

Contents lists available at ScienceDirect

Chemical Engineering Journal



journal homepage: www.elsevier.com/locate/cej

Rationale of lead immobilization by ball milling in synthetic soils and remediation of heavy metals contaminated tailings

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ARTICLE INFO

Article history: Received 14 January 2009 Received in revised form 2 July 2009 Accepted 4 July 2009

Keywords: Ball milling Soil remediation Heavy metals Immobilization

ABSTRACT

In this work, the use of mechanical milling for the remediation of heavy metals in synthetic soils and tailings sampled from the mining area of "Barraxiutta", SW of Sardinia, Italy is investigated. Specifically, Pb(II) contaminated synthetic soils of sandy, bentonitic and kaolinitic type are taken into account following the results obtained in previous works. Suitable sequential extraction procedures have been performed on both untreated and treated synthetic soils. It is found that mechanical loads which occur during collisions among milling media and soils are able to modify the distribution of Pb(II) onto the different solid fractions of contaminated synthetic soils. Specifically, for sandy soils the milling treatment induces a significant increase in Pb(II) content in the Fe–Mn oxides fraction. On the other hand, for bentonitic and kaolinitic soils, Pb(II) content in both carbonate and Fe–Mn oxide fractions is augmented after treatment. Such phenomena may contribute to Pb(II) immobilization efficiency since the heavy metal trans-speciation occurs in favor of fractions characterized by stronger bonds and lower solubility.

As for the heavy metals contaminated tailings, their immobilization is obtained using both ball and attrition milling devices under specific ball to powder ratio values. The degree of metals immobilization is evaluated by analyzing the corresponding leachable fraction obtained through the Synthetic Precipitation Leaching Procedure (SPLP) proposed by EPA. X-ray diffraction and granulometric analyses revealed no significant alterations of the intrinsic character of the tailings after milling except for a relatively small increase in particles size.

The increase in immobilization efficiency when tailings are mechanically treated may be due to specific phenomena induced during milling such as entrapment of heavy metals into aggregates, solid diffusion of metals into the crystalline reticulum of soil particles, the formation of new fresh surfaces onto which heavy metals may be irreversibly adsorbed as well as metal trans-speciation onto tailings fractions characterized by stronger bonds and lower solubility.

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1. Introduction

As a consequence of industrial activities, such as metal mining, smelting and refining, atmospheric deposition, land application of sewage sludge and industrial by-products, gasoline processing, storage, distribution and production of painting materials and their use, heavy metals are widespread in urban and industrial areas [1,2].

The remediation of heavy metals contaminated soils is still recognized nowadays to be one of the most difficult problems to be

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solved even if few, albeit costly, technologies may be employed [3–5]. For this reason the development of economically feasible remediation technologies represents a very interesting technological and scientific issue.

Immobilization processes are generally preferred for the treatment of heavy metals contaminated soils due to the intrinsic limitations of extractive techniques [1]. In fact 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 [6]. Immobilization processes are characterized by mixing the contaminated soils with suitable binders in order to reduce heavy metals leachability [7,8]. For the case of heavy metals contaminated soils, a variety of binders have been investigated. The use of rock phosphate [9], zeolites, calcium hydroxide [10] and phos-

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^{1385-8947/\$ –} see front matter $\ensuremath{\mathbb{C}}$ 2009 Elsevier B.V. All rights reserved. doi:10.1016/j.cej.2009.07.005

Operating conditions used in the sequential extraction method.

Pb(II) fraction	Extracting agent	Shaking or contacting time	Temperature
Exchangeable Bound to carbonates Bound to Fe-Mn oxides	8 mL NaCH3COO (1 M, pH 8.2) 8 mL NaCH3COO (1 M) + HNO3 until pH 5 20 mL NH2OH HCI (0.04 M) in CH3COOH 25%(v/v)	1 h 5 h 6 h	25 °C 25 °C 96 ± 3 °C
Bound to organic matter	3 mL HNO ₃ (0.02 M) + 5 mL H ₂ O ₂ 30% (pH 2 with HNO ₃) 5 mL H ₂ O ₂ 30% (pH 2 with HNO ₃) 8 mL NaCH ₃ COO (1 M) in HNO ₃ 20%(v/v)	2 h 3 h 0.5 h	85±2°C 85±2°C 25°C
Residual	9 mL HNO ₃ + 3mL HF	In contact until total dissolution	Microwave oven 180°C

phates [11] gave rise to very promising results. In particular, the use of hydroxylapatite $(Ca_{10}(PO_4)_6(OH)_2)$, for the immobilization of leachable Pb(II) in soils [12,13], was characterized by remarkable efficiency values. However, the use of hydroxylapatite (HA) for the remediation of heavy metal contaminated soils may also inhibit the growth of specific plant species, if HA percentages higher than 5% are used [13].

