Chemical Engineering Journal 149 (2009) 19–24

Contents lists available at ScienceDirect

Chemical Engineering Journal

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

Valorization of coal fly ash by mechano-chemical activation
Part II. Enhancing pozzolanic reactivity

P. Stellacci[a,*], L. Liberti[a], M. Notarnicola[a], P.L. Bishop[b]

[a] *Technical University of Bari, Department of Environmental Engineering and Sustainable Development, Viale del Turismo 8, 74100 Taranto, Italy*
[b] *University of Cincinnati, Department of Civil and Environmental Engineering, Cincinnati, OH 45221, USA*

ARTICLE INFO

Article history:
Received 22 May 2007
Received in revised form 14 May 2008
Accepted 20 June 2008

Keywords:
Coal fly ash
Mechano-chemical activation
Stabilization/solidification
Phenol
Lead

ABSTRACT

The pozzolanic and adsorptive characteristics of coal fly ash have been enhanced by mechano-chemical activation in order to evaluate their potential utilization in the stabilization/solidification treatment of hazardous wastes. To that aim a soil artificially contaminated by large amounts of Phenol and Pb underwent that treatment, wherein increasing amounts of powder activated carbon and Portland cement were substituted by mechano-chemically activated fly ash. Under the experimental conditions investigated, very encouraging results, in terms of contaminants leaching and mechanical properties of the stabilized/solidified matrix, were obtained when up to 100% of the powder activated carbon and up to 50% of the Portland cement were substituted by mechano-chemically activated fly ash, thus opening improved possibilities for using this latter in environmental applications.

1. Introduction

The stabilization/solidification (S/S) process is a widely used technology for treating hazardous waste wherein the stabilization with proper additives minimizes the rate of contaminant migration (leaching) into the environment while the addition of a solidifying agent produces a harmless solidified mass [1]. The highly alkaline environment ($pH \geq 11$) provided by cementitious binders like Portland cement, lime and other pozzolanic materials ensures that most inorganic contaminants (e.g. toxic heavy metals) may be effectively immobilized [2].

Due to the large differences among their hydrophobicity and polarity, however, most organic compounds do not react with inorganic binders and can leach relatively rapidly [3–4]. Consequently, the need exists to develop effective and economic S/S systems that can reliably treat hazardous wastes that also contain organic contaminants.

The addition of cheaper adsorbents like coal fly ash (FA, i.e. the organic and inorganic residue resulting from coal combustion, representing an abundant industrial waste worldwide) rather than the effective, but expensive, activated carbon (AC) during S/S treatment would represent an excellent choice to achieve that aim. The organic fraction (i.e. the unburned coal residue) of FA may behave potentially similar to AC while its inorganic fraction (consisting mainly of siliceous and/or aluminous material) may exhibit potential cementitious properties. If properly enhanced, both the adsorptive and pozzolanic potentials of coal FA can turn this abundant industrial waste into a new opportunity for the protection of the environment.

Accordingly, coal FA has been submitted to mechano-chemical activation, a well established procedure already in use in several industrial applications [5–28], with the aim of using it as a potential substitute for AC and/or Portland cement during the S/S treatment of soil contaminated by Phenol and Pb, typical organic and inorganic industrial pollutants [29]. The results concerning the enhancement of the adsorptive behaviour of mechanically activated fly ash (MAFA) towards Phenol have already been presented in Part I of this study [30]. The effective capability of MAFA to prevent the leaching of both Phenol and Pb is described in this Part II.

2. Materials and methods

The characteristics of the commercial powder activated carbon (PAC) and the coal fly ash investigated, before and after its mechanical activation together with the best operating conditions for this latter, have already been described [30].

Abbreviations: AC, activated carbon; FA, fly ash; FA_x, fly ash with *x* LOI content; FTIR, Fourier transform infra red; GAC, granular activated carbon; HEM, high energy mill; LOI, Loss On Ignition (%); MA, mechanochemical activation; $MAFA_x$, mechanochemically activated fly ash with *x* LOI content; NMR, nuclear magnetic resonance; PAC, powdered activated carbon; S/S, stabilization and solidification treatment.

[*] Corresponding author. Tel.: +39 099 4733203; fax: +39 099 4733203.
E-mail address: p.stellacci@poliba.it (P. Stellacci).

1385-8947/$ – see front matter © 2009 Published by Elsevier B.V.
doi:10.1016/j.cej.2008.06.042

Table 1
Main components of Portland cement

Component	Formula	Percentage by mass (%)
Tricalcium silicate	$3CaO*SiO_2$	45–60
Dicalcium silicate	$2CaO*SiO_2$	5–30
Tricalcium aluminate	$3CaO*Al_2O_3$	6–15
Tetracalcium ferroaluminate	$4CaO*Al_2O_3*Fe_2O_3$	6–8
Gypsum	$CaSO_4*2H_2O$	3–5

The natural siliceous cube test standard sand (Societé Nouvelle du Littoral, Leucate, France), consisting mostly (≥98%) of rounded silica particles, was used as a soil substitute because sand represents the least adsorptive and most conservative component of soil, wherein any adsorption mechanism can be neglected.

Type I 42.5N Portland cement containing small variable amounts of Na and K oxides was used. The typical characteristics are shown in Table 1.

