtures (CLP 2008)

Acute toxicity	M_{acute} factor	Chronic toxicity	$M_{chronic}$ factor	
$L(E)C_{50}$ value mg/l		NOEC value mg/l	Non-rapidly degradable components	Rapidly degradable components
$0.1 < L(E)C_{50} \leq 1$	1	$0.01 < NOEC \leq 0.1$	1	-
$0.01 < L(E)C_{50} \leq 0.1$	10	$0.001 < NOEC \leq 0.01$	10	1
$0.001 < L(E)C_{50} \leq 0.01$	100	$0.0001 < NOEC \leq 0.001$	100	10
$0.0001 < L(E)C_{50} \leq 0.001$	1 000	$0.00001 < NOEC \leq 0.0001$	1 000	100
$0.00001 < L(E)C_{50} \leq 0.0001$	10 000	$0.000001 < NOEC \leq 0.00001$	10 000	1 000
(continue in factor 10 intervals)		(continue in factor 10 intervals)		

M_{acute} factors are available in the CLP annex (CLP 2008) for pesticides and nickel substances. A large panel of M_{acute} and $M_{chronic}$ factors for mineral and organic substances, derived from the Portal of Chemical substances from INERIS (http://www.ineris.fr/substances/fr/) are reported in Hennebert and Rebischung, 2013.

3.4.1 "Worst case" approach and generic entries when the mineral substances are not known

The Tables 5 and 6 show the minimum EC_{50} and NOEC values extracted from the Portal of chemical substances from INERIS (http://www.ineris.fr/substances/fr/) of March 2013 and other data source among the species of metallic elements and metalloids. **The elements in bold have generic entries**. No further speciation work is required, as far as you can prove or judge that the "compounds specified elsewhere in this Annex" are not present in the waste.

If the waste contains only one element that can form a substance with H400 or H410 hazard statement code (and no organic substances with those codes), in a worst case approach, compare the total content with the concentration limit (penultimate column). If it is lower, the waste will not be H400 or H410.

If the waste contains more than one element that can form a substance with H400 or H410 hazard statement code (and no organic substances with those codes), in a worst case approach, compute the sum of ratios (concentration/concentration limit). If it is < 1, the waste will not be H400 or H410.

Note: Concentration of element or concentration of substance ?

In the worst case approach, normally the substance concentration is used for hazard calculation. But for HP 14, in the worst case approach, taking into account that EC_{50} and NOEC of heavy metals and metalloids are frequently expressed in element concentrations (mg/l), the element concentration is used rather than the substance concentration. For the generic entries, the element concentration is used for hazard calculation.

Table 4: Minimal EC_{50}, maximal M_{acute} factor, maximal concentration limit and cut-off value for "worst case" approach in HP 14 acute ecotoxicity

Element	Acute ecotoxicity hazard statement code	EC_{50} min (mg element/l)	Substance	M_{acute}	Concentration limit acute (mg element/kg)	Cut-off value acute (mg element/kg)
Hg	H400	0.0007	n.s.	1 000	250	1
Cd	H400	0.0034	$CdCl_2$	100	2 500	10
Cu	H400	0.011*	n.s.	10	25 000	100
As	H400	0.011	AsH_2KO_4	10	25 000	100
Pb	H400	0.026	$Pb(NO_3)_2$	10	25 000	100
Cr(VI)	H400	0.030	$K_2Cr_2O_7$	10	25 000	100
Zn	H400	0.032	$ZnCl_2$	10	25 000	100
Ni	H400	0.060	$NiCl_2$	1	250 000	1 000
Se	H400	not found		1	250 000	1 000
Tl	-	0.01	n.s.	-	-	-
U	-	0.04	n.s.	-	-	-
Be	-	0.1	n.s.	-	-	-
Sb	-	1.77	$SbCl_3$	-	-	-
Ba	-	14.5	n.s.	-	-	-
Mo	-	29	n.s.	-	-	-

n.s.: not specified / *: a lower value can be found in a European Commission - European Voluntary Risk Assessment Report

(EU-VRAR) report but it is proposed to use this value instead

Table 5: Minimal NOEC, maximal $M_{chronic}$ factor, maximal concentration limit and cut-off value for “worst case” approach in HP 14 chronic ecotoxicity

