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Remediation of Heavy Metals Contaminated Soils by Ball Milling

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Heavy metals are widespread in urban and industrial areas as a consequence of several anthropic activities. Strong efforts have been made to develop remediation techniques of heavy metals contaminated soils. Typical remediation techniques are constituted by extraction and immobilization processes. Nevertheless, the ex situ extractive technologies are rarely adopted because of high risks and costs related to the use of hazardous reactants and the consequent need of treating secondary effluents. On the other hand immobilization processes are generally preferred as cost-effective technologies for treating heavy metals contaminated soils. Specifically, the immobilization techniques prevent migration of heavy metals into the environment due to leaching by improving soil physical characteristics, increasing and subsequently decreasing surface area, or limiting the solubility or mobility of the hazardous compounds. In the present work, we analyze the efficiency of mechanical treatment for the remediation of real soils contaminated by heavy metals and tailings from the mining area of "Diga su Fangu", SW of Sardinia, Italy. The characterization of possible modification of soil physical, chemical and mineralogical properties induced by the milling process is also addressed. Possible mechanisms involved during the mechanical treatment and responsible of the increase of soil immobilization capacity are discussed.

1. Introduction

The remediation of heavy metals contaminated soils is still recognized nowadays to be one of the most difficult problem to be solved even if few, albeit costly, technologies may be employed (Concas and Cao., 2004; Tica D. et al., 2011; Xu M. et al., 2012). For this reason the development of economically feasible remediation techniques represent a very interesting technological and scientific issue. Immobilization techniques prevent heavy metals migration since for example surface area across which pollutants can be mobilized becomes smaller and solubility or toxicity of certain hazardous compounds is decreased. Immobilization processes are characterized by mixing the contaminated soils with suitable binders in order to reduce heavy metals leachability (Concas and Cao, 2004). For the case of heavy metals contaminated soils, a variety of binders have been investigated. The use of rock phosphate (Cao et al., 2003), zeolites, calcium hydroxide (Castaldi et al., 2005) and phosphates (Raicevica et al., 2005) gave rise to very promising results. In particular, the use of hydroxylapatite ($Ca_{10}(PO4)_6(OH)_2$), for the immobilization of leachable Pb(II) in soils was characterized by remarkable efficiency values. However, the use of hydroxylapatite (HA) for the remediation of heavy metal

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contaminated soils may also inhibit the growth of specific plant species, if HA percentages higher than 5 % are used. Recently, the effect of mechanical treatment on the immobilization capacity of heavy metals contaminated soils has been addressed (Montinaro et al., 2008).

Specifically, the use of ball milling for the remediation of synthetic soils of sandy, bentonitic and kaolinitic type was investigated by Montinaro et al. (2007; 2008). The weak transformations of soils induced by the collisions occurring in the milling process, determine the immobilization of heavy metals (Cd(II), Pb(II), Zn(II)). In particular, specific ball-milling treatments, without the use of additive, were able to reduce the leachable fraction of metals to levels lower than the USEPA (USEPA, 1996) regulatory thresholds, even when heavy metals contaminated soils showed concentration values similar to field ones. Since the results obtained by Montinaro et al. (2007; 2008) appeared to be very promising, so that ball milling technique may be considered potentially applicable for the remediation of heavy metal contaminated soils, the applicability of the ball milling technique to real contaminated soils is evaluated. Specifically, heavy metals contaminated tailings sampled in the mining area of "Diga su Fangu" (Sardinia, Italy) are mechanically treated using both ball and attritor milling devices.

2. Materials and methods

Tailings sampled from the mining area above mentioned were named "DSF". Solid samples were sieved at 2 mm in order to remove the coarser (not contaminated fraction) and then chemically characterized through strong acid digestion. Specifically, microwave assisted acid digestion has been carried out according to the Method 3052 (USEPA, 1996) to obtain the complete dissolution of siliceous and organically based matrices. This method consists of putting the solid sample in contact with an acid solution which consists of 3 mL of HF and 9 mL of HNO_3. A solid to liquid weight ratio equal to about 33 was employed and the contact time was equal to 15 min within the microwave oven operated at 180 °C. The concentration of heavy metal in the leachate was determined by an Inductively Coupled Plasma-Optical Emission Spectrometer (ICP-OES, Vista MPX, Varian).

Once characterized, the contaminated samples were mechanically treated by ball milling using a Spex Mixer/Mill mod. 8000. Specifically, 4 g of soil sample were introduced inside the vial together with two stainless steel balls of 8 g and 10 mm in diameter in order to obtain a ball to powder ratio (BPR) equal to 4. Once sealed, the vial was fixed to the mill through a vice and subsequently milling trials for different time intervals under air atmosphere were performed, according to the procedure reported by Montinaro et al. (2007; 2008).

