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Mechanochemical Treatment of Soils Contaminated by Heavy Metals in Attritor and Impact Mills: Experiments and Modeling

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An integrative approach was developed to support the scale-up from lab- into pilot-scale mechano-chemical reactors for immobilize heavy metals in contaminated mining soil.

1. Introduction

Heavy metals (HMs) are soil pollutants resulting from anthropic activities such as metal mining, electronic waste disposal, metallurgy, smelting and refining, car shredding, etc. (Sannia et al., 2001). Because the environmental risks of HMs depend on their mobility, immobilization techniques are attractive strategies for soil remediation (Yuan et al. 2019). HMs mobility in contaminated soils can be reduced with minor changes of their chemical and structural properties (Concas et al. 2007) by mechano-chemical treatment. This treatment is based on supplying mechanical energy to the soil particles with suitable ball mills without using reagents. The motion of the milling chamber allows milling bodies to collide or shear thus transferring high mechanical loads to the soil entrapped between them. The energy provided leads to physic-chemical transformations of the soil/contaminant system with immobilization of HMs in the solid matrix (Montinaro et al. 2009).

Soil remediation studies reported high efficiency of HMs immobilization in soils with mechanical treatment: mica/fibrolite soil mixed with Ca/CaO to immobilize As, Cd, Cr and Pb (Mallampati et al. 2012a); Fe/Ca/CaO or NaH2PO4 to immobilize Cs-contaminated soils (Mallampati et al. 2012b); artificial soils to immobilize Pb, Cd and Zn (Montinaro et al. 2009). Laboratory scale mills such as SPEX mixer, planetary and tumbling ball mills were used for the mechanochemical treatments. Despite these high efficiencies of HMs immobilization, they were mainly referred to scenario with artificial samples mimicking contaminated soils and milling devices that do not represent the full-scale operations. More recently, mechanically promoted HMs immobilization was obtained in contaminated real soils without integrating any reactant using an attritor mill up-scaled for pilot- and full-scale applications (Montinaro et al. 2012). However, the scalability of the proposed processes has not been analysed.

The application of mathematical models that describe the immobilization processes is suitable to perform analysis of the scalability of the mill devices relating key design parameters with the mechano-chemical processes and HMs immobilization desired. Thus, we proposed an integrative approach that combines experimental data with mathematical modelling, to analyse the scalability to efficiently immobilize HMs in real contaminated mining soil by milling devices for pilot and full-scale application. The integrative approach based on a mathematical model (Concas et al. 2020a, 2020b) with modifications, provided information for scale-up from bench to pilot-scale. The application of the model at different scales was tested and validated by comparing simulation with experimental data obtained with bench and pilot-reactors.

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2. Materials and methods

2.1 Contaminated soil and mechanical treatment: Spex Mixer/Mill and Attritor Mill

HMs contaminated soils were sampled from the abandoned mining area of "Barraxiutta" in the SW of Sardinia. In this area, after mine cessation, HMs mobilization by meteoric and ground-waters led to their dispersion in the soil of the entire hydrographic basin. Currently, soils are strongly contaminated by HMs and represent themselves a threat for sensitive targets such as rivers, lakes or population. A chemical characterization of the contaminated soils has been previously reported (Montinaro et al. 2012). The contaminated soils were mechanically treated at different time intervals with a SPEX Mixer/Mill mod. 8000 (Caschili et al. 2006) using a charge ratio $C_R = 4$. The charge ratio is the ratio between the mass of milling bodies and the mass of precessed soil. To evaluate the scale-up potential of the technology and mathematical model proposed, additional milling experiments obtained with an Attritor Mill mod. 01HD/01HDDM were used. This mill is preferred for pilot-scale application in comparison to the Spex Mixer Mill because it is capable to treat higher amounts of soils.

2.2 Post treatment leaching test

To evaluate the degree of metal immobilization was used the "synthetic precipitation leaching procedure" (SPLP) which consisted in the procedure reported by Montinaro et al. (2012). The procedure to analyze the concentration of HMs in the leachate $C_f^{HM}(mg\ L^{-1})$ was published elsewhere (Concas et al., 2020a). This measure allows to determine if the treatment could lead to remediate the soil according to international regulations.

