

Heavy Metal Immobilization using Fly Ash in Soils Contaminated by Mine Activity

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ABSTRACT

Often the remedial measures required to clean up sites contaminated with heavy metals are so complex that their implementation becomes economically unsustainable. In these cases immobilization of the metal contaminants, by means of suitable soil amendments, is a promising and economically feasible technique for soil remediation. In this context, an experimental investigation has been carried out to assess the potential use of fly ash from coal-fired power stations for immobilizing the heavy metals contained in soils in a severely contaminated Italian mine site. Parallel experiments have been carried out in columns, one containing the soil as received, the other the soil mixed with fly-ash. The tests lasted for more than one year and the results obtained so far have shown that the heavy metal content of percolating waters can be drastically diminished when the soils are admixed with fly ash.

INTRODUCTION

Pollution resulting from industrial growth has often been overlooked in the past, due to a lack of awareness of the extent of the problem and the environmental hazard it creates as well as for economic reasons. What is more, the lack of specific environmental protection laws meant that any necessary remedial action was left to the discretion of the single operators, with the result that once activity had ceased the sites, generally severely degraded, were often simply abandoned. However, more recently, a heightened awareness of the harmful effects of soil, air and water pollution and enhanced public perception have changed attitudes towards environmental issues. Nowadays remedial measures for eliminating or confining sources of pollution or for the remediation and reclamation of contaminated soils are more frequently being adopted, also with the economic objective of converting the degraded land to other uses. In a similar context, the abandonment of mining activities, especially in countries with a long mining tradition has left an enormous environmental legacy. Apart from devastating the original landscape, the large open pits, networks of galleries and underground cavities, mine waste dumps and settling ponds left behind in derelict mine sites have also altered the chemico-physical environmental parameters, often transforming the soils into an unstable, toxic substrate exposed to water and wind erosion.

Acid mine drainage, tailings ponds, mineralised waste dumps and slag heaps in particular are sources of hazardous heavy metal pollutants. Several options ^{1,2,3}, can be pursued for cleaning up contaminated sites, the ultimate choice depending on a number of often conflicting technical, economic and legislative parameters.

Current legislation regulating the rehabilitation of contaminated sites and their protection against possible contamination generally prescribes the use of the best available technology at acceptable costs ⁴. This allows to assess whether the complexity and cost of remedial measures are commensurate with the benefits to be derived. Thus for those sources of pollution for which elimination of the toxic elements proves economically unsustainable, given the characteristics and amount of material to be removed, then immobilization techniques based on the use of appropriate additives are generally accepted, conditional upon a favourable environmental impact assessment. Within the frame of a comprehensive laboratory investigation aimed at identifying low cost metal immobilizing agents such as certain industrial waste products, we explored the possibility of using fly ash produced by coal-fired power stations. The effectiveness of fly ash in immobilizing metals has been demonstrated for the heavily contaminated soils in an extensive area downgradient from the settling ponds of the Montevicchio-Levante lead and zinc mine in SW Sardinia (Italy) that has lain abandoned for over ten years. Laboratory experiments have been under way for over a year now in columns containing soils mixed with fly-ash and the as received soil as controls. The Pb, Zn, Cd and Cu contents of the eluates are determined periodically as well as pH and conductivity. The results obtained so far demonstrate that mixing with fly-ash drastically reduces the heavy metal content in the leachate.

MATERIALS

The soil sample concerned, collected downgradient of the tailings pond at the Montevicchio-Levante mine site is a brown soil of volcanic origin contaminated by reddish tailings from flotation and gravity concentration processes.

Particle size distribution, chemical composition (Table 1), qualitative mineralogic composition, by means of SEM and diffractometric analysis and pH were determined.

Table 1. Particle size analysis and chemical composition of the soil.

Size Class (mm)	Weight (%)	Metal content (ppm)			
		Pb	Zn	Cu	Cd
+1	7,86	9644	2257	454	16
-1+0.5	6,03	8836	2447	452	20
-0.5+0.21	12,58	7601	2434	467	19
-0.21+0.106	13,50	7979	2740	421	16
-0.106+0.074	5,45	9328	2120	362	14
-0.074+0.038	10,99	13901	2143	365	15
-0.038+0.020	13,37	18039	2370	347	18
-0.020	30,22	16869	4868	583	34
Calculated total	100,00	12870	3140	461	22
Analysed total		12245	3366	444	25

As can be seen from Table 1, the soil has a rather fine particle size and elevated metal concentrations that tend to increase as particle size decreases..