In order to evaluate the scaling up of the proposed technology from the laboratory scale results, further mechanical treatment experiments were carried out by using an Attritor Mill mod. 01HD/01HDDM. In fact, the latter one allows to perform experimental trials using larger amount of contaminated soil with respect to the Spex Mixer Mill, thus providing more appropriate information about the industrial scale applicability of this technology.

The Attritor Mill is operated at the standard milling frequency of about 4200 rpm using a zirconium vial of 8.2 cm internal diameter and 11 cm internal height. 70 g of soil were introduced inside the vial together with 282 g of zirconium balls of 0.44 g and 5 mm in diameter, i.e. 641 balls, to obtain a value of ball to powder ratio (BPR) equal to 4. As for the ball-milling trials, the vial has been sealed under atmospheric pressure, fixed to the mill, and mechanically treated for different time intervals.

Unmilled and milled soils were then submitted to the "synthetic precipitation leaching procedure (SPLP)" reported by USEPA (1996) in order to evaluate the degree of metal immobilization. The SPLP test, US EPA SW 846 Method 1312 (USEPA, 1996), was carried out by using an acid mixture which consists of a 60/40 wt% sulphuric/nitric acid diluted with 18.2 MΩ water up to a final pH of 4.2 ± 0.05. During the SPLP test, a solid to liquid weight ratio equal to 1:20 and a contact time of 18 h was guaranteed. Samples were filtered using a Whatman GF/F 0.45 µm filter and the concentration of metals in the leachate were determined by ICP-OES (Vista MPX, Varian), whose analysis was performed at least two times for each treated sample.

The immobilization efficiency $\eta(t)\%$ of the mechanical treatment after a time interval equal to t was evaluated, through the following equation, after each treatment:

$$\eta(t)\% = \left(1 - \frac{C(t) \cdot V_{leach}}{q^0 \cdot W_{solid}}\right) \cdot 100 \quad (1)$$

where $C(t)$ ($mg\ L^{-1}$) is the heavy metal concentration in the leachate, V_{leach} is the leachate volume (L), q^0 ($mg\ kg^{-1}$) is the initial heavy metal concentration in the untreated soil and W_{solid} (kg) is the soil weight which undergoes the test.

In order to evaluate possible immobilization mechanisms and verify if significant soil alterations occurred during mechanical treatment, further analyses were performed. The identification of crystalline phases in solid samples was obtained by X-ray diffraction (XRD) through a RIGAKU GEIGERFLEX diffractometer by employing CuKα Ni-filtered radiation (λ =15.418 Å). Measurements of particle size distributions after each ball milling treatment were performed using a laser granulometer CILAS 1180 in the wavelength range of 0.04 μm – 2500 μm.

3. Results

The content of heavy metals in the samples "DSF" from the overburden mining area of Diga Su Fangu was analyzed and the results reported in Table 1 were obtained.

Table 1. Concentration (mg/kg) of heavy metals in the soils DSF obtained by complete soil digestion

Sample	Al	As	Cd	Hg	Mn	Ni	Pb	Se
DSF	13657.5	416.1	85.5	244.6	1340.0	44.7	24688.0	313.5

The real contaminated tailings were subjected to mechanical treatment. As mentioned above mechanical treatment trials were performed by using either the Spex Mixer/Mill or the Attritor Mill. In fact, the latter one allows to treat a mass of soil per batch 28 times greater than that one of the Spex Mixer Mill, thus providing more detailed information about the possible industrial application of the proposed process. Moreover, the same ball to powder ratio (BPR=4) ratio used in the Spex mill is maintained, thus evaluating whether the BPR could represent a suitable scale-up factor. Once milled, tailing samples have been extracted from the mills and submitted to the SPLP leaching procedure. Concentrations of heavy metals released from the treated tailing sample "DSF" in the leachate from SPLP test and the corresponding immobilization efficiencies are shown in Figure 1.

