CHEMICAL ENGINEERING TRANSACTIONS, Volume 11, 2007
Edited by Sauro Pierucci

Immobilization of heavy metals in contaminated soils

Selena Montinaro[1], Alessandro Concas[2], Massimo Pisu[2], Sarah Fadda[3], Alberto Cincotti[3] and Giacomo Cao[1,2,3*]
[1]Centro Interdipartimentale di Ingegneria e Scienze Ambientali (CINSA) and Cagliari Laboratory of Consorzio Interuniversitario Nazionale "La Chimica per l'Ambiente" (INCA), Via San Giorgio 12, 09123 Cagliari, Italy.
[2]CRS4, Center for Advanced Studies, Research and Developement in Sardinia Parco Scientifico e Tecnologico, POLARIS, Edificio 1, 09010 PULA (CA - Italy)
[3]Dipartimento di Ingegneria Chimica e Materiali, Università degli Studi di Cagliari and Unità di Ricerca del Consorzio Interuniversitario Nazionale "La Chimica per l'Ambiente" (INCA), Piazza d'Armi, 09123 Cagliari, Italy

1. Introduction

It is well known that specific transformations such as combustive or gradual reactions, amorphization, activation, microstructural refinement, comminution, cold welding and alloying (Suryanarayana, 2001), can be promoted through mechanical treatments performed by means of ball milling (BM). The degradation of organic pollutants such as exachlorobenzene (Mulas et al., 1997), PCBs and other organo-halogenated compounds (Rowlands et al., 1994) have been successfully accomplished by mechanically induced BM reactions. The latter ones 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). 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). 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 been analyzed only by Montinaro et al. (2007). In this paper 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 with or without the use of additional reactants (hydroxylapatite) through the exploitation of weak transformations induced on the treated soil by mechanical loads taking place during collisions among milling media (Concas et al., 2006).

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 soils (SS), kaolinitic soils (KS) and bentonitic soils (BS). The amount of each compound used for preparing synthetic soils, has been calculated according to the procedure suggested by Lo and Yang (1999). Soil contamination has been carried out in a temperature controlled shaker at 25°C by contacting known weights of each synthetic 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 $Zn(Cl)_2$ were 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. 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). When considering the experiments conducted with additives, hydroxylapatite ($Ca_{10}(PO_4)_6(OH)_2$) was added to the polluted soil on a 3%, 4% and 5% wt/wt basis (related to the total weight of the soil-hydroxylapatite mixture). Once contaminated, soils with or without hydroxylapatite (HA), were mechanically treated for different time intervals by Spex Mixer/Mill mod. 8000 whose characteristics and operating conditions are reported by Montinaro et al. (2007). Different soil amounts were introduced inside the vial together with two stainless steel balls of 8 g and 10 mm in diameter in order to investigate the effect of the ball to powder ratio (BPR). At the end of each programmed time interval of mechanical treatment, as well as for untreated soils (i.e. milling time equal to 0), soils and soil-HA mixtures were suitably sampled to be analysed. The degree of immobilization of heavy metals was evaluated using the "synthetic precipitation leaching procedure (SPLP)" reported by USEPA (1996). Immobilization efficiency was calculated through the following equation:

$$\eta(t)\% = \left(1 - \frac{C(t)\cdot V_{leach}}{q^{24h}\cdot W_{solid}}\right)\cdot 100 \qquad (1)$$

where $\eta(t)$ *%* is the immobilization efficiency (%) of the soil mechanically treated for a time interval equal to *t* (s), *C(t)* (mg L^{-1}) is the heavy metal concentration in the leachate, V_{leach} is the leachate volume (L), q^{24h} (mg kg^{-1}) is the initial heavy metal concentration in the untreated soil (cf. equation 1) and W_{solid} (kg) is the soil weight which undergoes the test. Further analyses were performed in order to elucidate immobilization mechanisms and verify if soil alterations occurred during mechanical treatment. X-ray diffraction (XRD) were used to identify crystalline phases in solid samples. Also analyses of particle size distributions after each ball milling treatment were performed (cf. Montinaro et al., 2006).