2.1. Soil contamination procedure

In order to study separately the S/S mechanisms for both organic and inorganic contaminants, two contaminated soils were prepared. The first was obtained by mixing 2 kg (on dry basis) of sand with 1 l of a solution containing 4000 mg l^{-1} of Phenol prepared in deionized water (*Phenol-contaminated soil*, loaded with ≈2000 mg Phenol kg^{-1} dry soil), while the second was prepared with 1 l of a solution containing 20,000 mg l^{-1} of Pb as $Pb(NO_3)_2$ prepared in deionized water (*Pb-contaminated soil*, loaded with ≈10,000 mg Pb kg^{-1} dry soil). A minimum headspace was maintained in the jars and the periodic end-over-end mixing was used. After preliminary tests confirmed that there was no appreciable adsorption of lead or Phenol on sand particles (≥99% of the contaminants remained in solution after 30 days of mixing), both soil samples were allowed to age for 7 days and, after separation from the liquid phase, were dried at 105 °C overnight.

2.2. S/S sample preparation

In order to determine MAFA's adsorptive capacity to prevent Phenol leaching, in a first set of tests used increasing amounts (1–2–5% w/w sand) of $MAFA_{27}$ and $MAFA_{80}$ (i.e. fly ash from a near-by coal power station with 27 and 80% LOI which had been mechano-chemically activated by 4 h milling in a high energy mono-planetary ball mill under N_2 atmosphere) were used and compared with similar addition of a commercial PAC (Darco G-60 by J.T. Baker, Phillisburg, NJ). These amounts were mixed with 100 g of Phenol-contaminated soil and submitted to the S/S treatment under the mix-design conditions reported in Table 2, and Phenol leaching was ascertained by the subsequent leaching tests.

In a second set of tests, aimed at assessing whether the pozzolanic fraction of FA could efficiently replace cement binders, increasing amounts (10–20–50% w/w cement) of FA_3, FA_{27}, $MAFA_3$ and $MAFA_{27}$ (i.e. non-activated or activated fly ash with 3 or 27% LOI) were used in substitution of Portland cement and mixed with 100 g of Pb-contaminated soil, as reported in Table 3. The S/S treatment without any cement substitution was also carried out as a blank.

Table 2
Mix design for S/S treatment to prevent Phenol leaching

Soil (g)	Addition (%)	Addition (g)	Cement (g)	Water (g)
100	0	0	33.3	16.65
100	1	1	33.3	16.65
100	2	2	33.3	16.65
100	5	5	33.3	16.65

Table 3
Mix design for S/S treatment to prevent Pb leaching

Soil (g)	Substitution (%)	Substitution (g)	Cement (g)	Water (g)
100	0	0	33.3	16.65
100	10	3.33	29.97	16.65
100	20	6.66	26.64	16.65
100	50	16.65	16.65	16.65

A soil/water/binder ratio of 1/0.5/0.33 was used to prepare the stabilizing mixture. After proper hand mixing, the slurry was put into moulds, covered with a lid to produce a zero-headspace and allowed to cure for 28 days.

2.3. Leaching test

Samples of the original contaminated soil, as well as its 3–7–14–28 days cured S/S specimens, were crushed to a ≤4 mm grain size for ≥95% of their mass and extracted with distilled water for 24 h at a 10 l kg^{-1} liquid/solid ratio, according to the European Standard EN 12457-2 leaching test [31]. The suspensions were then filtered through a 0.45 μm Iso-Disc filter (Supelco, San Francisco, CA, USA) and the leachate was analyzed for Phenol and Pb with a Lambda 25 UV/visible spectrophotometer and an AAnalyst 300 Flame Atomic Absorption spectrophotometer (both by PerkinElmer, Wiesbaden, Germany) by the direct aspiration method, respectively. Simple mass balances between the solid and the liquid phases allowed one to calculate the leaching (%) of each contaminant.

A Nicolet Magna 760 Fourier Transform Infrared (FTIR) spectrometer (Thermo Electron Co., Madison, WI) was used at different curing times for the Pb-contaminated soil samples in order to understand in which form Pb had been stabilized in the solidified waste. Spectral analyses were carried out over the 4000–400 cm^{-1} range at 4 cm^{-1} resolution by averaging 256 scans. Specimens were prepared by mixing 1 mg of sample in 300 mg of KBr.

XRD analysis was also carried out and compared with FTIR spectra.

3. Results and discussion

The contaminated soil was tested for chemical leaching and it was found to yield Phenol and Pb concentration in the leachate equal to 50 and 321 mg l^{-1}, respectively, greatly exceeding the Italian allowable limits currently in force.

In order to explain the effect of these pollutants on the hydration reactions of the binders during the S/S treatment, their influence on the treated waste microstructure (and therefore on the performance of the treated product) needs to be discussed.

3.1. Phenol–cement interaction

Better understanding of the soil-binder interaction is essential in the S/S treatment of soil contaminated by organic waste since various mechanisms (adsorption, interference with cement setting, etc.) could control the process [32]. According to Pollard et al. [33], when cement is dispersed in water Ca ions are rapidly leached out from the solid to form a solution of (mainly) calcium hydroxide, leaving behind silica-rich cement grains. Aqueous $Ca(OH)_2$ is thought to react with silicic acids on cement surfaces to form a gelatinous semi-permeable C–S–H membrane around cement particles, which then extends to interconnect all the granules. This membrane allows the transport of water, but not of Ca ions, thus

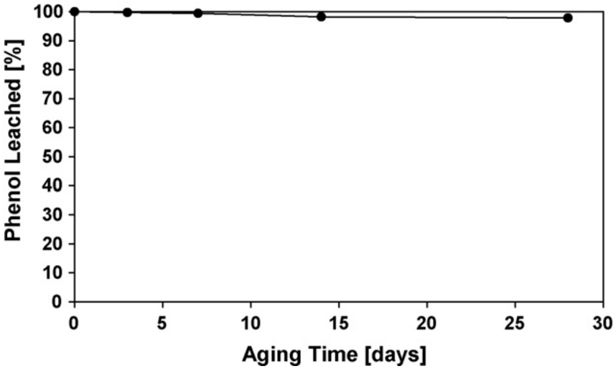

Fig. 1. Phenol leaching from S/S specimens with 0% adsorbent addition.

