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

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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. 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.

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 (cf. Sheppard and Thibault, 1992; Concas et al., 2004).
Immobilization processes are generally preferred for the treatment of heavy metals contaminated soils due to the intrinsic limitations of extractive techniques (Paff and Bosilovich, 1995).
Recently the effect of mechanical treatment on the immobilization capacity of heavy metals contaminated soils has been addressed (Montinaro et al., 2007; Concas et al., 2007; 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). 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, 1995; 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) 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 $CaCO_3$ (99%), SiO_2 (99%), bentonite (99%), kaolin (99%), Fe_2O_3 (99%), MnO_2 (99%), humic acid (99%) were mixed in order to prepare sandy (SS), kaolinitic (KS) and bentonitic (BS) soils, respectively. The amount of each of them used for preparing synthetic soils is reported by Montinaro et al., (2007). Synthetic soil contamination was performed according to the procedure reported by Montinaro et al. (2007; 2008). Contaminated soils were then mechanically treated using a Spex Mixer/Mill mod. 8000, following the procedure reported by Montinaro et al. (2007).

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. (1979) 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. (1979), 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 heavy metals concentration in the solution obtained after contacting contaminated soils with each extractant was determined using an Inductively Coupled Plasma-Optical Emission Spectrometer.

Table 1. Operating conditions used in the sequential extraction method.

Pb(II) Fraction	Extracting agent	Shaking or contacting time	Temperature
Exchangeable	8mL $NaCH_3COO$ (1 M, pH = 8.2)	1 h	25°C
Bound to carbonates	8mL $NaCH_3COO$ (1 M) +HNO_3 until pH = 5	5 h	25°C
Bound to Fe-Mn oxides	20mL $NH_2OH \cdot HCl$ (0.04M) in CH_3COOH 25%(v/v)	6 h	96 ± 3°C
Bound to organic matter	3mL HNO_3 (0.02 M) + 5mL H_2O_2 30% (pH = 2 with HNO_3)	2 h	85 ± 2°C
	5mL H_2O_2 30% (pH = 2 with HNO_3)	3 h	85 ± 2°C
	8mL $NaCH_3COO$ (1 M) in HNO_3 20%(v/v)	0,5 h	25°C
Residual	9mL HNO_3 + 3mL HF	In contact until total dissolution	Microwave oven 180°C

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.

Soils sampled from this area were named "B", while tailing samples were named "DSF". Solid samples were chemically characterized through strong acid digestion. Specifically, microwave assisted acid digestion has been carried out according to the Method 3052 (SW-846 EPA Method 3052,1995) to obtain the complete dissolution of siliceous and organically based matrices. 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 according to the procedure reported by Montinaro et al. (2007; 2008).

Table 2. Heavy metals in the soils DSF and B obtained after complete soil digestion.

Sample	Al (mg/kg)	As (mg/kg)	Cd (mg/kg)	Hg (mg/kg)	Ni (mg/kg)	Pb (mg/kg)	Se (mg/kg)	Zn (mg/kg)
DSF	13657,5	416,1	85,5	244,6	44,7	24688,0	313,5	28434,1
B	4522,5	221,0	54,3	144,2	25,1	17582,9	249,9	32652,9

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. Unmilled and milled soils were then submitted to the "synthetic precipitation leaching procedure (SPLP)" reported by USEPA (1995, 1996) in order to evaluate the degree of metal immobilization. Immobilization efficiency η(t)% of the mechanically treated soil after a time interval was evaluated through the following equation.

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

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^{-1}) is the initial heavy metal concentration in the untreated soil and W_{solid} (kg) is the soil weight which undergoes the test.

3. Results And Discussion

In Table 3 the distribution of Pb(II) between the main synthetic soil components before and after mechanical treatment (7h prolonged) is outlined.

Table 3. Distribution (mg) of Pb(II) in the 5 fractions that constitute the synthetic soils.