3. Results and discussion

Different contaminated soils mixtures were prepared as described in the experimental section: a sandy soil (SS), a clayey bentonitic soil (BS) and a clayey kaolinitic soil (KS) characterized by a Pb(II) concentration in the solid phase of 39000, 102000 and 185000 mg kg^{-1}, respectively. Once contaminated, soils were mixed with HA amounts on a 5% wt/wt basis. As far the soil-HA mixtures obtained, concentration of Pb(II) from the SPLP test was equal to to 333 mg L^{-1}, 228 mg L^{-1}, 1783 mg L^{-1} for the SS, BS and KS, respectively. The effect of mechanical treatment on Pb(II) immobilization efficiency, under different milling regimes (i.e. BPR equal to 2, 4 and 6) and for different treatment times, is shown in Figures 1a – 1c.

From Figure 1 it should be noted that immobilization efficiency increases when the soil-HA mixtures are mechanically treated. This last effect is more evident when the milling time is augmented. These results highlight that mechanical treatment may induce specific transformations on soil and HA particles that cause an increase of the immobilization efficiency of the corresponding soil-HA mixtures. As far as the modifications induced on HA particles by mechanical treatment are concerned, it is reasonable to assume that a particle refining is obtained as a result of milling. This fact probably leads to an increase in the specific surface area of HA particles. Moreover, the accumulation of crystalline defects (amorphization) on the HA lattice may determine a thermodynamic instability of HA particle surfaces which may determine an higher tendency to react or dissolve. As for the soil particles only some considerations may be formulated about 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 (Weng, 2004) between soil surface sites and heavy metal complexes. When ball milling process starts, soil particles are subjected to high energetic collisions that may promote aggregation and breakage phenomena. 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 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 result in higher adsorption capacity thus increasing the corresponding immobilization efficiency of heavy metals.

Because the use of high percentages of HA may affect the economical feasibility of the proposed technique and, at the same time, potentially induce negative effects such as phyto-toxitcity and chemical modification of the intrinsic properties of soils, further trials with less HA wt/wt percentages were performed. Figure 2 shows the results of the milling trials on the soil-HA mixtures containing 0%, 3%, 4% and 5% wt/wt of HA, respectively. The BPR parameter was fixed to 4 for each trial. From Figure 2 it may be seen that by prolonging mechanical action up to 5h, immobilization efficiency of the soil HA mixtures reaches approximately the same value when different percentages of HA (0%, 3%, 4%) are used for all the considered soils. This fact indicates that, within the compositional range 0%-4%, a suitably prolonged mechanical action may represent a valid alternative to the use of HA for immobilization of Pb(II) in sandy soils. On the basis of these last results further experiments were performed in order to verify if higher immobilization efficiencies may be achieved by mechanically treating soils without HA. The following synthetic soils contaminated by heavy metals (Cd(II), Pb(II), Zn (II)) were prepared: a sandy soil (SS) contaminated with Pb(II), Cd(II) and Zn(II) concentrations of 32875, 20000 and 28000 mg kg^{-1}, respectively; a bentonitic soil (BS) with Pb(II), Cd(II) and Zn(II) concentration levels of 107181, 20000 and 10000, respectively; a kaolinitic soil (KS) contaminated by Pb(II), Cd(II) and Zn(II) concentrations of 107857, 24000 and 17000 mg kg^{-1}, respectively.

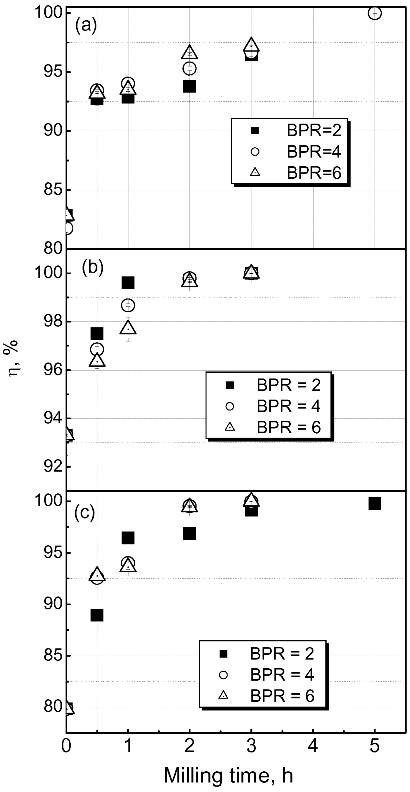

Figure 1 Effect of mechanical treatment on immobilization efficiencies of soil-HA (5%) mixtures obtained using different BPR: (a) SS, (b) BS, (c) KS.