Element	**Chronic ecotoxicity hazard statement code**	**NOEC min (mg/l)**	**Substance**	**$M_{chronic}$**	**Concentration limit chronic (mg element/kg)**	**Cut-off value chronic (mg element/kg)**
Hg	H410	0.0001	n.s.	100	250	10
Cd	H410	0.00016	$CdCl_2$	100	250	10
Se	H410	0.0018	Na_2SeO_3	10	2 500	100
Cu	H410	0.0022	$CuCl_2$	10	2 500	100
Cr(VI)	H410	0.0047	$K_2Cr_2O_7$	10	2 500	100
As	H410	0.0050	$AsHNa_2O_4$	10	2 500	100
Pb	H410	0.0063	n.s.	10	2 500	100
Zn	H410	0.01	$ZnSO_4$	10	2 500	100
Ni	H410	0.011*	$NiCl_2$	1	25 000	1 000
Be	H411	0.0038	n.s.	-	250 000	10 000
Sb	H411	1.13	$SbCl_3$	-	250 000	10 000
Tl	H411	0.002	n.s.	-	250 000	10 000
U	H411	0.0007	n.s.	-	250 000	10 000
Ba	-	2.9	n.s.	-	-	-
Mo	-	54	n.s.	-	-	-

n.s.: not specified / *: a lower value can be found in a European Commission - European Voluntary Risk Assessment Report (EU-VRAR) report but it is proposed to use this value instead

Table 6: Most hazardous substances by element (worst case approach) and corresponding concentration limit of element for HP 14 acute and chronic, for other elements than in Tables 14 and 15

Element	**HP 14 Min. Concentration limit /substance**	**Worst case substance**	**Formula**	**CAS#**	**Worst case Concentration limit /element**
Ag	2.50%	Silver sodium zirconium hydrogenphosphate	$AgNaZrHPO_4$	155925-27-2	0.85%
Al	0.25%	Aluminium phosphide	AlP	20859-73-8	0.12%
B	2.50%	Trinickel boride	BNi_3	12007-02-2	0.14%
Ca	0.25%	Calcium phosphide; tricalcium diphosphide	Ca_3P_2	1305-99-3	0.055%
Co	0.25%	Cobalt dinitrate	$Co(NO_3)_2$	10141-05-6	0.081%
Cr III					
Fe	2.50%	$Pb_2Fe(Cyanide)_6$	$Pb_2Fe(Cyanide)_6$		0.22%
K	0.25%	Potassium dichromate	$K_2Cr_2O_7$	7778-50-9	0.066%
Li	2.50%	Cobalt lithium nickel oxide	CoLiNiO	131344-56-4	0.12%
Mg	0.25%	Magnesium phosphide; trimagnesium diphosphide	Mg_3P_2	12057-74-8	0.14%
Mn	2.50%	$MnSeO_4$:5H2O	$MnSeO_4:5H_2O$		0.48%

Element	HP 14 Min. Concentration limit /substance	Worst case substance	Formula	CAS#	Worst case Concentration limit /element
Na	0.25%	Sodium arsenite	$NaAsO_2$	7784-46-5	0.044%
P	0.025%	Trizinc diphosphide; zinc phosphide	P_2Zn_3	1314-84-7	0.0060%
S	0.25%	Propoxycarbazone-sodium	$C_{15}H_{17}N_4NaO_7S$	181274-15-7	0.019%
Si	2.50%	Lead hexafluorosilicate	F_6PbSi	25808-74-6	0.20%
Sn	2.50%	$SnSe_2$	$SnSe_2$	20770-09-6	1.07%
Sr	2.50%	$SrSeO_4$	$SrSeO_4$	7446-21-1	0.95%
V	2.50%	$Pb_3(VO4)_2$	$Pb_3(VO_4)_2$		0.30%

3.4.2“Worst case” approach for acute ecotoxicity with the total concentrations and the minimal EC_{50}

The CLP regulation allows calculating the EC_{50} of a part of a mixture like a waste by combining individual EC_{50} of the substances and their total concentration. This should at best be done with EC_{50} values of the same taxonomic group (CLP 2008 p.136). The result is a calculated EC_{50m} of the mixture. This is valid **only for acute hazard** (4.1.3.3.1 of CLP). The EC_{50m} of a mixture (the waste) is calculated from the concentration of substances and the EC of each substance:

$$\frac{\sum Ci}{L(E)C50\,m} = \sum \frac{Ci}{L(E)C50\,i}$$

where:

Ci = concentration of component i (weight percentage)

L(E)C50 i = (mg/l) LC50 or EC50 for component i

L(E)C50 m = L(E) C50 of the part of the mixture with test data

The mixture is classified according to Table 4.1.0 of CLP regulation: it is acute Category 1 if $CE_{50m} \leq 1$ mg/l.