Recently the effect of mechanical treatment on the immobilization capacity of heavy metals contaminated soils has been addressed [14–16]. Specifically, the use of ball milling for the remediation of synthetic soils of sandy, bentonitic and kaolinitic type was investigated by Montinaro et al. [14,16]. 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 [17,18] regulatory thresholds, even when heavy metals contaminated soils showed concentration values similar to field ones.

Since the results obtained by Montinaro et al. [14,16] on synthetic soils appeared to be very promising, so that ball milling technique may be considered potentially applicable for the remediation of heavy metal contaminated soils, further investigations are performed in the present work with the aim of elucidating the immobilization mechanisms promoted by mechanical treatment. In particular milled and unmilled synthetic soils are subjected to specific sequential extraction procedures in order to estimate the corresponding effects induced by mechanical treatment with respect to the speciation of heavy metals within the soil phases.

In the second part of the work, the applicability of the ball milling technique to real contaminated soils is evaluated. Specifically, heavy metals contaminated tailings and soils sampled in the mining area of "Barraxiutta" (Sardinia, Italy) are mechanically treated using both ball and Attritor Mills devices.

2. Materials and methods

High purity CaCO₃ (99%), SiO₂ (99%), bentonite (99%), kaolin (99%), Fe₂O₃ (99%), MnO₂ (99%), humic acid (99%) were mixed in order to prepare sandy (SS), kaolinitic (KS) and bentonitic (BS) soils, respectively. All compounds were obtained from Sigma–Aldrich, Inc, while the amount of each of them used for preparing synthetic soils is reported by Montinaro et al. [14].

Synthetic soil contamination was carried out in a temperature controlled shaker at 25 °C by contacting, for suitably prolonged times, known weights of each synthetic soil with Pb(II) solutions of prescribed concentration levels and volume in suitable flasks, according to the procedure reported by Montinaro et al. [14,16]. Contaminated soils with or without additives were then mechanically treated by ball milling using a Spex Mixer/Mill mod. 8000, following the procedure reported by Montinaro et al. [14,16].

Sequential extractions were then performed both on unmilled and milled soils with the purpose to assess whether the mechanical treatment could have led to changes in the distribution of heavy metals among the different soil fractions. The five-step sequential extraction scheme developed by Tessier et al. [19] was used in order to determine the amount of metals associated with the different soils phases. It should be noted that the last extraction step was modified with respect to the procedure indicated by Tessier et al. [19], in order to reach the total dissolution of the soil silicate phase. The extractants used, the extraction conditions, and the soil phases from which the metal is extracted are reported in Table 1. The Pb(II) concentration in the solution obtained after contacting contaminated soils with each extractant was determined using an Inductively Coupled Plasma-Optical Emission Spectrometer (ICP-OES, Vista MPX, Varian).

The second part of the work was dedicated to the evaluation of the capability of the mechanical treatment to immobilize heavy metals within real contaminated soils. To this aim, soils and tailings contaminated by heavy metals were sampled from the overburden mining area of "Barraxiutta" in the SW of Sardinia, Italy. The area is nowadays abandoned and heavy metals are continuously leached by surface and filtrating waters and thus mobilized far away from the site, thus potentially threatening sensitive targets around such as rivers, lakes or population.

Soils sampled from this area were named "B", while tailing samples 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 (SW-846 EPA Method 3052 [17]) 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 HNO₃. 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 ICP-OES (Vista MPX, Varian). Analytical results of the acid soluble portion of metals are reported in Table 2 where high levels of heavy metals bound to the solid phase may be seen.

Once characterized, the contaminated samples were mechanically treated by ball milling using a Spex Mixer/Mill mod. 8000. Specifically, 4g of soil sample were introduced inside the vial together with two stainless steel balls of 8g and 10 mm in diam-

 Table 2

 Concentration of heavy metals in the soils DSF and B obtained after complete soil digestion.

