

REDUCTION OF Pb, Zn AND Cd AVAILABILITY FROM TAILINGS AND CONTAMINATED SOILS BY THE APPLICATION OF LIGNITE FLY ASH

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Abstract. The effectiveness of lignite fly ash for stabilization of Pb, Zn and Cd in tailings and contaminated soils was examined. Fly ash was mixed with the contaminated soil or oxidic tailings samples at various doses and pot experiments were performed. The effectiveness of stabilization was mainly evaluated by the standard US EPA TCLP toxicity test. The 5-stage sequential extraction procedure was also applied to determine the form of contaminants in the fly ash amended soil or tailings samples. Complementary EDTA extraction tests were also carried out. The fly ash treatment resulted in the reduction of TCLP solubility of Pb, Zn and Cd to below the respective regulatory limits at 5 and 10% w/w fly ash addition rates in tailings and soil, respectively. Speciation of lead, in the treated soil and tailings samples indicated that there was a significant transition of the heavy metals form from the exchangeable and carbonate fractions to reducible and residual, suggesting that the potential mechanisms of heavy metals retention are, apart from increase of pH, sorption on the oxides and hydroxides surfaces and binding with the hydrated fly ash compounds.

Keywords: cadmium, EDTA, lead, lignite fly ash, stabilization, TCLP, toxicity, zinc

1. Introduction

Oxidic tailings from the mineral processing industry and soils contaminated by heavy metals or toxic elements, due to interaction with these tailings, may pose a high risk to the ecological and biological cycle. Only few innovative technologies have been developed and applied on a commercial scale for remediation of metal-laden soils and oxidic wastes. They include metals removal from soils or their fixation in an insoluble form by solidification/stabilization techniques. Contaminants removal by physical or chemical/electrochemical methods is often viewed as effective, since almost the entire amount of the contained heavy metals and toxic elements is removed. However, these techniques are complex and generally suffer from high cost, which in some cases is moderated by the recovery of heavy metals value. *In situ* stabilization-immobilization methods aiming at converting the contaminants to low solubility, mobility and bioavailability forms, are relatively simple and of low-cost, however, a long term monitoring is required to ensure the contaminant stability.



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Various methods have been proposed and developed for the stabilization of oxidic tailings and contaminated soils. They involve mixing of the contaminated soil or waste *in situ* with appropriate substances and curing for the reactions to proceed. The basic mechanisms for immobilization of metals in wastes and contaminated soils are the following (Conner, 1990):

- *pH control*, using alkaline additives such as lime, hydrated lime, limestone, cement and fly ash.
- *Chemical precipitation as low-solubility species*, i.e., hydroxides, sulfides, silicates and phosphates.
- *Organic complexation*, where materials with many oxygen-containing functional groups, particularly -COOH and -OH, immobilize metal ions.
- *Sorption*, using natural materials such as clays, peat moss and sawdust, or synthetic materials such as fly ash, zeolite, activated carbon and metal oxides.
- *Ion exchange*, which is involved at some degree in almost all stabilization methods.

One of the most common mechanisms for chemical fixation of metals in wastes and soils is the pH control, since pH regulates metal solubility and rate of metal uptake by plants (Eriksson, 1989). Alkaline materials such as lime (CaO), hydrated lime (Ca(OH)₂) and fly ash have been extensively applied for this purpose. In stabilization systems the contaminants remain in the solid product; therefore, given conditions favorable, the reverse reaction may occur (Conner, 1990). Fundamentally both sorption and to an even greater degree, ion exchange are reversible. Thus, long-term monitoring of the stabilized material is required to ensure that the leachability of toxic elements remains safely low.

Fly ash, which is a low cost and abundant industrial by-product, has been known since the 60's for its effectiveness on the remediation of different kinds of industrial wastes in Europe and the U.S.A. by applying solidification techniques so that they are safely disposed of at landfills.

Much research has been recently conducted to examine the effects of fly ash addition in soils on heavy metals retention, as well as on plant growth and uptake of elements naturally occurring in soils (Scotti *et al.*, 1999; Wright *et al.*, 1998; Shende *et al.*, 1994). Moreover, alkaline fly ash is used in agriculture as a soil additive in small amounts (e.g. <5%), because of its capacity to supply plants with small amounts of nutrients, or as a liming material for treating acidic soils (Mishra and Shukla, 1986, Shende *et al.*, 1994). In addition, mixtures of fly ash with other materials were investigated for a variety of applications. They include sewage sludge/fly ash co-composting for agriculture uses (Fang *et al.*, 1999; Wong and Su, 1997), red mud/fly ash for waters detoxification (Apak *et al.*, 1998; Kilinckale *et al.*, 1997) and lime/fly ash for contaminated sandy soil stabilization.