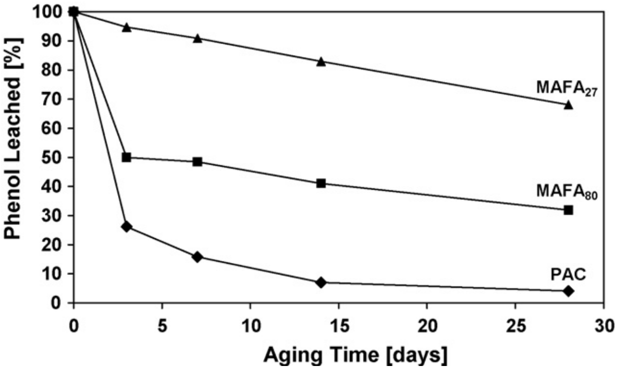

Fig. 3. Phenol leaching from S/S specimens with 2% adsorbent addition.

inducing a dormant phase in the hydration process. Water passing through this semi-permeable membrane causes the hydration of the cement grains enclosed therein. Ca ions and hydrates remain within the membrane until build-up of the osmotic pressure causes the rupture of the membrane with development of new hydration products.

Scouten and Dougherty [34] suggested that the reaction of $Ca(OH)_2$ and Phenol at room temperature forms a Ca–Phenate complex (hydroxycalcium phenoxide) according to:

$$Ca(OH)_2 + C_6H_5OH \rightarrow Ca(OH)O\text{–}C_6H_5 + H_2O$$

In the presence of an aqueous solution of Phenol, as in the present case, the Ca released by the initial dissolution of cement reacts with Phenol dissolved in the pore water and thus becomes unavailable to form the C–S–H gel membrane. This forces the hydration products to enter the solution, causing a local peak in the concentration of Ca^{2+} ions. When the solution is saturated with the Ca–phenol complex, the Ca ions further released start to complex with silicates to form the C–S–H gel membrane. This mechanism retards the hydration of cement and yields a significant reduction in the leaching of Phenol.

Present experimental results show that the leaching behaviour of Phenol from the S/S matrix is influenced by the amount and nature of the adsorbent used and by the curing period. It should be primarily remembered that at the alkaline pH (≥ 11) provided by the cement matrix, Phenol (pK 9.89 at 20 °C) is largely dissociated and the Phenate anion prevails. Compared with Fig. 1, showing that it is almost totally and rapidly leached out when no adsorbent is added, Figs. 2–4 indicate that Phenol leaching decreases drastically and almost vanishes after the 28 days curing period upon addition of 1–5% amounts of PAC. Furthermore, it is interesting to note that quite comparable results were achieved with a similar addition (1–5%) of MAFA, with performance obviously increasing with its LOI content (i.e. $MAFA_{80} > MAFA_{27}$), and that the largest part of Phenol immobilization occurs in the first 3 days of curing.

A possible explanation of this effect may be the encapsulation of Phenol in the C–S–H gel matrix of the cement: as curing time progresses, Phenol may actually have been adsorbed on the adsorbent rather than being chemically locked into the cement pores.

The experimental results presented in Figs. 1–4 conclusively confirm the effective ability of $MAFA_{80}$ to prevent Phenol leaching when used to substitute equivalent amounts of PAC during the S/S treatment of contaminated soil under the conditions investigated.

3.2. Pb–cement interaction

As cement hydrates, the C–S–H gel forms, followed by hardening of the material while thin densely packed silicate fibrils grow and interlace. In the highly alkaline environment of the cement paste, many heavy metals in the hazardous waste are converted into insoluble hydroxides and/or silicates and remain trapped within the pores of the cement paste matrix and/or they become physically bound to the paste lattice. These mechanisms yield a significant reduction in the leaching of contaminant metals.

A vast literature, however, indicates that impurities such as Pb in the matrix may inhibit the setting and curing of cement by interfering with the hydration process due to coating of the reacting surfaces. Such metal-induced retardation can limit the formation of major cement hydration products, and this may affect its microstructural and physical properties, including metal leaching [35–46].

It is known that the efficiency of the S/S process for treating hazardous wastes containing heavy metals greatly depends on solution pH [2]. Amphoteric metals such as Pb exhibit enhanced solubility at

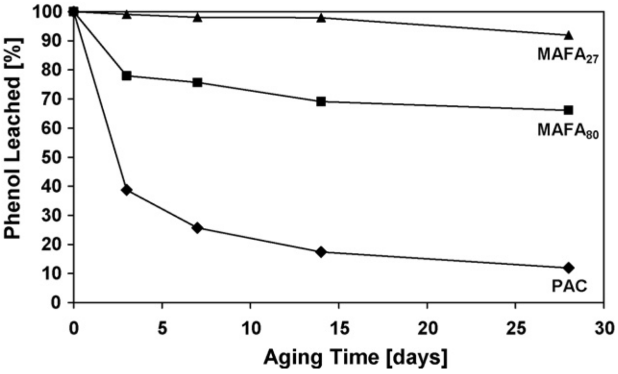

Fig. 2. Phenol leaching from S/S specimens with 1% adsorbent addition.

