II-O-10. DETERMINING THE DANGEROUSNESS OF WASTE

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Summary: Producers and holders of waste - legal entities - are forced to classify each type of waste generated by their activity in the national list of waste (for Romania, waste list is enclosed in the Government Decision no. 856/2002). Therefore, occur frequently requests to characterize the waste in order to their classification. This has made to be necessary a methodology to establish (in a consistent and reproducible manner that take into account the legislative provisions and the needs of those working in the production, transport and capitalization/waste disposal) the hazardous/non - hazardous nature of a waste. The methodology established and used in the INCD ECOIND Bucharest was based on Romanian legislation (legislation harmonized with the European one), which, however, is not able to make easy work of framing a waste.

Methodology for determining the dangerousness of waste is laborious. A correct methodology requires as much information about the analyzed waste: data obtained from the client, from literature, from safety data sheets of the raw materials used in waste-generating processes or in waste – treating processes, from data obtained by analytical determinations performed on waste samples analyzed; it is important, therefore, to correctly identify the quality indicators to be determined. Further, the method includes identifying risk phrases of all determined or potential components existing in waste. The quantification of dangerous properties of analyzed waste samples is achieved by summing the total concentration of compounds that shows the same risk phrase, responsible for a particular dangerous property.

To minimize the effort of applying this methodology, it was necessary to develop a database (with the names of substances, CAS Registry Number, molecular weight, solubility in water, risk phrases risk statements etc.) for the potential constituents of a wide variety of waste, database remaining open.

1. INTRODUCTION

To establish the dangerousness wastes, especially industrial ones, is a matter of great importance of the waste management. Need for a methodology to determine whether a waste is hazardous or not derived from the provisions of the Romanian legislation in the field of waste, of which the most important are:

- *Resolution No. 856 of 16 August 2002 regarding evidence of waste management and to approve the list of waste, including hazardous waste -*

which shows the list of wastes and their framing codes, and boundaries of features for classification of a waste as hazardous waste;

- *Law No. 211 of 15 November 2011 on waste* (Chapter 7, Article 8):
  - Forcing producers and holders of waste businesses to fit each type of waste generated from its work in the waste list;
  - Require the determination of waste dangerousness to be performed by the waste producers and holders of such waste only based on an analysis of the origin, by means of testing, on the basis of analysis report and other relevant documents;
  - Provides the Reference Laboratory of the National Environmental Protection Agency (NEPA) to analyze and resolve cases of doubt regarding the characterization and classification of waste.
- *The Ministerial Order No. 95 of 12 February 2005 establishing acceptance criteria and preliminary waste acceptance procedures in the storage and the national list of waste accepted in each class of landfill* and the *Decision no. 349 of 21 April 2005* (*updated*) *regarding waste storage* also contain provisions / regulations which are in direct connection with the hazardous/not hazardous nature of waste.
- *Decision No. 1061 of 10 September 2008 regarding the transport of hazardous and non-hazardous in Romania* - requires knowledge of the dangerous/non dangerous character of the waste in order to complete the form for hazardous waste shipment approval and the form for hazardous waste expedition/ transport.

To all these imposition can not be respond only by general characterization of the waste and by assessment of their dangerousness according to certain criteria.

The current situation in the country: Taking into account legislative impositions, economic agents face the problem of determining the dangerousness of waste and of associating their code. If the legislative provisions and the application thereof are largely clear in establishing the category of landfills and in transport waste, about how to determine the waste dangerousness is not explicit in the content of legislative documents. There is no structured work methodology with clearly defined steps that can serve all those interested (the waste generator, transporter, economic entities that eliminate / harness the waste or relevant competent authority). Therefore, each work to evaluate the hazardous/non-hazardous nature of waste involved a considerable effort to study and to correlate of technical, scientific and legal information.

International situation: both the EU and outside the EU (USA, for example), methodologies (well-structured, detailed and accessible) for determining the dangerousness of waste exist and are used.

Taking into account the above mentioned, **it was considered necessary to establish a methodology by which can be determined the hazardous/non hazardous nature of waste in a consistent and reproducible manner and which takes into account the provisions of national legislation and the**

needs of the undertakings involved in the production, transport and capitalization/ disposal waste.