Mineralogical analysis indicated the main phases containing heavy metals to be siderite, sphalerite and galena; the secondary minerals included pyrite, cerussite, smithsonite, chalcopyrite, anglesite and iron oxides.

The pH, measured in compliance with official soil chemical analysis procedures ⁵, was 5.13.

Leaching and sequential extraction tests, not reported here for the sake of brevity, showed the soil to be highly toxic ⁶.

By way of example, Table 2 gives the Pb, Zn, Cd and Cu concentrations of the eluates after leaching at pH 5 with acetic acid and the corresponding Italian regulatory limits for emission into surface waters

Table 2. Leach tests using acetic acid on the as received soils

	Cu (ppm)	Pb (ppm)	Zn (ppm)	Cd (ppm)
Eluate	<0,1	3,5	15	0.13
D.Lgs.152/99(*)	<0,1	<0,2	<0,5	<0,02

(*) regulatory limits for emission into surface waters ⁷.

Fly ash from the Portovesme coal-fired electric power station in SW Sardinia was used as an additive for immobilizing the heavy metals. The fly-ash had pH of 12.17 and a bulk density of 2.24 g/cm³;

The particle size analysis shown in Table 3, revealed that the residual combustible fraction tends to concentrate in the coarser particle sizes.

Table 3. Particle size analysis and LOI of the fly ash .

Size class (μm)	Mass (%)	LOI (%)	LOI Distrib. (%)
+45	27,99	20,80	68,3
-45+37	7,78	5,91	5,4
-37	64,34	3,46	26,3
Total	100,00	8,49	100,0

The non-combustible fraction is made up of individual, prevalently spherical particles while the carbon is composed of irregularly shaped highly porous particles often in clusters.

Table 4 shows the chemical analysis of the non-combustible fraction.

Table 4. Chemical composition of the non-combustible fraction

SiO ₂ (%)	Al ₂ O ₃ (%)	Fe ₂ O ₃ (%)	CaO (%)	MgO (%)	Na ₂ O (%)	K ₂ O (%)	TiO ₂ (%)	MnO (%)
40,63	24,84	3,61	10,28	8,42	8,37	1,28	1,26	0,04

Figures 1 and 2 show the scanning electron microscope images of the ash and unburnt particles respectively.

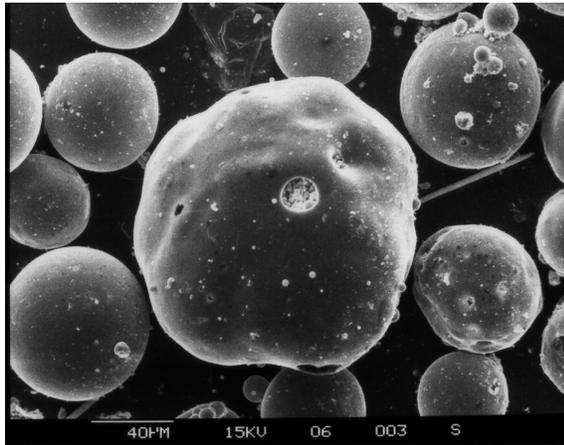


Figure 1. Ash.

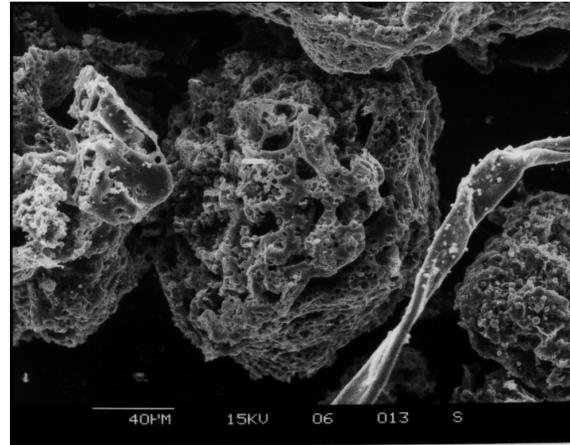


Figure 2. Unburnt carbon.

