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A Comprehensive Methodology for Assessing the Hazardousness of Waste Categorized in the European Union Legislation as "Mirror Entries"—Case Studies

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Abstract: In the European Union List of Wastes, the category of "mirror entry" waste refers to either hazardous or non-hazardous waste, depending on their composition and specificity. Classifying waste as hazardous or non-hazardous is essential because it influences the feasibility and economic viability of subsequent management methods. Thus, waste classification represents a challenge both for the scientific community and for the producers/holders of waste. The methodology presented in this paper describes the stages that are the basis for evaluating the dangerousness of "mirror entry" waste and the potential factors that influence the evaluation process. Three case studies that represented three types of industrial waste were selected: waste from the non-metallic minerals industry (W1), waste from glass manufacturing (W2), and waste from the iron and steel industry (W3). The case studies were characterized and evaluated according to hazardous properties and the assignment of a waste code. The W1 and W2 waste samples did not present the hazardous properties HP1–HP15 and were included in the non-hazardous waste list. The W3 waste sample exhibited five dangerous properties and was classified as hazardous waste. The assessed wastes maintain the classifications as long as there are no changes in the technological process generation and in their composition.

Keywords: industrial waste; mirror entries; hazardousness assessment; waste management; methodology

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1. Introduction

Currently, as a result of industrial developments and imposed legislation regarding both reductions in generated waste and implementation of waste management with respect to environmental protection, at the global level, the problem of waste occupies a priority place for authorities, the scientific community, and the economic environment. Whether we talk about wastes generated from processing raw materials or wastes generated from the treatment/recycling/recovery of other wastes, wastes are becoming increasingly challenging to manage due to their specificity and complex matrix. Waste classification is essential in all management stages, starting with production and ending with the final treatment. Therefore, identifying a suitable code in the European Union List of Wastes (LoW) is crucial [1,2]. The classification of waste as hazardous or non-hazardous affects the feasibility and economic viability of its collection, recycling, disposal, and subsequent management methods [3]. Moreover, classifying waste as hazardous can have important legal consequences [4]. The EU Waste Framework Directive imposes clear restrictions regarding the management of hazardous wastes. The directive imposes measures that guarantee the tracking and control of hazardous wastes, starting with their generation and ending with their final destination (Article 17), which include prohibitions regarding mixing (Article 18), specific obligations regarding labeling and packaging (Article 19), and special treatment only in installations that are arranged based on special authorization

(Articles 23–25) [5]. In addition to these measures, the establishment of an electronic register at the level of the member states for chronologically recording hazardous waste is required (Article 35 of Directive 851/2018 amending Directive 98/2008) [6]. According to the LoW, waste codes are grouped into three categories: codes for absolutely hazardous (AH) waste, which are marked with an (*); codes for absolutely non-hazardous (ANH) waste; and "mirror entry" codes, which can be assigned based on their composition and specificity as "mirror hazardous" (MH) or "mirror non-hazardous" (MNH) waste.

Producers and holders of waste and legal entities must include each type of waste generated from their activity in the LoW. "Absolutely hazardous" waste is noted in the list as AH waste and includes mainly wastes for which the hazardous properties are known (for example, flammable, oxidizing, explosive wastes, wastes containing persistent organic pollutants, and used oils). "Absolutely non-hazardous" (ANH) waste is, in general, known waste that does not contain hazardous chemical substances. Therefore, an additional hazardous or non-hazardous character assessment is not necessary for AH and ANH types of waste. For the absolutely hazardous (AH) and absolutely non-hazardous (ANH) types of waste, inclusion in the List of Wastes is evident; however, for waste with "mirror entry" codes, an evaluation of the hazardous properties HP1–HP15 is necessary [5,7–13]. This evaluation involves a set of complex theoretical and experimental investigations [14–16]. At the European Union level and beyond, various guides have been developed to classify waste to support waste producers and owners. Under various approaches, these guides present general and specific aspects that must be considered for hazard assessment and the establishment of a waste code [7,17–19]. In practice, however, there are multiple challenges faced by laboratories and specialists when it is necessary for them to evaluate the dangerousness of waste assigned a "mirror entry" code. The challenges arise because each waste is considered to be a unique sample due to its specificity and heterogeneity. If the composition of the waste is unknown, the hazardous substances present in the waste are identified based on additional physical-chemical analyses or by applying knowledge about the technological process/activity that led to the waste generation. Additionally, if the domain and technological process are known, it is essential to know the analyses/characteristics of the initial raw materials used [18].

At the international level, the management of hazardous waste is regulated by international protocols and conventions, such as the Basel Convention and the OECD Control System for Waste Recovery, and by local regulations enforced at each country's level [20,21]. For example, in the USA, hazardous waste is defined according to the Environmental Protection Agency (EPA) in chapters, subchapters, parts, and subparts by the Code of Federal Regulation (CFR) [22,23]. In China, hazardous waste is regulated by the Standard for Pollution Control on Hazardous Waste Storage [24]. In Taiwan, industrial waste is divided into hazardous and general industrial waste [25]. In order to reduce the generation of hazardous waste and the potential risks after treatment and disposal, the EPA formed a regulatory framework for managing industrial waste in 1999 [26].