In general, fly ash properties depend on the initial coal composition, combustion temperature, and the efficiency and type of emission control device. Some invest-

igators believe that the predominant mechanism of heavy metal retention by fly ash is precipitation (Conner, 1990). Others attribute the activity of fly ash in binding heavy metals to pure sorption, which is influenced by the pH of the medium. The main advantage of the fly ash application as compared with other alkaline additives is its effectiveness in immobilizing a variety of metals. However, in some cases the composition of fly ash is inappropriate for use in soils. This is due to the presence of increased amounts of potentially toxic elements (such as Ni, Cd, Mo), high salinity and the pH increase of fly ash amended soil (Adriano *et al.*, 1980). The latter results in deficiencies of both macro- and microelements in plants such as P, Cu, Fe, Mn and Zn (Furr *et al.*, 1976; Mishra and Shukla, 1986; Scotti *et al.*, 1999).

Two major classes of fly ash are specified in ASTM C618 on the basis of their chemical composition resulting from the type of coal burned. These are designated Class F and Class C. Class F is fly ash normally produced from the burning anthracite or bituminous coal [$(\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3) \geq 70\%$]. Class C is normally produced from the burning of subbituminous coal and lignite [$(\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3) \geq 50\%$]. Class C fly ash has cementitious properties in addition to pozzolanic properties due to free lime, whereas Class F is rarely cementitious when mixed with water alone.

In Greece, 8 million tonnes of different fly ash types are produced per year from lignite power stations where lignite is combusted at temperatures of 700–800 °C (Stamatakis *et al.*, 1997). About 10% of this fly ash is used in the cement industry. Recently, large quantities of fly ash were used in civil engineering works such as dam or road construction. Other uses of Greek fly ash were investigated including rehabilitation of various types of industrial wastes (Papahristou, 1982) and detoxification of water from organic substances (Albanis and Danis, 1997). Almost 90% of the produced fly ash quantity is disposed in open pits at the lignite mine sites.

In this study, class C fly ash originated from Ptolemais lignite power plant is used as a stabilizing agent for immobilization of heavy metals in mining wastes and contaminated soil originating from Montevicchio, Sardinia, Italy. In this area, mining activities along a 10 km long hydrothermal vein system of quartz-siderite with Pb-Zn mineralization were conducted for 150 yr. Huge amounts of oxidic tailings with elevated heavy metals and toxic elements content were produced and disposed at the Levante tailings dam. The combined action of wind and water erosion resulted in dispersing the contaminants to the surrounding soils which exhibit elevated Pb, Cd and Zn content in an area of 30–40 km² around the inactive mine (Dessi *et al.*, 1999). Measurements in edible plants (e.g. oats, strawberry, pear), grown in spoils and contaminated soil along the drainage catchment showed that Pb, Zn and Cd contents are increased posing a high risk to the foodchain, livestock and humans (Dessi *et al.*, 1999). Therefore, rehabilitation of the entire area is an important issue still to be addressed. Stabilization methods using various additives were investigated including phosphates (Xenidis *et al.*, 1999), alumina red mud, biological sludge, peated lignite, bentonites and zeolites. In this paper

the efficacy of fly ash as stabilizing agent for both Montevecchio tailings and contaminated soils is presented.

2. Methodology

2.1. MATERIALS

The efficacy of fly ash as stabilizing agent was evaluated on two samples collected from Montevecchio, Sardinia, Italy. The first sample represents the material disposed at the Levante tailings dam in the Montevecchio mining site. The second is a soil sample that represents the soil horizons typical of the contaminated area, at the banks along the river flowing from the Levante tailings dam. It consists of brownish clayey topsoil, which is mixed with ocraceous tailing muds. The composite samples were sieved to remove the coarse fractions (>2 mm) and the <2 mm fractions were used as working samples for conducting characterization tests, analyses and stabilization experiments. The fly ash sample used in this study was supplied from the lignite-fired power station in Kardia, Ptolemais, Northern Greece. It is a very fine material and it was used without any further treatment.

2.2. ENVIRONMENTAL CHARACTERIZATION

A detailed environmental characterization of the working samples was carried out using conventional analytical techniques and standard and non-standard leaching tests. Analyses included:

- Chemical analysis carried out in duplicate on the bulk samples as well as the various particle size fractions. These were conducted by digestion and measurement of the ion concentrations in solution by Atomic Absorption Spectrophotometry (AAS), while a graphite furnace attachment was used for analysis of trace elements in solution. Total sulfur content was determined with a LECO Sulfur analyzer. Loss on ignition was measured by ignition of sample at 1000 °C for 1 hr.
- Mineralogical analysis by X-ray diffraction (XRD, Siemens D5000 Diffractometer) using Cu-K α radiation and Scanning Electron Microscopy techniques with Energy Dispersive Spectroscopy using X-rays (SEM/EDS system, JEOL 6100/NORAN TN 5500) for elemental microanalysis of the solid phases.
- Particle size analysis by wet screening for particle size coarser than 63 μm and laser particle size analyses for finer fractions in the 63 to 1 μm range.
- Paste pH measurements at a water to solid ratio of 2 to determine the pH of the soil and tailings samples.
- Toxicity Characteristic Leaching Procedure (U.S. EPA TCLP, 1990) to determine the toxicity of the tailings and contaminated soil samples.