Diffraction analysis revealed the presence of mullite and a phase similar to graphite, that may correspond to the coking product.

Microprobe investigation showed the ash to be composed for the most part of an amorphous phase with strongly variable chemical composition.

EXPERIMENTAL

The experimental investigation was conducted in 140 mm diameter by 40 cm high plexiglass columns. The soil was kept at the bottom of the column by means of a filter system, through which the leach solution percolates. This system consists of a perforated plexiglass disk overlain by a second disk of glass wool in turn overlain by a bed of 15-20 mm diameter ceramic beads⁸.

The test procedure was as follows:

- the as received soil sample (3 kg) in column A and the soil-fly ash mixture (ratio 10:1.5 by weight, i.e. 3 kg soil and 450 g fly ash) in column B were agglomerated by adding 10% by weight distilled water and mixing in rotating cylindrical containers;
- each column was filled with the agglomerated material which was then compacted and left to age for 60 h prior to initiating the test;
- 150 cc of leach solution (distilled H₂O) was supplied to the columns in a single addition each day using the pulse method;
- flow rate, pH (Hanna Instruments HI 92240 pH-meter) conductivity (LF 92, WTW conductimeter) and Pb, Zn, Cd and Cu assays (SS-7 DCP, ARL plasma spectrometer) of the leachate were determined daily, or every 2-3 days, at the beginning of the test, then every week;

The experiment lasted for about 17 months. During this time the supply of distilled water addition was suspended for brief periods of the duration of 20-30 days to simulate a dry weather. At the end of the dry period when supply was resumed slight increases in conductivity and in the content of some metals were observed in the eluate, that

became totally negligible after a few days; this can be attributed to the contact time between the residual liquid and the material in the column.

A total of about 55 litres of leach solution were consumed over the 17 month test period. The results obtained so far have been evaluated referring to the metal assays observed in the eluate and to the metal units extracted, calculated as the product of the weight of the percolated solution times the corresponding metal content. Clearly the total units of metal contained in the soil sample are the product of its weight (3000 g) times the respective assays reported in Table 1.

Thus the units of metal initially contained in each column were as follows: Pb = 36,735,000; Zn = 10,098,000; Cd = 75,000; Cu = 1,332,000.

Figures 3-5 show and compare pH and conductivity (Fig.3), Pb and Zn content (Fig.4) and Cd and Cu content (Fig.5) of the leachates from columns A and B. Figures 6 and 7 give the cumulative units of Pb and Zn (Fig.6) and of Cd and Cu (fig.7) extracted so far from the two columns.

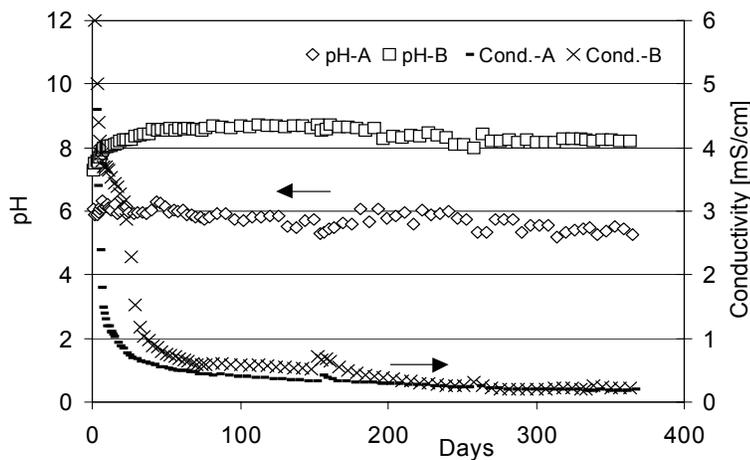


Figure 3. pH and conductivity versus time. (A) soil as received, (B) soil+fly-ash.

