Partial stabilization of hazardous wastes: An approach for a safe landfill disposal

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Abstract

The issues of the treatment of hazardous wastes cannot be solved easily and must be properly faced to avoid management and legal problems. In this work the stabilization process of different hazardous wastes containing metals was investigated at lab and full scale to understand if a “common approach” can be defined, at least for some categories of wastes, in order to provide useful information to the managers of waste treatment plants on the wastes that can be more efficiently and safely treated together within the same “mix”. Results indicated that, for the investigated metals, most of the wastes shows a similar predictable pH-dependent behavior, with the exception of the molybdenum. For waste containing this metal a different approach is proposed in order to achieve the partial stabilization goal. Specifically, the efficiency of using of zero valent iron and the sodium sulphate was confirmed by experimental results indicating that this approach can be used successfully. However, the narrow border of economic convenience in applying this treatment to such specific typologies of wastes strictly depends on the current market scenario.

Keywords: Stabilization, metals, treatment, landfill, molybdenum

1. Introduction

Waste characterization for the proper final disposal selection is regulated in Italy by DM 27/09/2010 so to ensure that the landfill receiving the waste has no environmental impact in the surrounding area, especially with regards to groundwater contamination. However, also hazardous wastes can be disposed into not-hazardous waste landfill if the waste are properly treated before the disposal so to respect some specific conditions regulated by Art. 6 of DM 27/09/2010 (now updated by DM 24.6.2015).
The main requirement is that the eluate from the leaching test on the treated waste [1] respects the limits of table 5a of the DM 27/09/2010. Other important requirements for the stabilized and not reactive waste to be disposed-off in a not-hazardous waste landfill are:

- A total organic carbon concentration (TOC) less than 5%;
- A pH higher than 6;
- A dry matter content higher than 25%;
- The treated waste has to be subjected to appropriate geotechnical tests that demonstrate adequate physical stability and load capacity.

One of the potential treatment, able to achieve all these requirements, is the stabilization or partial stabilization of the waste consisting in creating a mixture with additives defined as ‘chemicals’ [2] which have the main purpose of reducing the release in the eluate of the target pollutants and so its potential impacts.

There is only one specific legal prohibition for this treatment, as stated by Article 6, co. 2 of Legislative Decree 36/2003 and Directive 1999/31/EC, that forbids to mix the wastes with the sole purpose of reducing the contaminants’ concentrations. This prohibition prevents the mixing of waste with other substances to reduce the concentration of contaminants in the eluate from the treated waste and therefore to achieve the compatibility with Table 5a by "mere dilution".

Waste stabilization processes) are widely used in the treatment of a large variety of industrial hazardous wastes such as by-product of industrial production, exhausted catalysts, incineration products, etc [3,4,5,6].

On one hand these processes allow to considerably reduce the release to the environment of the polluting substances present in the waste through the formation of insoluble compounds that create a stable polymeric or crystalline structure capable of trapping the toxic elements,elements [7]; on the other hand, they improve the physical characteristics of the material and therefore its manipulability, lowering the risks for the operators and the environment [8,9] The wide heterogeneity of wastes of different origin, composition and response to the treatment [10] makes particularly difficult for the operators to accurately identify the multiple reactions that takes place within the treatment process [11]. As a consequence, there is no definitive scientific and technical literature that regulates the percentage of chemicals to be used as the variety of wastes makes a schematic procedure complicated to be uniquely defined [12,13].

pH is however fundamental to understand the chemical behavior that occurs when a mix is created [14] Generally, the mixes achieve a high alkaline pH that rarely fall below 12. Most of the metals react positively to this high increase in pH [15,16,17]. On the contrary, it is necessary to correct the pH of the waste if it is too low, since waste with a pH less than 6 is not allowed in the landfill. An exception is represented by wastes containing Molybdenum as in the case of some by-products of industrial production, exhausted catalysts, incineration products, etc.

Molybdenum responds to the increase in pH becoming more soluble; this behavior causes a serious issue to deal with when wastes containing molybdenum have to be treated together with other classes of wastes which responds better to alkaline condition.

In literature various treatments applying additives have been investigated such as Portland cement, Cement kiln dust, Fly ash (e.g. Class F and C pozzolanic fly ashes), Lime (e.g. quicklime, hydrated lime, lime kiln dust) Slag (e.g. ground granulated blast furnace slag), Organoclay, Activated carbon, Cement-based proprietary mixtures, Silicate, phosphate, and sulphate[4,18] among which the ones based on cement and lime, appears to be the most widespread and economically convenient. The amount of additives can be quite relevant, the type and the percentages being considerably variable from case to case, depending on the characteristics of the pollutant, its concentration and the chemical-physical characteristics of the waste (e.g: granulometry, pH, humidity etc).