This approach could be used in “worst case” calculation with the EC_{50} values:

- If $EC_{50\ m}$ is lower than 1 mg/l, that part of the waste (sum of C_i) has a hazard statement code H400. If it is higher, it has no hazard statement code;
- If $EC_{50\ m}$ is lower than 0.1 mg/l, assign a M_{acute} factor to that part of the waste with the Table 3;
- Calculate the acute ecotoxicity of the waste with that part of the waste (sum of C_i) and all the substances having H400 hazard statement code: the waste is Aquatic Acute if:

$$\sum(c\ Aquatic\ Acute\ 1 \times M) \geq 25\ \%.$$

3.4.3 The total and leachate concentrations of elements are known

One could consider that the leachate concentration of elements could be used for classification for aquatic ecotoxicity.

In waste leachate with liquid/solid ratio of 10 l/kg, soluble substances are totally dissolved in the leachate and less soluble (partially dissolved) substances control the concentration of the element in the leachate (solid/liquid equilibrium). In both cases, the soluble concentration cannot be higher. The leachate concentration represents the maximum concentration of the element that will be in contact with organisms during aquatic ecotoxicity tests.

Proposition of Method

If the leachate concentration of an element is lower than the ecotoxic concentration (EC_{50} and NOEC) of that element from a soluble form (Tables 5 and 6), the substance(s) that contain(s) that element is/are not hazardous and receive no hazard statement code, whatever that substance is. The waste is then classified according to the total content.

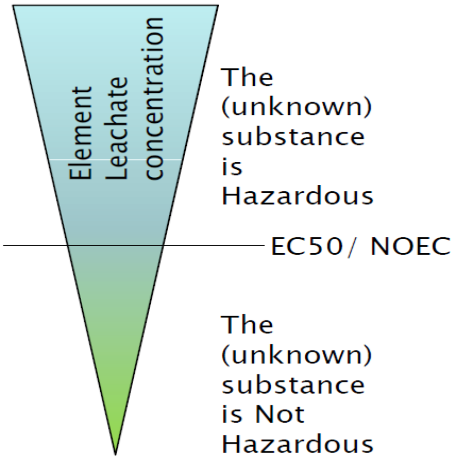

Figure 2: Scheme of attribution of hazard statement to unknown substances with leachate concentration

In practice

1. Measure the element concentration in the leachate C_L (like for landfill acceptance);

2. Compare with minimal EC_{50} and NOEC of the element (Tables 5 and 6;

3. If $C_L < EC_{50}$ and NOEC, the substance containing that element is not soluble enough to be ecotoxic;

4. If $C_L \geq EC_{50}$ or NOEC, the substance containing that element is soluble enough to be ecotoxic: attribute the hazard statement code of the Tables (H400, H410, H411, or no code), the EC_{50} and NOEC, and the M_{acute} and Mc_{hronic} factors to that substance.

Hazard assessment (in progress) for 41 waste for HP14 acute classifies 7 waste hazardous for with the worst case method (3.4.1), 3 waste for the mixture method (3.4.2) and 2 waste for the leachate method (3.4.3).

For HP 14 acute (the most frequent HP property), the scores are 25 times hazardous for with the worst case method (3.4.1) and 22 times for the leachate method (3.4.3).

4. PROPOSITION OF TESTS

4.1 Tests for HP 1 ‘Explosive’, HP 2 ‘Oxidising’ and HP 3 ‘Flammable’

According to the DG ENV proposal, a waste will be hazardous if it contains substances with given hazard statement codes Hxx, without concentration limits. The substances for HP 1 and 2 and some substances for HP 3 are not measured in routine by service laboratories. Most of the time the presence of those substances for HP 1 and HP 2 will be known by the origin of the waste rather than by analysis at laboratory. An easy alternative to that is laboratory tests.