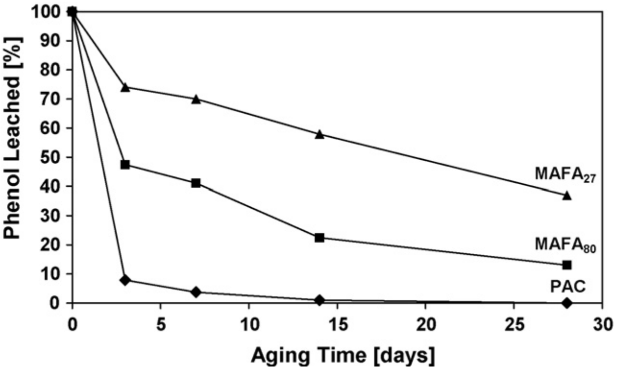

Fig. 4. Phenol leaching from S/S specimens with 5% adsorbent addition.

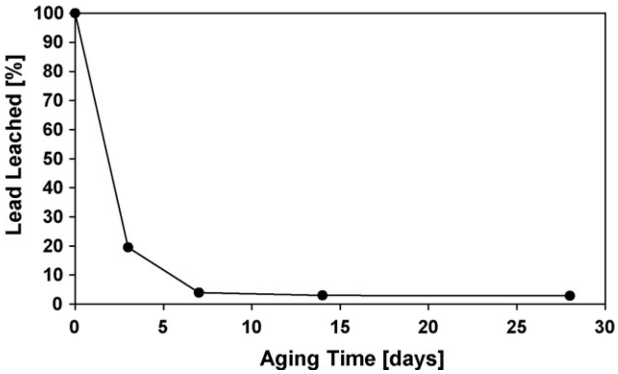

Fig. 5. Pb leaching from S/S specimens with 0% adsorbent addition.

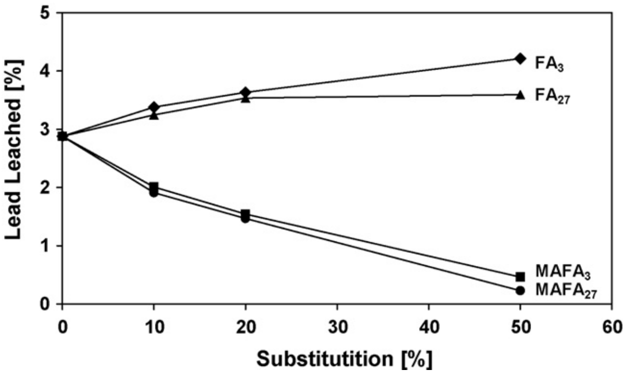

Fig. 6. Pb leaching from S/S specimens as a function of cement substitution (28 days aging).

elevated pH, significantly increasing from pH 9.5 to ≥11 [47]. Upon the S/S application treatment with cement, pH would always be ≥8 and in most cases ≥11 [48]. Thus, the mechanism responsible for the great decrease in leaching of Pb in the 12.4–13 pH range is mainly due to its entrapment in the crystal structures of the cementitious compounds formed as a result of the pozzolanic reactions.

Bishop [49] found that Pb leached out at much slower rates than expected on the basis of its hydroxide solubility and explained this phenomenon as due to strong Pb complexation in the silica matrix, so it would not leach to any great extent until this latter breaks down. Other investigators suggested that Pb immobilization in cement was due to its inclusion by an addition reaction in calcium silicate hydrates (C–S–H), whose exact stoichiometry is still unknown [50–52]. Studying a Pb-polluted cement sample submitted to sequential extraction, Bishop [53] found that Pb was bound along with Ca, Si, and, to a lower extent, Fe and Al.

In conclusion, immobilization of Pb by the hydraulic binders during the S/S treatment probably occurs by one or a combination of the following mechanisms:

$$\text{Addition}: \quad \text{C–S–H} + \text{Pb} \rightarrow \text{Pb–C–S–H}$$

$$\text{Substitution}: \quad \text{C–S–H} + \text{Pb} \rightarrow \text{Pb–S–H} + \text{calcium}$$

$$\text{Precipitationofanewcompound}:$$

$$Pb^{2+} + OH^{-} + Ca^{2+} + SO_4{}^{2-} \rightarrow \text{mixedsalts}$$

As shown in Fig. 5, Pb leaching from the S/S treated contaminated soil with no adsorbent addition was as low as ≤4% after 7 days of aging and remained constant thereafter. This result clearly confirms the effectiveness of Portland cement *per se* in stabilizing Pb in contaminated soil [54,55].

As previously seen for Phenol, substitution of Portland cement with MAFA not only confirmed, but also improved this result. As shown in Fig. 6 and compared with the experimental results in Fig. 5, substituting up to 50% of the Portland cement with non-activated FA (FA_3 and FA_{27}) provided comparable results with the former after 28 days curing time (≤4% Pb leaching). Furthermore, still better results (≤1% Pb leaching) were obtained when the substitution occurred with $MAFA_3$ and $MAFA_{27}$, thus confirming the beneficial effect of mechano-chemical activation of coal fly ash for S/S purposes.

