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Bottom Ashes From Waste Incineration Characterization: Concentration of Heavy Metals and Environmental Hazard

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Abstract

The Italian law about waste, has recently introduced (L. 28/2012) a new way to classify the waste, taking into account its Ecotoxicity (assignment of hazardous characteristic H14 according to ADR criteria). Pending EU guidelines, different procedures have been followed leading to distinct results in the hazardous characterization.

The problem is particularly complex in the cases of bottom ashes because of the content of heavy metals potentially hazardous for environment. Due to the nature of bottom ash, it is very difficult to define the exact chemical species of an heavy metal. In order to classify the waste, this aspect is very important since different chemical species of the same metal present different concentration limits to assess the environmental hazard using additive methods.

In this study, a comparison between available classification methods is performed, showing their applicability to bottom ashes. It is also shown how the results may change using CLP and ADR criteria.

Key words: Heavy metals, bottom ashes, waste classification, environmental hazard, H14.

Introduction

New modification in the Italian law about waste, has changed once again the classification criteria for environmental hazard. According to law n. 205 of 2010, hazardous wastes for environment (H14) were classified according to Classification Labelling and Packaging (CLP) criteria, although the law was not so clear about it. As L. 28/2012 has become effective, the criteria defined in the ADR have to be followed. As a result, many of the wastes previously classified as hazardous for environment could be now considered not hazardous.

The two criteria above are different because they have different tasks: CLP regards the "whole life" of a substance or a mixture, while ADR concerns only with transportation and so it doesn't consider long-term impacts on environment. According to CLP, in fact, a mixture can be classify as Acute 1 (short period) and Chronic 1-4 (long term), while ADR doesn't consider Chronic 3 and 4 as hazardous classes.

This topic can be very relevant for some particular wastes as bottom ash (identified with mirror entries CER 190112 or 190111*), because of their content of heavy metals potentially hazardous for environment.

As revealed in several studies (Clozel-Leloup et al.,1999; Zevenbergen and Comans, 1994; IAWG, 1997), the incineration bottom ash is mainly composed of a mix of slag, ferrous and no-ferrous metal, ceramics, crystals, glassy material and others non-combustible material. Furthermore, fresh incinerator bottom ash is characterized by a low-density slag phase and a vitreous dense phase (Filipponi et al. 2003). Typically, mineralogy composition includes silicates (quartz), sulphates, carbonates, metal oxides, hydroxides (portlandite), as well as metals and alloys (Kirby and Rimstidt, 1993; IAWG, 1997; Eusden et al., 1999; Speiser et al., 2000). Due to the presence of portlandite, the bottom ash is an alkaline material.

The concentration of heavy metals, such as lead, nickel, mercury, cadmium, arsenic and zinc, depends on the waste composition and the operating conditions of the plant. Due to the nature of bottom ash is very difficult to define the exact chemical species of an heavy metal. In order to classify the waste, this aspect is very important since different chemical species of the same metal present different concentration limits to assess the environmental hazard, using additive methods.

Both of the regulations allow to use three

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alternative methods to classify mixture in relation to the hazard for environment:

- Ecotoxicity testing: in order to directly determine impacts on living beings;
- Bridging principles: using data from similar substance or mixture or a mix of data available and data from test;
- “summation of classified components" and/or an "additivity formula": calculation of ecotoxicity on the basis of known toxicological properties of the known components of the mixture or sum of concentration of every chemical component of the mixture.

In this study, a comparison between available classification methods is performed, showing their applicability to bottom ash. It is also shown how the results may change using CLP and ADR criteria.

Materials and Methods

In this issue a total of 16 chemical analysis for wastes characterization of bottom ashes, are considered, all of them hazardous according to CLP. In particular 2 certifications from Puglia for bottom ashes from municipal waste incinerators, before 2010, have been taken (LeIU-1, LeIU-2); 2 certifications from plants in Lombardia, (Bs-1 of 2011, Bs-2 of 2012). Moreover, chemical concentration data of metals, related to 12 bottom ash samples, presented in the paper “ecotoxicological characterisation of 12 incineration ashes (mwi) using six terrestrial and aquatic tests” (J.Roembke et al, 2012), are considered too.