Firstly, from Figure 1 it may be observed that for DSF samples, no significant differences exist between the results obtained when using the Spex Mill with respect to the Attritor one thus confirming that the BPR may be considered as a suitable scale-up factor. In particular, it may be noticed from Figures 1b and 1c that a milling time of about 3 h is sufficient to decrease Cd and Ni released below the EPA regulatory limits. Instead, for heavy metals such as As and Pb a more prolonged time is needed in order to achieve the desired reduction of the corresponding leachable fractions. However, it is worth noting that after mechanical treatment applied for relatively short times (i.e. 10 h), concentrations of all heavy metals in leachate from SPLP test are lower or very close to the corresponding regulatory limits (dashed lines in Figure 1) proposed by USEPA for drinkable water. In Figure 1 the increase in heavy metals immobilization efficiency obtained by augmenting the milling time is also shown. It may be seen that, for almost all the considered heavy metals, a significant increase in immobilization efficiency takes place after only 1 h of mechanical treatment. The results obtained when treating DSF samples suggest that the mechanochemical technology is able to promote heavy metal immobilization also in tailing sample when both the Spex or the Attritor Mill are used. Furthermore, the results from the trials carried out with the DSF sample confirm that the BPR ratio may be assumed as the main scale-up factor for the application of the technology to the real scale.

In order to further elucidate the mechanism which determines the increase in the immobilization capacity of the contaminated tailing and to verify if mechanical treatment causes drastic alterations of the original soil properties, further analyses on untreated and treated tailings were performed. Specifically, XRD analyses on untreated and mechanically treated (10 h, BPR = 4) tailing sample DSF may be seen in Figures 2a and b, respectively.

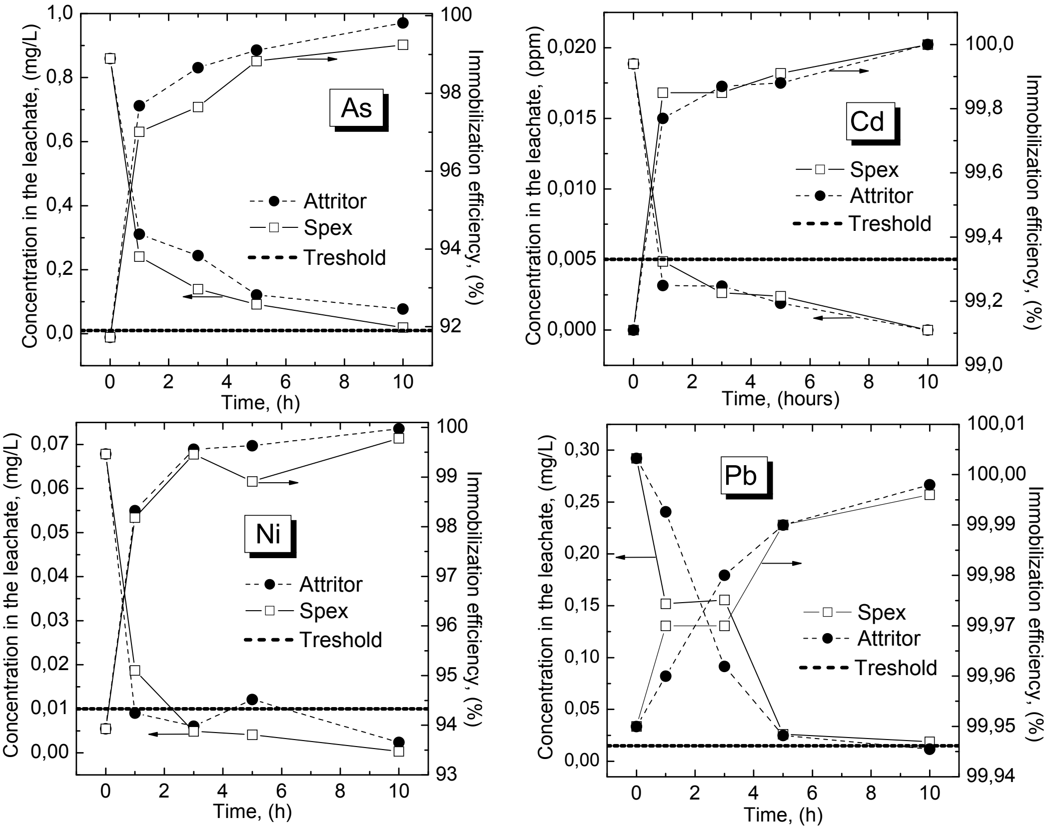

Figure 1a – 1d. Heavy metal's concentration in the SPLP leachate and immobilization efficiency after mechanical treatment for different times with Spex and Attritor Mill.

In particular, it is apparent from Figures 2a and 2b that the main crystalline phases, i.e. quartz, calcite and goethite are detected for the DSF sample before and after the mechanical treatment, thus indicating that the latter one cause no substantial alterations of the sample's mineralogy, except for hemimorphite which is on the other hand a minor component of the DSF sample (Figure 2a). Finally, the analysis of the full width at half maximum peak was used to evaluate the crystallite sizes and lattice distortion. The results of such analysis show that the DSF samples are characterized by diffraction patterns without remarkable peaks broadening after milling. It is then possible to assume that no substantial peak reduction occurs during tailings milling.