The negligible influence of LOI in Fig. 6, for both MAFA and FA, indicates that, under the conditions investigated, Pb leaching from the S/S matrix depended only on the curing period and the amount of fly ash added, not on its carbonaceous content.

The experimental results in Figs. 5 and 6 thus clearly confirm the effective ability of MAFA, almost independently of its organic content, to prevent heavy metal leaching when used in substitution for Portland cement during the S/S treatment of soil contaminated by Pb under the conditions investigated.

As described elsewhere [56–63], the basic mechanical properties of the S/S matrix in the present investigation were not seriously impaired by substituting up to 50% Portland cement with fly ash, mechanically activated or not.

3.3. Mineralogy modifications

Fig. 7 shows the variations of the FTIR spectra with aging of the blank sample (i.e. an S/S specimen with no adsorbent addition). The FTIR spectra present particular regions where the main vibration and deformation bands of Si–Al, S, C, N and OH are concentrated [64].

1. Si (Si–O and Si–O–Si) and Al (Al–O and Al–O–Al) vibrational bands are detected in the 1100–400 cm^{-1} region, where the 1100–900 cm^{-1} and 500–400 cm^{-1} regions correspond to υ_3 (Si–O) and υ_4 (O–Si–O) stretching vibration of the SiO_4 tetrahedron, respectively. Mineralogy in this interval is mainly quartz, pozzolans and calcium silicates.
2. Sulphur shows vibrational bands (S–O) in three regions: 1300–1100, 1685–1620 and 3600–3100 cm^{-1}, with gypsum being the best represented mineral in these mortars.
3. C-vibrational bands (C–O) in the 1500–700 cm^{-1} region (with minor bands at 3000–2500 cm^{-1}) correspond to $CaCO_3$, with mineralogy resulting from cement carbonation.
4. N–O vibrational bands occur between the 1515–1560 and 1345–1385 cm^{-1} regions, where Pb nitrate has been detected.

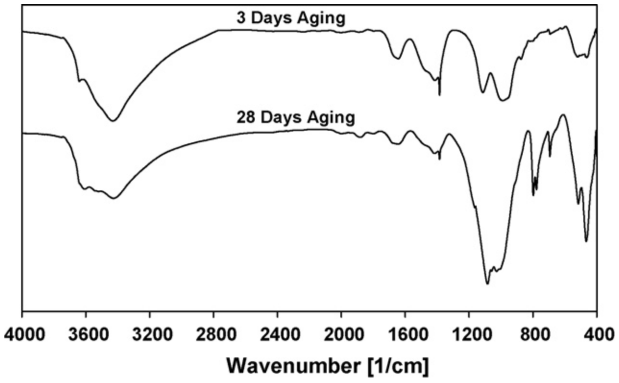

Fig. 7. FTIR spectra of blank sample with 0% adsorbent addition.

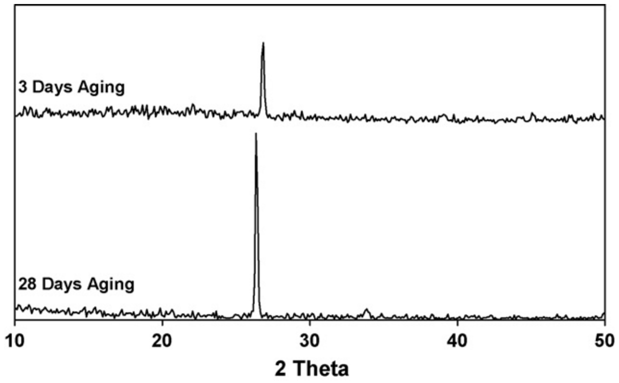

Fig. 8. XRD patterns of blank sample with 0% adsorbent addition.

5. Vibrational and deformational bands of constitutive water (O–H) appear in the 3450–3400 and 1650–1620 cm^{-1} regions, where hydrated minerals, $Ca(OH)_2$ and C–S–H, are also detected.

Some differences appear between the 3 and 28 days aged FTIR spectra, indicating the formation of reaction products as a consequence of cement hydration. The nature of such products evolves with time: after 28 reaction days, the FTIR spectra show a more intensive absorption band in the 1100–400 cm^{-1} region due to the formation of a C–S–H gel-type hydrated Ca silicate.

On the contrary, a less intensive band between 1500 and 1300 cm^{-1} indicates the dissolution of Pb nitrate and the subsequent possible development of insoluble gel products of Pb–C–S–H around cement grains [53]. In addition, water stress (O–H) and deformation (H–OH) bands, in the 3500 and 1600 cm^{-1} regions, respectively, become less intense due to the formation of reaction products such as $Ca(OH)_2$ and C–S–H.

Fig. 8 shows XRD patterns for the blank sample after 3 and 28 days of aging. There appears to be no evidence of Lead hydroxide $Pb(OH)_2$, cerussite $PbCO_3$, hydrocerussite $Pb(CO_3)_2(OH)_2$ or anglesite $PbSO_4$ in the substantially crystalline form. The consistent peak around 27° 2θ was identified as Lead silicate PbO^*SiO_2, confirming that the dissolved Pb may be incorporated as a minor component of a Pb–C–S–H gel formed by adsorption to the leached layer of the cement grain, as found in previous studies [51–53]. The occurrence of Pb–C–S–H is significant from the very beginning and it continues to increase with time.

