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Mechanochemical remediation of heavy metals contaminated soils: Modelling and experiments

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Abstract

The use of mechanochemistry for the remediation of heavy metals contaminated soils is investigated. Specifically, synthetic sandy soils contaminated by $Cd^{(II)}$, $Pb^{(II)}$ and $Zn^{(II)}$ are prepared. The degree of metal immobilization is evaluated after the soil is subjected to mechanical treatment by analyzing the leachable fraction of heavy metals obtained through the "synthetic precipitation leaching procedure (SPLP)". For the case of soils contaminated by heavy metals concentration levels similar to field contaminated soils, their leachability is reduced to levels lower than the USEPA regulatory threshold for drinkable water. In addition impact velocity of milling media as well as impact energy and frequency are evaluated by means of a simulation model of the used milling apparatus.

Keywords: Soil remediation; Heavy metals; Ball milling; Immobilization; Mathematical modelling

1. Introduction

Mechanical treatments by ball milling (BM) are typically used to promote specific transformations such as combustive or gradual reactions, amorphization, activation, microstructural refinement, comminution, cold-welding and alloying (Boldyrev, 1995; Suryanarayana, 2001).

Mechanically induced reactions by BM have been successfully used for the degradation of organic pollutants such as exachlorobenzene (Mulas et al., 1997), hexabromobenzene (Zhang et al., 2002), PCBs (Birke, 2002) and other organohalogenated compounds (Rowlands et al., 1994; Monagheddu et al., 1999). Such degradation reactions occur by either gradual conversion paths or combustion-like reactions which take place, after an induction period, in a very short time (Schaffer and McCormick, 1992; Mulas et al., 1997; Saeki et al., 2001). In the first case, the increasing amount of defects in the solid matrix permits a continuous degradation of the organic compound (Schaffer and McCormick, 1992; Saeki et al., 2001; Birke, 2002). In the second one, the complete degradation of organic compounds take place through strong exothermic reactions in relatively short times as a consequence of the high temperatures reached by powders inside the mechanochemical reactor (Mulas et al., 1997; Cao et al., 1999; Caschili et al., 2006). While a significant amount of papers have been devoted to investigate degradation reactions of organic contaminants, to our best knowledge the effect of mechanical treatment on immobilization capacity of heavy metals in soils has not been analyzed to date. In addition, very few papers (Delogu et al., 2003) have been devoted to assess possible quantitative correlations between observed results and specifics parameters of milling processes.

Thus, the present paper consists of two parts. In the first, with the aim of quantitatively evaluating process variables (i.e., impact energies and collision frequency), which influence

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chemical and physical transformations of soils during milling, a suitable model for the appropriate simulation of the dynamics of a Spex Mixer/Mill, which will be used to perform the experiments, is presented.

In the second part, experimental results related to the remediation of $Pb^{(II)}$, $Zn^{(II)}$ and $Cd^{(II)}$ contaminated soils are reported. $Pb^{(II)}$, $Zn^{(II)}$ and $Cd^{(II)}$ immobilization is achieved without the use of additional reactants but only through the exploitation of weak transformations induced on the treated soil by mechanical loads taking place during collisions among milling media.

2. Modelling section

As it will be seen in the experimental section, contaminated soils have been mechanically treated by ball milling inside suitable vials. Specifically, a Spex Mixer/Mill mod. 8000, operating at the standard milling frequency of about 870 rpm, is employed together with a stainless steel vial, 606.75 g in weight, having the internal diameter equal to 3.8 cm and the internal height of 5.8 cm. Mill characteristics and operating conditions adopted during milling are reported in Table 1.

In a Spex Mixer/Mill, balls and soils are placed in a vial which is agitated at high frequency in complex three dimensional cycles. In order to simulate the dynamic of the milling bodies within the ball milling equipment, a model which takes into account the motion of one sphere, therefore subjected to wall-sphere impacts, is presented. Then, the impact between the vial wall and the sphere is identified when position, velocity and acceleration of each point of the vial and of the sphere during the process is known. Along these lines, the 3D vial motion has been firstly simulated according to Concas et al. (2006).

Once the movement of the vial is quantitatively described, in order to check possible impacts of the sphere with the vial wall and to quantify the energetic inputs related to the corresponding impacts, the sphere motion within the vial needs to be simulated. To this aim the vial wall has been considered to be constituted by bounded spheres, being the diameter of such spheres equal to the vial wall thickness. In this way, the impact between the sphere and the vial wall is represented as an impact between two spheres of different diameter.