2.3 Mathematical model

The ball milling treatment (BM) can trigger the transformation of soil-bound HMs from the state of leachable (L) to the state of immobilized (I) according to the following reaction:

$$HM, L \xrightarrow{BM} HM, I \tag{1}$$

For a generic grinding time τ, the mechanical treatment has the following relationships:

$$\xi^{HM,L}(\tau) \leq \xi^{HM,L}(0) \quad \text{and} \quad q^{HM}(\tau) = q^{HM}(0) \tag{2}$$

indicating with 0 the time before the mechanical treatment. The symbols $\xi^{HM,L}(mg\ kg^{-1})$ and $\xi^{HM,I}$ indicate the leachable mass fraction of the generic metal HM with respect to the total mass of soil being processed and the immobilized fraction of metal, respectively. The total mass fraction of HMs irrespective of its leachability $q^{HM}(mg\ kg^{-1})$ is unchanged during the milling treatment. With the integration of the macro-kinetic model proposed to simulate a generic solid-state transformation in the soil during milling with the probability that a generic mass would face *j* effective collisions out of a total of n ones taking place in the milling device, it is possible to quantify this probability with a Poisson distribution for mechanical treatment by ball milling involving a large number of collisions as reported by Garroni et al., (2014) and Delogu et al., (2004):

$$P_j(n) = \lim_{n\to\infty} \binom{n}{j} K^j (1-K)^{n-j} = \frac{(K\,n)^j}{j\,!} e^{-Kn} = \frac{(k\,\tau)^j}{j\,!} e^{-k\,\tau} \tag{3}$$

Where the parameter $k\ (h^{-1})$, equal to the product $K\,f$, is related to the dynamics of milling conditions by directly accounting for the impact frequency *f* and, implicitly for the collision energy and the charge ratio. The parameter K is the ratio between the mass of solid (m^*) entrapped between two milling bodies during a collision and the total mass (m) of powders in the milling device. The probability defined in Eq. (3) permits a good estimation of the mass fraction of soil sample which faces *j* effective collisions during a prolonged milling process for a time τ. The mass fraction $\xi_j^{HM,L}(\tau)$ of leachable HMs experiencing j effective hits after processing for a time τ can be calculated as follows (Garroni et al. 2014):

$$\xi_j^{HM,L}(\tau) = \xi^{HM,L}(0) \frac{(k\,\tau)^J}{j!} e^{-k\,\tau} \tag{4}$$

By considering the mass conservation law and accounting for the mass fraction of immobilized metal $\psi^{HM,I}(\tau)$ for the milling time τ, the immobilized fraction of HM during milling can be calculated as (Concas et al., 2020b):

$$\psi^{Me,I}(\tau) = \xi^{Me,L}(0) - \sum_{j=0}^{J_{min}} \xi_j^{Me,L}(\tau) = \xi^{Me,L}(0)\left[1 - \sum_{j=0}^{J_{min}} \frac{(k\,\tau)^j}{j!} e^{-k\,\tau}\right] \tag{5}$$

Where J_{min} is the minimum number of effective collisions that should be experienced by the soil for the transformation of Eq. (1) to occur while the constant k is linearly related to the charge ratio (C_R) through the relationship: $k' = k/C_R$. Since the leachable fraction of HMs content in the solid phase ($\xi^{HM,L}$) cannot be measured, a strategy has been previously developed to evaluate HMs concentration in the liquid phase accessible for measurements and thus allowing a comparison with experimental data (Concas et al., 2020). The time profile of the leached concentration $C_f^{HM}(\tau)$ can be simulated as:

$$C_f^{HM}(\tau) = C_f^{HM}(0)\left[\sum_{j=0}^{J_{min}} \frac{(k' C_R\, \tau)^j}{j!}\right] e^{-\,k' C_R\, \tau} \tag{6}$$

This equation quantifies the concentration of the HMs released from the solid to the liquid phase after the time τ of mechanical treatment. The immobilization efficiency of the treatment was then evaluated as:

$$\eta(\tau) = \frac{C_f^{HM}(\tau) - C_f^{HM}(0)}{C_f^{HM}(0)} \tag{7}$$

The scalability of this expression in predicting the effect of the mechanical treatment at different experimental conditions represented by different size of the mills has been validated.

3. Results and discussion

The concentration (C^0) of heavy metals in the liquid phase obtained by leaching untreated soil samples are reported in Table 1. Only As, Hg, Pb and Se concentrations are shown because they were the only HMs whose concentration overcame their corresponding USEPA (United States Environmental Protection Agency) thresholds for drinkable water (cf. C^{lim} in Table 1). Leached concentrations of As, Hg, Pb and Se were about 33, 850, 60 and 3 times greater than their corresponding regulatory thresholds.

Table 1: Initial (C^0) and USEPA limit (C^{lim}) concentrations in the leachate; model parameters (k') and mean relative errors (ε) obtained by fitting the experimental data in Figure 1.