The FTIR and XRD investigations thus conclusively confirm that adsorption by amorphous polymerized silicates is responsible for significantly reducing Pb leaching from the S/S matrix.

4. Conclusions

The capability to effectively prevent the leaching of typical organic and inorganic contaminants like Phenol and Pb when mechano-chemically activated coal fly ash (MAFA) is used as a substitute for PAC and Portland cement during the S/S treatment of contaminated soil has been demonstrated.

The leaching tests indicated that, while the massive release of Phenol ($\leq$98%) from the solid matrix may be drastically reduced ($\leq$4%) by a small addition (1–5%) of PAC during the S/S treatment of the contaminated soil investigated, even better results may be achieved by a similar addition (1–5%) of MAFA, with performance increasing with its LOI content ($MAFA_{80} > MAFA_{27}$).

Still more encouraging performance may be recorded if MAFA is used as a Portland cement substitute for preventing Pb leaching from the S/S matrix. Compared with the small ($\leq$4%) Pb leaching achieved by Portland cement under the conditions investigated, substitution of up to 50% of this latter with MAFA provided an even lower Pb leaching ($\leq$1%) while maintaining acceptable values of the basic mechanical properties of the S/S matrix.

It may be concluded accordingly that proper mechanical activation discloses a new scenario for utilizing coal fly ash in environmental applications such as the S/S treatment of contaminated soil, where it may be used in a valuable and cost effective manner to substitute for PAC and Portland cement.

Acknowledgments

The authors would like to thank Covecom S.p.A. (Milan, Italy) for financial support of this study as well as Prof. Federico Cangialosi, Technical University of Bari, Italy, for precious suggestions throughout this investigation.

References

[1] M. LaGrega, P. Buckingham, J. Evans, Hazardous Waste Management, McGraw-Hill, New York, NY, 1994.
[2] D. Dermatas, Stabilization/solidification of lead contaminated soils. II. Flow through column leaching, in: Restoration and Protection of the Environment II, Patra University Press, Greece, 1994, pp. 165–172.
[3] H.A. Arafat, V.M. Hebatpuria, H.S. Rho, N.G. Pinto, P.L. Bishop, R.C. Buchanan, Immobilization of phenol in cement-based solidified/stabilized hazardous wastes using regenerated activated carbon: role of carbon, J. Hazard. Mater. B70 (1999) 139–156.
[4] C. Vipulandan, S. Krishnan, Solidification/stabilization of phenolic wastes with cementitious and polymeric materials, J. Hazard. Mater. 24 (1990) 123–136.
[5] N.J. Welham, J.S. Williams, Extended milling of graphite and activated carbon, Carbon 36 (1998) 1309–1315.
[6] V.V. Molchanov, R.A. Buyanov, Scientific grounds for the application of mechanochemistry to catalyst preparation, Kinet. Catal. 42 (2001) 366–374.
[7] N.J. Welham, V. Berbenni, P.G. Chapman, Increased chemisorption onto activated carbon after ball milling, Carbon 40 (2002) 2307–2315.
[8] K.G. Korolev, O.I. Lomovsky, O.A. Rozhanskaya, V.G. Vasil'ev, Mechano-chemical preparation of water-soluble forms of triterpene acids, Chem. Nat. Compd. 39 (2003) 366–377.
[9] V.V. Zyryanov, Ultrafast mechanochemical synthesis of mixed oxides, Inorg. Mater. 41 (2005) 378–392.
[10] H. Onoda, D. Mori, K. Kojima, H. Nariai, Mechanochemical effects on the formation and properties of various nickel phosphates, Inorg. Mater. 41 (2005) 1089–1096.
[11] A.K. Hall, J.M. Harrowfield, R.J. Hart, P.G. McCormick, Mechanochemical reaction of DDT with calcium oxide, Environ. Sci. Technol. 30 (1996) 3401–3407.
[12] S. Saeki, J. Kano, F. Saito, K. Shimme, S. Masuda, T. Inoue, Effect of additives on dechlorination of PVC by mechanochemical treatment, J. Mater. Cycles Waste Manage. 3 (2001) 20–23.
[13] N.J. Welham, Mechanochemical processing of gold-bearing sulphides, Miner. Eng. 14 (2001) 341–347.
[14] H. Mio, S. Saeki, J. Kano, F. Saito, Estimation of mechanochemical dechloration rate of poly(vinyl chloride), Environ. Sci. Technol. 36 (2002) 1344–1348.
[15] F. Cavalieri, F. Padella, Development of composite materials by mechanochemical treatment of post-consumer plastic waste, Waste Manage. 22 (2002) 913–916.
[16] K.G. Korolev, A.I. Golovanova, N.N. Maltseva, O.I. Lomovski, V.L. Salenko, V.V. Boldyrev, Application of mechanical activation to decomposition of toxic chlorinated organic compounds, Chem. Sustain. Develop. 11 (2003) 489–496.
[17] P. Plescia, D. Gizzi, S. Benedetti, L. Camillucci, C. Fanizza, P. De Simone, F. Pagletti, Mechanochemical treatment to recycling asbestos-containing waste, Waste Manage. 23 (2003) 209–218.
[18] S. Saeki, J. Lee, Q. Zhang, F. Saito, Co-grinding $LiCoO_2$ with PVC and water leaching of metal chlorides formed in ground product, Int. J. Miner. Process. 74S (2004) S373–S378.
[19] M.D.R. Pizzigallo, A. Napola, M. Spagnuolo, P. Ruggiero, Mechanochemical removal of organo-chlorinated compounds by inorganic components of soil, Chemosphere 55 (2004) 1485–1492.
[20] J. Ryou, Improvement on reactivity of cementitious waste materials by mechano-chemical activation, Mater. Lett. 58 (2004) 903–906.
[21] V. Birke, J. Mattik, D. Runne, Mechanochemical reductive dehalogenation of hazardous polyhalogenated contaminants, J. Mater. Sci. 39 (2004) 5111–5116.
[22] K. Miyoshi, T. Nishio, A. Yasuhara, M. Morita, T. Shibamoto, Detoxification of hexachlorobenzene by dechlorination with potassium-sodium alloy, Chemosphere 55 (2004) 1439–1446.
[23] G. Intini, L. Liberti, M. Notarnicola, T. Pastore, Mechanochemical treatment for remediation of harbour sediments contaminated by PCBs and PAHs, in: R.F. Olfenbuttel, P.J. White (Eds.), Remediation of Contaminated Sediments. Finding Achievable Risk Reduction Solutions, Battelle Press, Columbus, OH, 2005, ISBN: 1-57477-150-F, CD-ROM.