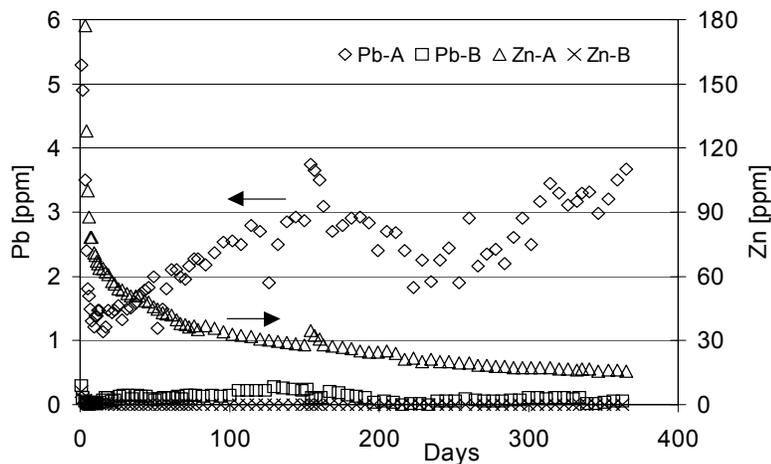


Figure 4. Pb and Zn content versus time. (A) soil as received, (B) soil+fly-ash.

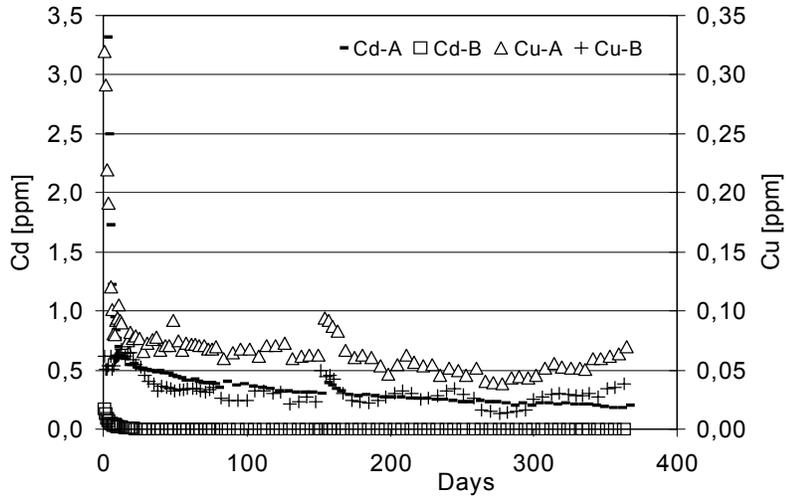


Figure 5. Cd and Cu content versus time. (A) soil as received, (B) soil+fly-ash.

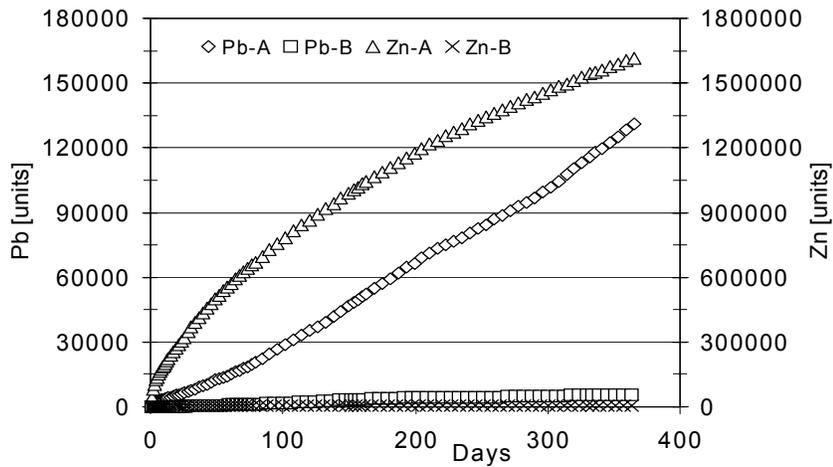


Figure 6. Pb and Zn cumulative units versus time. (A) soil as received, (B) soil+fly-ash.