2. METHODOLOGY FOR DETERMINING THE HAZARDOUS/NON HAZARDOUS NATURE OF THE WASTE ESTABLISHED AND USED IN THE INCD ECOIND

The methodology discussed is based both on the current legislation and the need to address them in a scientific way and valorization of results in the form of environmental services.

2.1. Steps methodology

This methodology includes the following **steps:**

- **Establishing identification data of the sample waste** (waste type, the process from which the waste comes, the evident features of the waste such as physical state, appearance etc.);
- **Obtaining as much information about the waste (**from the analysis of technological flow that generate the waste, from the waste generation conditions, information on raw materials used in the generation and/or treatment of the waste, information on quality indicators previously determined etc., information from the generator/owner, from the literature, from the safety data sheets for materials used in the technological process generating the waste);
- **Identifying a waste stream, typical for the waste in question,** in the list of waste enclosed in Government Decision No. 856/2002; if you can identify, without reserve, a good flow, it is possible to framing the waste without the need for further analysis. If, however, you can not do this or if it is not sure that the waste is non hazardous, analysis of the waste is continued**;**
- **Establishing the potential constituents of waste** in order to set the indicators to be determined; as analysis to determine the dangerousness of waste is based on several indicators, the result will be all the more argued; from this can see how important the capacity of analytical determination of the laboratory which performs the determinations;
- **Analytical determinations of the quality indicators that have been set and their registration;** it is very important to correctly determine the quality indicators, but equally important is achieving the correct sampling and all operations (storage, transport, storage, pre-treatment) to which is subjected waste before proper analysis.
- **Identifying the risk statements for the waste components** (determined analytically or estimated on the basis of all information available), using reliable sources; significance of risk phrases used in the methodology for determining the dangerousness of waste, developed and used by INDC ECOIND, complies Decision No. 1408 of 4 November 2008 concerning the Classification, Packaging and Labeling of Dangerous Substances (referred

to Law No. 211/2011 in Annex 4, point 1). Considering the importance of risk phrases in determining the dangerousness of substances and implicitly of waste, should be noted about the changes concerning the classification, packaging and labeling. In the Globally Harmonized System (GHS - Globally Harmonized System), EC 1272/2008 (CLP*) shall come into force from 2015, June 1. According to him, the risk phrases (R) will replace the hazard (H). Currently, however, all the guides still refer to classifications established under CHIP (CHIP: the Chemicals (Hazard Information and Packaging for Supply) Regulations or Regulations for chemicals (Information about dangerous products and the packaging for the supply) - [1, 2, 11, 12].

- **Assigning of dangerous properties** (properties that make the waste be hazardous: properties H1÷H15 stipulated in annex no. 4 to Law no. 211/2011) based on identified risk phrases for the waste components. Significance of the 15 properties that induce danger are shown in Table no.1
- **Quantifying the level of hazardous properties** by summing the total concentration of the waste components which shows the same risk phrase, responsible for a specific property potentially dangerous - if properties H4, H5, H6, H7, H8, H10, H11 (as result of Government Decision no. 856/2002, Article 8, paragraph 2); Regarding H3 property, it must be analyzed by measuring the flash point. H1, H2 properties as well as H12 - H15 properties are determined by special methods. The Romanian legislation is unclear regarding the application of these methods in case of waste.
- **The evaluation of the results** by comparing the determined level of the dangerous properties with the limits covered by Government Decision no. 856/2002, Article 8, paragraph 2; the result of comparison, in conjunction with the definition of hazardous waste given by the Law no. 211/2011 - Annex no.1, Item 11 ("any waste which displays one or more of the hazardous properties listed in the Annex no. 4 to the law") allows for the analyzed waste sample to be categorized as hazardous or non-hazardous waste; so if at least for one dangerous property (H3, H4, H5, H6, H7, H8, H10, H11) it exceeds the limit imposed by GD. 856/2002, then the waste is hazardous; if none of the hazardous properties` level will reach the limit imposed by Government Decision 856/2002, then the waste is non-hazardous.

In order to minimize the effort of implementing the methodology that establishes the degree of danger in waste, a database was created. It has a large pool of useful information (names of substances, CAS number, molecular mass, solubility in water and other solvents, risk statements etc.). The database is still in progress, and the list is open to further additions, including found constituents or those possible to be found in different types of waste. [4, 5, 10, 13, 14, 15, 16, 17]

The analysis of the informations related to the assessment of dangerousness of waste in the UK and in the U.S. [1, 2, 3, 4, 6, 7, 8, 9] has shown that there are no notable differences compared to procedure as outlined.