Sample	Al (mg/kg)	As (mg/kg)	Ba (mg/kg)	Cd (mg/kg)	Hg (mg/kg)	Mn (mg/kg)	Ni (mg/kg)	Pb (mg/kg)	Se (mg/kg)	Sr (mg/kg)	Zn (mg/kg)
DSF	13657.5	416.1	11547.9	85.5	244.6	1340.0	44.7	24688.0	313.5	178.8	28434.1
В	4522.5	221.0	15939.4	54.3	144.2	523.9	25.1	17582.9	249.9	230.0	32652.9

Table 3

Distribution (mg) of Pb(II) in the five fractions that constitute the synthetic soils.

	SS 0 h BM	SS 7 h BM	SB 0 h BM	SB 7 h BM	SK 0 h BM	SK 7 h BM
Exchangeable (mg)	0.096	0.011	0.094	0.0	0.054	0.000
Bound to carbonates (mg)	0.310	0.301	0.474	0.182	0.484	0.074
Bound to Fe–Mn oxides (mg)	0.144	0.429	0.210	0.848	0.113	0.625
Bound to organic matter (mg)	0.039	0.034	0.040	0.052	0.014	0.059
Residual (mg)	0.404	0.232	0.327	0.114	0.375	0.246

eter 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. [14,16].

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 [17,18] in order to evaluate the degree of metal immobilization. The SPLP test, USEPA SW 846 Method 1312 [17,18], 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 concentrations 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 mechanically treated soil after a time interval equal to *t* was evaluated, through the following equation, after each treatment:

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

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) 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



Fig. 1. Comparison of heavy metals' concentration in the SPLP leachate of Barraxiutta soil "B" treated with Spex and Attritor Mill, respectively, for different times: As (a), Hg (b), Pb (c) and Se (d).



Fig. 2. Comparison of heavy metals' immobilization efficiency for Barraxiutta soil "B" after mechanical treatment for different times with the Spex Mixer/Mill and the Attritor Mill, respectively: As (a), Hg (b), Pb (c) and Se (d).

diffraction (XRD) through a RIGAKU GEIGERFLEX diffractometer by employing Cu K α 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 0.04–2500 μ m.

3. Results and discussion

The possibility to immobilize heavy metals such as Pb(II), Cd(II) and Zn(II) which contaminate synthetic sandy and clayey soils through mechanical treatment was demonstrated by Montinaro et al. [14,16]. When mechanical treatment was applied to soils which simulate real contaminated ones, after relatively short milling time, leachable fraction of heavy metals were reduced under the EPA regulatory limits for drinkable water [14,16].

In order to clarify the mechanisms which determine the increase in the immobilization capacity of the contaminated soils once mechanically treated, a sequential extraction was carried out both on milled and unmilled soils. In particular, synthetic soils mechanically treated for 7 h were subjected to sequential extraction, since such a prolonged treatment time guaranteed the total immobilization of heavy metals [14].

In Table 3 the distribution of Pb(II) between the main soil components before and after mechanical treatment is outlined. From Table 3 it is possible to observe that the amounts of Pb(II) bound to the different soil components changes when the soil is mechanically treated. In particular for the case of the sandy soil (SS), mechanical treatment results in a decrease in exchangeable and residual Pb(II), since the corresponding value changes from 0.096 and 0.404 mg, for the unmilled soil, to 0.011 and 0.232 mg, respectively, for the milled one (Table 3). On the other hand, a significant increase (from 0.144 to 0.429 mg) of Pb(II) bound to Fe–Mn oxides is observed for the SS soil subjected to milling treatment.

On the contrary, for the bentonitic (SB) and kaolinitic (SK) soils, a different behaviour may be observed. In particular, for these soils mechanical treatment results in a remarkable decrease in Pb(II) bound to carbonate fraction and in a simultaneous increase in Pb(II) amount bound to oxide fraction.

These results highlight that mechanical treatment strongly influences the Pb(II) distribution between the different soil phases. This phenomenon may probably contribute to the increase in immobilization efficiency observed for milled soils. In fact the increase in immobilization efficiency deriving from mechanical treatment of SS soil may be probably ascribed to trans-speciation of Pb(II) which preferably binds to oxides fraction under milling. Since the bond to oxides is stronger than that one to the exchangeable fraction, such a trans-speciation may result in a decreased leachability of Pb(II). Moreover lead oxides are characterized by low solubility.

