Industrial waste characterization as a tool for sustainable management: The case of secondary aluminum wastes

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Abstract Waste characterization and classification provides the basis for ensuring their sustainable collection, transportation, storage and treatment in compliance with legal requirements. The aim of this article is to summarize the prevailing framework for industrial waste classification in EU and its application in the characterization of wastes that present mirror entries in the European Waste Catalogue. Within this framework a methodology based on the Commission Regulation (EU) No 1357/2014 was developed for the characterization of dross wastes from a secondary aluminum unit plant in Greece and presented in this article. Chemical and mineralogical analyses and laboratory tests for the assessment of the hazardous properties were conducted in accredited European laboratories. Then based on the evaluation of analytical & experimental results the properties of the materials under study were recorded and compared with the prevailing regulated limits. The methodology developed can be generally applied for the characterization of aluminum bearing wastes, and their classification as hazardous, or as their respective non-hazardous mirror entry. Based on the above the sustainable management of these wastes will be designed with the implementation of the measures corresponding to their respective properties.

Keywords: aluminum dross wastes, waste classification, hazardous properties

1. Introduction

The classification of waste as hazardous or non-hazardous is crucial for their sustainable management in compliance with the prevailing legislation. The EU framework for classification of waste and the list of properties that render them hazardous have been recently updated. The key guidance documents for waste classification include a) Commission Decision of 18 December 2014, amending Decision 2000/532/EC on the list of waste pursuant to Directive 2008/98/EC of the European parliament and of the Council 2014/955/EU [The List of Waste (LoW)] and b) Commission Regulation (EU) No 1357/2014of 18 December 2014, replacing Annex III to Directive 2008/98/EC of the European Parliament and of the Council on waste and repealing certain Directives. The LoW establishes a harmonised classification system for wastes. More specifically, depending on their hazard classification the wastes are labelled in three different ways:

- absolute hazardous entry: The code is marked with an asterisk (*) and the waste is classified as hazardous waste,
- mirror entry: The waste is potentially hazardous or non-hazardous depending on its hazardous properties and/or the content of hazardous substances. The waste hazardous properties have to be assessed prior to assigning the appropriate waste code, and
- absolute non-hazardous entry: The waste is classified as non-hazardous (no further assessment required).

Hazardous waste is defined as waste that displays one or more of the 15 hazardous properties (HPs) included in the revised Annex III to Directive 2008/98/EC. The 15 HPs are divided into physical hazards (HP1: Explosive, HP2: Oxidising, HP3: Flammable), health hazards (HP4: Irritant, HP5: Specific Target Organ Toxicity (STOT)/Aspiration Toxicity, HP6: Acute toxicity, HP7: Carcinogenic, HP8: Corrosive, HP9: Infectious, HP10: Toxic for reproduction, HP11: Mutagenic and HP13: Sensitising) and environmental hazards (HP14: Ecotoxicity). Additional hazardous properties include HP12: Release of an acute toxic gas and HP15: Waste capable of exhibiting a hazardous property listed above not directly displayed by the original waste. In Commission Regulation (EU) No 1357/2014, under each HP, a number of hazard categories, each corresponding to a Hazard Statement Code (HSC) is listed. The assessment of hazardous properties is based on concentration limits of contained hazardous substances specified in above regulation or on the result of tests performed in accordance with Regulation (EC) No 440/2008 or other internationally recognised test methods and guidelines (Maraboutis *et al.*, 2016). The classification rules are based on Regulation (EC) No 1272/2008 (CLP) on the Classification, Labeling and Packaging of substances and mixtures. The waste classification has several implications given that a number of European regulations set special requirements for the management of hazardous waste (Figure 1). Given, that the waste generally consists of a complex mixture of numerous substances whereas the CLP refers to specific substances, the assessment of hazardous properties is not a trivial task. Several issues in the implementation of the procedure have been reported, including difficulties in the assessment of some hazardous properties, lack of harmonised threshold values (HP14, HP15), lack of guidance on the selection of test methods (BiPRO and Prognos, 2015, Wahlström *et al*., 2016). The development of procedures, including a combination of methods for the comprehensive characterization of waste is therefore needed, (Zomeren *et al*., 2015). In this paper the integrated methodology developed and applied for the assessment of hazardous properties of aluminum dross wastes from a secondary aluminum unit plant in Greece is presented. Aluminum dross is generated when impurities and oxidation layers are skimmed from the surface of molten metal. The waste is listed as mirror entry in the LoW:

10 03 15* skimmings that are flammable or emit, upon contact with water, flammable gases in hazardous quantities

10 03 16 skimmings other than those mentioned in 10 03 15.

10 03 15* and 10 03 16 are assigned based on the waste displaying hazardous property HP 3 Flammable or containing POPs (EA, 2015). To ensure the non hazardous character of the waste, all fifteen (15) HPs have been examined.

2. Methodology

2.1 Sampling and characterisation

Sampling of aluminium dross was performed based on European standard EN 14899. A representative subsample of 50 kg was collected from the plant's storage area according to CEN/TR 15310-3. The dross sample was prepared according to the requirements of standard EN 15002. The analyses and tests performed for the characterization of the examined waste sample are given in Table 1.. Quality control procedures specified in ISO 17025 were applied.. Particle size analysis was performed by dry sieving. The fine fraction (-500 μm) was analysed with the laser light diffraction technique in Mastersizer Microplus analyser of Malvern Instruments. Chemical analysis involved fusion of the solid sample with lithium tetraborate and analysis of major elements with Atomic Absorption Spectrophotometer, AAS PE 2100 (APHA, 2005). For the analysis of minor elements, the sample was digested with a mixture of HCl/HNO_3 with ratio 3:1 (aqua regia). The solutions were analysed with ICP MS. Total carbon and sulphur content of the sample was determined by LECO CS 200 analyser. For the determination of pH and alkalinity of aluminium dross sample, OECD/OCDE Test Guideline 122 was followed. For the determination of Cr(VI), alkaline digestion with 0.28M Na_2CO_3/0.5M NaOH solution (EPA Method 3060A) was performed. Hexavalent chromium in the produced solution was determined colorimetrically according to EPA Method 7196A using a Hitachi U 1100 UV/Vis Spectrophotometer.

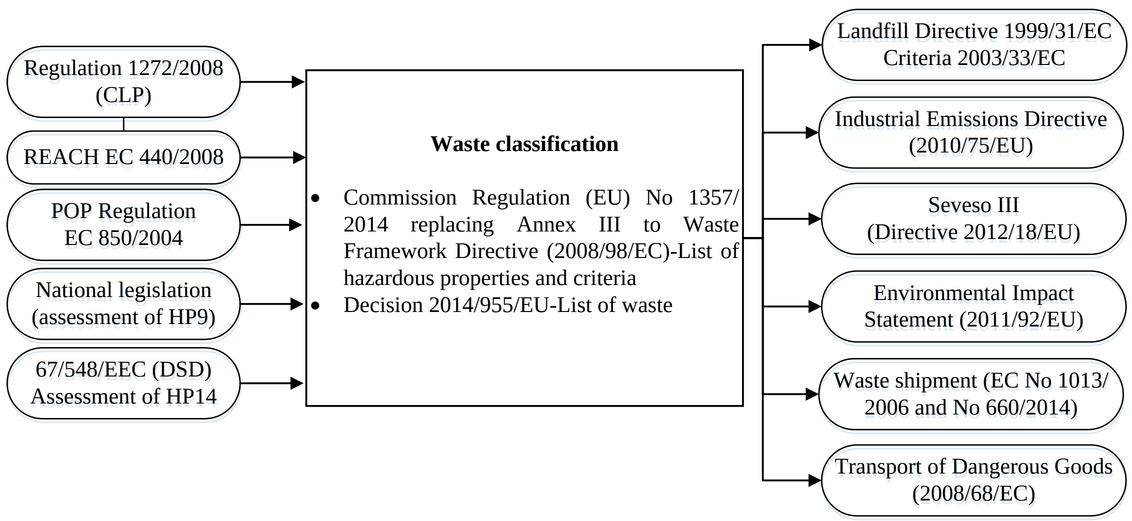

Figure 1: Legislative framework for waste classification

Table 1. Methods of aluminium dross characterization applied in the present study