The model proposed by Cundall and Strack (1979) and subsequently modified by Brilliantov et al. (1996), Salueña et al. (1999), is used for impacts simulation. In particular, by evaluating the deformation taking place as $\xi_{ij} = R_i + R_j - |\vec{r}_i - \vec{r}_j|$, being $\vec{r}_i$ and $\vec{r}_j$ the position vectors of spherical particles having radius R_i and R_j, respectively, the colliding sphere is subjected to force $\vec{F}_{ij} = \vec{F}^N_{ij} + \vec{F}^T_{ij}$, where $\vec{F}^N_{ij}$ and $\vec{F}^T_{ij}$ are the components along normal and tangential directions, respectively. If more than one sphere pertaining to the simulated wall ($j = 1, \ldots, n_{\mathrm{imp}}$) interacts with the sphere i, the resulting force acting upon it is given by $\vec{F}_i = \sum_{j=1}^{n_{\mathrm{imp}}} \vec{F}_{ij}$. The normal and tangential components of the interaction forces and momenta may be written as follows (cf. Concas et al., 2006 and references therein):

$$\vec{F}^N_{ij} = \left[\frac{2\Upsilon}{3(1-\nu^2)}\sqrt{R_{\mathrm{eff}}}\left(\xi_{ij}^{\frac{3}{2}} + \frac{3}{2}A\sqrt{\xi_{ij}}\frac{\mathrm{d}\xi_{ij}}{\mathrm{d}t}\right)\right]\cdot\vec{n}, \tag{1}$$

$$\vec{F}^T_{ij} = \mathrm{sgn}(v^{\mathrm{rel}}_{ij})\ \min\{m^{\mathrm{eff}}_{ij}\gamma_T|v^{\mathrm{rel}}_{ij}|, \mu|\vec{F}^N_{ij}|\}\cdot\vec{t}, \tag{2}$$

$$\vec{M}_i = \vec{F}^T_{ij} \wedge \vec{n}R_i, \tag{3}$$

$$\vec{M}_j = -\vec{F}^T_{ij} \wedge \vec{n}R_j, \tag{4}$$

$$\vec{\tau}_i = -\mu_{\mathrm{rol}}|\vec{F}^N_{ij}|\cdot\frac{\vec{M}_i}{|\vec{M}_i|}, \tag{5}$$

$$A = \frac{1}{3}\frac{(3\chi_2-\chi_1)^2}{(3\chi_2+2\chi_1)}\left[\frac{(1-\nu^2)(1-2\nu)}{\Upsilon\nu^2}\right], \tag{6}$$

$$\vec{v}^{\mathrm{rel}}_{ij} = \left(\frac{\mathrm{d}\vec{r}_i}{\mathrm{d}t} - \frac{\mathrm{d}\vec{r}_j}{\mathrm{d}t}\right) + (R_i\vec{n}\wedge\vec{\Omega}_i - R_j\vec{n}\wedge\vec{\Omega}_j), \tag{7}$$

where symbols' significance is reported in the notation. It is worth noting that also a resistant torque $\vec{\tau}_i$ opposite to the rolling motion of the sphere on the cylindrical surface of the vial wall has been considered. Once forces and momenta acting upon the sphere are evaluated, it is possible to express the equations of motion for the sphere i, as follows:

$$\frac{\mathrm{d}\vec{r}_i}{\mathrm{d}t} = \vec{v}_i, \tag{8}$$

$$\frac{\mathrm{d}\vec{v}_i}{\mathrm{d}t} = \varepsilon\frac{\vec{F}_i}{m_{\mathrm{eff}}} + \vec{g}, \tag{9}$$

$$\frac{\mathrm{d}\vec{\Omega}_i}{\mathrm{d}t} = \varepsilon\frac{\vec{M}_i - \phi\vec{\tau}_i}{I_i}, \tag{10}$$

along with the corresponding initial conditions:

$$\vec{r}_i = \vec{r_i^0}, \quad \vec{v_i} = \vec{0} \text{ and } \vec{\Omega_i} = \vec{0} \text{ at } t = 0. \tag{11}$$

The significance of the symbols' shown in the equations above is reported in the notation. It should be noted that the equations above need two auxiliary parameters namely ε and ϕ, to discriminate the occurrence of impact and rolling: $\varepsilon = 1$ and $\phi = 1$ if impact and rolling take place, respectively, $\varepsilon = 0$ and $\phi = 0$ if no impact and no rolling occur, respectively. The system of ordinary differential equations (8)–(10) represents an initial value problem that is solved by means of the subroutine DIVPAG of the IMSL libraries.