This work proposes a detailed methodology for evaluating the dangerousness of "mirror entry"-type wastes. The methodology was developed based on the legislation in force, the guidelines from waste classification tools, the specificity of various types of waste analyzed in our laboratory, and some relevant factors necessary in the waste evaluation and classification process. Three types of waste generated from various industrial activities were selected to exemplify the methodology's applicability. The methodology is valuable for assessing the dangers of "mirror entry" waste and for providing critical information for effective waste classification. The methodology proposed in this paper can be applied at both the European Union and international levels, regardless of the form of implementation of legislative regulations for hazardous waste management. The assessment of waste involves establishing indicators, conducting physical-chemical analyses, and calculating the concentration of dangerous compounds/elements using EPA methods and EU and international standards that are generally valid all over the world. The only stage that requires harmonization according to each state's legislation is the classification of waste as hazardous or non-hazardous based on concentration limits imposed at the state level.

2. Methodology for Assessing Hazardous "Mirror Entry" Waste

The evaluation of waste hazardousness was carried out based on the composition of a waste, which was detected through chemical analyses and/or through information on the technological process of the production, the balance of raw materials, and other chemical substances used in the process, only if the composition of the waste had not changed during its generation or temporary storage. Chemical analyses do not always identify the hazardous compounds in waste, but individual anions and cations can be identified (especially for predominantly inorganic waste). In such cases, the dangerous compounds resulting from the combination of anions and cations in the sample are established based on knowledge of the technological process/activity from which the waste was generated and based on specific parameters, such as pH, humidity/water content, and organic matter content. To evaluate the dangerousness of a "mirror entry"-type of waste, the steps described below are necessary.

Stage I. Obtaining relevant information about process of wastes generation

The waste origin/generation source, i.e., identify the industry and field of activity from where the waste originated.

(a) The technological process of waste production, i.e., identify the technological process and the physical-chemical treatments applied to the process flow (if applicable).
(b) The raw materials, i.e., prepare an inventory of the raw materials that enter the technological process and of the substances used in different stages of the technological process, including their balance sheets.
(c) The material safety data sheets (MSDSs), i.e., use the MSDSs of the materials to identify the component substances and related concentrations (if applicable).
(d) Information regarding the appearance of the waste, i.e., obtain information on the state of aggregation, color, estimated humidity, smell, and with or without petroleum product content.
(e) The purpose of assessing the dangerousness and classification of the waste, i.e., depending on the method of subsequent management, simultaneously with the assessment of the dangerousness, determine other characteristics/parameters of the waste that can influence the final destination. This step is not mandatory, but it supports the producer/owner of the waste by providing additional helpful information. For example, in the case of waste that is managed through disposal in a waste deposit, it is necessary to carry out a leaching test to establish the type of waste deposit (i.e., inert, non-hazardous, or hazardous). Also, in the case of waste that is managed through energy recovery, it is essential to determine the calorific value, ash content, volatile substances, and other useful parameters, in addition to the potentially dangerous compounds in the waste.

Figure 1 shows a schematic presentation regarding the possibilities of waste management after the coding stage. The methods shown in Figure 1 were developed by the authors in accordance with the European Union laws related to waste management transposed into Romanian laws. These methods can be applied in a similar manner at the European Union level unless there are any other country-specific regulations that apply.

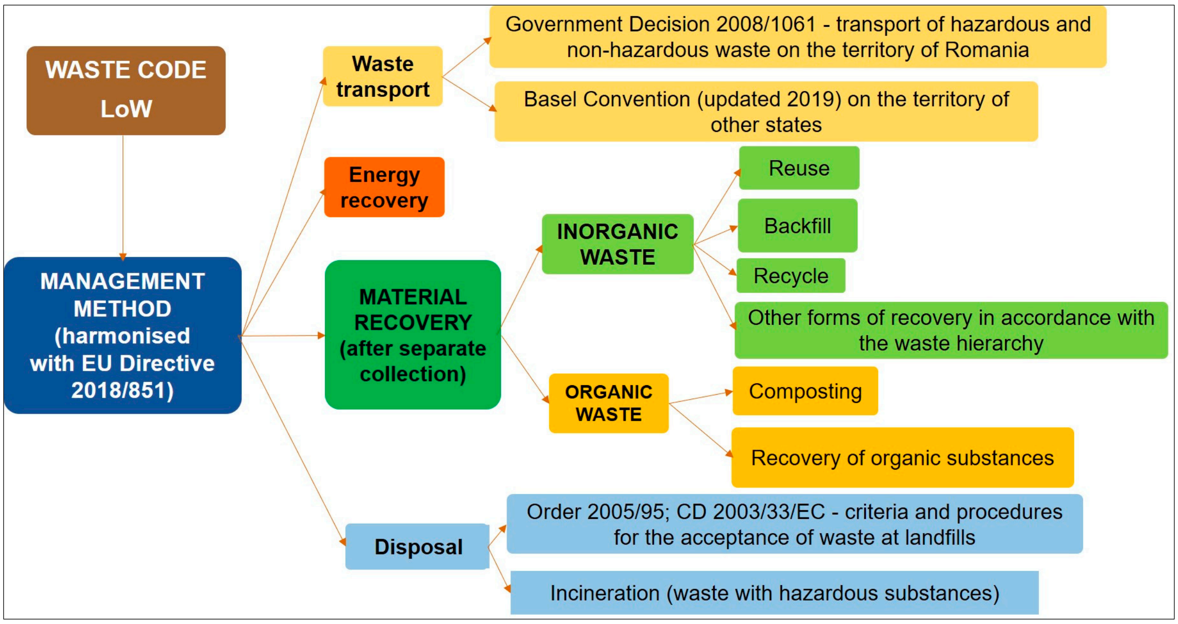


Figure 1. A schematic presentation of the management methods following the codification of waste [20,27–29].