As frequently reported [19], several wastes can also be used as an additive, as in the case of combustion ash which, thanks to its high concentration of active oxides, can facilitate the stabilization goals. The additives used to stabilize a single waste within the mix, should not exceed 25%, to limit the dilution undesired effects.

The objectives of this work can be summarized as follow:

- To verify which categories of wastes/pollutants can be considered sensitive to the same treatment conditions;
- To investigate some alternative treatment conditions for those waste having pollutants which show different behavior (e.g. wastes containing molybdenum) and not respond positively to the classic high-alkaline approach of stabilization

2. Materials and methods

2.1 Wastes and mixture preparation

A mix is here defined as a mixture between one or more types of wastes with the addition of additives. The purpose of creating a mix is to obtain a reduction in the concentration of pollutants (heavy metals in particular) following the leachate test.

Generally, a mix is composed of waste considered dangerous, which are those with a concentration of heavy metals in the eluate from the leaching test higher than the legal limit, provided for in Table 5a of Article 6 of the Ministerial Decree of 27 September 2010. The lab mix is created on the basis of 100 g.

Twelve different mixed were analyzed having different target contaminants including Sb, Mo, Cu, Zn and Ba respectively.

Once the composition of the mixture is proposed, its components are weighted individually and mixed manually in a baker, by means of a glass rod. In this mixture consisting of the waste and the additives (lime and ferrous sulphate), water must be added to ensure that all the needed reactions take places.

In order to reduce the gap between the laboratory results and the full scale treatment in the plant, leachate from the landfill where the same stabilized waste are disposed was added to the mixtures, as in the full-scale treatment conditions. The addition of leachate allows all the components of the mix to react but attention must be payed in order not to worsen the consistency of the mix so to compromise its handling within the plant. The amount of leachate added is closely related to the initial humidity of the mixture both in the full scale treatment and in the lab scale experiments;

A two-hour maturation time is necessary to let the mix maturing and to allow all the reactions to reach an equilibrium. It was observed that a longer wait does not entail any improvement in the stabilization process;

2.2 Stabilization tests on wastes containing molybdenum

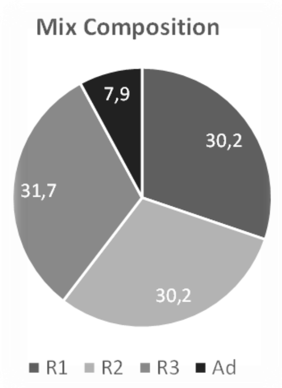
6 mixes were specifically prepared for wastes containing molybdenum. Fly ashes from incineration of industrial wastes characterized by a concentration of molybdenum in the eluate of 1,7 mg/l were treated using as additive the same percentage of sodium sulphide (1%), and percentages of zero iron valence variable from 0.5% to 1%.

2.3 Leachate analysis

The sample of the waste was placed for a 24-hours in an overhead shaker set at a speed of 9 rpm. The sample was then acidified with 65% purity nitric acid; 100 µl of 65% nitric acid were added to both tubes and 200 µl of internal standard were added to the first tube. An ICP mass (Perkin Elmer nexION 350x) was used for heavy metal concentration analysis.

3. Results and discussion

The main characteristics of a mixture of two hazardous wastes containing both Molybdenum and Antimony



respectively are reported, in Table 1 and Figure 1, as a first example of the procedure. Both the elements cause a release in the leachate in excess with respect to the corresponding legal limit.

Table 1: an example of mix composition containing three wastes with different target contaminants

	Waste	Target contaminant	Concentration in the eluate	Law Limit
R1	Carbonate sludge (190814*)	Antimonium	5.64	0.07
R2	Exhaust catalysts (160807*)	Molibdenum	1.3	1
R3	Sludge (100120) as additive			
Ad	Additive (Lime and Iron sulfate)			