In France the battery of test applicable to waste for (present) properties H1, H2 and H3 is defined by the Order of 08.07.03. The methods are listed in Table 7. These tests are conducted by laboratories specialised in product characterization.

4.2 Tests for ecotoxicity

A battery of test emerging from a ring test with 64 laboratories from European countries and the U.S. (Moser and Römbke, 2009) is proposed by Pandard and Römbke (2013). This step-wise approach begins with tests performed with waste eluates. The results of these tests can be expressed as EC_x values (concentration of eluate or solid in the mixture with the control substrate producing an effect of x %) or as LID values (lowest ineffective dilution rate). Preparation of eluates (liquid/solid ratio = 10 l/kg dry matter, 24h) and mixtures of waste with control substrate are carried out according to EN 14735 (CEN 2006). If one of the EC values in the eluate tests is below a specific limit value (or one of the LID values is above a specific limit value), the waste is classified as hazardous. Otherwise, solid waste tests are carried out. The waste is considered as non-hazardous only if all the results are above the limit values.

Results of tests overwhelm results of calculations. If the results of calculations are dubious (by lack of information), the test battery (eventually step-wise) should be performed. The test is performed with various dilutions without pH adjustment, and the test is then repeated for dilution(s) with toxic pH adjustment between 6.5 and 8.5. (Pandard,2004).

Table 7: Tests for H 1, H 2 and H 3 applicable to waste in France, and proposed for HP 1, HP 2 and 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

In practice, the test UN N1 (flammable solids) and EC method A9 (flash point of liquids) are the most frequent. An alternative is to use the analytical package results to detect substances with a flash point < 55 °C.

Table 8: Recommended test battery for assessing HP 14

Test	Endpoints	EC or LID limit values: the waste is HP 14 if	Duration	Standard
1. Aquatic tests				
Inhibition of the light emission of *Vibrio fischeri* (Luminescent bacteria test)	Eluate concentration which results in 50% inhibition of light emission (EC_{50}), *or* Dilution step at which light emission is inhibited by more than 20% in comparison to the control	$EC_{50} \leq 10\%$ LID > 8	30 min	EN ISO 11348-3(2007)
Freshwater algal growth inhibition test with *Desmodesmus subspicatus* or *Pseudokirchneriella subcapitata*	Eluate concentration which results in 50% inhibition of population growth (EC_{50}), *or* Dilution step at which population growth is inhibited by more than 25% in comparison to the control	$EC_{50} \leq 10\%$ LID > 8	72 h	EN ISO 8692 (2012)
Inhibition of the mobility of *Daphnia magna* -	Eluate concentration which results in 50% inhibition of mobility (EC_{50}), *or* Dilution step at which mobility is inhibited by more than 20% in comparison to the control	$EC_{50} \leq 10\%$ LID > 8	48 h	EN ISO 6341 (2012)
2. Terrestrial tests				
Soil contact test with *Arthrobacter globiformis* (bacteria contact test)	Waste concentration which results in 50% inhibition of enzyme activity (EC_{50}), *or* Dilution step at which enzyme activity is inhibited by more than 30%	$EC_{50} \leq 10\%$ LID > 8	6 h	ISO/DIS 10871 (2008)
Effects of chemicals on the emergence and growth of higher plants (*Avena sativa*, *Brassica napus*)	Waste concentration which results in 50% inhibition of growth (EC_{50}), *or* Dilution step at which growth is inhibited by more than 30%	$EC_{50} \leq 10\%$ LID > 8	14 d	ISO 11269-2 (2012)
Avoidance test with earthworms (*Eisenia andrei/fetida*)	Waste concentration which affects behaviour by 50% (EC_{50}), *or* Dilution step at which behaviour is impacted by more than 40%	$EC_{50} \leq 10\%$ LID > 8	48 h	ISO 17512-1 (2007)

4. CONCLUSION

This paper proposes methods for some aspects that have not yet been fully defined for the assessment of the hazard waste. Within the European objectives of priority reuse, recycling and recovery, the hazard must be measurable.

A tiered approach and a unified analytical method for minimizing the effort of waste classification are proposed. The analytical results are useable for classification of product as well, in case of end-of-waste status.

Users are encouraged to share their experience to improve the methods or clarify the practical cases that are not covered here.

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