Based on above-mentioned information, i.e., (a)–(f), the EU LoW is inventoried to determine the chapter and subchapter where the waste can be classified. A schematic representation of the LoW proposed by the authors is presented in Figure 2. After identifying the chapter and subchapter, the most suitable code is searched for the waste generated. If the identified code is for an AH or ANH waste, the waste is coded as such. If the waste is identified as a "mirror entry" waste (MH or MNH), the evaluation process continues with stages II, III, and IV. In the List of Waste, the name of a type of waste can be repeated for several types of industries/fields of activity. This aspect must be considered when identifying the chapter and subchapter, and the waste code is selected from the most suitable activity field [30].

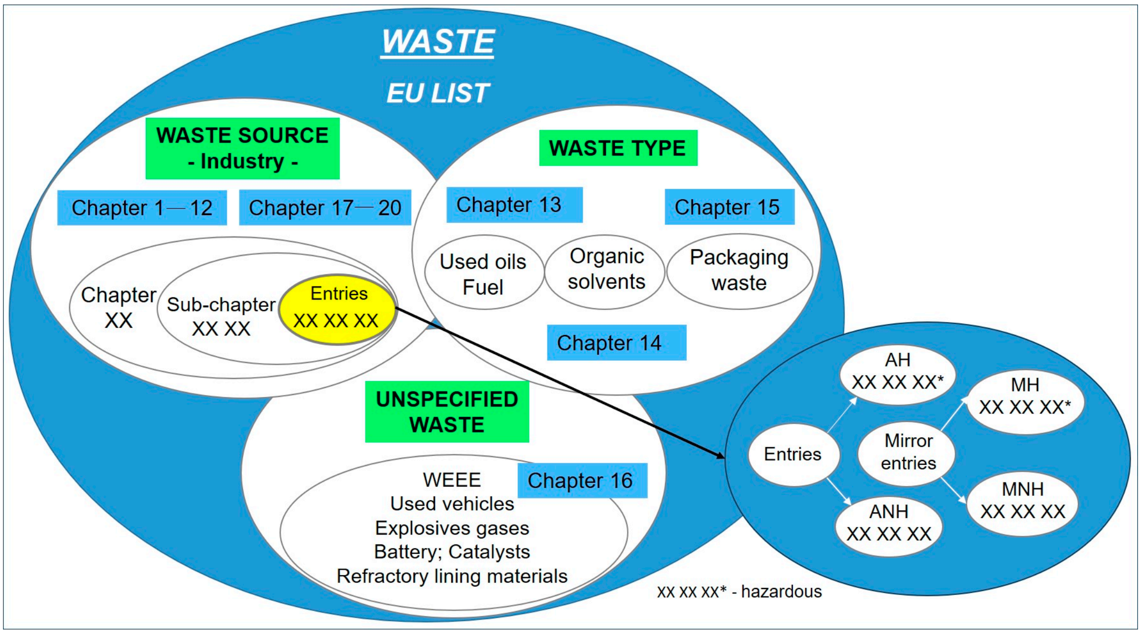


Figure 2. The schematic structure of the European Union List of Wastes [1].

Stage II. Establishing the physical-chemical indicators/waste composition to identify the potentially dangerous compounds in waste

The composition of waste is determined based on information about the technological process or through chemical analyses. If chemical analyses are required, and there are no analysis/testing methods for specific indicators at the laboratory level, the establishment of their concentrations is determined based on information about the technological process and in the MSDSs of the materials used in the process. In general, depending on the state of aggregation of the waste, the physical-chemical analyses carried out at the laboratory level aim at the following indicators:

Solid waste, i.e., pH, moisture (W), loss on ignition (LOI), total organic carbon (TOC), carbonates, and acid neutralization capacity (ANC);

Liquid waste, i.e., pH, water content, chemical oxygen consumption (CCOCr), dissolved organic carbon (DOC), density, and flash point (for emulsion);

Solid/liquid waste, i.e., salts, such as chlorides, nitrates, nitrites, phosphates, sulphates, silicon, metals (calcium, total iron, aluminum, magnesium, potassium, manganese, cadmium, chromium, mercury, copper, nickel, zinc, arsenic, fluoride, sulfur, titanium, vanadium, antimony, selenium), and organic pollutants, such as polycyclic aromatic hydrocarbons (PAH), polychlorinated biphenyls (PCB), benzene, toluene, ethylbenzene, and xylene (BTEX). Depending on the type of waste, it is evaluated to determine if persistent organic pollutants (POPs) could also be present in the waste.