Test/Analyses	Methods	Relevance to hazardous properties
Particle size distribution	Dry sieving (ASTM E276, E 389), Laser particle size analysis (ISO 13320)	HP6
Chemical analysis		HP1-HP15
– Major elements (Al, Ca, Fe, Mg, Na, Si, Ti, V)	CEN/TR 15018/APHA 3111	
– Minor elements (As, Cd, Co, Cr, Cu, Hg, Mn, Mo, Ni, Pb, Sb, Se, Zn)	EN 13657/EN ISO 17294.02	
– Total sulphur and carbon analysis	ASTM E 1915	
Speciation		
Determination of Cr(VI)	EPA Method 3060A/7196A	
Determination of $S(SO_4)$	APHA 4500-SO_4-C	
Mineralogical analysis	X-Ray Diffraction, Scanning Electron Microscopy	HP1-HP15
pH/Alkalinity	OECD/OCDE 122	HP4, HP8
Metals leachability	EN 12457.04	HP14, HP 15
Flammability in contact with water	A.12 (440/2008/EC)	HP 3, HP 12
Analysis of Persistent Organic Pollutants (POPs)	US EPA 808, US EPA 8082, ISO 10382	-

Mineralogical analysis was performed with X-Ray Diffraction (XRD) using a Bruker D8-Focus diffractometer. The morphology of the solid particles was examined by scanning electron microscopy (SEM), using a Jeol 6380LV microscope, at 20 kV accelerating voltage. Chemical composition of the sample particles was determined by an Oxford INCA Energy Dispersive Spectrometer (EDS), connected to the microscope. To determine the leachability of contained metals and oxyanions from the waste sample, the standard leaching tests EN 12457.02 was applied. The release of flammable gases in contact with water was determined by A.12 method, Regulation (EC) No 440/2008. Analysis of Persistent Organic Pollutants (POPs) specifically mentioned in the LoW was also performed. The last two parameters were determined in external accredited laboratories.

2.2 Hazard assessment procedure

For the assessment of hazardous properties of aluminium dross sample, the guidelines given in the Commission study performed by BiPRO were followed (BiPRO, 2015). The methodology applied is shown in Figure 2. Based on the characteristics of the aluminium dross examined, substances potentially contained in the waste and having Hazardous Statement Codes (HSC) were identified. Given that the lower limit for substances specified in EU regulations is 0.1%, the elements contained in the aluminium dross at a concentration higher than 0.01% were taken into account for the assessment of hazardous properties. The hazard categories presented in Table 3.1 of Annex VI to CLP regulation (e.g. Al powder: Flammable solid/H228, Water-react. 2, In contact with water releases flammable gases, H261) were considered. The hazardous properties were assessed based on the content of the substances listed in the relevant HSCs as compared to the limit values specified in EU regulation 1357/2014. For HP 3, evaluation was based on the results of A.12 test method specified in regulation (EC) 440/2008. A.12 test results were also used to evaluate HP12, regarding the release of toxic gases in contact with water. For each HP, the Hazard Index (HI) i.e. the ratio of the sum or maximum of relevant substances concentration to the concentration limit was calculated (Hennebert *et al*, 2014). In the case that HI≥1, the waste is classified hazardous.