Tabel 1 - Hazardous Properties [based on information provided in table 2.1 of 2nd ed (v2.3) of Technical Guidance WM2] - UoE update Jul 2011 [18]

Hazard Group - Category	**Description**
H1 - Explosive	substances and preparations which may explode under the effect of flame or which are more sensitive to shocks or friction than dinitrobenzene
H2 - Oxidising	substances and preparations which exhibit highly exothermic reactions when in contact with other substances, particularly flammable substances
H3A - Highly flammable/H3B - Flammable	Liquid substances and preparations having a flashpoint of below 21C / Liquid substances and preparations having a flashpoint of greater than 21C and less than or equal to 55C
H4 – Irritant	non-corrosive substances and preparations which, through immediate, prolonged or repeated contact with the skin or mucous membrane, can cause inflammation
H5 – Harmful	substances and preparations which, if they are inhaled or ingested or if they penetrate the skin, may involve limited health risks
H6 – Toxic	substances and preparations (including very toxic substances and preparations) which, if they are inhaled or ingested or if they penetrate the skin, may involve serious, acute or chronic health risks and even death
H7– Carcinogenic	substances and preparations which, if they are inhaled or ingested or if they penetrate the skin, may induce cancer or increase its incidence
H8 – Corrosive	substances and preparations which may, on contact with living tissues, destroy them
H9 - Infectious	substances containing viable micro-organisms or their toxins which are known or reliably believed to cause disease in man or other living organisms
H10 - Toxic for Reproduction	substances and preparations which, if they are inhaled or ingested or if they penetrate the skin, may produce or increase the incidence of non-heritable adverse effects in the progeny and / or an impairment of male or female reproductive functions or capacity
H11 - Mutagenic	substances and preparations which, if they are inhaled or ingested or if they penetrate the skin, may induce heritable genetic defects
H12	substances and preparations which release toxic or very toxic gases in contact with water, air or an acid
H13 - Sensitising	substances and preparations which, if they are inhaled or if they penetrate the skill, are capable of eliciting a reaction of hypersensitisation such that on further exposure to the substanceor preparation, characteristic adverse effects are produced. [As far a stesting methods are available.]
H14 - Ecotoxic	substances which, were they to enter into the environment, would present or might present an immediate or delayed danger for one or more components of the environment
H15	substances and preparations capable by any means, after disposal, of yielding another substance, e.g. a leachate, which possesses any of the characteristics listed above

Note, however, that in the UK, documented materials on this domain are well structured and very affordable (The Technical Guidance WM2, designed to be the reference document for all legislation relating to hazardous waste management). Regarding the methodology applied in the U.S., the lists of wastes which are used in the first steps of procedures are more detailed lists that can also differ from state to state, and to determine toxicity of waste is done indirectly, by the results of an approach based on leaching, where what it

counts is the measure in which toxic materials from waste can leach into the soil and then into groundwater, polluting the environment.

The applicability of this methodology is demonstrated in the paper through a case study, presented below.

Case study for implementing the methodology used by INCD ECOIND for determining the hazardous/non hazardous nature of waste

To illustrate how to work on the application of the methodology developed for the case study was chosen: *The determination of dangerousness and framing of waste resulting from the mechanical blasting with metal shot.*

- **Identifying a waste flow,** corresponding to the respective waste in the list enclosed in the *Government Decree no. 856/2002:* The „waste flow made by the sanding blasting materials" was identified at the category 12: *Waste from mechanical and physical modeling and treating of metallic surfaces and plastic materials.* Because of the fact that this category may include both hazardous and non-hazardous waste (code 12 01 16* - „waste from sanding materials that contain hazardous substance", and code 12 01 17 – „sanding materials, other than those mentioned in code 12 01 16", this kind of situation being named „mirror entrances" in specialty literature), the analysis must be continued in order to determine the degree of danger for waste and its classification.
- **Information about the manner of generating the waste was required from the waste generator,** in order to establish the indicators. **T**he established and analyzed indicators, the results of analytical determinations and work methods are presented in table no. 2.