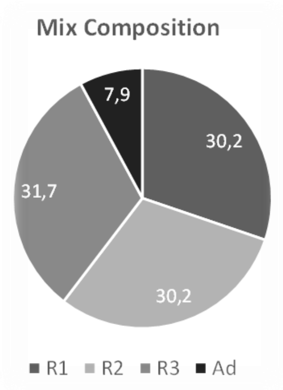
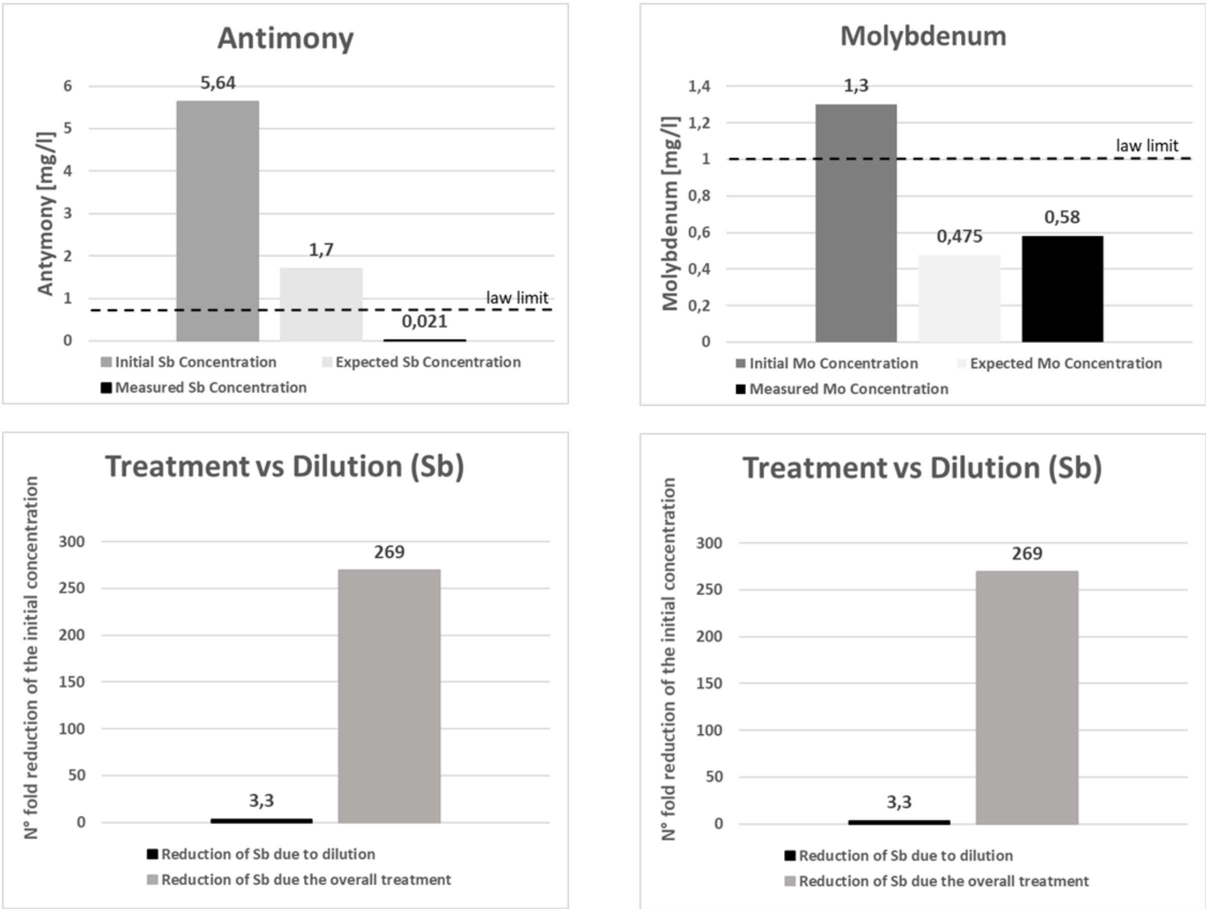


Figure 1: Mix composition of the three wastes and additives

The calculation of the single contaminant concentration (i.e. Antimony and Molybdenum) in the whole mix, is performed as a simple weighted average of its concentration in each individual waste. In the weighted average additives have been considered, as they contribute to the 'dilution' of the contaminant.

While it is evident that antimony in the mixtures has responded well to the treatment, since its reduction is 81 times greater than that one due to the simple dilution in the case of Molybdenum it is evident how the treatment is not only been ineffective, but even detrimental.
Considering the dilution factor, the mix has obviously made the molybdenum leachable, thus increasing its concentration in the eluate of the test so remaining below the legal limit (1 ppm) only as an effect of the dilution (Figure 2).



a) b)

Figure 2: Different stabilization effects and comparison with concomitant dilution factors for the target contaminants contained in the examined mix a) Antimony; b) Molybdenum.