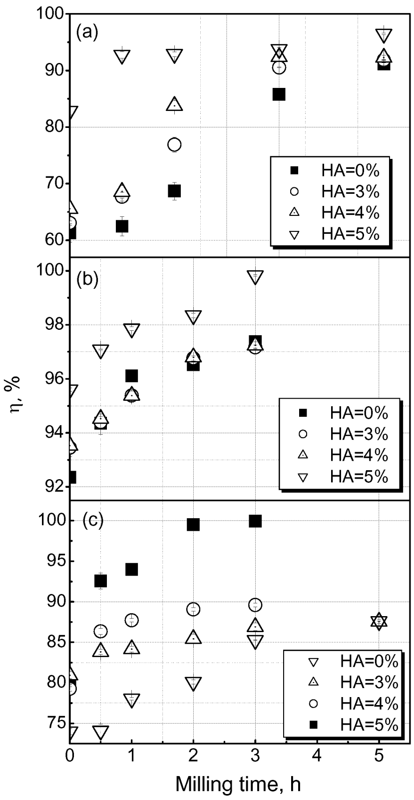

Figure 2 Effect of mechanical treatment on immobilization efficiencies of soil-HA mixtures obtained using different amounts of HA: (a) SS, (b) BS, (c) KS.

The effect of mechanical treatment, suitably prolonged for different milling times, on heavy metals (Pb(II), Cd(II), Zn(II)) immobilization efficiency and the corresponding concentration released in the leachate from SPLP test are shown in Figure 3, 4, 5, respectively. From these Figures 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. By considering the results reported in Figures 3, 4 and 5, it may be pointed out that mechanical action determines an important increase of immobilization capacity of the investigated soils for all the considered heavy metals.

In order to elucidate the mechanisms which determine the increase of 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 have been performed. XRD analyses revealed that only a partial amorphization occurs when the soils are milled. 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. This effect may be explained considering that aggregation phenomena may prevail on breakage.

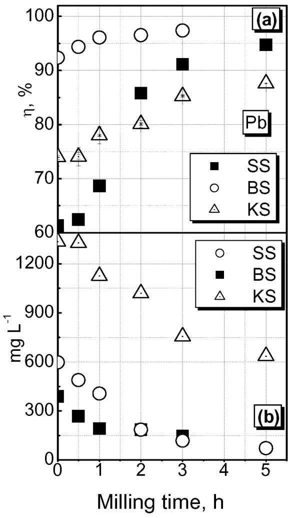

Figure 3. Effect of mechanical treatment on (a) immobilization efficiency of Pb(II) and (b) Pb(II) concentration in leachate.

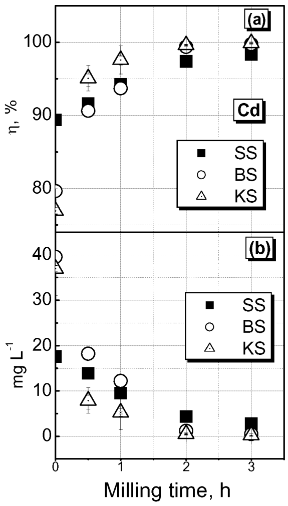

Figure 4. Effect of mechanical treatment on (a) immobilization efficiency of Cd(II) and (b) Cd(II) concentration in leachate.

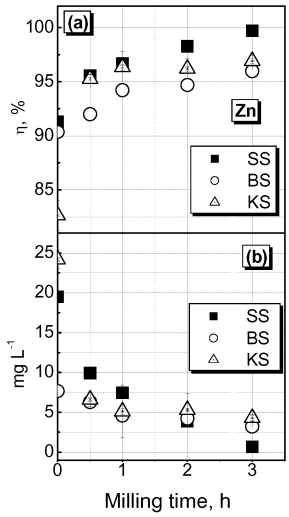

Figure 5. Effect of mechanical treatment on (a) immobilization efficiency of Zn(II) and (b) Zn(II) concentration in leachate.