Tabel 2 - The results of analytical determinations

Current No.	Indicators	Unit	Sample: waste resulting from the mechanical blasting	Method of analysis
1	pH	pH units	6,15	ISO 10390:2005
2	Dry matter	%	99,88	SR ISO 11465-98
3	Iron	mg/kg s.u	607875	SR EN ISO 11885:2009
4	Manganese	mg/kg s.u	6905	SR EN ISO 11885:2009
5	Silica	mg/kg s.u	20760	SR EN 15309:2008
6	Total chromium	mg/kg s.u	605,24	SR EN ISO 11885:2009
7	Chromium VI	mg/kg s.u	<0,05	SR ISO 11083-98
8	Cooper	mg/kg s.u	1443	SR EN ISO 11885:2009
9	Nickel	mg/kg s.u	446	SR EN ISO 11885:2009
10	Calcium	mg/kg s.u	501,46	SR EN ISO 11885:2009
11	Titanium	mg/kg s.u	399	SR EN ISO 11885:2009
12	Carbonates	%	0,14	STAS 7184/7:1987

- **Identifying the risk statements** for the sample; the source for the risk phrases was the database performed in the institute;
- **The calculation of the total concentration of the compositions that show the same risk phrase**, responsible for a certain hazardous property, in order to evaluate the level of the respective property (the quantification of hazardous properties in the sample of the analyzed waste is done by summing up the total concentrations of the components that present themselves with the same risk statement, responsible for a certain hazardous property).
- **Comparing the rezult of the calculus with the limit** (indicated by the Government Decision no. 856/2002, art 8 paragraph 2), for a certain hazardous property (between properties H4, H5, H6, H7, H8, H10, H11 – according to Annexe 4 of the law 211/2011), the limit that represents the threshold between classifying waste in either the hazardous or non-hazardous category); Properties H4, H5, H6, H7, H8, H10, H11 were analyzed based on the concentrations of the indicators identified in the waste sample. For the identified metals, within each property named above, were analyzed the forms established according to their assigned CAS numbers, mentioned in the Files with Security Data of the components used in the sandblasting process. The risk statement incriminated by the property that induces the degree of danger was considered in the analysis. For properties H9, H13 si H14 the limit values are not provided in the GD no. 856/2002. On the other hand, considering the way the waste was generated (in the process of mechanical sandblasting with metal pellets), from its physical and chemical state and from the sample's visual exam, we can appreciate the fact that the waste does not hold the hazard-inducing properties, type H2, H3, H12 and H15 (according to Annexe 4 of law 211/2011). The H1 property was not a subject of this analysis.
- **Evaluation of the results**: if the value of at least one hazardous property is equal or above the limit imposed by GD no. 856/2002, then the waste is dangerous; if none of the dangerous properties have a value below the limit imposed by GD no. 856/2002, then the waste is considered non-hazardous.

The results of these last 4 steps of the methodology designed to establish the degree of danger of the waste are compiled in table no 3.

Thus, considering the results shown in table 3 and the definition of hazardous waste according to Law 211/2011 (Annexe no. 1, point 11): *"any waste that presents itself with one or more dangerous properties included in the law's Annexe no. 4)* we can conclude that t**he analyzed waste – resulted from the process of mechanical sandblasting with metal pellets – is hazardous.**

Considering the source area and its corresponding category, **the analyzed waste is framed in code: *12 01 16 – Waste from sanding materials containing hazardous substances.***

4. CONCLUSIONS

- The methodology presented is a useful tool for characterizing waste with a view their classification
- After researching similar methodologies used in other countries (United Kingdom, USA), one can ascertain that the methodology established and used by our institute to determine the hazardous/non-hazardous nature of waste is a competitive one.
- Apply the methodology for determining the dangerousness of waste is a laborious demarche. To minimize the effort of applying this methodology, it was necessary to establish a database (including substance names, CAS number, molecular masses, solubility in water and other solvents, risk statements etc.) for the constituents found in the analyzed waste or for other possible constituents, database that remains open for further additions.