Error! Reference source not found. shows the results of the stabilization treatment for the 8 different mixes, evaluating and comparing the effect of the dilution versus the treatment for each target pollutant having the concentration in the eluate of the original wastes higher than the legal limit.

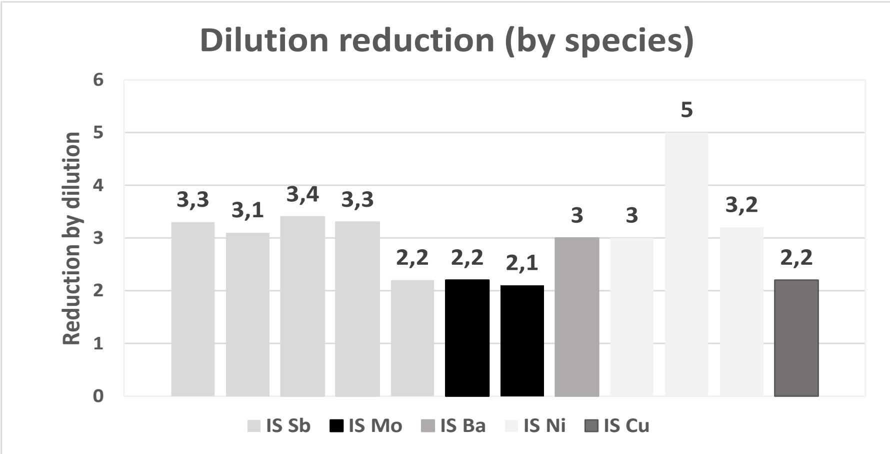
Three main behavior can be identified for different target contaminants. For those mixtures containing metals such as Antimony and Cu the treatment is significantly effective compared to dilution whose effects are limited to a range between 2 and 5 folds. The graph shows that the antimony has substantially the same trend in all the mixtures, with reductions that can exceed even 100 folds. These wastes reacts well to the addition of lime and ferrous sulphate.

For waste containing molybdenum the effects of the treatment is questionable: in one mixture, it is clear how the decrease in concentration is due mainly to dilution while in the other investigated mixture the result of the treatment is pejorative as it slightly increases the solubility of the metal. The stabilization with lime of wastes contain of molybdenum is two orders of magnitude less effective than that one of the antimony.

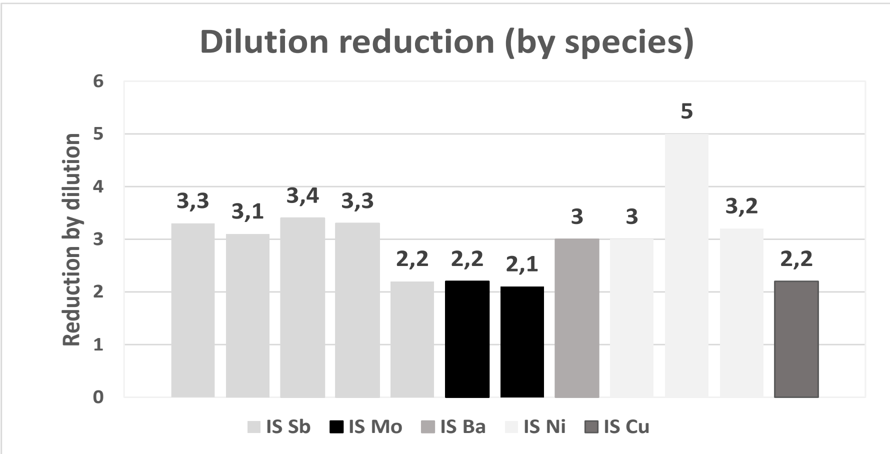
Molybdenum responds to the increase in pH becoming more soluble; this behavior causes a serious issue to deal with when waste containing molybdenum have to be treated together with other classes of wastes which responds better to alkaline condition.

A third behavior is shown by the mixtures containing wastes contaminated by nickel whose results show different responses to the treatment achieving a ratio between stabilization and dilution effects ranging between 2.8 and 50. In any of these cases, the effect of the treatment is higher than the one caused by simple dilution. The lower treatment effects are obtained with lime and ferrous sulphate, while, in the last mixture, where cement is used the reduction on nickel leaching is significantly lower.