[24] V.V. Boldyrev, N.Z. Lyakhov, Proceedings of the V International Conference on Mechano-chemistry and Mechanical Alloying “Income 2006”, Novosibirsk, Russia, 2006, http://www.solid.nsc.ru/INCOME2006.

[25] F. Cangialosi, G. Intini, L. Liberti, M. Notarnicola, T. Pastore, S. Sasso, Investigation on Degradation of PAHs by Mechanochemical Treatment, Proceedings of the V International Conference on Mechanochemistry and Mechanical Alloying “Income 2006”, Novosibirsk, Russia, 2006, http://www.solid.nsc.ru/INCOME2006.

[26] V.A. Drebushchak, G. Intini, L. Liberti, M. Notarnicola, T. Pastore, T.N. Drebushchak, V.V. Boldyrev, Dechlorination of contaminated sediments of Ionian sea: thermo-analytical investigation, J. Therm. Anal. Calorim. 90 (2007) 143–146.

[27] V.V. Boldyrev, F. Cangialosi, G. Intini, L. Liberti, O.O. Lomovsky, D. Lupo, M. Notarnicola, T. Pastore, Mechanochemical treatment of contaminated marine sediments. Part I. PCBs degradation, Chem. Sustain. Develop. 15 (2007) 147–156.

[28] V.V. Boldyrev, F. Cangialosi, G. Intini, L. Liberti, O.O. Lomovsky, S. Sasso, M. Notarnicola, T. Pastore, Mechanochemical treatment of contaminated marine sediments. Part II. PAHs degradation, Chem. Sustain. Develop. 15 (2007) 139–145.

[29] P. Stellacci, Valorization of coal fly ash in stabilization/solidification of contaminated soil, Ph.D. thesis, Technical University of Bari, Italy, 2007.

[30] P. Stellacci, L. Liberti, M. Notarnicola, P.L. Bishop, Valorisation of coal fly ash by mechano-chemical activation. Part I. Enhancing adsorption capacity, Chem. Eng. J., submitted for publication.

[31] EN 12457-2, Characterisation of waste. Leaching—compliance test for leaching of granular waste material and sludges. Part 2. One stage batch test at a liquid to solid ratio of 10 l kg^{-1} for materials with particle size below 4 mm (without or with size reduction), 2004.

[32] S. Asavapisit, G. Fowler, C.R. Cheeseman, Solution chemistry during cement hydration in the presence of metal hydroxide wastes, Cem. Concr. Res. 27 (1997) 1249–1260.

[33] S. Pollard, D. Montgomery, C. Sollars, R. Perry, Organic compounds in the cement-based stabilization/solidification of hazardous mixed wastes—mechanistic and process considerations, J. Hazard. Mater. 28 (1991) 313–327.

[34] C.G. Scouten, H.W. Dougherty, Organic chemistry of calcium. Part 3. Steam stripping of metal phenoxides liberates phenol and regenerates the metal oxide, Ind. Eng. Chem. Res. 29 (1990) 1721–1725.

[35] D.L. Cocke, J.D. Ortego, H. McWhinney, K. Lee, S. Shukla, A model for lead retardation of cement setting, Cem. Concr. Res. 19 (1989) 156–159.

[36] D.L. Cocke, M.Y.A. Mollah, The chemistry and leaching mechanisms of hazardous substances in cementitious solidification/stabilization systems, in: R.D. Spence (Ed.), Chemistry and Microstructure of Solidified Waste Forms, Lewis Publishers, 1993.

[37] M. Yousuf, A. Mollah, K. Vempati, T.C. Lin, D.L. Cocke, The interfacial chemistry of solidification/stabilization of metals in cement and pozzolanic material systems, Waste Manage. 15 (1995) 137–148.

[38] C. Tashiro, Hardening property of cement mortar adding heavy metal compound and solubility of heavy metal from hardened mortar, Cem. Concr. Res. 7 (1997) 283–290.

[39] N.L. Thomas, D.A. Jameson, D.D. Double, The effect of lead nitrate on the early hydration of Portland cement, Cem. Concr. Res. 2 (1981) 143–153.

[40] J.D. Ortego, S. Jackson, G.S. Yu, H. McWhinney, D.L. Cocke, Solidification of hazardous substances—A TGA and FTIR study of Portland cement containing metal nitrates, J. Environ. Sci. Health. A 24 (1989) 589–602.