- 5-stage Sequential Extraction Procedure (SEP, Tessier *et al.*, 1979) that provides valuable information on the chemical form of the contaminants. The soluble-exchangeable and the carbonate fractions, determined in the initial two extraction stages, represent the readily available fractions of the contained metals to the ecosystem.
- Determination of the EDTA leachable fraction by leaching with EDTA (ethylenediaminetetraacetic acid, $C_{10}H_{16}N_2O_8$) – ammonium acetate solution (0.02 M Na_2 -EDTA in 1 N CH_3COONH_4 at pH 7) The EDTA extracts of soils have been found to give an indication of the plant available fraction for Cd, Pb, Zn, Cu and Ni (Quevauviller *et al.*, 1996). However, it is widely accepted that the EDTA test overestimates the bioavailable content of pollutants.

2.3. STABILIZATION PROCEDURE

To evaluate the efficacy of fly ash as a stabilizing agent in oxidic tailings and soils, pot experiments were performed. Soil or tailings samples weighing 600 g were thoroughly mixed with 5, 10, 15, 20 or 25% w/w fly ash and placed in 1 L pots. The mixtures were then systematically saturated with deionized water to promote the chemical reactions. The excessive quantity of drainage water was reused, hydrating the same pot again, several times a day. When this excess water was depleted by evaporation, a new quantity was supplied and the recycling of the water was continued. Preliminary experiments on fly ash amended tailings and soil samples indicated that after one month curing no significant variation on the TCLP solubility of heavy metals occurred. Based on these results the mixtures were kept saturated with water for one month.

2.4. EVALUATION OF STABILIZATION

The stabilization efficacy was evaluated by applying chemical tests on the mixtures of fly ash with oxidic tailings or contaminated soils. Chemical tests, which were conducted in duplicate, included:

- U.S. EPA TCLP test,
- EDTA leaching test, and
- 5-stage sequential extraction to examine the changes in heavy metals speciation after treatment.

The efficiency of fly ash as a stabilizing agent was evaluated based mainly on the TCLP results and supplemented with the EDTA and SEP results. An effective fly ash dose was one that resulted in reducing the TCLP solubility of the metals below their respective regulatory limits. The EDTA extracts were not used as an absolute criterion, due to the lack of respective limits, but were used as an indicator for the relative success of the various doses applied. Furthermore, the SEP results provided an indication of the change in contaminants form after fly ash amendment.

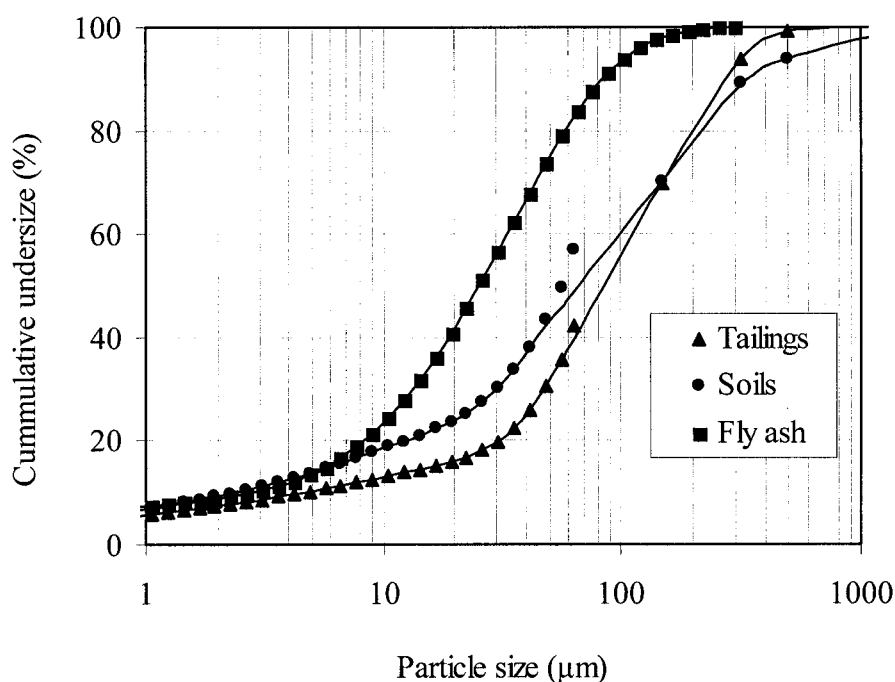


Figure 1. Particle size analyses of the tailing, soil and fly ash sample.

3. Results and Discussion

3.1. ENVIRONMENTAL CHARACTERIZATION OF SAMPLES

3.1.1. Tailings

Particle size analysis of the tailings sample revealed that the material is characterized as sandy loam, where the fine fraction ($<63 \mu\text{m}$) was 41% (Figure 1).

Chemical assays showed that the Pb, Zn and Cd contents were higher than the Dutch intervention values (Dutch soil standards, 1994) suggesting that remediation is required (Table I). Chemical analysis of the six (6) different particle size fractions of the tailings sample showed that 80% of Pb, 65% of Zn and 73% of Cd were accumulated in the fine fraction ($<63 \mu\text{m}$). The increased heavy metal accumulation in the fine fractions raises the risk of aerial contamination emanating from the site.