By integrating Eqs. (8)–(10), position ($\vec{r}_i$), velocities ($\vec{v}_i$ and $\vec{\Omega}_i$) and acceleration of the milling sphere can be obtained, thus allowing one to evaluate the most important energetic parameters which influence soil transformations within the milling apparatus, namely the impact energy ($E_i = \frac{1}{2}m_i|\vec{v}_i|^2 + \frac{1}{2}I_i|\vec{\Omega}_i|^2$) and the impact frequency (number of impacts/time).

From statistical distribution of impact velocity modulus obtained through the presented model, it is established that its average value is equal to about $4\,\mathrm{m\,s^{-1}}$ (cf. Table 1) which is in good agreement with experimental results available in the literature (cf. Caravati et al., 1999; Delogu et al., 2000). The obtained time evolution of the impact frequency during the

Table 1
Operating conditions for milling trails

Parameter	U.M.	Value	Ref.
Mille type	–	spex Mixer/Mill mod. 8000	–
Vial length	m	5.8×10^{-2}	Spex industries
Vial internal radius	m	1.9×10^{-2}	Spex industries
Mill arm length	m	1.0×10^{-1}	Spex industries
Weight of treated soil	g	8, 4, 2.66	This work
Milling spheres weight	g	8	This work
Ball to powder radio (BPR)	–	2, 4, 6	This work
Mill frequency	rpm	870	Spex industries
Impact velocity	$m\,s^{-1}$	4.168	This work
Impact energy	$J\,hit^{-1}$	0.093	This work
Impact frequency	$hit\,s^{-1}$	142	This work
Milling time	h	0.5–7	This work

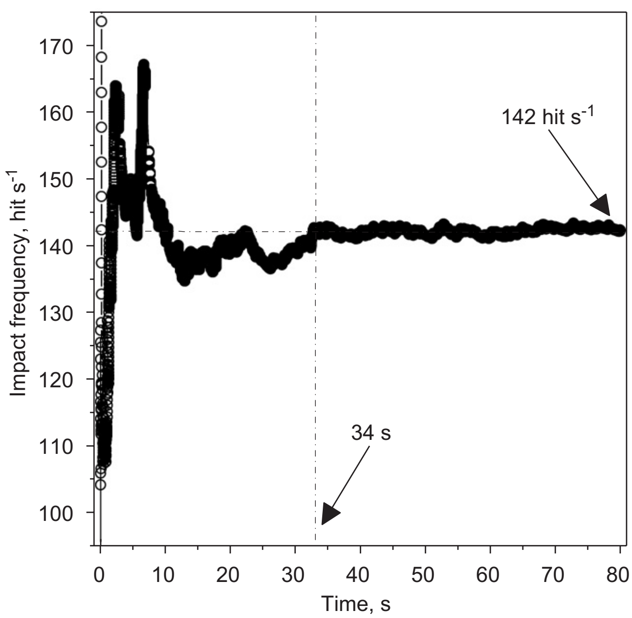

Fig. 1. Time evolution of the sphere impact frequency. Stabilization after a period of 34 s may be observed.

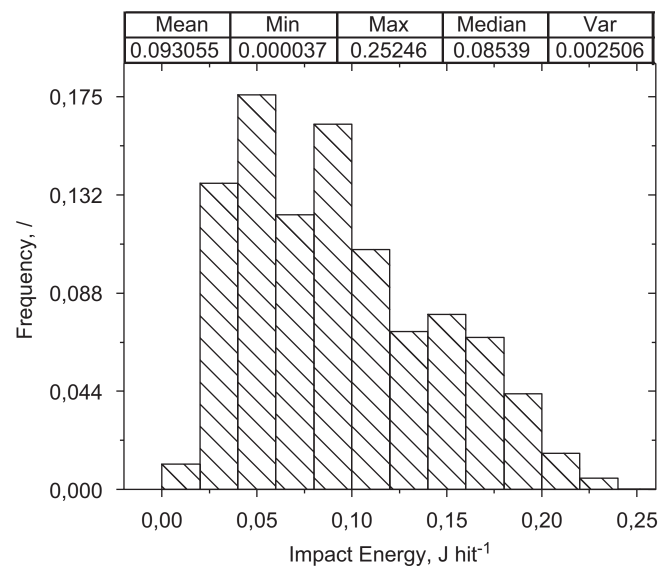

Fig. 2. Statistical distribution of impact energy.