Stage III. Assessment of hazardous properties HP1–HP15

According to the EU Directive 2008/98 on waste, updated by the EU Directive 2018/851, hazardous waste is defined as "any waste that presents one or more of the hazardous properties listed in Annex III". Any reference to this annex is considered to be associated with the EU Regulation 2014/1357, which provides, in the annex attached to the regulation, the limit values for the dangerous properties HP4, HP5, HP6, HP7, HP8, HP10, HP11, and HP13 [31]. The quantification of these properties is based on the concentrations of the components that present a specific danger phrase responsible for a dangerous property. The concentration values are compared with the limits indicated by the legislation, and the results obtained allow the analyzed waste to be classified as hazardous or non-hazardous waste. The HP1 (explosive), HP2 (oxidant), HP3 (inflammable), and HP12 (sensitive) properties of waste with unknown composition are detected via specific tests (Regulation CE 2008/440 or by assessing the hazard phrases of substances from MSDSs) [32]. For the HP9 property, no limit values are provided by the mentioned annex. The United Kingdom Guide mentions the following two general aspects of assessing the HP9 property: (1) If the waste contains a toxin produced by a microorganism in a concentration in which the waste presents the dangerous property HP5 or HP6, then it must be classified under the MH heading based on HP9. (2) If the waste comes from the sanitary system and its collection and disposal are subject to special measures regarding the prevention of infections, the waste must be classified under the MH heading based on HP9 [18]. In the EU Regulation 2017/997, the dangerous property HP14 "ecotoxic" limit values are defined and regulated. Recital 8 of the regulation reiterates that when the hazardous property of waste is evaluated based on a test and by using the concentrations of hazardous substances according to annex III of the EU Directive 2008/98, the test results prevail. To evaluate the dangerous properties of HP4, HP5, HP6, HP7, HP8, HP10, HP11, HP13, and HP14, the potentially dangerous compounds from the waste determined through analyses or based on MSDSs are considered. The inventory of hazard phrases is based on Regulation 2008/1272 (CLP), the C&E inventory database (ECHA), or MSDSs (where available) [33,34]. After assigning the hazard phrases, the dangerous property is determined by relating the concentrations of potentially dangerous compounds to the limit values of the hazard phrases established according to the EU Regulation 2014/1357. For the hazardous property HP15, apart from the hazard phrases mentioned in the annex, member states can classify waste under the heading MH by HP15 based on other applicable criteria, such as leaching tests.

2.1. Acid/Alkaline Reserve

For HP4/HP8 properties, if the pH of the waste is <4 units pH, the acid reserve of the waste solution is determined with NaOH solution, and if the pH is >10 units pH, the basic reserve is determined with an H_2SO_4 solution [35]:

$$AC = \frac{V_1 \times C_1 \times 4.904}{w} \tag{1}$$

$$ALK = \frac{V_2 \times C_2 \times 4.001}{w} \tag{2}$$

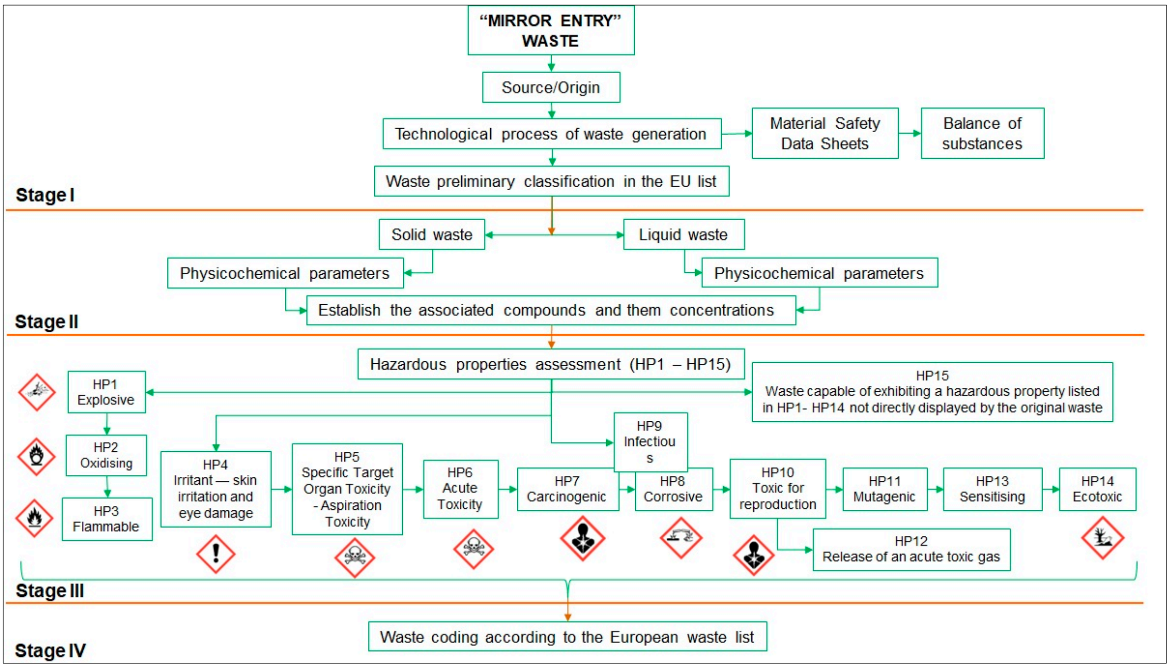
where AC represents acidity (calculated as H_2SO_4) (% m/m); ALK represents alkalinity (calculated as NaOH) (% m/m); C_1, C_2 is the normality of the solution NaOH/H_2SO_4 (mol/L); V_1, V_2 is the volume of the solution NaOH/H_2SO_4 (mL) (endpoint pH 7, 4.904 grams of H_2SO_4 0.05 M for preparation of 1 L solution 0.1 N and 4.001 grams of NaOH 0.1 M for preparation of 1 L solution 0.1 N); and w is the weight of waste (g).

A waste with a pH $\leq$2 or $\geq$11.5 should generally be considered to be a "corrosive" hazardous waste (HP8). If the acid or alkaline reserve is $\geq$1% but $\leq$5%, the waste is irritant (HP4), and if the acid or alkaline reserve is $\geq$5%, the waste is corrosive (HP8).