In Figure 2c the effect of ball milling treatment on particle size distribution of DSF tailing is shown. From Figure 2c it is noted that mechanical action induced an initial particle size refinement followed, after 30 min, by an increase in particles mean size. This effect may be explained by considering that aggregation phenomena take probably place as the result of electrostatic interaction between small particles produced during the first instants of milling process. On the other hand, it is worth noting that, according to the Rumpf's theory (Rumpf, 1962), Van der Waals forces play a significant role only at particle size lower than 1μm. Moreover, the corresponding bond energy increases as the size of the aggregating particles is reduced.

4. Conclusions

The understanding of phenomena involved during mechanical treatment of soil and specifically those ones related to the immobilization capacity of soils is quite difficult. Solid matrix of contaminated soils is a very complex system and its interactions with heavy metals is still not well understood. Moreover, the application of impulsive mechanical loads further complicates the picture. On the basis of experimental results, only some hypotheses may be formulated about mechanisms responsible of the immobilization capacity enhancement due to mechanical treatment. In what follows the case of Pb(II) contaminated soil is taken into account.

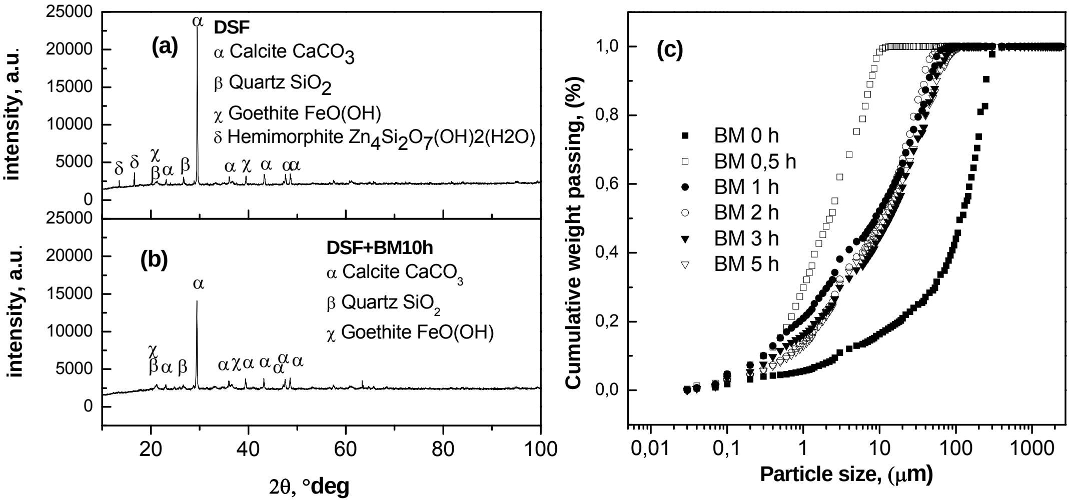

Figure 2. Effect of ball milling on the structure of the DSF sample: XRD patterns for untreated tailings (a) and for tailings after 10 h of mechanical treatment (b). Particle size evolution with ball milling (c).