first 80 s of vial motion is shown in Fig. 1. It may be observed that after a transient period of about 34 s, impact frequency reaches a stable value of about 142 impacts/s (cf. Table 1). This behavior highlights that after a certain critical time, during which large oscillations occur, the system reaches a stationary milling regime. The obtained statistical distribution of the impact energy over 80 s of milling is shown in Fig. 2. An average value of 0.093 J per hit has been calculated and reported in Table 1. The latter one is in good agreement with the experimental results reported in the literature (cf. Davis et al., 1988; Caravati et al., 1999; Delogu et al., 2000).

The obtained values of process parameters typical of Spex Mixer/Mill, as reported in Table 1, represent the starting point for a quantitative understanding of the experimental results related to the use of ball milling reactors for the remediation of heavy metals contaminated soils as described in the next section.

3. Experimental section

High purity $CaCO_3$ (99%), SiO_2 (99%), bentonite (99%), Fe_2O_3 (99%), MnO_2 (99%), humic acid (99%) have been mixed in order to prepare sandy soil (SS). All compounds have been obtained from Sigma-Aldrich, Inc. The amount of each compound used for preparing the synthetic soil according to the procedure suggested by Lo and Yang (1999) is reported as follows: SiO_2, 78%wt, bentonite (Al_2O_3 $4SiO_2$ H_2O), 20%wt, $CaCO_3$, 0.5%wt, Fe_2O_3, 0.25%wt, MnO_2, 0.25%wt, humic acid, 1%wt.

Soil contamination has been carried out in a temperature controlled shaker at 25 °C by contacting known weights of the synthesized soil, with a solution of known solute ($Pb^{(II)}$, $Cd^{(II)}$ and $Zn^{(II)}$) concentration and volume in suitable flasks. $Pb(NO_3)_2$, $Cd(Cl)_2$ and $Zn(Cl)_2$ (99.99%, Alfa Aesar) have been employed to obtain the solution at the desired $Pb^{(II)}$, $Cd^{(II)}$ and $Zn^{(II)}$ concentration, respectively. The flasks were sealed and shaken for 24 h, which has been experimentally proved to be a sufficient time to reach equilibrium conditions. Finally, the solutions were sampled in order to determine the solute concentration and pH. Heavy metal concentration in the soil solid phase at equilibrium has been obtained as reported by Montinaro et al. (2007).

Once contaminated, soils have been mechanically treated under air atmosphere for different time intervals by Spex Mixer/Mill mod. 8000, whose characteristics and operating conditions are reported in Table 1.

At the end of each programmed time interval of mechanical treatment, as well as for untreated ones (i.e., milling time equal to 0), soils have been suitably sampled to be analyzed. The degree of immobilization of heavy metal has been then evaluated using the "synthetic precipitation leaching procedure (SPLP)" reported by USEPA (1995, 1996), which is performed according to Montinaro et al. (2007). Immobilization efficiency, after each treatment interval, has been evaluated through the following equation:

$$\eta(t)\% = \left(1 - \frac{C(t)\cdot V_{\mathrm{leach}}}{q\cdot W_{\mathrm{solid}}}\right)\cdot 100, \qquad (12)$$

where symbols' significance is reported in the notation.

The effect of mechanical treatment under different milling regimes (i.e., BPR equal to 2, 4 and 6) and for different treatment times on $Pb^{(II)}$ immobilization efficiency and $Pb^{(II)}$ concentration released in the leachate (SPLP test) is shown in Fig. 3a and b, respectively.

It clearly appears that the immobilization efficiency increases when the soil is mechanically treated and this effect is more evident when the milling time is augmented. It should be noted that the SS soil seems to be very sensitive to the mechanical action since immobilization efficiency increases from 61.3% in absence of treatment to 94.8% when the soil is treated for 5 h with a BPR equal to 4. Correspondingly, the concentration of $Pb^{(II)}$ released in the leachate dramatically decreases being its concentration reduced from 596 to 70 mg L^{-1}. Similar results, not reported here for the sake of brevity, are obtained for $Cd^{(II)}$ and $Zn^{(II)}$ contaminated soils.