Stage IV. Establishing the waste code

Based on the evaluation of the hazardous properties HP1–HP15, it is established whether the waste is of the MH or NMH type. If at least one hazardous property exceeds the EU Regulation 2014/1357 limit, the waste is a "mirror hazardous" (MH) waste. If no hazardous property exceeds the imposed limit, the waste is a "mirror non-hazardous" (MNH) waste.

A scheme for evaluating "mirror entry" waste proposed by the authors based on European Union legislation and current practices regarding the waste generation process is presented in Figure 3.



Legend: Stage I—Obtaining relevant information about process of wastes generation;
Stage II—Establishing the physical-chemical indicators/waste composition to identify the potentially dangerous compounds in waste;
Stage III—Assessment of hazardous properties HP1–HP15;
Stage IV—Establishing the waste cod;

Figure 3. General scheme for evaluating the dangerousness of a "mirror entry" waste [5,7,31].

2.2. Determining the Concentrations of Pollutants: Calculation Formulas

(*a*) *Determination of the concentrations of hazardous substances based on the physical-chemical indicators*

It is considered that, for subsequent management, waste is managed in a wet state, as it was generated. Therefore, the concentration of the analyzed indicator is determined relative to the wet mass of waste:

$$C_{MAI} = C_{AI} \times d.m. \, (\%) \tag{3}$$

where C_{MAI} is the concentration of the indicator found in one kilogram of wet waste (mg/kg), C_{AI} is the concentration of the indicator related to the dry substance of the waste (mg/kg *d.m.*); *d.m.*- dry matter existing in 100 g of wet waste.

Based on the C_{MAI} determined in Formula (3), the concentration of the associated compound (hazardous substance) in the waste is determined:

$$C_{AC} = \frac{C_{MAI} \times M_{AC}}{M_{AI} \times 10^6} \times 100 \tag{4}$$

where C_{AC} is the concentration of the associated compound (%), M_{AC} is the molecular mass of the associated compound that could be found in the waste (g/mol), M_{AI} is the molecular mass of the indicator in the waste (g/mol), and 10^6 is the kilogram to milligram conversion factor.

(*b*) *Determination of the concentrations of hazardous substances in the waste based on MSDSs and the information provided by the waste producer*

If the waste is sludge from a treatment plant, the concentrations of hazardous substances in the sludge are determined based on the following known data:

- Weight of sludge generated in a month X (tonne);
- Sludge humidity W (%);
- The volume of wastewater treated in one month Y (sqm);
- Mass of dangerous substance m_S (kg) used in the technological process in a month related to the concentration indicated in the safety data sheet.

Starting from these known data, the volume of water Z (sqm) found in the mass of sludge X is determined:

$$Z = \frac{X \times W}{100} \tag{5}$$

The total volume of used water is calculated $V_w(sqm)$:

$$V_w = Y + Z \tag{6}$$

Therefore, the concentration of the dangerous substance/element C_S (%) found in the mass of waste is:

$$C_S = \frac{Z \times m_S}{V_W \times X \times 10^3} \times 100 \tag{7}$$

If the waste is generated from other technological processes, only Formulas (3) and (5) are taken into consideration.

3. Materials and Methods

3.1. Case Studies

To assess the hazardousness of waste and to establish the code, three types of waste identified in the European Union List of Wastes as "mirror entries" generated from various industrial activities were selected:

W1 W1 is dust waste from an asphalt mixture production station. The waste was generated from the process of dedusting the mineral aggregates using filter bags after the aggregates were heated to 190 °C. A light liquid fuel was used in the heating process.

W2 W2 is sludge from glass manufacturing. The sludge was generated after glass processing. The sludge resulted from the glass grinding process from a Vitrosep-type glass particle separator. In the sludge, in addition to glass particles, the components of two cooling liquids used in the process can be found.

W3 W3 is dust waste from the production of steel in the electric furnace. The waste was generated from the dry dedusting of the burnt gases captured by a gas absorption hood with a bag filter from the dry dedusting installation.

Through the LoW inventory, considering the activity and the technological process of generation, it was found that the waste samples could be classified into the following codes:

W1: Code 01 04 07—waste containing hazardous substances resulting from the physical and chemical processing of non-metallic minerals (MH), or 01 04 10—waste in the form of dust and powders, other than those mentioned in 01 04 07 (MNH)* (chapter 1—waste from the exploration and exploitation of mines and quarries, as well as from the physical and chemical treatment of minerals, subchapter 01 04—waste from the physical and chemical processing of non-metallic minerals);

W2: Code 10 11 13—sludge from grinding and polishing of glass containing hazardous substances (MH), or 10 11 14—sludge from grinding and polishing of glass, other than that specified in 10 11 13 (MNH)* (chapter 10—waste from thermal processes, subchapter 10 11—waste from the production of glass and glass products);

W3: Code 10 02 07—solid waste resulting from gas purification containing hazardous substances (MH), or 10 02 08—solid waste from gas purification, other than that specified in 10 02 07 (MNH)* (chapter 10—waste from thermal processes, subchapter 10 02—waste from the iron and steel industry).

3.2. Test Leaching

Considering the intention of managing the three wastes through final storage, a leaching test was carried out to evaluate the behavior of the wastes during leaching (which can be associated with the dangerous property HP15) and to establish the class of storage where the three types of waste could be stored. The leaching test was carried out under the requirements of the SR EN 12457-2/2003 and CEN/TR 16192:2020 standards [36,37]. The method involves bringing the waste into contact with distilled water (the leachant) at a ratio between the leachant and the solid sample L/S of 10:1 and keeping it in contact for 24 h. After this period, the leachate is separated from the solid phase through filtration (filter porosity 0.45 μm) and analyzed. The results are compared with the maximum allowed values established by the Council Decision 2003/33/CE, transposed into Romanian legislation by the MMGA Order 2005/95 [27,29].

