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The validation of converting pyrite ashes contaminated soils into End-of-Waste by High-Performance Solidification/Stabilization process application

# The validation of converting pyrite ashes contaminated soils into End-of-Waste by HPSS application

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## CONFLICT OF INTEREST

The authors declare that there are no conflicts of interest.

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**DATA AVAILABILITY STATEMENT**

Data on test results are available upon reasonable request to corresponding author Petra Scanferla (petra.scanferla@unive.it)

**AUTHOR CONTRIBUTION STATEMENT**

**Petra Scanferla**: Conceptualization; Data curation; Funding acquisition; Methodology; Validation, Writing–original draft. **Calgaro Loris**: Conceptualization; Data curation; Formal analysis; Visualization; Writing–original draft; Writing–review & editing. **Roberto Quaresmini**: Data curation; Investigation; Writing–original draft. **Martino Zambon**: Data curation; Formal analysis; Validation. **Roberto Pellay**: Conceptualization; Funding acquisition; Project administration; Resources. **Giorgio Ferrari**: Formal analysis; Funding acquisition; Project administration; Resources. **Antonio Marcomini**: Formal analysis; Funding acquisition; Project administration; Supervision.

EDITOR'S NOTE: This article is part of the special series "Remtech Europe 2021: International Approaches to Contamination Management." The series documents and advances the current state of the practice, with respect to the sustainable management of contaminated sites, high resolution techniques for characterization, disrupting technologies for remediation of soil and groundwater, and risk assessment frameworks.

**ABSTRACT**

One of the major challenges to establish more sustainable management strategies than landfill disposal of metal contaminated soils is the lack of End of Waste (EoW) criteria defined at the European and national level. Another limitation stems from the scarcity of information on industrial scale applications of treatment technologies able to obtain safe and reusable materials from such contaminated waste. In this context, the High-Performance Solidification/Stabilization process was applied for the full-scale remediation of pyrite ashes contaminated soil (ca. 24000 $m^3$), and a dedicated sampling and analytical protocol was developed and implemented to verify if the treated material obtained complied with the general EoW criteria established by article 6 of the Waste Framework Directive 2008/98/EC. The results of the leaching, ecotoxicological, and mechanical tests carried out on representative samples of the treated soil showed that this material (ca. 19000 $m^3$) could be classified as EoW and thus was deemed reusable both *in-situ* as filler for the excavation and *ex-situ* as road construction material. These results improve the knowledge on the performance of a state-of-the-art technique for the treatment of a metals contaminated soil. Furthermore, the developed monitoring plan can support future assessments on the compliance of materials obtained from contaminated soil with the general EoW criteria.

Key Points: A sampling and analytical validation protocol was developed and implemented to establish the compliance to the End of Waste criteria of a stabilized granular material obtained from contaminated soil A safe and reusable material that could be classified as End of Waste was obtained from pyrite ashes contaminated soil by applying the High Performance Solidification/Stabilization (HPSS) process

**KEYWORDS**

End-of-Waste; metals contamination; soil remediation; Stabilization/Solidification.

**INTRODUCTION**

Land resources are of utmost importance for human survival and development, but anthropogenic pollution of soils, sediments, and waters have caused severe global land degradation in the past decades (Bonetto et al. 2022). In particular, several concerns have been raised on the most suitable methods to be used for the reclamation of contaminated soils and sediments. Considering the increasing problems caused by soil deterioration (e.g., worsening of water quality, biodiversity decline, ecosystem service degradation, and land use capability losses) (Thomas et al. 2013; UNCCD 2014; Yang et al. 2020) the development and application of industrial-scale technologies capable to obtain safe and reusable materials starting from contaminated soil and sediments is fundamental (Contessi et al. 2020; Calgaro et al. 2021).