Heavy Metal	C^0 $(mg\ L^1)$	C_{lim} $(mg\ L^1)$	k' (h^{-1})	**ε (%)**
As	1.71×10^{-1}	1.0×10^{-2}	7.75×10^{-2}	22.8
Hg	3.34×10^{-1}	2.0×10^{-4}	5.50×10^{-2}	3.6
Pb	8.91×10^{-1}	1.5×10^{-2}	1.87×10^{-1}	34.3
Se	1.46×10^{-1}	5.0×10^{-2}	3.00×10^{-2}	6.7

Soil samples were milled for different times (τ) with the SPEX mill using a Cr equal to 4 and then subjected to the SPLP. The evolution with milling time of normalized concentrations of HMs, expressed as the ratio between the actual concentration in the leachate and the corresponding threshold ($C^*(\tau) = C(\tau)/C_{lim}$), is shown in Figure 1a. It can be clearly seen that the longer was the milling time the lesser were HMs concentrations in the leachate.

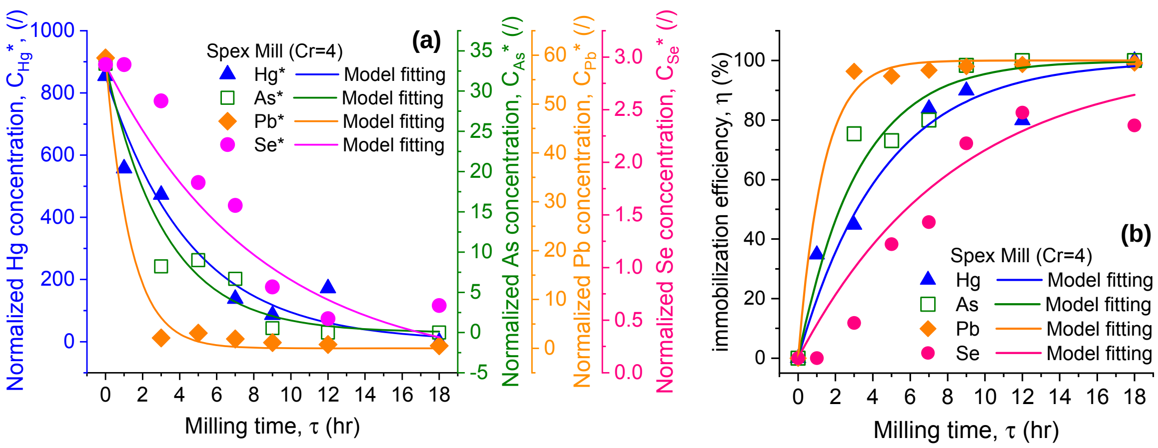

Figure 1. Time evolution of normalized HM concentrations (a) and immobilization efficiency (b) using the SPEX

Hence, structural changes resulting in a better entrapment of HMs clearly took place in the soil with milling. According to Concas et al. (2020a) such changes could be ascribed to the synergy of different phenomena triggered by the mechanical treatment. Among these the most relevant were assumed to be the breakage of soil particles and the opening of new surfaces onto which HMs could adsorb; the cold-welding of particles that determined the subtraction of HMs originally adsorbed in the welded surfaces to the action of leaching agents; the diffusion of HMs from the surface to the inner of the crystalline lattice due to the accumulation of vacancies and defects triggered by the mechanical loads and finally amorphization of solid particles.

While further research activity is needed to understand the mutual role of the above phenomena, the experimental evidence confirms that increasing the milling time promoted the immobilization efficiency (h) of the soil to increase (cf. Figure 1b). As it can be inferred from the Figures and the mean relative errors of the fitting procedure in Table 1, the experimental behaviour is well captured by the mathematical model using the values of parameter k' reported always in Table 1. The parameter J_{min} was instead assumed equal to 1 for all the HMs. Because Attritor Mill can treat a mass of soil 28 times greater than that of the Spex Mixer Mill, further experiments were performed with the former by adopting the same Cr=4 of the previous trials. The experimental results (cf. Figure 2) well reproduced the ones already obtained with the SPEX Mill thus demonstrating that Cr represents the most important scale up parameter irrespective of the adopted milling device. To test the predictive capability of the model, the experimental data were simulated by keeping fixed the parameters in Table 1.