3. Classification of aluminium dross

3.1 Characteristics of aluminium dross sample

Based on particle size analysis, 50% of aluminium dross had particle size lower than 3 mm (d_{50}: 3 mm). The percentage of material that fall in the range of silt and clay (d<0.06 mm), sand (d: 0.06-2 mm) and gravel (d>2mm) amounted to 12%, 33% and 55% respectively. Based on the chemical analysis, the sample examined consists mainly of Al (Al_2O_3: 84%), followed by Mg (MgO: 3.8%), Ti (TiO_2: 3.4%), Ca (CaO: 2.5%), Si (SiO_2: 3.1%), Na (Na_2O: 1.3%), Fe (Fe_2O_3: 1.0%), Ba (BaO: 0.64%) and K (K_2O: 0.42%). Minor elements content is Mn (1225 mg/kg), Cr (236 mg/kg), Cu (230 mg/kg) and Zn (215 mg/kg) whereas the concentration of other elements analysed was very low (i.e. <0.01%). The concentration of Cr(VI) was below quantification limit of the analytical method, i.e. <0.24 mg/kg. Carbon and sulphur content of the waste sample was 0.87% and 0.11% respectively. The main

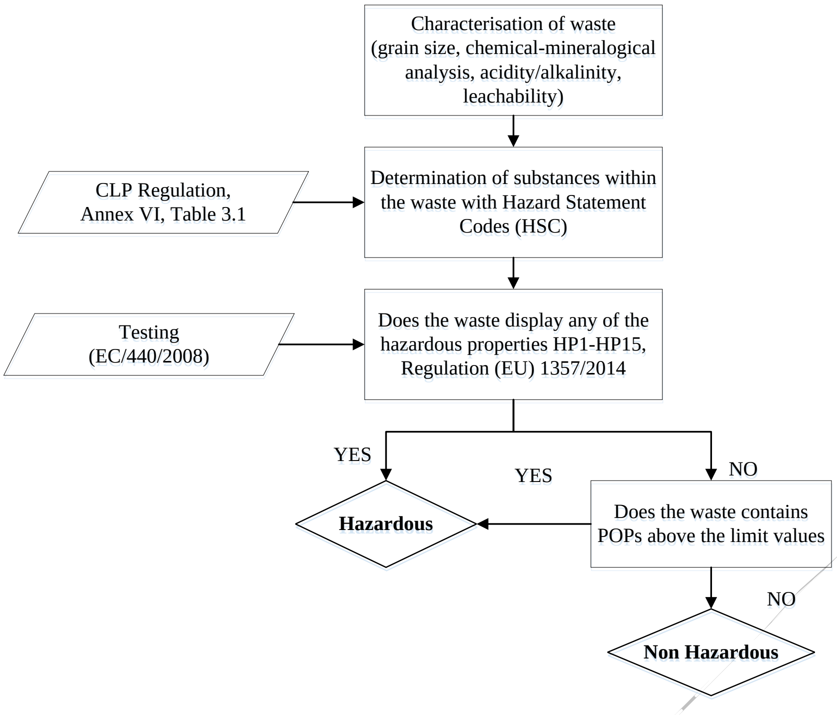

Figure 2. Methodology for assessment of hazardous properties and waste classification

crystalline phases detected include Al compounds such as corundum (Al_2O_3), spinel ($MgAl_2O_4$, $Mg_{0.388}Al_{2.408}O_4$), aluminium nitride (AlN), aluminium oxynitride, metallic aluminium (Al) and sodium aluminium oxide ($NaAl_{11}O_{17}$). Calcium carbonate was also detected. Furthermore, SEM examination indicated the presence of Aluminium Carbide and KCl. The sum of the concentration of the compounds identified exceeded 90% of sample mass, in agreement with proposed analytical protocol (Hennebert *et al*., 2013) The alkalinity of sample, expressed as % NaOH was determined to 0.5%. Leaching of the Aluminium dross sample with deionized water at a liquid to solid ratio of 10 L/kg resulted in the production of alkaline leachates with pH: 9.7 with increased concentration of Al, Na, K, Ca and chlorides. The leachability of metals of environmental interest was generally in compliance with the limits for the acceptance of waste in the landfill for inert wastes. The dissolution of Sb, chlorides and fluorides satisfies the criteria for the landfill of non hazardous wastes. Based on the results of A.12 test, no gas generation or spontaneous ignitions were observed and it was thus concluded that the sample does not generate flammable gases in contact with water. Finally, POPs analysis indicated that the concentration of these pollutants are well below the limits specified in Regulation (EC) 850/2004.