Given this context, article 6 of the Waste Framework Directive 2008/98/EC (EC 2008) defines the criteria specifying when a waste ceases to be classified as such (i.e. End-of-Waste, EoW) and becomes a new product. Although the EoW approach has been promoted as an alternative to landfill disposal (Calgaro et al. 2019) and as a fundamental step in establishing a more circular management of resources, nowadays the implementation of this approach has largely failed in the European Union (Johansson and Forsgren 2020). The general criteria established by article 6 of the Waste Framework Directive 2008/98/EC (EC 2008) were supposed to be translated into detailed and waste-specific criteria valid across the whole European Union (EU). However, this process was carried out only for a very limited number of waste types as it has proven difficult to agree on common criteria (Zorpas et al. 2021). This issue was therefore entrusted to the management of local authorities, which often lack the capability to determine suitable criteria to establish when a waste satisfies the general provisions established by the Waste Framework Directive 2008/98/EC (EC 2008; Johansson and Forsgren 2020). Nevertheless, some technologies have been recognized as a valid alternative to produce materials satisfying the EoW criteria from contaminated soils and sediments, even in the absence of a specific regulation at the European level. In particular, processes used to immobilize pollutants into a matrix by modifying its physical-chemical characteristics by mixing the matrix with different ligands (Bates and Hills 2015) (i.e., solidification and stabilization (S/S) treatments) have been applied with good results to reclaim soils and sediments contaminated by multiple metals (Scanferla et al. 2012; De Gisi et al. 2022). In detail, the term "solidification" refers to the physical retention of pollutants through their encapsulation in a solid matrix characterized by low levels of permeability and porosity, while the term "stabilization" denotes the chemical transformation of contaminants into less soluble, mobile or toxic forms (Calgaro et al. 2019). While Portland cement remains the most used hydraulic binder among these technologies, several by-products-based binders such as furnace slag, soda production residual slag, fly ash, metakaolin and red mud (Jiang et al. 2022; Tian et al. 2022) have also shown promising results as alternatives for the treatment of metals contaminated wastes.

However, most research regarding the development of S/S processes suitable to obtain safe and reusable materials from polluted soils and sediments has been mostly carried out focusing on laboratory scale applications (Karamalidis et al. 2008; Nikolić et al. 2014; Liu et al. 2018; Zhang et al. 2018; Contessi et al. 2020; Contessi et al. 2021), or focuses mostly on specific aspects related to the material mechanical properties (Bougharraf et al. 2018; Wang et al. 2020) (e.g., mechanical resistance and leaching of contaminants) or ecotoxicological assays (Bamze Attoumani et al. 2020). For this reason, there is still a lack of information on the use of S/S processes for the remediation of real contaminated sites at the industrial scale. Furthermore, this information is of great relevance since the most implemented practices to remediate metals contaminated soils are usually landfill disposal or capping (Liu et al. 2018), which are not sustainable in the long run. Then, considering that more than five million contaminated sites (i.e., ca. 20 million hectares of land) have been identified globally (He et al. 2015), it is clear that large-scale technologies for the management of such sites are needed (Shah and Daverey 2020; Thinh et al. 2021).

In this context, this work reports on the first industrial scale application of the HPSS® (High Performance Solidification Stabilization) technology to reclaim a metals contaminated soil to produce a cement-based granular aggregate classified as EoW that can be used as filler for excavation or as a building material (Ferrari and Pellay 2007; Scanferla et al. 2012; Calgaro et al. 2021). The HPSS® is carried out in suitable mixing and granulation installations to obtain a hardened granular material by mixing a finely divided (≤2-6 mm) contaminated matrix with a hydraulic binder (typic ally Portland cement) and special additives. The obtained granular material shows a reduced leaching of inorganic contaminants and a better mechanical resistance with respect to the untreated soil (Ferrari and Pellay 2007; Calgaro et al. 2019) since the cement causes the immobilization of metals as poorly soluble compounds (e.g., carbonates and hydroxides) and their incorporation in the hydration products (e.g., aluminosilicate phases and tobermorite gels) (Careghini et al. 2010), while the additives (superplasticizers and water-repellent) ensure the formation of a dense solid material characterized by a low residual porosity and low leaching of pollutants into the environment.

During this study, different tests were carried out according to international standards to evaluate the leaching of metals from the obtained granular material, its mechanical resistance (i.e., resistance to fragmentation), and its toxicity towards different types of organisms.

Since this was the first Italian case study where the EoW classification has been used for a polluted soil treated with a S/S process, the monitoring and quality control protocols reported in this work could also serve as support for the definition of EoW criteria also for other S/S industrial scale processes both at the national and European level.