[41] C. Tashiro, J. Oba, The effects of Cr_2O_3, $Cu(OH)_2$, ZnO, PbO on the compressive strength and the hydrates of the hardened C_3A paste, Cem. Concr. Res. 9 (1979) 253–258.

[42] N.M. Alford, A.A. Rahman, The effect of lead nitrate on the physical properties of cement pastes, Cem. Concr. Res. 11 (1981) 235–245.

[43] S. Balzamo, G. De Angelis, F. De Poli, Cementation of toxic sludges: Italian experience, In: Cement industry solution to waste management, in: Proceedings of the 1st International Symposium, Calgary, Alberta, Canada, October 7–9, Calgary, CPCA, 1992, pp. 189–209.

[44] D.L. Cocke, H.G. McWhinney, D.C. Dufner, An XPS-EDX investigation of Portland cement doped with Pb^{2+} and Cr^{3+} cations, Hazard. Waste Hazard. Mater. 3 (1989) 251–267.

[45] M.W. Grutzeck, Hazardous waste (organic, heavy metal): cement disposal, in: Proceedings of the 9th International Congress on the Chemistry of Cement, New Delhi, India, vol. VI, 1992, pp. 119–125.

[46] C.R. Cheeseman, S. Asavapisit, Effect of calcium chloride on the hydration and leaching of lead-retarded cement, Cem. Concr. Res. 29 (1999) 885–892.

[47] D. Geysen, C. Vandecasteele, M. Jaspers, G. Wauters, Comparison of immobilization of air pollution control residues with cement and with silica, J. Hazard. Mater. B107 (2004) 131–143.

[48] D. Dermatas, X. Meng, Utilization of fly ash for stabilization/solidification of heavy metal contaminated soils, Eng. Geol. 70 (2003) 377–394.

[49] P.L. Bishop, Leaching of inorganic hazardous constituents from stabilized/solidified hazardous wastes, Hazard. Waste Hazard. Mater. 5 (1988) 129–143.

[50] M.S.Y. Bhatty, Fixation of metallic ions in Portland cement, Superfund’87, Proceedings of the 4th National Conference on Hazardous Wastes and Hazardous Materials (PCA & D serial No. 1834), Washington, DC, 1987, pp. 140–145.

[51] L. Chatelet, J. Yvon, J.Y. Bottero, A. Bouchelaghem, Statut des sels de Plomb et de Zinc dans les matrices à base de ciment, 1er Congrès International sur les P.S.S., Nancy, J.M. Cases, F. Thomas, Eds., S.té Alpine de Publication, Grenoble, Feance, 1995, pp. 199–206.

[52] D. Lee, Formation of leadhillite and calcium lead silicate hydrate (C–Pb–S–H) in the solidification/stabilization of lead contaminants, Chemosphere 66 (2007) 1727–1733.

[53] P.L. Bishop, Prediction of heavy metals leaching rates from stabilized/solidified hazardous wastes, in: Proceedings of the 18th Mid-Atlantic Industrial Waste Conference, College Park, Lancaster, Boardman Technomic, 1986, pp. 237–252.

[54] B. Alpaslan, M.A. Yukselen, Remediation of lead contaminated soil by stabilization/solidification, Water Air Soil Pollut. 60 (2002) 253–263.

[55] S.L. Lin, W.H. Cross, E.S.K. Chian, J.S. Lai, M. Giabbai, C.H. Hung, Stabilization and solidification of lead in contaminated soils, J. Hazard. Mater. 48 (1996) 95–110.

[56] T.R. Naik, S.S. Singh, M.M. Hossain, Enhancement in mechanical properties of concrete due to blended ash, Cem. Concr. Res. 26 (1996) 49–54.

[57] I. Kula, A. Olgun, Y. Erdogan, V. Sevinc, Effects of colemanite waste, cool bottom ash, and fly ash on the properties of cement, Cem. Concr. Res. 31 (2001) 491–494.

[58] Ž. Sekulić, S. Popov, M. Duričić, A. Rosić, Mechanical activation of cement with addition of fly ash, Mater. Lett. 39 (1999) 115–121.

[59] R. Siddique, Effect of fine aggregate replacement with Class F fly ash on the mechanical properties of concrete, Cem. Concr. Res. 33 (2003) 539–547.

[60] J. Payá, J. Monzó, M.V. Borrachero, E. Peris, E. González-López, Mechanical treatments of fly ashes. Part III. Studies on strength development of ground fly ashes (GFA)—cement mortars, Cem. Concr. Res. 27 (1997) 1365–1377.

[61] F. Blanco, M.P. Garcia, J. Ayala, G. Mayoral, M.A. Garcia, The effect of mechanically and chemically activated fly ashes on mortar properties, Fuel 85 (2006) 2018–2026.

[62] V. Sata, C. Jaturapitakkul, K. Kiattikomol, Influence of pozzolan from various by-product materials on mechanical properties of high-strength concrete, Constr. Build. Mater. 21 (2007) 1589–1598.

[63] N. Bouzoubaâ, M. Lachemi, Self-compacting concrete incorporating high volumes of Class F fly ash. Preliminary results, Cem. Concr. Res. 31 (2001) 413–420.

[64] M.J. Varas, M. Alvarez de Buergo, R. Fort, Natural cement as the precursor of Portland cement: methodology for its identification, Cem. Concr. Res. 35 (2005) 2055–2065.