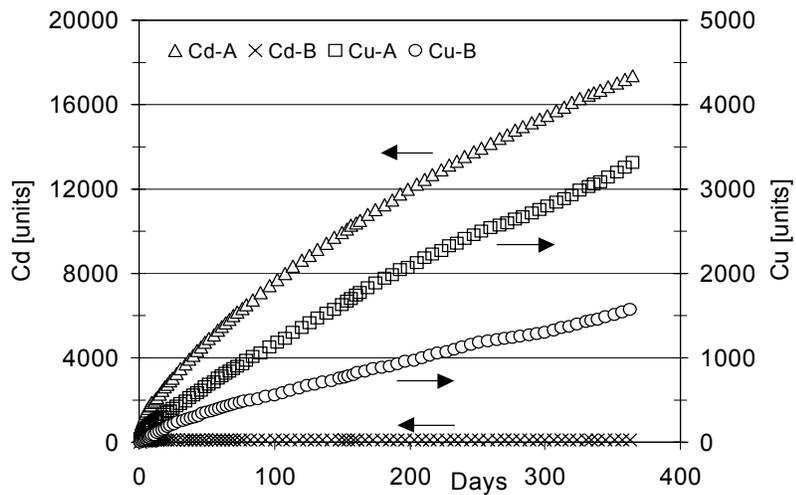


Figure 7. Cd and Cu cumulative units versus time. (A) soil as received, (B) soil+fly-ash.

The results of the test can be summarised as follows:

- pH in column A remained substantially constant (around 6) during the first year, decreasing slightly down to 5.5-5.4 thereafter, while pH in column B was always over 8 varying between 8.6 and 8.2;
- conductivity decreased almost exponentially down to about 0.2 mS/cm in both columns;
- Pb concentrations in the eluates from the as received soil (column A) generally ranged from 1 to 4 ppm, far higher than in the eluates from the soil-fly ash mixture (column B), which, always yielded values lower than 0.2 ppm except for the initial concentration. Further, as can be seen from Fig. 6., the total amount of metal extracted from column B was 23 times lower than the corresponding value for column A;
- Zn concentrations, which decreased over time, ranged from 325 (not shown in Fig. 6) to 16 ppm in the eluates of column A. These were far higher than those measured in column B where a Zn content of over 0.5 ppm was only observed in the first ten days, after which it decreased to between 0.5 and 0.1 ppm at 10-30 days and to less than 0.1 ppm thereafter, in some cases to below the instrument's detectability limit (0.006 ppm). As can be seen from Fig. 6, the total amount of metal extracted from column B was more than 400 times lower than column A;
- Cd concentrations, decreasing over time, varied between 3.3 and 0.2 ppm in the eluates of column A, while for column B Cd concentrations of below 0.02 ppm were observed after 10 days and below the instrument's detectability limit (0.005 ppm) after 20 days. In addition, Fig. 7 shows that the total amount of metal extracted for column B was 140 times lower than column A;
- Cu concentrations in both columns were less than 0.1 ppm, except for the first two days in column A. The total extracted metal for column B (Fig. 7) is roughly twice that of column A.

The soil-liquid-fly ash exchange mechanisms depend on the physical and chemical properties of the single phases and are governed by the variations in pH. In the soil mixture tested here the immobilization of the heavy metals contained therein is fundamentally related to the neutralization of the soils and to a decreased aggressivity of the leach solution by the strongly alkaline fly ash. The initial attack of the leach solution is able to solubilise the metals, that once in solution precipitate in the form of hydroxides as the liquid phase becomes alkaline. The potential absorbing properties of some fly ash constituents, such as the highly porous combustible fractions activated by the furnace temperatures and the silico-aluminate complexes, should not be overlooked.

CONCLUSIONS

The potential of fly ash produced by coal fired power stations in immobilising the heavy metals contained in severely contaminated soils has been experimentally assessed. The results obtained so far demonstrate that relatively small additions of fly ash can drastically reduce the heavy metals content of the soil leachates. However, it should be stressed that the process warrants further investigation so as gain a better understanding of the influence of certain parameters such as climatic conditions at the

site (temperature, rainfall, etc.) and permeability of the substrate, which govern the contact time between percolating leach solution and the soil as well as the effluent flowrate.

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