## MATERIALS AND METHODS

### *Contaminated area*

The contaminated site investigated in this study is located in the southern part of Brescia Province (North-West of Italy) within the city of Bagnolo Mella. The site included an agrarian consortium dedicated to different industrial activities, such as sulfuric acid production through pyrite roasting (lead chambers process), synthesis of phosphate fertilizer (through the reaction of phosphate minerals and sulphuric acid) and fuel and mineral oil storage. These industrial installations were active from 1898 to 1985, and during this period tailings and wastes heavily contaminated by several metals where incorrectly disposed of by burial inside the site (Contessi et al. 2020). In detail, the pyrite roasting process leaves a residue consisting of iron oxides (i.e., amorphous iron oxides and hematite), and other minerals of anthropogenic origin (e.g., gypsum, jarosite, bassanite, anglesite, brushite, phosphoferrite, lithargite and esperite) (Bonetto et al. 2022) polluted by a considerable amount of several metals, in particular As, Pb, Cu, Cd, V, and Zn. Table 1 reports the average and maximum concentrations of the main pollutants found during the characterization of the study area. The contaminated area was found to be equal to about 16,000 m2, with an average depth of 1.5 m, thus resulting in about 24,000 m3 of contaminated soil to be treated (Figure S1 and Figure S2).

### *The HPSS® application*

The HPSS® technology was applied to treat *in-situ* the contaminated soil by assembling and using at the remediation site a dedicated plant capable to treat 6 $m^3$ $h^{-1}$ of soil. In detail, the contaminated soil was sieved to remove the coarse material (i.e., with a diameter (Ø) larger than 4 mm) mainly composed of brick and stone debris, which was either reused on site after being washed to remove finer material's residues or sent offsite to a waste recovery plant. The fine fraction (i.e., Ø ≤ 4 mm) was treated with the HPSS® process by mixing it with Portland cement (CEM 52.5 R), two additives (i.e., superplasticizer and water-repellent additives Mapeplast ECO 1A and 1B, respectively), and water on a sloping and rolling-plate system, thus obtaining a granular material. In detail, the granulate material diameter was maintained within the 2-4 mm range by changing the rotation speed and the inclination of the rolling plate. The typical mix used was composed of 1 kg dry weight (d.w.) of soil fine fraction, 400 g d.w. of Portland cement; 7 g of Mapeplast ECO 1-B, 7g of Mapeplast ECO 1-A and about 45 g of water. After 28 days of curing in a dedicated onsite storage area to allow for cement hydration, the stabilized granulates were investigated by applying the protocol described in the following sections.

In detail, following the High-Performance Concrete approach reported by Aïtcin and co-workers (Aïtcin 1998), the additives used drastically reduce the water/cement ratio (W/C) under a value of 0.35, thus both significantly reducing the capillary porosity and increasing the mechanical properties of the stabilized material (Powers et al. 1959). In addition, the use of these additives leads to using a significantly lower quantity of binder with respect to other S/S processes (ca. 28 *vs* 35-45 $g_{binder}$/ $g_{stabilized\ material}$) (Fan et al. 2018; Yang et al. 2022).

The HPSS technology shows several advantages with respect to other S/S processes, such as i) lower application cost, ii) higher number of possible uses for the stabilized granular material produced (e.g., filler for excavation, aggregate for non-structural concretes and road substrate) (Ferrari and Pellay 2007) and iii) ease of subjecting this material to additional treatments (e.g., thermal desorption for the removal of mercury and organic contaminants and wet conditioning for further cement hydration) (Careghini et al. 2010; Calgaro et al. 2019) without the use of complex equipment to manage both the abatement of dust emissions and the filtration of loose soil particles from the produced wastewater. (Ferrari and Pellay 2007; Ferrari et al. 2008).

***Sampling of the stabilized granular material***

Following the treatment of the contaminated soil excavated from the study area, about 18450 tonnes of stabilized granular material were obtained. According to UNI 10802:2013 standard (BSI 2013a), representative samples (ca. 15 kg) were taken for each 500 m3 lot of granular material produced by collecting 20 aliquots of granular material at regular intervals directly from the rolling plate. The 39 obtained samples were then quartered to obtain portions suitable for the following tests.

To confirm the results obtained from these 39 samples, an additional composite sample composed by randomly sampling over the whole granular material produced after it had been collocated to refill the excavation was tested with the same validation protocol. In detail, the statistical approach reported in Appendix B of the CEN/TR 15310-1:2013 standard (CEN 2013) was followed to determine the number of sub-samples needed to obtain a composite sample statistically representative of the whole amount of granulate produced. According to this standard, to check if the data obtained on each metal concentration in the leachates produced using the previously selected 39 samples (the test procedure is described in the next section) followed a normal distribution, a non-parametric statistical test (Kolmogorov Smirnov test) (Berger and Zhou 2014) was applied. After verifying the normality of the leaching data, a statistical analysis was carried out according to CEN/TR 15310-1:2013 standard (CEN 2013) to quantify the spatial variability of the samples' population (i.e., $\sigma_W$). The highest value of $\sigma_W$ was obtained for the concentrations of Pb in the eluates (i.e., 14.39 µg/L), and this value was used to apply Eq. 1 to establish of the number of randomly distributed sub-samples:

$$N = \sigma_W{}^2/[n \cdot 2(d/U_a) - (\sigma_b{}^2 \cdot \sigma_e{}^2)] = 56 \qquad \text{Eq. 1}$$

where:

N: number of sub-samples to be taken to obtain a sample representative of the whole stabilized material production

$\sigma_W$: spatial variability of the samples' population = 14.39 µg/L

$\sigma_b$: spatial-temporal deviation between the composite samples = 1

$\sigma_e$: type of error deviation (i.e., analytical) = 1

C: desired level of confidence = 0.99

n: cumulative probability = $1 - (1 - C)/2$ = 0.995

d: desired precision = 5 µg/L

$U_a$: normal deviation = 2.58

Following this approach, the final sample (i.e, COMP59 sample) was composed of 56 sub-samples taken at random points inside the remediated area, each made by sampling at two different depths (i.e, one from 0 to 1.0 m depth and one from 1.0 to 2.0 m depth).

***End-of-Waste validation protocol***

In order to certify and validate the effectiveness of the HPSS® technology for the treatment of the contaminated soil and to classify the obtained granular material as "End-of-Waste", the leaching of the selected metals (i.e., As, Cu, Zn, Co, V, Cd, and Pb) from the stabilized material, the toxicity of the eluate, and the resistance to fragmentation of the granular material were investigated by applying the following tests to the set of 39 representative samples defined above, as well as to the sample made of 56 randomly selected sub-samples.

According to the Italian Ministerial Decree No 186 of 05th April 2006 (EMD 2006), a leaching test was carried out by applying the UNI EN 12547-2:2004 (BSI 2004a) standard. In detail, each sample was placed in a HDPE bottle with ultrapure water (solid/liquid ratio = 1/10) and shaked with an end-over-end tumbler (10 rpm) for 24 hours, then the leachate obtained was filtered at 0.45 m under vacuum and analysed for metals concentration by Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES, Spectro Genesis - AMETEK, Berwyn, PA, USA) applying the APAT CNR IRSA 3020 Man 29 2003 standard (IRSA-APAT-CNR 2003).

In detail, to reach a suitable detection limit for each metal the instrument was calibrated and optimized for a 1 g/L solution of CsCl to compensate for the high saline content of the analysed matrix. Spectral lines were selected according to the severity of the interference and relative intensities of each analyte (all the instrumental settings are reported in Table S1). The results were then compared with the regulatory limits established for the End-of-Waste classification in Annex III of Ministerial Decree n°186 of 05$^{th}$ April 2006 (EMD 2006).

The eluates obtained by carrying out the UNI EN 12547-2:2004 leaching test on 7 composite samples, each representative of about 3000 $m^3$ of the stabilized granular material, were also used to carry out the ecotoxicological tests based on the ISO 11348-3:2009 (i.e., determination of the inhibitory effect of water samples on the light emission of *Vibrio fischeri* (Luminescent bacteria test using freeze-dried bacteria) (BSI 2009), ISO 8692:2012 (i.e. algal growth inhibition test with unicellular green algae *Pseudokirchneriella subcapitata*) (BSI 2012a), and ISO 6341:2013 (i.e., determination of the inhibition of the mobility of *Daphnia magna* Straus (Cladocera, Crustacea) - Acute toxicity test) (BSI 2013b) standards.

The stabilized granular material resistance to fragmentation was investigated by applying on 20 samples, each representative of about 1000 $m^3$ of granular material, the UNI EN 1097-2:2010 standard test (BSI 2010). In detail, the percentage (weight/weight) of the granular material with a diameter lower than 1.6 mm after the test (i.e., Los Angeles %) was considered as the fragmented fraction.

The UNI EN 12547-2:2004 leaching test requires to decrease the diameter of the sampled granulates under 4 mm by means of a jaw crusher or a hammer mill if more than 5% of the sample has a higher diameter than this threshold. Since this will greatly increase the surface area of the granulate exposed to the leaching solution through the formation of fine material in contrast with the principles of the HPSS® technology, a comparison between milled and un-milled granular material was made by using an especially prepared sample of stabilized granules with a diameter between 4 and 10 mm. In detail, the leaching test of the un-milled sample was carried out following the same leaching protocol described in the UNI EN 12547-2:2004 standard, thus reflecting what is established by the UNI EN 12547-4: 2004 (BSI 2004b) standard (i.e., Characterisation of waste - Leaching - Compliance test for leaching of granular waste materials and sludges - Part 4: One stage batch test at a liquid to solid ratio of 10 L/kg for materials with particle size below 10 mm without or with size reduction). The size distribution of the granulates before and after the leaching test was investigated by applying the UNI EN 933-1: 2012 (BSI 2012b), and the concentration of metals in the leachates was investigated using the same methodology reported above for the eluates obtained from the tests carried out following the UNI EN 12457-2:2004 standard.