3.3. Techniques and Methods of Analysis

Standardized analysis methods were used to determine the indicators from the three waste samples (from both the solid sample and the leachate) (Table 1).

Table 1. Quality indicators—standard methods.

Indicator	Standard Method	Techniques/Equipment
pH	EN ISO 10390:2022 [38]	pH meter
Total moisture	SR EN 15934:2012 [39] SR EN 15002:2015 [40]	Gravimetry
Chloride	STAS 7184/7-87 [41]	Volumetry
Sulphates	SR ISO 11048:1999 [42]	Gravimetry
Carbonates	STAS 7184/7-87 [43]	Gravimetry
Total nitrogen	SR EN 16168:2013 [44]	CHNS-O Analyzer EA 1112

Table 1. *Cont.*

Indicator	Standard Method	Techniques/Equipment
Total organic carbon (TOC)	SR EN: 15936:2022 [45]	Carbon/Sulfur Analyzer 580A
Silicon and major elements (total iron, calcium, magnesium, potassium, zinc)	SR EN 15309:2007 [46]	X-ray fluorescence (XRF)
Heavy metals minor elements (manganese, cadmium, total chromium, mercury, copper, nickel, arsenic, titanium, vanadium, antimony, selenium, barium)	SR EN 16171:2017 [47] SR EN 16173:2013 [48] SR EN 54321:2021 [49]	Mass spectrometry with inductively coupled plasma (ICP-MS), Agilent 7900
Dissolved organic carbon (DOC)	SR EN 1484:2001 [50]	Combustion and IR detection

4. Results

Table 2 shows the results for the indicators in the W1, W2, and W3 samples. The indicators were selected based on information on the waste generation process and on the basis of data from the MSDSs (where applicable).

Table 2. Physical-chemical analysis.

Indicators	W1		W2		W3	
	mg/kg d.m.	%	mg/kg d.m.	%	mg/kg d.m.	%
Na	15.38	0.0013	5086	0.47	-*	-*
Ca	83,000	6.83	2208	0.20	50,870	4.79
Si	52,380	4.31	24,1916	22.42	-*	-*
K	-*	-*	1592	0.15	-*	-*
Mg	-*	-*	1367	0.13	12,410	1.17
Mn	-*	-*	5.07	4.7×10^{-4}	21,180	1.99
Pb	0.65	5.4×10^{-5}	15.5	0.0014	9870	0.93
As	-*	-*	-*	-*	<0.05	-
Co	-*	-*	15.6	0.0015	-*	-*
Total iron	4300	0.35	156	0.015	395,500	37.2
Cd	0.10	8.2×10^{-6}	-*	-*	-*	-*
Total chromium	0.16	1.3×10^{-5}	8.63	8×10^{-4}	770	0.072
Cu	-*	-*	65.9	0.0061	830	0.078
Ni	0.45	3.70×10^{-5}	-*	-*	-*	-*
Zn	0.39	3.2×10^{-5}	-*	-*	345,000	32.5
V	<0.15	-	-*	-*	<0.15	-
Ba	-*	-*	-*	-*	182	0.017
B	-*	-*	128.1	0.012	-*	-*
Al	16,200	1.33	522	0.048	3820	0.36
Chloride	493	0.041	-*	-*	17,090	1.61
Total nitrogen	-*	-*	-*	-*	-*	0.01
Total organic carbon (TOC)	-*	0.39	-*	0.32	-*	-*
Carbonates	-*	23.1	-*	1.5	-*	-*
Sulphate	310	0.025	545	0.05	5682	0.54

*, not applicable; <, under the methods determination limit.

According to the standardized analysis methods, the results are reported for the dry weight of the waste. For the assessment of hazardous properties, the percentage concentration of a compound is considered by reference to the weight of the waste in a wet state.

Table 3 presents the results for the three leachates (LW1, LW2, and LW3) obtained after the leaching tests.

Table 3. Results of the leaching test.

Indicators	Leachate Test				Order 2005/95 (MAV)		
	Units	**LW1**	**LW2**	**LW3**	**(I)**	**(NHA)**	**(HA)**
Arsenic	mg/kg d.m.	<0.07	<0.07	<0.07	0.5	2	25
Barium	mg/kg d.m.	0.43	0.80	3.76	20	100	300
Cadmium	mg/kg d.m.	<0.05	<0.05	<0.05	0.04	1	5
Total chromium	mg/kg d.m.	<0.05	<0.05	0.23	0.5	10	70
Copper	mg/kg d.m.	<0.01	0.19	1.88	2	50	100
Mercury	mg/kg d.m.	<0.05	<0.05	<0.05	0.01	0.2	2
Molybdenum	mg/kg d.m.	<0.10	0.11	0.26	0.5	10	30
Nickel	mg/kg d.m.	<0.03	0.05	**0.82**	0.4	10	40
Lead	mg/kg d.m.	<0.07	0.21	**12.8**	0.5	10	50
Antimony	mg/kg d.m.	<0.50	<0.50	<0.50	0.06	0.7	5
Selenium	mg/kg d.m.	<0.13	<0.13	<0.13	0.1	0.5	7
Zinc	mg/kg d.m.	<0.03	0.54	**568**	4	50	200
Chloride	mg/kg d.m.	229	15.8	**8542**	800	15,000	25,000
Fluoride	mg/kg d.m.	<0.05	<0.05	5.96	10	150	500
Sulphate	mg/kg d.m.	111	98	**3478**	1000	20,000	50,000
Phenol index	mg/kg d.m.	<0.20	<0.20	<0.20	1	-*	-*
Dissolved organic carbon (DOC)	mg/kg d.m.	**630**	**527**	128	500	800	1000
Total dissolved solids (TDS)	mg/kg d.m.	**5060**	**7012**	**33,460**	4000	60,000	100,000