It should be noted that the performed XRD analyses shows the same crystalline phases, i.e., quartz and bentonite, before and after 5 h of mechanical treatment. The only detectable effect is a partial amorphization of phases confirmed by a small decrease of XRD peak intensity. In addition, by analyzing the effect of ball milling treatment on particle size distribution, it is seen that the mechanical action induces an increase of particle size rather than a size refinement (cf. Fig. 4). This effect may be explained considering that aggregation phenomena may prevail on breakage.

On the basis of the experimental results described above, only some hypotheses may be formulated about the possible mechanisms responsible for the immobilization capacity enhancement due to mechanical treatment. First, it is possible to assume that when soil is contaminated, heavy metals are adsorbed onto soil particles through a surface coordination process which may be represented as a complexation reaction between soil surface sites and heavy metal complexes

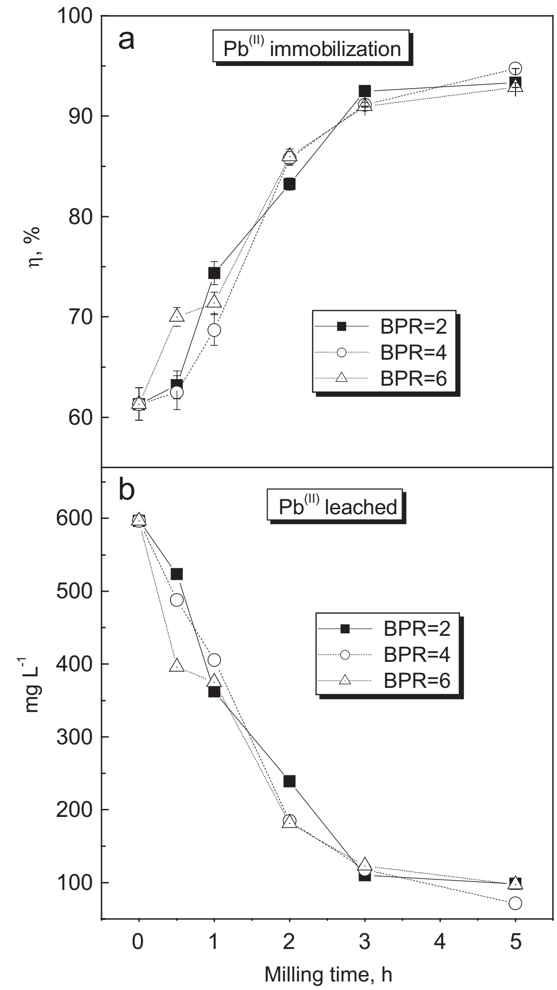

Fig. 3. Immobilization efficiency of treated SS soil (a) and leachate concentration (b).

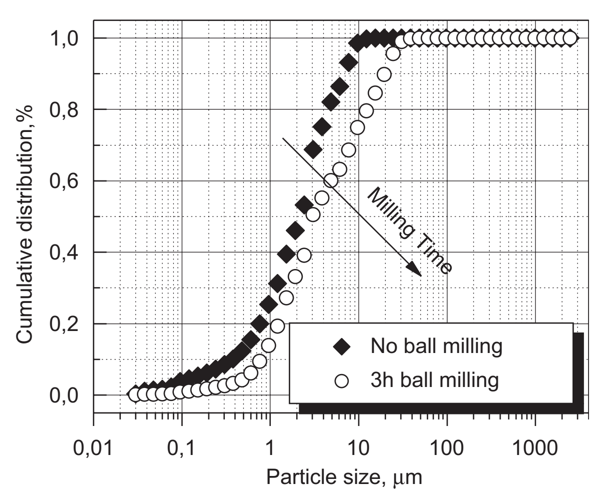

Fig. 4. Particle size distribution for untreated and treated SS soil after 3 h of milling.

(cf. Weng, 2004 for the case of $Pb^{(II)}$). When ball milling process starts, soil particles are subjected to high energetic collisions that may promote aggregation and breakage phenomena. The occurrence of aggregation phenomena, with a subsequent formation of stable aggregates, results in a net increase of soil particle size. When aggregation occurs, the amount of heavy metal adsorbed on the surface of two overlapping particles may be entrapped within the new formed aggregate. In this way the amount of heavy metal exposed to the leaching action is reduced thus determining a higher immobilization capacity. Moreover, since the accumulation of dislocations and vacancies in crystalline reticulum gives rise to an increase of diffusivity within the solid matrix (Lu et al., 1997), it is possible to assume that heavy metal complexes may diffuse within the crystalline reticulum of soil particles, thus leading to a very efficient chemical entrapment of heavy metals within the soil.