## RESULTS AND DISCUSSION

To verify and certify the industrial scale application of the HPSS® process for the production of a stabilized granular material from metal contaminated soil compliant with the EoW criteria, a validation protocol was established and tested, and the results are reported below. In detail, the use of the HPSS® process allowed for to recover and reuse *in situ* the contaminated soil treated through the production of a stabilized granular material (about 19000 $m^3$) which could be classified as EoW.

### *Leaching tests*

The results of the leaching tests carried out on the selected samples showed that all the lots of granulates were compliant with the criteria for reuse in Italian legislation, save for sample GR 37 which showed an excessive leaching of Pb (i.e., 0.07 mg/L) (Table S2). This lot of granular material was therefore treated a second time with the HPSS® process, and a new sample (i.e., GR39 bis) was tested, showing a concentration of metals in the leachate lower than the regulatory limits for reuse.

In particular, the concentration of Zn, Co, V, and Cd was below the ICP-OES detection limit (i.e., <0.5-5 µg/L) for all 40 samples (Table S2 and Table S1), while the concentration of As, Cu, and Pb in the eluates is shown in Figure 1. In detail, the concentration of As detected ranged between 2.5 and 32 µg/L, the concentration of Cu ranged between 10 and 40 µg/L, and the concentrations of Pb ranged between 2.5 and 46 µg/L (with a regulatory limit of 50 µg/L for As, Cu, and Pb).

According to previous studies carried out to elucidate the mechanisms involved in the solidification/stabilization of the contaminated soil found in this polluted area (Contessi et al. 2019; Contessi et al. 2020; Calgaro et al. 2021; Contessi et al. 2021), the retention of As, Pb, Zn, Co, and Cd can be ascribed to their entrapment within calcium silicate hydrates (formed by cement hydration) ettringite (formed by the reaction between calcium aluminates and sulphate ions derived from the dissolution of gypsum and anglesite present in the contaminate soil) structures. Furthermore, the stabilization of Cu and V was found to be mainly controlled by diffusion phenomena, thus closely related to their physical encapsulation and the different amounts of the superficial area exposed to the eluent during the leaching test.

The results also showed that in the case of stabilized granular material with a diameter larger than 4 mm, the sample size reduction carried out in accordance with UNI EN 12457-2:2004 standard caused a marked increase in the leaching of several investigated metals, in particular for Cu, Pb, As, Cd, and V with an increase of 3.0, 2.0, 3.2, 2.6, and 1.7 times, respectively (Figure 2 and Table S3). This can be ascribed to the higher surface area of the granular material exposed to the eluent during the leaching test when the sample was crushed to reduce its diameter under 4 mm (Diotti et al. 2021), as well as to the increase of the leachate pH when milling the sample (from 11.3 to 12.0) (Table S3) due to increased solubility of the investigated metals in more alkaline conditions (Lewis 2010; Calgaro et al. 2019).

***Mechanical characteristics***

To comply with the EoW criteria contained in article 6 of the Waste Framework Directive 2008/98/EC (EC 2008) about the use of the obtained material, we investigated the stabilized granular material resistance to fragmentation in order to verify if it could be used as a road substrate in accordance to the Italian Legislation. In detail, the results of the UNI EN 1097-2:2010 standard test (BSI 2010) showed a fragmented fraction (i.e., Los Angeles %) between 34.1% and 44.7% (Figure 4), thus classifying this material as usable for road construction and as restoration material based on the UNI EN 10006:2002 standard (BSI 2002) on road construction and maintenance. As reported by several authors this can be ascribed to the effects of the combined use of cement and water-repellent/superplasticizer additives (Wang et al. 2012; Li et al. 2020) to produce a dense and durable material from the contaminated soil.