<, under the methods determination limit; (I), inert; MAV, maxim admissible values; the values marked in bold font exceed the MAV; *- there are no imposed limits

5. Discussion

W1: The W1 waste sample presents in the form of coarse powder heterogeneous granulation with a soil appearance. It has a humidity of 17.7%, and it has 10.7 pH units. Considering the visual appearance of the sample, the low TOC content (0.39%), and the predominantly inorganic composition, it is considered that the waste cannot develop dangerous properties such as HP1, HP2, HP3, HP9, and HP12.

Evaluation of dangerous properties HP4_HP8, HP10, HP11, HP13, and HP14

The quantification of the dangerous properties was carried out based on an evaluation of the compounds that present dangerous phrases and based on an evaluation of the dangerousness of the sulfur in CLU used for heating the aggregates. The humidity and pH of the waste sample make it possible for heavy metals to exist in the form of oxyhydroxides and carbonates, with the carbonate concentration in the form of calcium carbonate being 17.06%. Considering the metal total chromium, sodium, vanadium, nickel, cadmium, zinc, and lead, which are in extremely low concentrations (Table 2), the association of these metals with sulphate or carbonate would lead to limit concentrations that do not exceed the limit value, i.e., 0.1% (the most restrictive limit, according to the Annex to the EU Regulation 2014/1357). For the silicon indicator expressed as silicon dioxide, there is information on its dangerousness only in the dry state in fine powder, which does not apply to the W1 waste managed in wet form. Also, according to the EC Regulation 2008/1272, calcium carbonate is not classified as a dangerous substance. Table 4 shows the hazardousness of the other compounds that may be in the waste.

For two of the evaluated dangerous properties (HP4 and HP5), the compounds that could induce the hazardousness of the waste had concentrations below the imposed limit concentration (Table 4). Regarding sulfur in CLU (hazard phrase H315), according to the MSDS, it is in a very low concentration (0.016%) in the fuel, with the risk of contamination of the waste with sulfur being practically zero, considering the concentration limit for the phrase hazard H315 (20%). Comparing the results obtained for LW1 with the maximum values allowed according to the MMGA Order 2005/95, Table 3 indicates that the waste can be stored in non-hazardous (ANH) sites. Therefore, the W1 waste is not hazardous by property HP15 (waste capable of exhibiting a hazardous property listed in HP1–HP14 not directly displayed by the original waste). Considering that none of the dangerous properties exceed the limit imposed according to Regulation 2014/1357, the analyzed waste is non-hazardous and can be classified under code 01 04 10 (MNH)—waste in the form of dust and powders, other than those mentioned in 01 04 07.

Table 4. Hazardous properties—W1.

Hazardous Property	Hazardous Phrase	Analyzed Indicator/ Associated Compound	Concentration of the Associated Compound (%)	Concentration Limit (%) Regulation EU 2014/1357
HP4	H318	Ca/CaO	9.56	**10**
	H315, H319	Ca/CaO	9.56	**20**
HP5	H335	Fe/FeO(OH) Ca/CaO	0.56 9.56	**20** **20**

W2: The sludge sample presents as a powdery mass that is slightly wet with a white-grey color. The humidity of the sludge is 7.33%, and it has 10.2 pH units. In addition to glass particles, component compounds in the waste from the two cooling liquids (L1, L2) may also exist. L1 is a liquid mixture that contains C_2H_7NO (2-aminoethanol) 5% and H_3BO_3 (boric acid) 3–5%. According to the MSDSs, the assigned hazard phrases for C_2H_7NO are H302, H312, H332, H314 (skin cor. 1B), and H335, and in the case of boric acid, the hazard phrase is H360. L2 is a liquid mixture containing $C_3H_9NO_2$ (hydroxymethyl amino alcohol) <3% (hazard phrases H302, H319, and H315) and triethanolamine, which is not classified as a dangerous substance according to Regulation 2008/1272/EC.

Assessment of Hazardous Properties HP1-HP14

Considering the technological process of generation and the visual appearance of the sample, the waste is considered to be not dangerous due to properties HP1, HP2, HP3, HP9, and HP12. The other dangerous properties were quantified by combining the anions and cations analyzed in the waste and by assessing the compounds from coolants L1 and L2. Table 5 shows the concentrations of the relevant hazardous compounds in the waste.

Table 5. Hazardous properties—W2.