The main minerals of the tailings sample identified by XRD technique were quartz, illite, plagioclase and siderite. Various ore minerals in trace amounts were identified by optical microscopy including pyrite, goethite, chalcopyrite, arsenopyrite and magnetite. Extensive replacement of sulfides and Fe-oxides by goethite was common and widespread, as seen under the optical microscope. Sulfate minerals, such as baryte, gypsum, anglesite and Fe-sulfates were identified in the fine fraction by SEM/EDS analyses. Heavy metals were mainly hosted in the Fe-Mn-oxides and hydrated Fe-oxides. More specifically, a significant amount of Pb was

TABLE I
Chemical assays of the materials used

(a) Major element oxides (%)					
Oxide	Tailings	Soil	Fly ash		
SiO ₂	71.00	68.00	33.4		
Al ₂ O ₃	6.08	8.86	13.26		
CaO	0.15	0.84	36.12		
MgO	0.33	0.65	5.11		
Fe ₂ O ₃	10.89	6.86	5.43		
K ₂ O	1.01	1.10	0.87		
Na ₂ O	0.17	0.36	0.42		
SO ₃	<0.05	0.30	2.74		
LOI ^a	5.33	7.71	3.60		

(b) Trace element content (mg kg ⁻¹)					
	Tailings	Soil	Fly ash	Canadian soil standards (industrial soil)	Dutch soil intervention values
Pb	2380	8900	<125	600	530
Zn	5040	7900	100	360	720
Cd	34	50	<10	22	12

^a Lost on ignition.

hosted, apart from anglesite, in limonites and baryte that were also the common host minerals for Zn and Mn.

The paste pH was moderately acidic with a mean value of 5.15 ± 0.03 . The tailings were characterized as toxic because they exhibited Pb solubility slightly above the US EPA TCLP regulatory limit (Table II). Zn solubility was also high (23.5 mg L^{-1}), while Cd solubility was well below the TCLP regulatory limit.

Metal speciation results from Sequential Extraction Procedure indicated (Figure 2a) that 60% of the total Pb content in tailings resided in reducible Fe-Mn oxides, such as limonite, while 19 and 10% were extracted during the carbonate and exchangeable stages, respectively. Zinc was mainly extracted during the residual (51%) and reducible (35%) stages, while Cd was almost equally associated with exchangeable and reducible forms (34%) and less with the carbonate form (16%). The readily available fractions (exchangeable and carbonate) of Pb, Zn and Cd were found to be 30, 9 and 49%, respectively.