***Ecotoxicological tests***

To ascertain the environmental safety of the stabilized granular material, the toxicity of the eluates obtained from the leaching tests carried on the 7 composite samples representative of the whole production was investigated considering different organisms (Table S5). In detail, the tests highlighted no significant effects on the life and development of the tested species (i.e., bioluminescence of *Vibrio fischeri*, growth of the algae *Pseudokirchneriella subcapitata,* and mobility of *Daphnia magna* Straus) for all samples. Furthermore, the test carried out on the eluates obtained from COMP59 sample showed only a slight adverse effect on *Daphnia magna* but this was not sufficient to calculate the Effect Concentration 20% (EC20) as established by the EN ISO 8692:2012 standard (BSI 2012a). These results show the high environmental compatibility of the produced stabilized granular material and can be linked to the efficacy of the HPSS in retaining the investigated pollutants in the presence of water.

***Recommendations and perspectives***

To limit landfill disposal of contaminated soil and sediments, criteria for the EoW classification of the materials obtained from the treatment of such matrixes are needed, and the results reported in this work show how the validation protocol used in this case could serve as an example for the definition of such national and European criteria. On the other hand, this study also showed the need to carefully consider the technical standards used to evaluate the performances of the materials produced by the EoW process, in order to evaluate the produced material in conditions reflecting real environmental situations. In particular, we recommend the use of the UNI EN

12457-4:2004 standard (i.e., without size reduction under 4 mm of diameter) to evaluate the leaching of pollutants from granulate materials obtained from the treatment of contaminated waste, since a granulate material of larger diameter could also be used for more used, such as aggregate for non-structural concrete (Limbachiya et al. 2000; Shi et al. 2016).

## CONCLUSIONS

Aiming to support a more sustainable management contaminated waste, the establishment of suitable EoW criteria to promote the use of technological processes allowing for the production of safe and reusable materials and limiting the practice of landfill disposal is fundamental. In this work we reported the results of the full-scale application of the HPSS® technology for the treatment of pyrite ashes contaminated soil, together with the validation protocol used to verify that the produced granular material complied with the general EoW criteria established by art. 6 of the Waste Framework Directive 2008/98/EC (EC 2008). Results of leaching, ecotoxicological, and mechanical tests highlighted that the granular material produced presented adequate physico-chemical, mechanical and ecotoxicological properties to obtain the EoW qualification as a filler for excavation.

The results of this study will also support the development of new EoW criteria for materials obtained from the application of Solidification/Stabilization processes by improving the knowledge: *i)* on the performance of a state-of-the-art technique for the treatment of a metals contaminated soil and *ii)* on a complete monitoring plan to assess if a material obtained from contaminated soil complies with the general EoW criteria to ensure a high level of protection of the environment and human health and facilitate the prudent and rational utilization of natural resources.

## CAPTIONS

**Table 1**: Average and maximum concentration of metals detected in the soil samples taken within the contaminated site.