Hazardous Property	Hazardous Phrase	Analyzed Indicator/ Associated Compound	Concentration of the Associated Compound(%)	Concentration Limit (%) Regulation EU 2014/1357
HP4	H314 (skin cor. 1A)	NaOH *Total*	0.82 ***0.82***	 **1**
	H318	NaOH Ca/Ca(OH)$_2$ Al/Al$_2$O$_5$Si Cu/CuSO$_4$x5H$_2$O *Total*	0.82 0.38 0.15 0.015 -*	 **10**
	H315, H319	Na/Na$_2$CO$_3$x10H$_2$O Fe/Fe$_3$O$_4$ Mg/Mg$_3$(Si$_4$O$_{10}$)(OH)$_2$ K/KOH TOC/C$_3$H$_9$NO$_2$ *Total*	2.93 0.02 0.66 0.21 0.809 **2.93**	 **20**
HP5	H335	Na$_2$SiO$_3$ Mg/Mg$_3$(Si$_4$O$_{10}$)(OH)$_2$ TOC/C$_2$H$_7$NO Fe/Fe$_3$O$_4$	1.25 0.66 0.813 0.02	**20** **20** **20** **20**

Table 5. *Cont.*

Hazardous Property	Hazardous Phrase	Analyzed Indicator/ Associated Compound	Concentration of the Associated Compound(%)	Concentration Limit (%) Regulation EU 2014/1357
HP6	H302	Cu/$CuSO_4x5H_2O$ K/KOH TOC/C_2H_7NO *Total*	0.015 0.21 0.813 -*	 **25**
	H332	Mg/$Mg_3(Si_4O_{10})(OH)_2$ TOC/C_2H_7NO *Total*	0.66 0.813 -*	 **22.5**
	H312	TOC/C_2H_7NO *Total*	0.813 -*	**55**
HP8	H314 (skin cor. 1B)	Na_2SiO_3 KOH *Total*	1.25 0.21 ***1.46***	**5**
HP10	H360	B/H_3BO_3 B/$Na_2(B_4O_5(OH)_4)$*$8H_2O$	0.017 0.114	**0.3** **0.3**

* The limit cut-off value from which a substance is assigned the danger phrases H318, H315, H319, H302, H332, and H312 is 1%. Since the concentration of each evaluated substance was <1%, it was unnecessary to sum up all the concentrations, the danger being practically zero.

Apart from the dangerous properties presented in Table 5, no compounds were identified that presented danger phrases in significant concentrations for the other dangerous properties. In the waste sample, there can also be compounds such as CrO_3 (0.0015%), PbCrO4 (0.0049%), MnO_2 (0.0007%), and $PbSO_4$ (0.0021%). These compounds are in extremely low concentrations and do not exceed the most restrictive limit of 0.1%. Comparing the results obtained for LW2 with the maximum values allowed according to the MMGA Order 2005/95, Table 3 indicates that the waste can be stored in non-hazardous (ANH) sites. Therefore, the W2 waste is not hazardous considering property HP15. Considering that W2 waste has no dangerous properties, it can be classified as non-hazardous waste under code *10 11 14 (MNH)—sludge from glass grinding and polishing, other than that specified in 10 11 13*.

W3: The W3 waste sample presents as a dense mass of fine powdery, dark-brown particles. The humidity of the waste is 5.82%, and it has 6.97 pH units. Considering the technological process of generation and the visual appearance of the sample, it is considered that the waste does not have dangerous properties of the types HP1, HP2, HP3, and HP12.

An evaluation of the other dangerous properties (Table 6) was carried out based on the potentially dangerous compounds in the waste detected through physical-chemical analyses. Since dust waste results from the dry dedusting of burnt gases, the majority of elements in the sample are the metals iron and zinc found in the form of oxides.

Table 6. Hazardous properties—W3.

Hazardous Property	Hazardous Phrase	Analyzed Indicator/ Associated Compound	Concentration of the Associated Compound(%)	Concentration Limit (%) Regulation EU 2014/1357
HP4	**H315, H319**	Fe/Fe_2O_3 Cr/Cr_2O_3 * Cu/CuO * Mn/MnO Ca/CaO Al/Al_2O_3 * Mg/MgO *Total* *	53.26 0.11 0.09 2.58 6.70 0.68 1.94 ***64.48***	 **20**

Table 6. *Cont.*

Hazardous Property	Hazardous Phrase	Analyzed Indicator/ Associated Compound	Concentration of the Associated Compound(%)	Concentration Limit (%) Regulation EU 2014/1357
HP5	**H335**	Zn/ZnO	***40.44***	**20**
		Mg/MgO	2.41	**20**
		Mn/MnO	2.58	**20**
		Al/Al_2O_3	0.68	**20**
		Cu/CuO	0.09	**20**
HP6	**H332**	Mg/MgO	2.41	
		Pb/PbO	1	
		Zn/ZnO	40.44	
		Total	***43.85***	**22.5**
HP10	**H360**	Pb/PbO	1	**0.3**
		Total	***1***	
HP11	**H341**	Cu/CuO	0.09	**1**
		Pb/PbO	***1***	**1**

*—same observation as Table 5.

Table 6 shows five dangerous properties (HP4, HP5, HP6, HP10, and HP11) for which the concentrations of inorganic compounds exceed the limits imposed by the European Union regulations. Also, the results obtained for the leaching test (Table 3) reveal that the W3 waste must be stored in hazardous waste sites because the concentrations for Pb, Zn, and TDS exceed the VMA for non-hazardous sites. Therefore, W3 waste is dangerous and can be included in the European Union List of Wastes under code 10 02 07* (MH)—solid waste resulting from purifying gases containing hazardous substances.

6. Conclusions

The methodology presented in this paper can be used to evaluate the hazardous properties of a solid/liquid waste that can be of the MH or MNH type, depending on its composition and specificity. The methodology was applied to evaluate the dangerousness of three industrial wastes, assigning two MNH-type codes and one MH code. These codes are valid as long as there are no changes in the technological process and in the waste composition. Even if the task of waste classification falls under the responsibility of waste producers and owners, to establish a suitable waste code, the support of specialists and laboratories is necessary throughout the characterization and evaluation of dangerousness.

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