With respects to the six mixtures containing Molybdenum results confirmed as the addition of zero valent iron and sodium sulphide can decrease the concentration on the molybdenum in the eluate.



(a)



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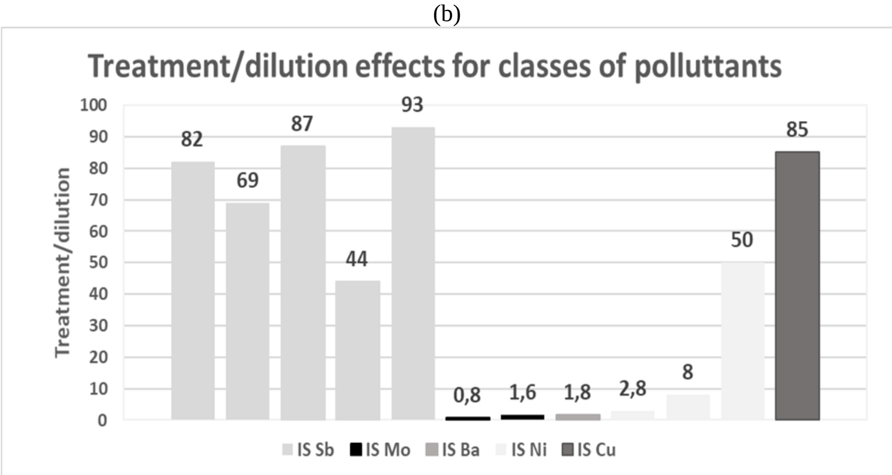
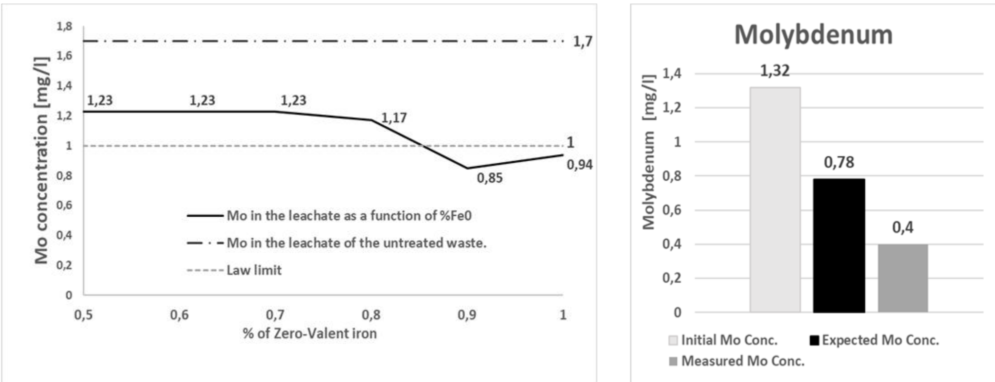


(c)

Figure 3: Separate effects of the dilution (a) and the treatment (b) for different mixes and their comparison by ratio

Figure 4a shows the trend of molybdenum release in the leachate as a function of the percentage of zero iron utilized in the mix and the comparison with the law limit (1 mg/l). Percentage of FeO exceeding 0,9% are needed to achieve the stabilization goal while lower percentages shows not significant effects. At this percentage the resulting concentration is 0,85 corresponding to a reduction of 50% in the leaching expected by simple dilution.

Higher percentage can be used for a safer management but it should be considered that zero-valent iron and sodium sulphide are very expensive additives (about 1100 € per ton), compared to additives such as lime, cement and ferrous sulphate. Therefore, it is necessary to optimize the amount of zero iron for each mixtures containing molybdenum as in the case of ashes from special wastes incineration.



a) b)

Figure 4: Release a) of Molybdenum in the leachate as a function of the increase of FeO in the mix and comparison b) between dilution and overall treatment

4. Conclusions

The issues of the treatment of hazardous wastes can't be easily solved and must be properly managed. From this work it results evident the difficulty of treating different types of wastes, through the stabilization process, because of their different origins, compositions and responses to the treatment. A multi-choice approach has been formulated to easily determine the effective contribution of the treatment versus dilution. The proposed approach, based can help the operators to understand which metals (i.e. wastes) can be treated together and how to improve the efficiency of the partial stabilization process so to increase its reliability and environmental safety.

Specifically, for those wastes contaminated by molybdenum, it has been demonstrated the effectiveness of using Zero-valent iron and Sodium sulphide, which are able to reduce the concentration of molybdenum in the eluate, allowing the safe disposal in a not – hazardous landfill.

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