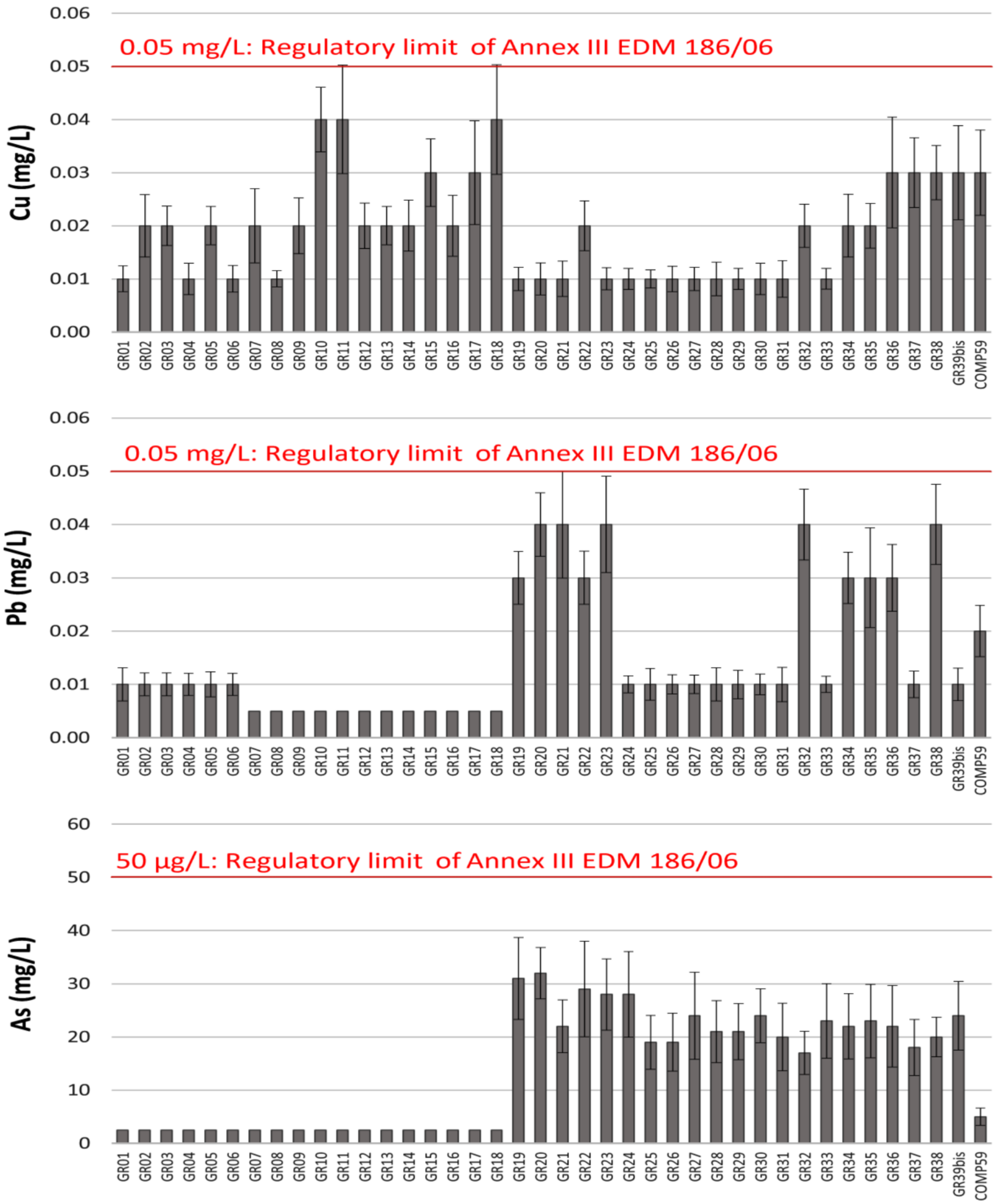


**Figure 1**: Concentration of Cu, Pb, and As in the leachate obtained from the UNI EN 12457-2:2004 leaching test carried out on the samples of stabilized granular material

used to validate the application of the HPSS® process (i.e., GR01-GR39bis, and COMP59). Error bars represent standard deviation of the results, and values below the ICP-OES detection limit are reported without an error bar.

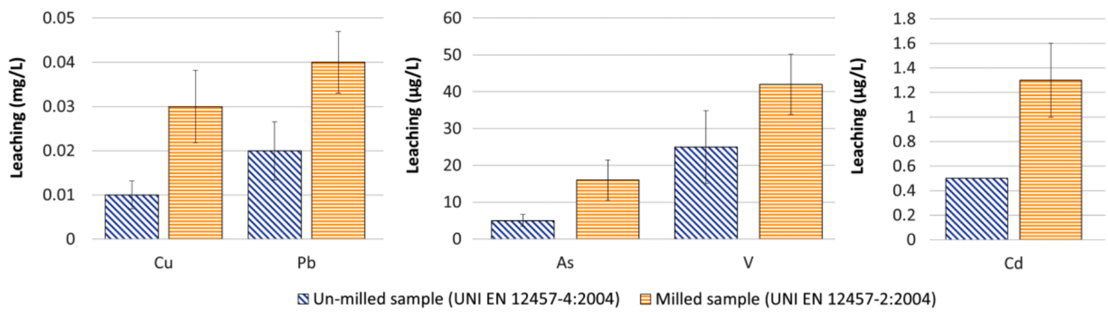


**Figure 2**: Concentration of Cu, Pb, and As, V, and Cd in the eluates obtained from the sample of stabilized granular material with diameter between 4 and 10 mm by applying the UNI EN 12457-2:2004 and UNI EN 12457-4:2004 leaching tests. Error bars represent standard deviation of the results, and values below the ICP-OES detection limit are reported without an error bar.