Starting from the analytical results, H14 classification is performed with CLP and ADR additive method, in order to compare the results. Heavy metals concentrations are elaborated in the first case, according to CLP using the following scheme:

Risk Phrases	Sum of components classified as	Mixture classified as
R50	Acute 1 x M ≥25%	Acute 1
R50/53	Chronic Category 1 x M ≥ 25 %	Chronic Category 1
R51/53	(M x 10 x Chronic Category 1) + Chronic Category 2 ≥ 25 %	Chronic Category 2
R52/53	(M x 100 x Chronic Category 1) + (10 x Chronic Category 2)	Chronic Category 3
R53	Chronic Category 1 + Chronic Category 2 + Chronic Category 3 + Chronic Category 4 ≥ 25 %	Chronic Category 4

Tab. 1. Classification of a mixture for acute (short period) and chronic (long term) hazards, based on summation of classified components (CLP directive, Annex I).

In the second case, ADR criteria, the used scheme is:

Risk Phrases	Sum of components classified as	Mixture classified as
R50	Acute 1 x M ≥25%	Acute 1
R50/53	Chronic Category 1 x M ≥ 25 %	Chronic Category 1
R51/53	(M x 10 x Chronic Category 1) + Chronic Category 2 ≥ 25 %	Chronic Category 2

Tab. 2. Classification of a mixture for acute (short period) and chronic (long term) hazards, based on summation of concentrations of classified components (ADR agreement, 2011).

In order to apply the hazardous classes to the metals in the waste, they are considered as “metal and its compounds”; if there isn’t such label in the Annex VI of CLP, the metal is considered as its most ecotoxic compound. Cu is relevant for environment only in its soluble form: if not specified in the analysis, Cu is considered as Total Cu after crossing data with eluate results.

In the above schemes, M-factor is a corrective factor which amplify limits for highly toxic substances, and it can be found, if available, in the annex VI to CLP.

In both cases, the value of factor M is given to each metal in the waste, according to following procedure:

- if there is a specific value for the “metal and its compounds” in the Annex VI to CLP, that is considered;
- if there ins’t the limit above, the limit belonging to the chemical specie of the metal which has the lowest value is considered.

Testing and bridging principles methods are evaluated in order to define their applicability to this particular kind of waste.

Results and Discussion

1. Additivity method.

The result of the comparison between additive methods for CLP and ADR is that CLP method is more conservative because, instead of ADR method, it considers two more hazardous classes depending on the substances formerly identified with risk phrases R 53 and R 52/53. Particularly relevant among the metals for the classification is Zn, and in a lighter way Pb. All the wastes have been classified H14 (Chronic 3) and so they are not hazardous with ADR.

Sample	Waste classification		Over limit metals
	CLP	ADR	
MWI-1	H14 (chronic 3)	Not hazardous	Zn
MWI-2	H14 (chronic 3)	Not hazardous	Zn
MWI-3	H14 (chronic 3)	Not hazardous	Zn
MWI-5	H14 (chronic 3)	Not hazardous	Zn

MWI-6	H14 (chronic 3)	Not hazardous	Zn, Pb
MWI-7	H14 (chronic 3)	Not hazardous	Zn
MWI-8	H14 (chronic 3)	Not hazardous	Zn
MWI-9	H14 (chronic 3)	Not hazardous	Zn
MWI-10	H14 (chronic 3)	Not hazardous	Zn
MWI-11	H14 (chronic 3)	Not hazardous	Zn
MWI-12	H14 (chronic 3)	Not hazardous	Zn, Pb
MWI-13	H14 (chronic 3)	Not hazardous	Zn
MWI-1	H14 (chronic 3)	Not hazardous	Zn
MWI-1	H14 (chronic 3)	Not hazardous	Zn
MWI-1	H14 (chronic 3)	Not hazardous	Zn
LeIU-1	H14 (chronic 3)	Not hazardous	Zn, Pb
LeIU-2	H14 (chronic 3)	Not hazardous	Zn, Pb
Bs-1	H14 (chronic 3)	Not hazardous	Zn
Bs-2	H14 (chronic 3)	Not hazardous	Zn

Tab. 3. Ecotoxicological hazard according to CLP and ADR additivity criteria.

From a technical point of view and considering environmental safety, it is important to point out that no one of the explained criteria is actually representative of a real environmental hazard. CLP additive method, in fact, can overestimate hazard (J.Roembke et al, 2012). It's easy to verify that concentrations of heavy metals in a soil close to the limits fixed for industrial/commercial soil contamination, can lead to an hazard classification of the soil itself.
Moreover, for this kind of waste, it is very important to know the real chemical formula of the heavy metal compounds in order to forecast their attitude to pollution and, first of all, their solubility. These information are very hard to find, since the structure of the waste, and, in the most of the cases, the formula is an hypothesis more or less reliable. In this case it's unreasonable to consider all the Zn or Pb as hazardous, knowing the properties of bottom ashes.
On the other hand ADR additivity method can underestimate the real hazard, although it has to be performed according by the recent law. ADR, in fact, doesn't consider the hazard classification Chronic 3 and 4.
For this reason, real ecotoxicological hazard can be evaluated after verifying CLP addivity results with other methods. The following table shows strengthens and weakness of possible verifying methods, to be performed after CLP additivity method leads to hazard classification.