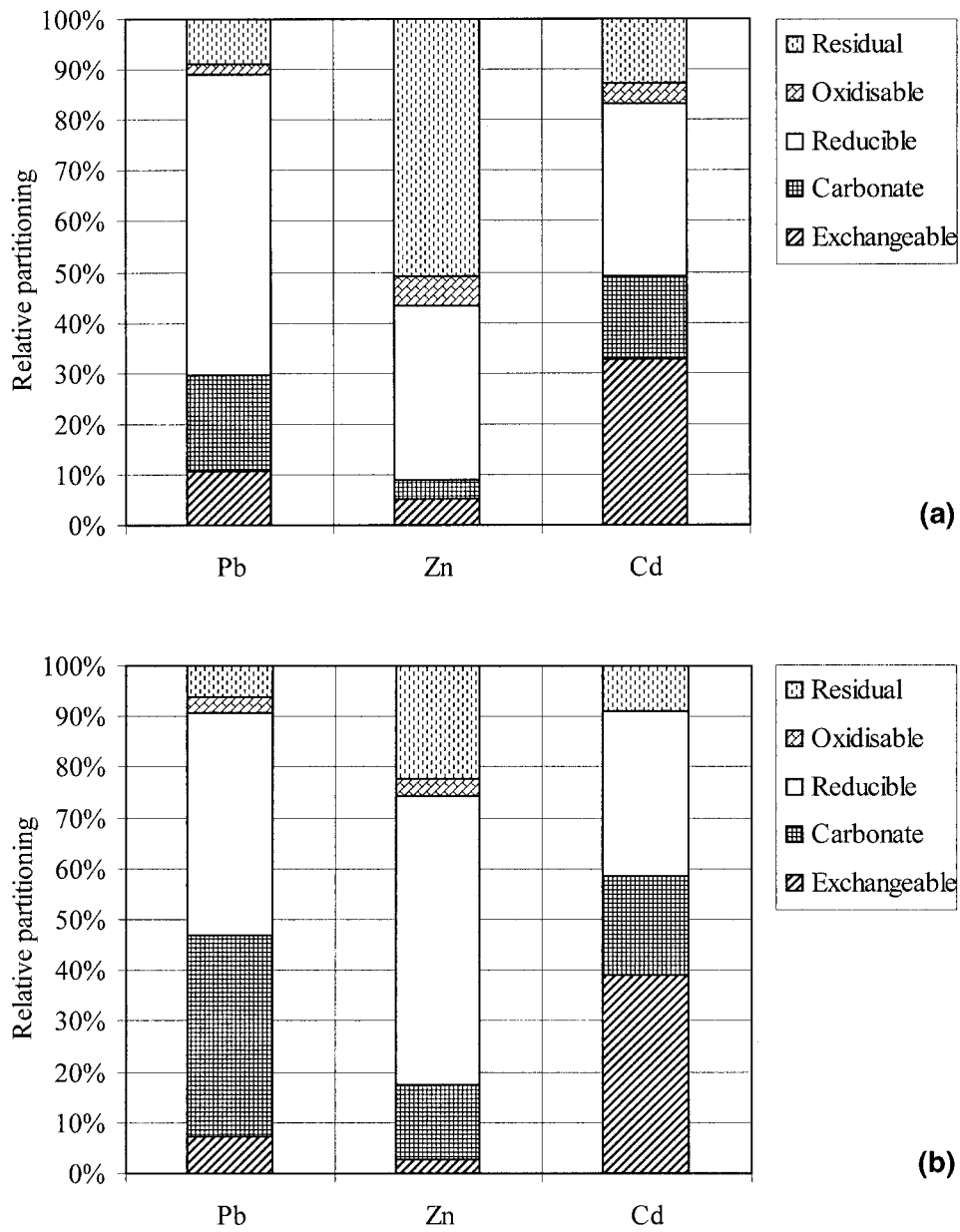


Figure 2. 5-stage sequential extraction results of the tailings (a) and soil (b) sample.

TABLE II
TCLP solubility values of the tailings and soil samples
(mg L⁻¹)

Element	Tailings	Soil	TCLP regulatory limit
Pb	10.70	57.30	5
Zn	23.50	87.50	–
Cd	0.52	1.20	1
As	<1.25	<1.25	5

3.1.2. Soil

Particle size analysis of the soil sample (Figure 1) revealed that the material is characterized as clay loam, where the fine fraction (<63 μm) was 56.9%.

Total Pb, Zn and Cd contents in the soil sample were higher than the Dutch intervention values and the recommended Canadian soil quality standards for industrial areas (CCME, 1999) (Table I), indicating that remediation of soil is required. More than 80% of total Pb, 80% of Zn and 78% of Cd were accumulated in the fine fraction (<63 μm).

The main minerals identified by XRD technique in all the particle size fractions of the soil sample were quartz (most abundant), clay minerals, illite and kaolinite, mica (muscovite) and alkali feldspars (albite and microcline). Carbonate minerals, such as calcite, siderite and ankerite, were identified in the silt and clay fractions. Trace amounts of galena (in the coarse grained fraction >1.18 mm), and baryte were identified by SEM/EDS. Optical microscopy revealed that pyrite and arsenopyrite occurred in trace amounts as well as goethite, as secondary replacement mineral of Fe-rich minerals. Furthermore, SEM/EDS analyses revealed that the carbonate minerals as well as the Fe and Mn oxides were the major repositories for Pb, Zn and Cd.

The paste pH was near-neutral with a mean value of 6.8 ± 0.05 . The Pb and Cd TCLP solubilities were greater than the respective regulatory limits, thus the material was characterized as toxic (Table II).

The sequential extraction results, presented in Figure 2b, indicate that the carbonate minerals (Ca-Mg-Fe carbonates and cerrusite) and Fe-Mn oxides (expressed as reducible fractions) were the most important mineral hosts for Pb, which confirmed the mineralogical analyses results. Zn was found mainly in the reducible fraction (57%) and less in the residual (22%) and carbonate (15%) fractions. Most of Cd was associated with exchangeable (39%), reducible (33%) and carbonate

(19%) forms. The readily available (exchangeable and carbonate) fractions of Pb, Zn and Cd were found to be 47, 17 and 58%, respectively.

In conclusion, both the Montevecchio tailings and soil samples were considered as hazardous because they presented (a) elevated levels of Pb, Zn and Cd as compared with Canadian and Dutch soil quality guidelines, (b) large readily available fractions of these heavy metals, determined by the two initial stages of the SEP, and (c) Pb and Cd solubilities in excess of the EPA-TCLP regulatory limits. Due to the increased environmental risk, remediation of contaminated soil and tailings using fly ash as the stabilizing agent was investigated.

3.1.3. Fly Ash

The fly ash was a very fine material with a d_{50} value of approximately $25 \mu\text{m}$ (Figure 1). Fly ash analyses (Table I) showed that it had high CaO, SiO₂ and Al₂O₃ content (36, 33 and 13 wt.%, respectively). According to the conventional classification of fly ashes (ASTM C-618), the used fly ash was characterized as calcic or class C. The main phases identified by XRD technique were quartz, anhydrite, lime, illite, calcite, gismondine (CaAl₂Si₂O₈·4H₂O) and portlandite. Additional minor phases identified were plagioclase, hematite and apatite.

The XRD pattern of the hydrated fly ash was similar to the original (non-hydrated) sample but showed the formation of ettringite (Ca₆Al₂(SO₄)₃(OH)₁₂·26H₂O), hydrated gehlenite (Ca₂Al₂SiO₇·8H₂O) and traces of hydrocalumite (Ca₁₆Al₈(OH)₅₄CO₃·21H₂O). Hydrocalumite is an anionic clay which is known to be formed in lime-treated class F fly ashes (Duchesne and Reardon, 1999).