On the other hand, also breakage phenomena, taking place in parallel with the aggregation ones, may determine an increase of immobilization efficiency. In fact when a contaminated soil particle breaks, it develops new "fresh" surfaces onto which heavy metals ions may re-adsorb. These phenomena may result in a higher adsorption capacity thus increasing the corresponding immobilization efficiency of heavy metals. However, the suggested mechanism should be considered only as a reasonable hypothesis which is also based on the observation that the net particle size after milling increases (cf. Fig. 4). On the other hand, further investigation is required for its validation. Work along these lines is in progress.

In any case, although all phenomena taking place during mechanical treatment are not yet completely understood the experimental evidence confirms that for the considered soil and for all milling regimes adopted, a significant increase of the immobilization capacity is obtained because of the effect of mechanical action.

For this reason, further investigations have been performed in order to assess the efficiency of mechanical treatment on soils contaminated by heavy metals when considering concentration levels close to those ones of field contaminated soils, i.e., 100–1000 $mg\,kg^{-1}$ for $Pb^{(II)}$ (Markus and McBratney, 2001), 1–180 $mg\,kg^{-1}$ for $Cd^{(II)}$ and 1000–50 000 $mg\,kg^{-1}$ for $Zn^{(II)}$ (Abollino et al., 2002). To this aim SS contaminated soils with $Pb^{(II)}$, $Cd^{(II)}$ and $Zn^{(II)}$ concentrations of 621.5, 88.6, 28 000 $mg\,kg^{-1}$, respectively, have been synthesized and then mechanically processed for different times (BPR = 4). $Zn^{(II)}$, $Cd^{(II)}$ and $Pb^{(II)}$ concentrations in leachate from SPLP test after each milling trial are reported in Fig. 5a–c, respectively. It may be clearly seen that leachable heavy metals concentration significantly decrease after milling. It is worth noting that after a mechanical treatment applied for relatively short times (i.e., 7 h for $Pb^{(II)}$ and 3 h for $Cd^{(II)}$ and $Zn^{(II)}$, respectively) heavy metals concentration in leachate from SPLP test is lower than the regulatory limit (i.e., 0.015 $mg\,L^{-1}$ for Pb(II), 0.005 $mg\,L^{-1}$ for $Cd^{(II)}$ and 5 $mg\,L^{-1}$ for $Zn^{(II)}$, respectively) proposed by USEPA (USEPA, 1996) for drinkable water.