	SS 0h BM	SS 7h BM	SB 0h BM	SB 7h BM	SK 0h BM	SK 7h BM
Exchangeable (mg)	0.096	0.011	0.094	0.000	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

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 of 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 (cf. 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 of Pb(II) bound to carbonate fraction and in a simultaneous increase of 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 of immobilization efficiency observed for milled soils. In fact the increase of 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 (PbCO$_3$, cerussite) to the oxide fraction determining a stronger bond of Pb(II) to the soil components. In particular, a thermal decomposition of PbCO$_3$ to PbO and CO$_2$ 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 particles, etc., to increase the immobilization efficiency of milled soils.

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. Moreover, the same ball to powder ratio (BPR) 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 Figure 1 while the corresponding immobilization efficiencies are shown in Figure 2.

Firstly, from Figure 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 Figure 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 (cf. Figure 1b, 1c and 1d respectively). The effect of mechanical treatment is more pronounced for milling times ranging from 0 to 9 hours while above 10 hours no substantial decrease of 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 Figure 1) proposed by USEPA for drinkable water.
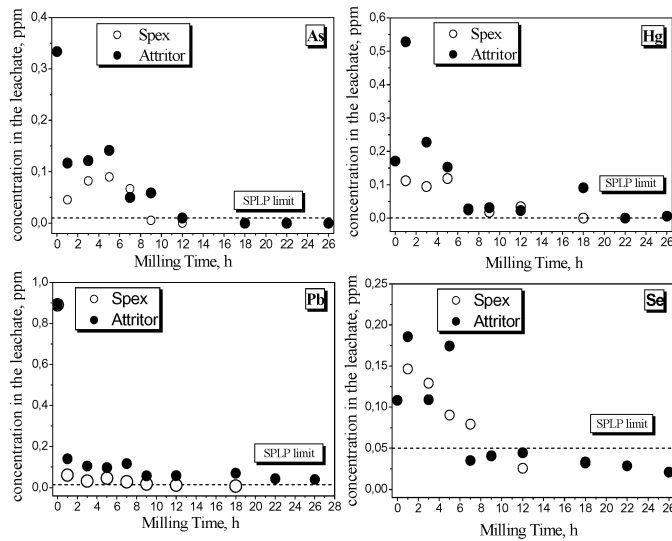

Figure 1. Comparison of heavy metal's concentration in the SPLP leachate of Barraxiutta soil "B" treated with Spex and Attritor Mill, respectively, for different times: As (a), Hg (b), Pb (c) and Se (d).
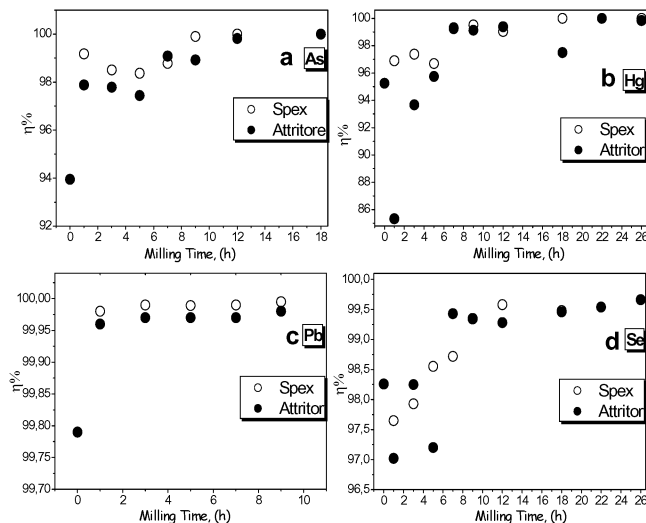

Figure 2. Comparison of heavy metal's immobilization efficiency of Barraxiutta soil "B" after mechanical treatment for different times with the Spex Mixer/Mill and the Attritor Mill, respectively: As (a), Hg (b), Pb (c) and Se (d).

From Figure 2 it may be observed that the corresponding immobilization efficiencies significantly increase after only 1÷2 hours of milling for all the considered heavy metals

except for Se (cf. Figure 2d) for which longer processing time are required to be effectively immobilized. From the analysis of Figure 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.

4. Concluding Remarks

It has been recently shown by Montinaro et al. (2007; 2008) 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 of 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 of 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 of 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.

5. References

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