3.2. STABILIZATION RESULTS

3.2.1. Tailings

The pH measurements of the fly ash amended tailings (Figure 3) revealed that fly ash addition resulted in a considerable increase in pH from 5.15 (control sample) to 10.3 (at the highest fly ash dosage).

As shown in Figure 4, heavy metals TCLP solubility decreased by increasing the fly ash dose. Pb solubility, which for the untreated sample was slightly above the TCLP regulatory limit, was reduced to below the regulatory limit at the minimum dose applied. Moreover, there was an abrupt decrease in Cd solubility with the addition of fly ash rate, while Zn solubility decreased in a linear fashion reaching 10 mg L^{-1} at 25% w/w fly ash addition. Fly ash addition also resulted in a significant reduction in the EDTA extractable fractions of Pb, Zn and Cd (Figure 5). At the maximum applied fly ash dose (25% w/w) the Pb EDTA extractable fraction was reduced by 78% (from 882 to 196 mg kg⁻¹) while the Zn and Cd fractions were reduced by 56 and 47%, respectively. The highest reduction rate was observed at the minimum applied dose (5% w/w), whereas limited if any changes in the EDTA extractable fractions were observed at fly ash additions greater than 10% w/w.

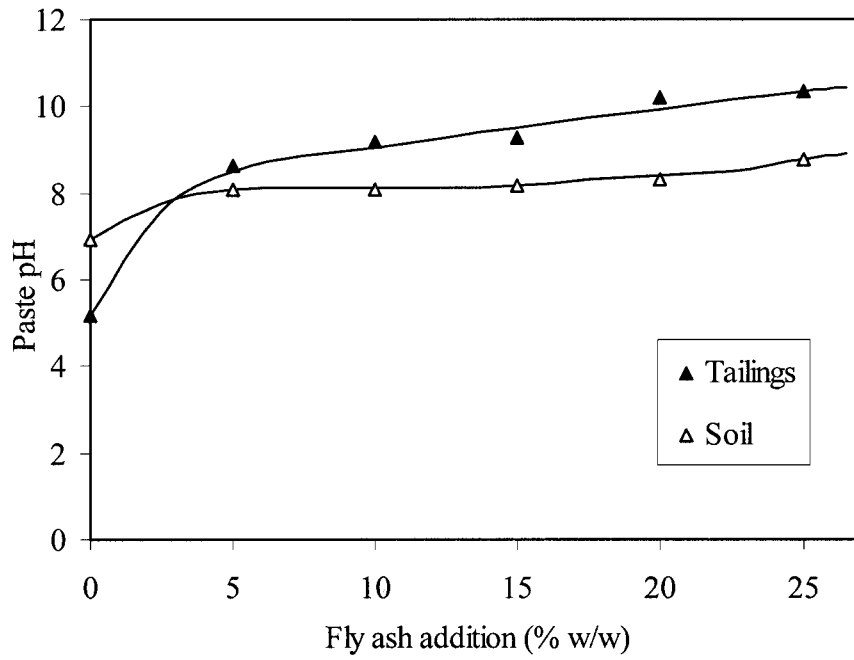


Figure 3. Paste pH versus fly ash addition rate.

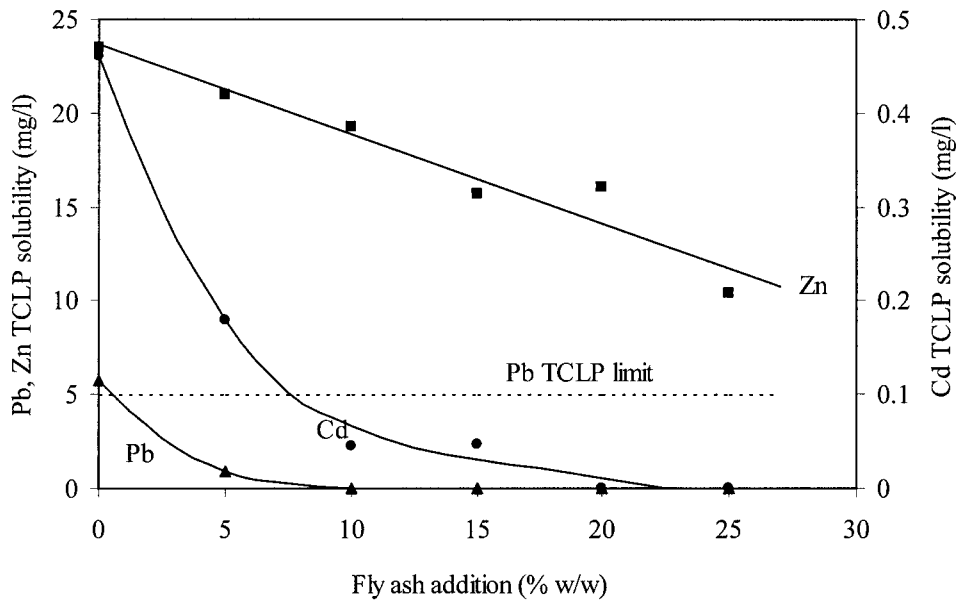


Figure 4. TCLP solubilities of lead, zinc and cadmium in the fly ash amended tailings.