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Tabel 3 - Data for classification of the waste

Current No.	Criteria for categorizing hazardous waste, see Law. 211/2011 and Government Decision no. 856/2002	Chemical element/ associated compound	Chemical element (mg/kg s.u.)	Associated compound (% masice)	Check criterion	Result evaluation in relation to criteria analyzed
0	**1**	**2**	**3**	**4**	**5**	**6**
1	**Property H4 – "'Irritant"** The total concentration of irritating materials classified as R41: ≥ 10%	$Ca/CaCO_3$	501,46	0,12	0,12%<10%	Waste is not irritant by irritating materials classified as R41
		TOTAL		**0,12**		
2	**Property H4 – "Irritant"** The total concentration of irritating materials classified as R36, R37 and R38: **≥ 20%**	Fe/Fe_2O_3 [1)]	607875	86,84	**87,85%>20%**	**Waste is irritant by irritating materials classified as R36, R37** and **R38**
		Cr/Cr	605,24	0,06		
		Cu/Cu	1443	0,14		
		Mn /Mn	6905	0,69		
		$Calciu/CaCO_3$	501,46	0,12		
		TOTAL		**87,85**		
3	**Property H5 – "Harmful"** [(2)] The total concentration of materials harmful to health classified as R20, R21, R22, R33, R39, R48, R65, R66 and R68: **≥ 25%**	Cr/Cr	605,24	0,06	O,89<25%	Waste is not harmful to health
		Cu/Cu	1443	0,14		
		Mn /Mn	6905	0,69		
		TOTAL		**0,89**		
4	**Property H6 – "Toxic"** The total concentration of highly toxic materials classified as R26, R27 andR28: **≥ 0,1%**	-	-	-	-	It was not identified any element that presents the risk phrases R26, R27 and R28
		TOTAL		-		
5	**Property H6 - "Toxic"** The total concentration of toxic materials classified as R23, R24 and R25: **≥ 3%**	Mn /Mn	6905	0,69	0,69%<3%	Waste is not toxic by compounds that are characterized by the risk phrases R23, R24 and R25
		TOTAL		**0,69**		
6	**Property H7 - "Carcinogens"** The total concentration of carcinogenic materials in category K1, K2 classified as R45 and R49: **≥ 0,1%**	-	-	-	-	It was not identified any element that presents the risk phrases R45 and R49

7	**Property H7 - "Carcinogens"** Total concentration of carcinogenic materials in category K3 classified as R40: **≥ 1%**	Ni/Ni	446	0,04	**0,1%<1%**	Waste is not carcinogenic by compounds that exhibit the risk phrase R40
		Cr/Cr	605,24	0,06		
		TOTAL		**0,1**		
8	**Property H8 - "Corrosive"** Total concentration of corrosive materials classified as R35: **≥ 1%**	-	-	-	**-**	It was not identified any element that presents the risk phrase R35
		TOTAL		**-**		
9	**Property H8 - "Corrosive"** Total concentration of corrosive materials classified as R34: **≥ 5%**	Ni/Ni	446	0,04	0,79%<5%	Waste is not corrosion by compounds that exhibit the risk phrase R34
		Cr/Cr	605,24	0,06		
		Mn /Mn	6905	0,69		
		TOTAL		**0,79**		
10	**Property H10 - "Toxic for reproduction"** Total concentration of materials toxic to reproduction in category K1, K2 classified as R60 and R61:**≥ 0,5%**	-	-	-	-	It was not identified any element that presents the risk phrases R60 and R61
		TOTAL		**-**		
11	**Property H10 - "Toxic for reproduction"** Total concentration of toxic materials for reproduction in category K3 classified as R62 and R63:**≥ 5%**	Cu/Cu	1443	0,14	0,14%<5%	Waste is not toxic for reproduction by compounds that exhibit the risk phrases R62 and R63
		TOTAL		**0,14**		
12	**Property H11 - "Mutagen" Total concentration of mutagenic materials in category K1, K2 classified as** R46:**≥ 0,1%**	-	-	-	-	It was not identified any element that presents the risk phrase R46
		TOTAL		-		
13	**Property H11 - "Mutagen" Total concentration of mutagenic materials in category** K3 clasificate ca R40:**≥ 1% -** It is similar to Property H7 - "Carcinogens" **-** Total concentration of carcinogenic materials in category K3 classified as R40: **≥ 1%**	Ni/Ni	446	0,04	0,04%<1%	Waste is not mutagenic by compounds that exhibit the risk phrase R40