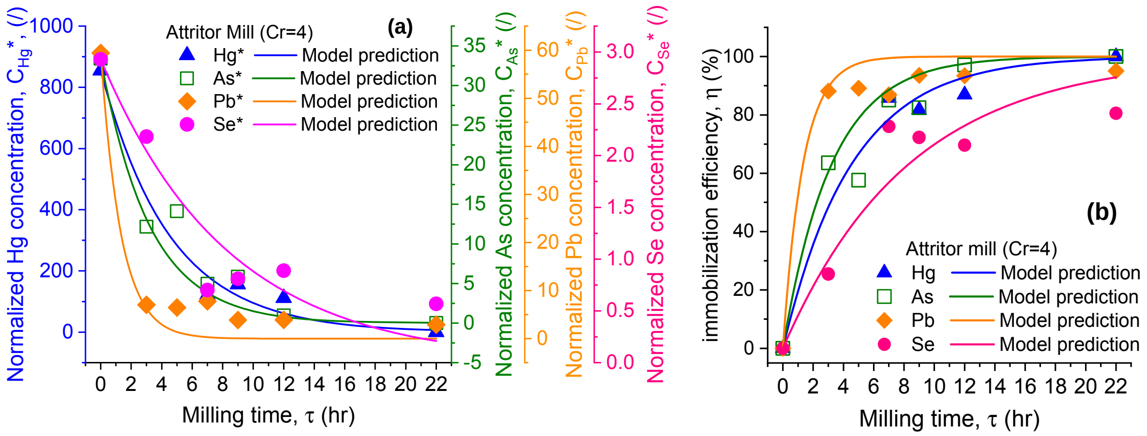

Figure 2. Time evolution of normalized HM concentrations (a) and immobilization efficiency (b) using the Attritor

The model well captures even the experimental results obtained with the Attritor without tuning any model parameter thus demonstrating its predictive capability. To further assess the reliability of the model, a sensitivity analysis has been performed by changing the parameter k' in the range -100% + 100% with respect to the base case values reported in Table 1. The final concentration of HMs in the leachate after 22 hours of milling was considered as monitored output in the sensitivity analysis (cf. Figure 3a).

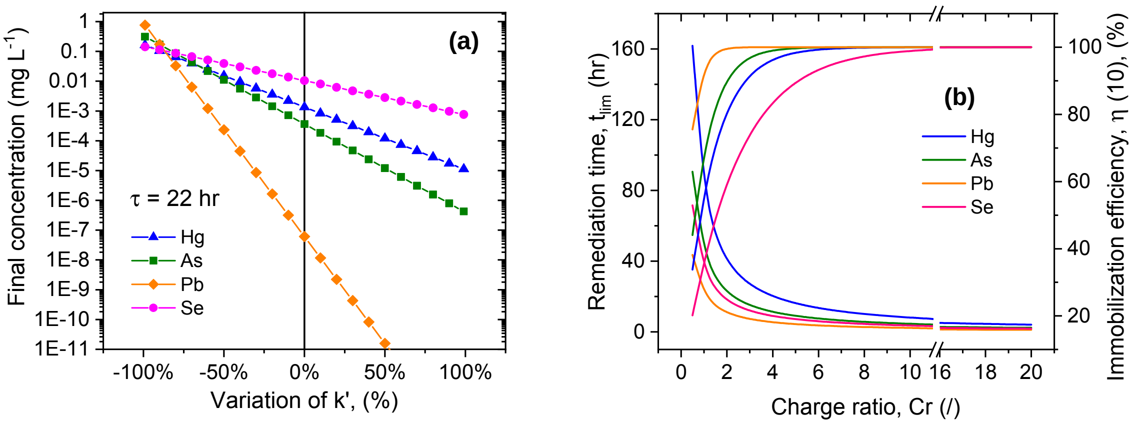

Figure 3. Sensitivity of simulated HMs concentrations in the leachate after 22 hours milling to the variation of the parameter k' (a); simulated effect of Cr change on the remediation time and immobilization efficiency after 10 hours of mechanical treatment (b).

Except for the case of Pb, the model is not very sensitive to the variation of k' values for the considered HMs (cf. Figure 3a). Hence, while further experiment and simulation should be devoted to assessing the effect of mechanical treatment on Pb immobilization, it can be reasonably stated that the parameter values and the model are reliable. Accordingly, the model can be used as a tool for the extrapolation of crucial information about the performance of the system under different operating conditions (charge ratios and milling times) and scales. An example of the application of the model to this aim is reported in Figure 3b where the effect of different charge ratios (Cr) on the time needed to remediate the soil (i.e reducing the HMs concentrations in the leachate below their regulatory limits) and the immobilization efficiency after a mechanical treatment prolonged for 10 hours, is simulated. As expected, the increase of charge ratio determines an exponential decrease of the remediation time and an increase of the immobilization efficiency after 10 hours. The interesting aspect to observe in Figure 3b is that, according to the model, by using a charge ratio of about 10, all the heavy metals would be effectively immobilized in the soil within 10 hours of mechanical treatment. To corroborate the above model extrapolation, a further experiment was performed by using a Cr = 10 and a milling time of 10 hr. The results are shown in Figure 4 in terms of leached HMs concentrations normalized to their corresponding regulatory threshold. It should be noted that the same untreated soil of the one considered in the previous experiments was adopted to perform this trial.