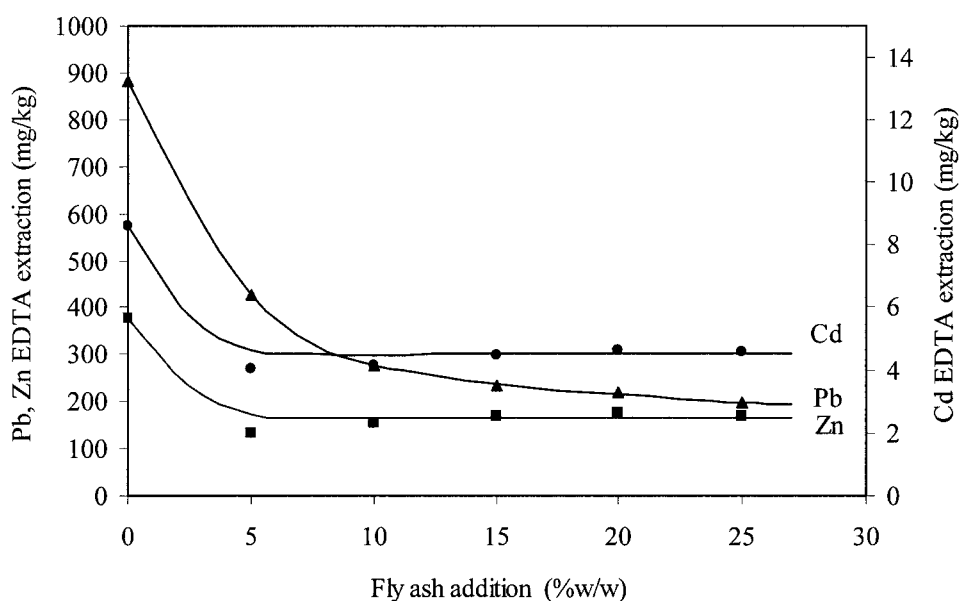


Figure 5. Lead, zinc and cadmium extraction using EDTA solution as a function of fly ash addition rate (tailings sample).

The 5-stage sequential extraction results indicated that fly ash amendment resulted in significant changes in the contaminants' forms. The exchangeable Pb fraction, which in the untreated sample was approximately 10% (Figure 6), decreased to below detection limit at 5% w/w fly ash addition. On the other hand, the reducible fraction of Pb increased by the same percentage, suggesting that Pb emanating from the dissolution of exchangeable lead compounds was possibly adsorbed by iron oxides and hydroxides. Fly ash addition at higher rates produced a decrease in Pb carbonate fractions from 19 to 7%, whereas the reducible and residual fractions increased.

The exchangeable Zn fraction, which initially amounted to 5.18%, decreased to 0.11 at 5% w/w fly ash addition and was reflected in an increase in the residual fraction (Table III); this suggests that zinc associated with exchangeable forms was dissolved and subsequently bound with the hydrated fly ash compounds. For higher fly ash addition rates, a decrease in the Zn reducible fraction was observed (from 30 to 25%), which was associated with a comparable increase in the residual fraction (from 60 to 67%). The Zn carbonate and oxidizable fractions of the untreated and treated tailings samples remained almost constant at around 4.5 and 4%, respectively.

As with Pb and Zn, the exchangeable Cd fraction was reduced significantly (from 33 to 20%) at 5% w/w fly ash addition. However, this reduction was associated with an increase in the carbonate, reducible and residual fractions. Fly ash addition at rates higher than 5% w/w resulted in a further decrease of the

TABLE III
Distribution of Zn and Cd as a function of fly ash addition rate (treated tailing and soil samples)