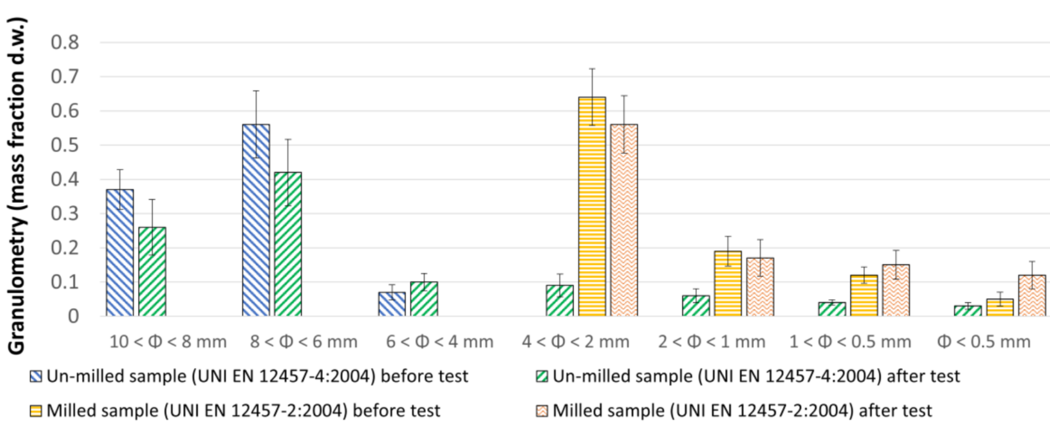


**Figure 3**: Granulometry of stabilized granular material sample with diameter between 4 and 10 mm subjected to the UNI EN 12457-2:2004 and UNI EN 12457-4:2004 leaching tests, before and after the tests. Error bars represent standard deviation of the results.

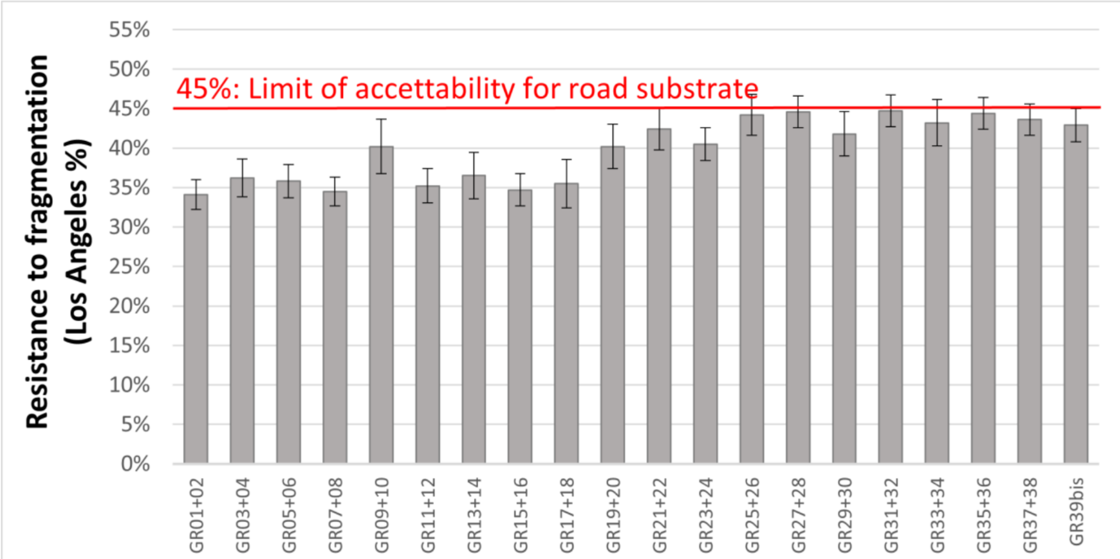


**Figure 4**: Results of the UNI EN 1097-2:2010 standard test (BSI 2010) for resistance to fragmentation for the 20 composite samples investigated. Error bars represent standard deviation of the results.

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Table 1: Average and maximum concentration of metals detected in the soil samples taken within the contaminated site.

| Heavy Metal | Unit of measure | Average concentration ± std dev. | Maximum concentration | Regulatory limit[b] |
|---|---|---|---|---|
| As | mg/kg d.w.[a] | 114 ± 186 | 662 | 50 |
| Cu | mg/kg d.w. | 395 ± 711 | 2351 | 600 |
| Pb | mg/kg d.w. | 843 ± 1948 | 7908 | 1000 |
| Cd | mg/kg d.w. | 19 ± 15 | 35 | 15 |
| Zn | mg/kg d.w. | 974 ± 865 | 3256 | 1500 |
| V | mg/kg d.w. | 85 ± 153 | 357 | 250 |
| Co | mg/kg d.w. | 64 ± 148 | 273 | 250 |

[a]: d.w. (dry weight)

[b]: Regulatory limit: Column B (commercial and industrial areas) of Table 1 of Annex V to Part IV of Title V of Legislative Decree No 152 of 03/04/2006 (EMD 2006).