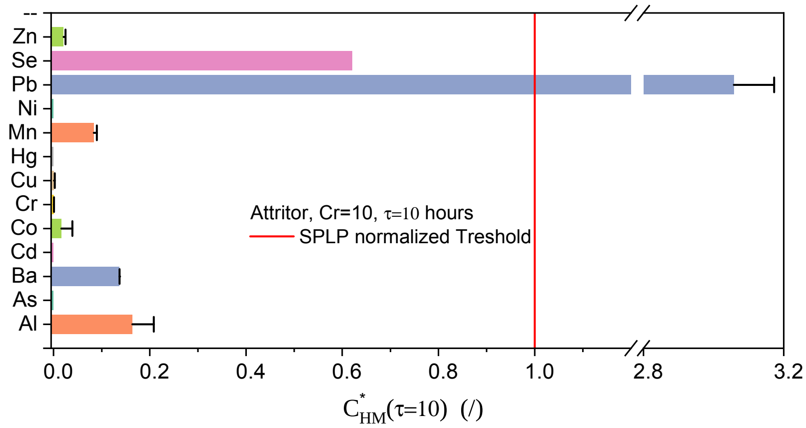

Figure 4. Effect of 10-h ball milling by the attritor using C_R=10 on the normalized concentrations of leached HMs

It can be observed that all the HMs normalized concentrations, except Pb, were well below their corresponding regulatory limit (cf. red line) for drinkable water thus corroborating modelling extrapolations. The peculiarity of lead is probably due to the fact that this metal is more sensitive to the impact action of SPEX rather than the attrition phenomena induced in the Atrittor Mill. In contrast, the concentration of Pb was still higher than its threshold limit after 10 hours milling even when using Cr=10. This might be because the attritor mill, where attrition actions prevail over impact ones, is probably less effective than the SPEX in triggering the transformations leading to Pb immobilization. However, it should be noted that much higher charge ratios than the ones here considered (i.e. Cr = 50 and even 100) are typically used to take advantage of attrition milling at the industrial scale. Therefore, according to model extrapolations and experimental evidence it is likely that a suitable Cr exists at which leached Pb concentration can be reduced below its regulatory threshold. Furthermore, according to Chen et al., (2019), suitable amounts of hydroxyapatite or $Ca_3(PO_4)_2$ could be mixed with the soil before the mechanical treatment to reduce Pb leachability. Finally, it should be highlighted that it is unrealistic assuming that groundwater filtrating through the soil, even if remediated, could be used for drinking purpose. Finally, large capacity mills exploiting high energetic collisions rather than attrition, such as for example Zoz mills (Boschetto et al. 2013), might better replicate the results obtained in the laboratory with the SPEX mill even with reference to Pb immobilization.

4. Conclusions

SPEX and Attritor Mills have been proved to be valuable devices to treat HMs-contaminated soils by mechano-chemical technique. The semi-empirical mathematical model proposed in this study was successfully used to evaluate the effects of the milling process on solid-state transformations by taking advantage of experimental data obtained during leaching procedures. To evaluate the scale up potentialities of the HMs immobilization technique, experiments were performed with an Attritor Mill that allows larger amounts of soil and investigation for pilot- and full-scale applications. The “charge ratio” parameter has been identified as a scale-up factor for both Spex and Attritor Mills. For most HMs in the leachate, the concentration was reduced below its corresponding regulatory threshold. Attritor mill was less efficient in reducing the leached concentration below Pb limit in comparison to the Spex. In part, this is related to the different mechanical action of the two devices and that higher charge ratios are needed for Attritor mill. Both mill performances were well predicted by the proposed model without tuning any model parameters for different operating conditions (i.e., charge ratio). The model represents a step towards the making of a tool for the design, optimization and control the mechano-chemical treatment at the field scale. Charge ratios or collision-based mills is a key factor in designing HM immobilization for scale-up of mechano-chemical reactors.

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