Verifying method	strengthens	weakness
X ray Difratto-metry	Can determine real hazard by identification of the exact molecular structure of metal compounds (speciation) and so its properties (solubility, dissolution). It is a direct and not destructive method.	Quantification level of the method: about 1%. Metals concentration in bottom ashes generally don't reach these levels. Moreover most of the CLP limits are lower than quantification level (0.25%).
Ecotoxico-logical tests	Independent from the real knowledge of the chemical formulas of metal compounds	Test need to be improved and specialized for wastes. According to CLP test must be preformed to all trophic levels (including fishes) for acute and chronic toxcicity. Sometime ecotoxicological hazard may depends on elements not classified as ecotoxic for CLP (K, Ca, Al), thus leading to possible misclassification (Breitholtz et al., 2012).
Chemical test for transforma -tion/ dissolution (annex 9 and 10 of GHS)	Can be an easy alternative to numerous, expensive and difficult ecotoxicological test	Need to improve for mixture in general, since they are validated only for substances.

Tab. 4. Verifying methods

2. Other methods.

For as regards other available methods, summation of classified components method is hard to use for wastes, since it is difficult to divide all their components in classified and not classified. So this method is useless both for CLP and ADR.
In the same way, bridging principles method is not feasible because it is impossible to find a similar and known mixture to the specific waste to be classified.
For as regards ecotoxicological testing, CLP and ADR provide for Acute Hazard and Chronic Hazard tests based on effects on living beings. Only for Chronic hazard, in addition to the previous tests, it should be also required a test for degradability and bioaccumulation for a more precise classification based on more complete information. However it is clearly specified that degradability and bioaccumulation tests for mixtures are not used as they are usually difficult to interpret, and such tests may be meaningful only for single substances (CLP –Annex I, 4.1.3.3.2, ADR – Part. II, 2.2.9.1.10.4.3.2). This topic is particularly relevant for heavy metal compounds.
As a consequence, without information about degradability and bioaccumulation, according to CLP, only Chronic 1 or 2 classification is possible. Eventually, when tests are negative, Chronic 4 class can be assigned if there are nevertheless reasons for concern (safety net classification). This class, for mixture, is not assessed by specific test results, as instead for substances (degradability results).

So even if CLP, and not ADR, also considers Chronic 3 and 4, in practice, only Acute 1 and Chronic 1 and 2 can be evaluated directly by tests, and so CLP and ADR lead to the same hazardous classes using tests.

Conclusion

CLP and ADR provide for the same methods to assess hazard for environment, but CLP is more conservative because it considers two more long term hazard classes (Chronic 3 and 4). Since waste disposal involves very long time, the approach of CLP, in our opinion, fits better on waste management, than ADR (long term impacts not evaluated).

Additivity and testing methods can apply to wastes.

For bottom ashes, because of heavy metals content, additive CLP method can overestimate the hazard, while ADR can underestimate it. By the comparison of the results from both the criteria, it is shown that all the hazardous wastes according to CLP are not hazardous for ADR. It depends mainly on Zn concentration and, in some cases, on Pb.

Even if law n. 28/2012 obliges to use ADR criteria for H14, through the modification of Annex D to D.Lgs 152/06, the Annex I to the same law, provides for CLP approach in order to classify hazardous properties. In our opinion, from a scientific point of view, CLP additivity approach should be the first step for hazard evaluation, because including Chronic 3 e 4 and long term effects, very relevant in case of waste management. If the waste is classified H14 according to this method (as Chronic 3, not included in ADR classification), possible overestimation could be avoided only by an additional control, using a verifying method suggested in table 4. These methods, chemical or biological, need however to be opportunely improved. The choice should depend on the comparison between the strengthens/weakness of the methods, the technological progress of the tests, the knowledge of the nature of the waste and its productive process.

Using validated ecotoxicological test for classification, there is no difference between CLP and ADR, in practice, because of the applicability of the tests to mixture. Biological tests on the waste is a concrete opportunity to overcome all the uncertainties related to the chemical formula of the wastes and can directly verify environmental impacts, but they need to be improved, specialized for wastes and reduced in number.

Considering that bottom ashes, in particular aged ones, have a low biological effect, probably for low solubility of the chemical species of metals due to the production during combustion in strong oxidant condition and high temperature, chemical test for transformation/dissolution (annex 9 and 10 of GHS) may be a valid verifying method.

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