3.2 Identification of dangerous substances

The many forms of aluminum compounds contained in the aluminium dross sample can potentially undergo a wide range of reactions when interacting with water during disposal. The reactions of metallic Al with water results in the production of the flammable gas $H_2(g)$. Given the alkaline properties of the sample examined, (pH>8), when mixed with water, reaction (1) occurs (Tolaymat and Huang, 2015):

$$2Al + 2OH^- + 6H_2O \rightarrow 2Al(OH)_4^- + 3H_2(g) + heat \quad (1)$$

The reaction of the contained AlN and Al_4C_3 with water results in the production of NH_3 (flammable and toxic gas) και CH_4 (flammable gas) respectively, according to reactions (2)-(30 (Bruckard, W. J., Woodcock, J. T., 2009, Tolaymat. and Huang, 2015):

$$AlN + 3H_2O \rightarrow Al(OH)_3 + NH_3(g) \quad (2)$$

$$Al_4C_3 + 12H_2O \rightarrow 4Al(OH)_3 + 3CH_4(g) \quad (3)$$

The reaction of Al_2S_3 with water results in the production of $H_2S(g)$ (flammable and toxic gas), according to reaction (4).

$$Al_2S_3 + 6H_2O \rightarrow 2Al(OH)_3 + 3H_2S(g) \quad (4)$$

Given the above, the aluminium dross sample examined contain compounds having HSCs relevant to HP3 and HP12 and thus further testing was necessary in order to assess these hazardous properties. Based on the chemical-mineralogical analysis of the aluminium dross sample, compounds of Ba, Ti, S, Mn, Zn, Cu and S that may be contained in the waste and have harmonized classification were identified. Taking into account the type and the production process of aluminium dross, substances that cannot be present in the waste were not considered. The HSCs of compounds identified were relevant to HP4, HP5, HP6, HP8, HP12 and HP14.

3.3 Assessment of hazardous properties

The overall assessment of hazardous properties is given in Table 2. Based on the Hazard Index (HI) calculated, as well as the results of testing performed, it was clearly documented that the waste is non hazardous.

Table 2. Assessment of hazardous properties of aluminium dross sample

Hazardous property	Hazard index	Justification
HP1	-	No relevant compounds are contained in the waste
HP2	-	No relevant compounds are contained in the waste
HP3	-	No flammable based on testing
HP4	0.0	Relevant compounds lower than the cut-off limit of 1%
HP5	0.03	Relevant compounds: BaS, CaS
HP6	0.23	Relevant compounds $BaCl_2$, Na_2S
HP7	0.0	No relevant compounds are contained in the waste
HP8	0.0	Relevant compounds lower than the cut-off limit of 1%
HP9	-	No relevant based on the waste type
HP10	0.0	No relevant compounds are contained in the waste
HP11	0.0	No relevant compounds are contained in the waste
HP12	0.8	No release of toxic gases in contact with water based on testing. Relevant compounds that emit toxic gases in contact with acid Ba, Ca, K, Na sulphides.
HP13	0.0	No relevant compounds are contained in the waste
HP14	0.01	Relevant compounds Ba, Ca, K, Na sulphides
HP15	0.0	No relevant compounds/ Leachability of the sample satisfies the criteria for the landfill of non hazardous wastes

4. Conclusions

To assess the hazardous properties of a waste, comprehensive knowledge of its constituents is required. The integrated testwork methodology described in this paper presenting a combination of chemical and mineralogical analyses, and environmental characterization tests allowed the detailed characterization of an aluminium dross sample, emanating from secondary aluminum production. Based on analytical test results, substances contained in the waste sample that present HSCs were identified. Comparison with regulatory limits clearly documented that the waste sample examined is non hazardous.

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