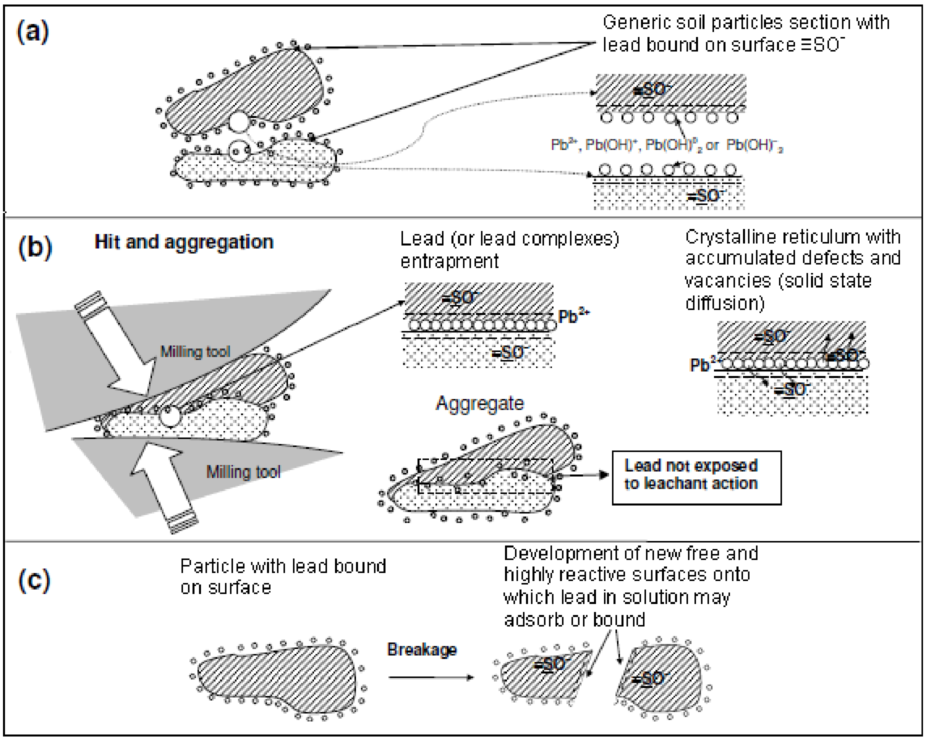

Figure 3. Schematic representation of possible mechanisms which may determine the increase of immobilization efficiency of tailings after milling: (a) Pb(II) adsorption, (b) aggregation, (c) breakage.

First it is possible to assume that when soil is contaminated, the metal is adsorbed onto soil particles (cf. Figure 3a). When ball milling process starts, soil particles are subjected to high energetic collisions that may promote breakage and aggregation phenomena as well as accumulation of crystalline defects and vacancies (amorphization). The occurrence of aggregation phenomena with a subsequent formation of stable aggregates results in a net increase of particle size of soils as confirmed by the granulometer data. When aggregation occurs, the amount of metal adsorbed on the surface of two overlapping particles may be entrapped within the new formed aggregate (cf. Figure 3b). In this way the amount of metal exposed to the leaching action is reduced, thus determining an higher immobilization capacity. Moreover, since the accumulation of dislocations and vacancies in crystalline reticulum determines an increase of diffusivity within the solid matrix (Lu et al., 1997), it is possible to assume that metal complexes may diffuse within the crystalline reticulum of soil particles thus leading to a very efficient chemical entrapment of metal within the soil (cf. Figure 3b). On the other hand, also breakage phenomena, taking place in parallel with the aggregation ones, may determine an increase of immobilization efficiency. In fact, as shown schematically in Figure 3c, when a contaminated soil particle breaks, it develops new "fresh" surfaces onto which metal ions may re-adsorb. These phenomena result in a higher adsorption capacity with respect to adsorb metal, thus increasing its immobilization efficiency. The same mechanisms may be reasonably taken into account in order to explain the increase of immobilization efficiency of soils related to each heavy metals investigated.

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References

Castaldi P., Santona L., Melis P., 2005, Heavy metal immobilization by chemical amendments in a polluted soil and influence on white lupin growth, Chemosphere 60, 365–371.

Cao R.X., Ma L.Q., Chen M., Singh S.P., Harris W.G., 2003, Phosphate-induced metal immobilization in a contaminated site, Environ. Pollut. 122, 19–28.

Concas A., Cao G., 2004, Technologies for the remediation of contaminated sites (Italian language), CUEC, 1–85.

Tica D., Udovic M., Lestan D., 2011, Immobilization of potentially toxic metals using different soil amendments, Chemosphere 85, 577-583. DOI: 10.1016/j.chemosphere.2011.06.

Xu M., Lu N., 2012, Research on Removing Heavy Metals From Mine Tailings, Disaster Advances 5, 116-120.

Lu L., Lai M.O., Zhang S., 1997, Diffusion in mechanical alloying, J. Mater. Process. Technol. 67, 100–104.

Montinaro S., Concas A., Pisu M., Cao G., 2007, Remediation of heavy metals contaminated soils by ball milling, Chemosphere 67, 631–639.

Montinaro S., Concas A., Pisu M., Cao G., 2008, Immobilization of heavy metals in contaminated soils through ball milling with and without additives, Chemical Engineering Journal 142, 271–284.

Raicevica S., Radoicicb T.K., Zouboulisc A.I., 2005, In situ stabilization of toxic metals in polluted soils using phosphates: theoretical prediction and experimental verification, J. Hazard. Mater. B117, 410–453.

Rumpf H., 1962, The strength of granules and agglomerate, in: W. Knepper (Ed.), Agglomeration, AIME, Interscience, New York (USA), 379-418.

USEPA (United States Environmental Protection Agency), 1996, Test Methods for Evaluating Solid Waste, SW846, third ed., Method 3052 - Microwave assisted acid digestion of siliceous and organically based matrices, Office of Solid Waste and Emergency Response, Washington, DC, (USA), http://www.epa.gov/wastes/hazard/testmethods/sw846/pdfs/3052.pdf