For the SB and SK soil, the trans-speciation occurs from the carbonate fraction (PbCO₃, cerussite) to the oxide fraction determining a stronger bond of Pb(II) to the soil components. In particular, a thermal decomposition of PbCO₃ to PbO and CO₂ probably occurred during milling as a result of high local temperatures reached at the impact point between the milling spheres. It is possible to assume that these mechanical induced trans-speciation phenomena may contribute, together with entrapment of heavy metals into aggregates, solid diffusion of metals into the crystalline reticulum of soil



Fig. 3. Comparison of heavy metals' concentration in the SPLP leachate of Diga su Fangu sample (DSF) treated with Spex and Attritor Mill, respectively, for different times: Al (a), As (b), Cd (c), Hg (d), Ni (e), Pb (f) and Se (g).



Fig. 4. Comparison of metals' immobilization efficiency of Diga su Fangu (DSF) treated with Spex and Attritor Mill, respectively, for different times: Al (a), As (b), Cd (c), Hg (d), Ni (e), Pb (f) and Se (g).



Fig. 5. XRD patterns of untreated soils (a) DSF and (c) B, respectively and of soils after 10 and 26 h of mechanical treatment, respectively: (b) DSF and (d) B.

particles, etc., to increase the immobilization efficiency of milled soils.

While, chemical and physical mechanisms involved during the mechanical treatment of soils may be the subject of further investigation, the results obtained so far further confirm that immobilization of heavy metals in synthetic soils may be achieved through the proposed technology.

In order to evaluate the possibility of scaling-up the latter one to the industrial level, in the second part of this work, real contaminated soils and tailings, sampled from an overburden mining area of Sardinia, Italy, 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) ratio used in the Spex Mill is maintained, thus evaluating whether the BPR could represent a suitable scale-up factor. To this aim mechanical treatments were carried out using the same treatment times and ball to powder ratio (BPR=4) when both the Spex or the Attritor Mill were used.

Once milled, soil and tailing samples have been extracted from the mills and submitted to the SPLP leaching procedure.

Concentrations of heavy metals released from the treated soil sample "B" in the leachate from SPLP test are shown in Fig. 1 while the corresponding immobilization efficiencies are shown in Fig. 2. Firstly, from Fig. 1 no significant differences between the results obtained using the Spex and the Attritor Mill, respectively may be observed, thus confirming that the BPR may be considered as a suitable scale-up factor. Moreover, from Fig. 1a it clearly appears that the concentration of As released in the leachate decreases when the soil is mechanically treated for suitably prolonged milling times. Similar behaviour may be observed for Hg, Pb and Se (Fig. 1b, c and d respectively). The effect of mechanical treatment is more pronounced for milling times ranging from 0 to 9 h while above 10 h no substantial decrease in the heavy metal leachable fraction may be observed. It is also worth noting that after mechanical treatment applied for relatively short times (i.e. 12 h), concentration levels of all the considered heavy metals in leachate result to be lower or very close to the regulatory limits (dashed lines in Fig. 1) proposed by USEPA for drinkable water.

From Fig. 2 it may be observed that the corresponding immobilization efficiencies significantly increase only after 1 or 2 h of milling for all the considered heavy metals except for Se (Fig. 2d) for which longer processing times are required to be effectively immobilized.

From the analysis of Figs. 1 and 2, it may be concluded that the mechanical treatment is effective in the immobilization of a wide range of heavy metals contained in real contaminated soil(B). Moreover, the results obtained when the Attritor Mill is used show that the proposed technique may be applied industrially when the BPR ratio is used as scale-up factor.

As for the tailings sample named "DSF", results obtained from milling trials are shown in Fig. 3 in terms of concentration of heavy metals released in the leachate by the samples subjected to different milling times. In Fig. 4 the same results are shown in terms of immobilization efficiency as a function of the milling time.

From Fig. 3 it may be observed that, as for the B soil, also for DSF samples, no significant differences exist between the results obtained when using the Spex Mill with respect to the Attritor one. In particular from Fig. 3a, c and e it may be noticed that a milling time of about 3 h is sufficient to decrease Al, Cd and Ni release below the EPA regulatory limits. Instead, for heavy metals such as As, Hg, Pb and Se (Fig. 3b, d, f and g, respectively) 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 than the corresponding regulatory limits (dashed lines in Fig. 3) proposed by USEPA for drinkable water.