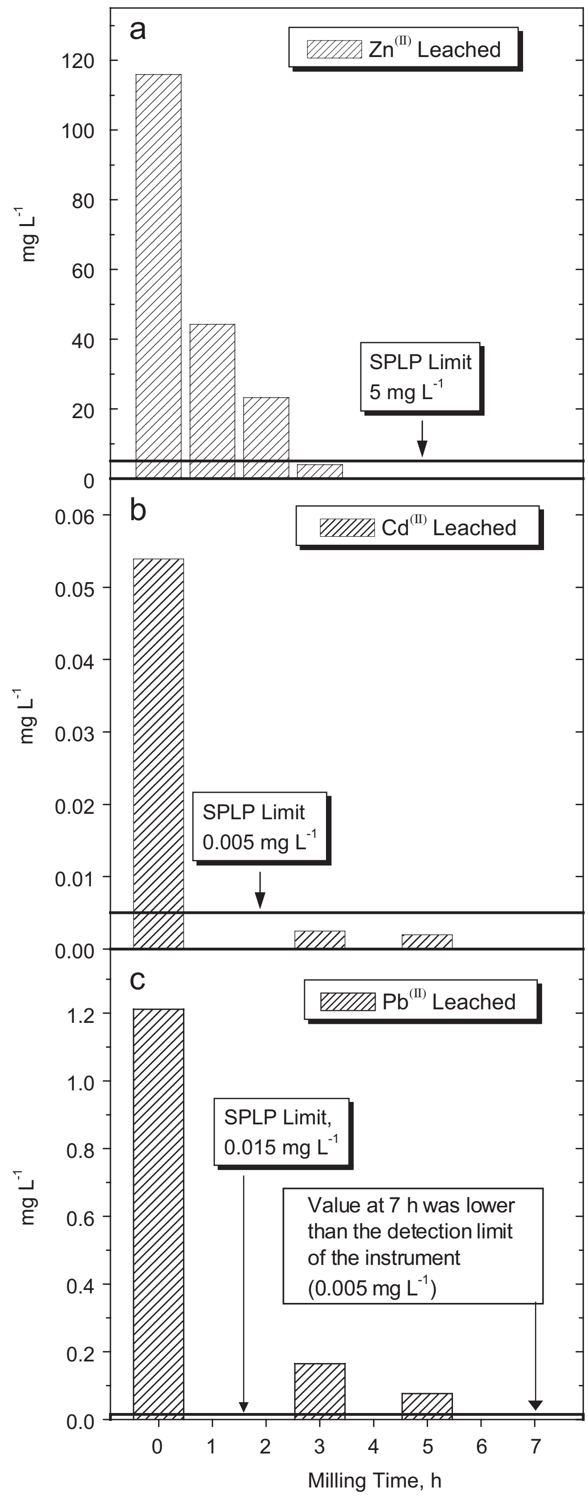

Fig. 5. Leachable heavy metals reduction after milling and comparison with EPA limits drinking waters: (a) $Zn^{(II)}$, (b) $Cd^{(II)}$ and (c) $Pb^{(II)}$.

4. Concluding remarks

In this work it is shown that immobilization of heavy metals in contaminated soils can be achieved through mechanical treatment. In particular, immobilization efficiency may be strongly increased as milling time is augmented. In addition, under the operating conditions investigated in this work, no significant alterations of the original characteristics of the synthesized SS soils are detected except for a weak amorphization and a relative increase of particle size. The immobilization capacity may be probably ascribed to phenomena such as entrapment of heavy metals into new formed aggregates due to aggregation of soil particles and their re-adsorption on new "fresh" surfaces produced through breakage.

When mechanical treatment is applied to soils which simulate real contaminated ones very promising results have been obtained. In fact, after relatively short milling times, leachable fraction of heavy metals has been reduced under the EPA regulatory limits for drinkable water for the considered SS soil. These results demonstrate the potential applicability of this technique for the remediation of field situations. Moreover, it is important to remark that, contrarily to what happen for classical immobilization technologies, these results have been obtained without any reactant addition and taking advantage of very simple apparatuses. Moreover, process simplicity makes this technology potentially feasible. While these aspects are particularly encouraging in view of possible technological applications of the proposed technique, it should be noted that quantitative correlations between the observed results and the process parameters, i.e., impact velocity, frequency and energy needs to be developed. The approach proposed in this work may represent a starting point which needs further investigations.

Notation

A	dissipative parameter, dimensionless
C	concentration, $\mathrm{mg\,L^{-1}}$
$\vec{F}$	forces, N
$\vec{g}$	gravitational acceleration, $\mathrm{m\,s^{-2}}$
I	inertial momentum, $\mathrm{kg\,m^{-2}}$
m	mass, kg
m_{eff}	effective mass $[m_i m_j/(m_i + m_j)]$, kg
$\vec{M}$	momentum, N m
$\vec{n}$	normal versor, dimensionless
n_{imp}	number of spheres of the simulated wall being impacted, dimensionless
q	heavy metal concentration in solid phase, $\mathrm{mg\,kg^{-1}}$
$\vec{r}$	position vector, m
R	radius, m
R_{eff}	effective radius $[R_i R_j/(R_i + R_j)]$, m
$\vec{t}$	tangential versor, dimensionless
t	time, s
$\vec{v}$	velocity, $\mathrm{m\,s^{-1}}$
V	volume, L
W	solid weight, kg

Greek letters

γ_T	damping coefficient in tangential direction, Hz
ε	auxiliary parameter, dimensionless
η	immobilization efficiency, %
μ	Coulomb static friction coefficient, dimensionless
μ_{rol}	rolling friction coefficient, dimensionless
ν	Poisson ratio, dimensionless
ξ	deformation, m
$\vec{\tau}$	rolling friction torque, N m
Υ	Young modulus, Pa
ϕ	auxiliary parameter, dimensionless
χ	viscous constants, dimensionless
$\vec{\Omega}$	angular velocity, $\mathrm{rad\,s^{-1}}$

Subscripts

i, j	impacting bodies
solid	solid phase
liquid	liquid phase

Superscripts

N	normal direction
0	initial condition
rel	relative velocity
T	tangential direction

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