Further investigations investigation is needed to elucidate the relevant mechanisms taking place (Montinaro et al., 2007). 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), 1-180 mg kg^{-1} for Cd(II) and 1000-50000 mg kg^{-1} for Zn(II) (Markus and McBratney, 2001) have been performed. To this aim, SS contaminated soils with Pb(II), Cd(II) and Zn(II) concentrations of 621.5, 88.6 and 1002 mg kg^{-1}, respectively; BS contaminated soils with Pb(II), Cd(II) and Zn(II) concentrations of 954.4, 98.0 and 1175 mg kg^{-1}, respectively; KS contaminated soils with Pb(II), Cd(II) and Zn(II) concentrations of 939.4, 76.28 and 915.0 mg kg^{-1}, respectively, were prepared 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 Figures 6a, 6b and 6c, 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 3h for Cd(II) and Zn(II), respectively) heavy metal concentration in leachate from SPLP test is lower than the regulatory limit (i.e. 0.015, 0.005 and 0.5 mg L^{-1} for Pb(II), Cd(II) and Zn(II) , respectively) proposed by USEPA (1996) for drinkable water.

In this work it is shown that mechanical treatment allows one to achieve the immobilization of heavy metals in contaminated soils either when HA is added or not.

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 soils are detected except for a weak amorphization and a relative increase of particle size.
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 related to drinkable water.

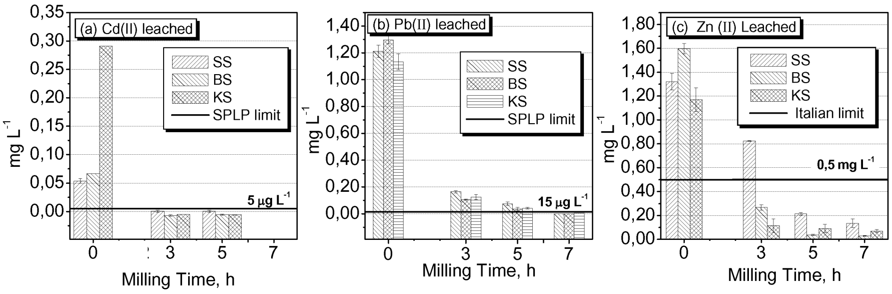

Figure 6. Effect of mechanical treatment on the leachable fraction of heavy metals in soils and comparison with USEPA thresholds for (a) Cd(II), (b) Pb(II) and (b) Zn(II).

5. 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.

6. References

Cao, G., Doppiu, S., Monagheddu, M., Orru', R., Sannia, M., Cocco, G., 1999, Ind. Eng. Chem. Res. 38, 3218.
Caschili, S., Delogu, F., Concas, A., Pisu, M. and Cao, G., 2006, Chemosphere 63, 987.
Concas, A., Lai, N., Pisu, M. and Cao, G., 2006, Chem. Eng. Sci. 61, 3746.
Lo, I. M. and Yang, X. Y., 1999, Water Air Soil. Pollut. 109, 219.
Lu, L., Lai, M.O. and Zhang, S., 1997, J. Mater. Process. Technol. 67, 100.
Markus, J. and McBratney, A. B., 2001, Environ. Int. 27, 399.
Montinaro, S., Concas, A., Pisu, M. and G. Cao, 2006, Chem. Eng. J., submitted.
Montinaro, S., Concas, A., Pisu, M. and G. Cao, 2007, Chemosphere 67, 631.
Mulas, G., Loiselle, S., Schiffini, L., Cocco, G., 1997, J. Sol. State Chem. 129, 263.
Rowlands, S.A., Hall, A.K., Mccormick, P.G, Street, R., Hart, R.J., Ebell, G.F.,
Schaffer, G.B. and McCormick, P.G., 1992, Metall. Trans. A, 23, 1285.
Suryanarayana, C., 2001, Prog. Mater. Sci. 46, 1.
USEPA, 1996, Test methods for evaluating solid waste, SW846, 3rd Edition. Office of Solid Waste and Emergency Response, Washington D.C.
Weng, C.H., 2004, J. Colloid Interface Sci. 272, 262.