In Fig. 4 the increase in heavy metals immobilization efficiency obtained by augmenting the milling time is shown. It may be seen that, for almost all the considered heavy metals, a significant increase in immobilization efficiency (i.e. close to 99%) takes place after only 1 h of mechanical treatment. Only for the case of Pb(II) more prolonged milling times (about 5 h) are needed in order to obtain an immobilization efficiency close to 99%.

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 soil and to verify if mechanical treatment causes drastic alterations of the original soil properties, further analyses on untreated and treated soils were performed. Specifically, XRD analyses on untreated and mechanically treated (10 h, BPR = 4) tailing sample DSF may be seen in Fig. 5a and b, respectively, while in Fig. 5c and d the XRD patterns of untreated and treated (26 h, BPR = 4) soil sample B are shown. The XRD patterns were analyzed by taking advantage of classical theories [20].

In particular, it is apparent from Fig. 5a and b 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 (Fig. 5a).

On the contrary, from Fig. 5c and d, it is possible to notice that, when subjected to mechanical treatment for 26 h, the soil sample B undergoes a transformation which determines the disappearance of lead carbonate detected in the untreated B sample.

This result is probably due to the thermal conversion of PbCO₃ in PbO and CO₂ determined by high local temperatures and pressures occurring at the impact point between two or more milling spheres. It should be noted that the same effect was observed for synthetic soils. The thermal decomposition of PbCO₃ appears to be a reasonable assumption although PbO peaks are very difficult to be revealed because they are covered by the CaCO₃ peaks.

Finally, the analysis of the full *width* at *half maximum* peaks was used to evaluate the crystallite sizes and lattice distortion. The results of such analysis show that the DSF and B 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 soils milling.

In Fig. 6 the effect of ball milling treatment on particle size distribution of B soil is shown. Similar results are obtained for DSF soils.

From Fig. 6 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 [22], Van der Waals forces play a significant role only at particle size lower than 1 μ m. Moreover, the corresponding bond energy increases as the size of the aggregating particles is reduced. Finally, the weak aggregates formed are then compacted by the impacts being so able to entrap heavy metals according to the mechanisms proposed by Montinaro et al. [14,16]. This behaviour probably plays a very important role,



Fig. 6. Particle size distribution for untreated and treated B soil at different milling times.

as discussed for the synthetic soils, in the immobilization efficiency induced by mechanical treatments.

4. Concluding remarks

It has recently been shown by Montinaro et al. [14,16] that immobilization of heavy metals contained in synthetic soils can be achieved through mechanical treatment without the use of additives. It was assumed that the increase in immobilization efficiency, obtained after soils are mechanically treated, can be ascribed to specific phenomena induced during ball milling, such as the entrapment of heavy metals into new formed aggregates due to cold-welding of soil particles and the re-adsorption of heavy metals on new "fresh" surfaces produced by particle breakage.

In this work it is found that another phenomenon, related to specific chemical transformation, may contribute to the increase in immobilization efficiency observed when the soils are mechanically treated. In fact, a significant change in chemical distribution of heavy metals among soil's phases is observed when the solid samples are subjected to mechanical treatment. In particular, an increase in the less leachable heavy metals complexes is achieved.

When mechanical treatment is applied to real contaminated soils and tailings very promising results are obtained. In fact, after relatively short milling times, leachable fraction of heavy metals was reduced under the EPA regulatory limits for drinkable water for both soil and tailing samples. No significant alterations of the original properties of soil and tailings samples were detected under the milling regimes and the milling times investigated.

These results demonstrate the applicability of this technique for the remediation of heavy metals contaminated soils and tailings. Moreover the trials performed by using an Attritor Mill confirm the possible applicability of the proposed technology at the industrial scale. Finally, the simplicity of the proposed process which makes use of classical comminution devices makes it quite interesting also from the economic point of view. In fact, from a preliminary evaluation performed in order to verify the economic sustainability of the process, the estimated cost of the technology, including electricity, labor and installation is of about $40-60 \in/ton [21]$.

Acknowledgements

The financial support of Ministero dell'Istruzione dell'Università e della Ricerca (MIUR), Italy, through the project "Nuove tecnologie per la bonifica e il ripristino ambientale di siti contaminati–PON Ricerca Scientifica, Sviluppo Tecnologico, Alta Formazione 2000–2006", is gratefully acknowledged. This work was also carried out with the financial contribution of the Sardinian Regional Authorities.

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