	Addition rate (% w/w)					
	0	5	10	15	20	25
(a) Tailings						
Zn fractions (%)						
Exchangeable	5.18±0.28	0.15±0.02	0.10±0.00	0.11±0.01	0.11±0.01	0.14±0.00
Carbonate	3.67±0.05	4.41±0.13	4.99±0.00	4.76±0.07	4.19±0.05	3.92±0.08
Reducible	34.48±0.20	30.72±0.18	27.93±0.18	28.03±0.32	26.42±0.30	25.24±0.02
Oxidisable	5.73±0.08	4.67±0.14	5.01±0.00	3.62±0.05	3.11±0.04	3.53±0.07
Residual	50.95±0.69	60.05±1.79	61.97±0.00	63.47±0.92	66.16±0.77	67.17±1.37
Cd fractions (%)						
Exchangeable	32.71±1.06	19.91±0.64	19.97±0.74	11.07±0.41	12.77±0.00	15.47±0.53
Carbonate	16.35±0.00	24.88±2.49	22.46±0.00	22.15±0.00	22.36±0.01	21.66±1.14
Reducible	34.07±1.10	37.33±1.20	37.44±1.39	48.44±1.79	47.90±0.03	46.42±1.60
Oxidisable	4.09±0.13	3.11±0.10	3.74±0.14	2.77±0.10	0.00±0.00	0.00±0.00
Residual	12.78±0.41	14.77±0.48	16.38±0.61	15.57±0.58	16.97±0.01	16.44±0.57
(b) Soil						
Zn fractions (%)						
Exchangeable	2.71±0.01	0.22±0.03	0.10±0.07	0.09±0.00	0.10±0.00	0.10±0.00
Carbonate	14.76±0.05	13.65±0.05	13.84±0.09	14.19±0.12	15.33±0.14	11.85±0.18
Reducible	56.94±0.96	58.38±0.99	58.02±2.28	56.48±0.00	52.66±1.04	57.46±0.41
Oxidisable	3.18±0.01	3.61±0.01	3.14±0.02	3.27±0.03	3.32±0.03	3.06±0.05
Residual	22.40±0.08	24.14±0.08	24.90±0.15	25.98±0.22	28.59±0.26	27.52±0.41
Cd fractions (%)						
Exchangeable	38.94±1.56	21.42±0.00	17.35±1.33	11.99±0.00	13.41±1.22	13.07±0.01
Carbonate	19.47±0.40	32.96±0.70	38.55±1.54	42.83±0.87	40.24±0.00	39.21±0.03
Reducible	32.74±1.31	37.90±1.52	35.66±1.43	37.69±0.00	37.37±0.00	40.14±0.03
Oxidisable	0.00±0.00	0.00±0.00	0.00±0.00	0.00±0.00	0.00±0.00	0.00±0.00
Residual	8.85±0.18	7.72±0.16	8.43±0.34	7.49±0.15	8.98±0.00	7.58±0.01

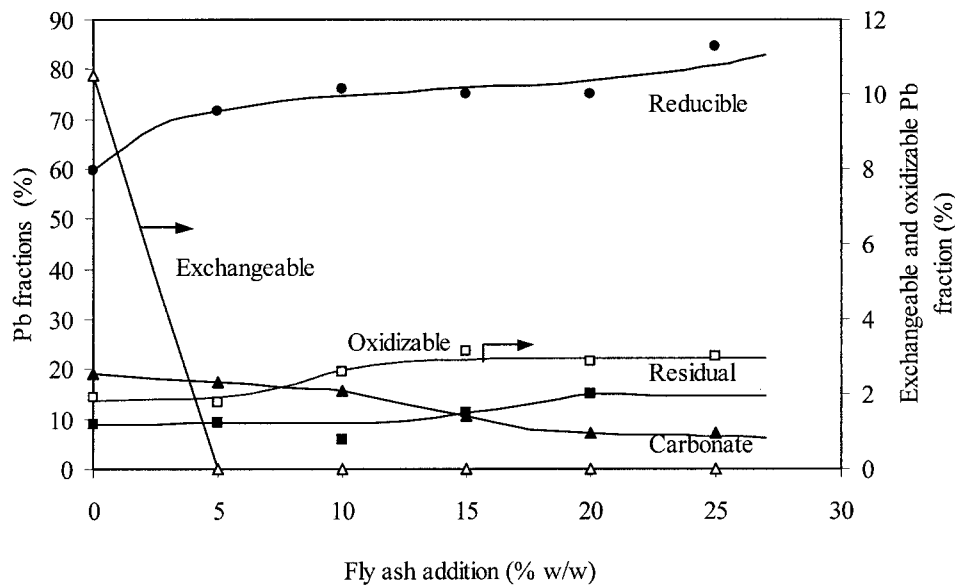


Figure 6. Distribution of Pb in the five fractions of the sequential extraction technique as a function of fly ash addition rate (tailings sample).

exchangeable (from 20 to 15%) and oxidizable (from 3 to 0%) fractions followed by an increase of the reducible fraction (from 37 to 46%).

3.2.2. Soils

Fly ash addition in soil increased the soil pH from 6.93 to 8.76 (Figure 3). The pH of the fly ash amended samples determines the solubility of Pb, Cd and Zn and prevents speciation as free ionic species (Lindsay, 1979; Chuan *et al.*, 1996; Song *et al.*, 1999). Furthermore, the TCLP solubilities of Pb, Zn and Cd were considerably reduced (Figure 7) with a steep decrease in TCLP solubility as the fly ash dose was increased. Lead solubility was reduced below the TCLP EPA regulatory limit of 5 mg L^{-1} at fly ash contents greater than 10%. Cadmium solubility, which for the untreated soil sample was slightly above the regulatory limit (1 mg L^{-1}), was reduced to below the limit at the minimum fly ash dose applied (5% w/w). In addition, zinc solubility decreased from 83 to 0.2 mg L^{-1} .

It was shown that addition of fly ash at the highest rate (25% w/w) resulted in 43, 52 and 20% decrease in EDTA extractable Pb, Zn and Cd, respectively (Figure 8). As was observed for the tailings and fly ash mixtures, the greatest reduction was observed at the minimum applied dose (5% w/w), while no significant change of the EDTA extractable fractions was observed at fly ash additions greater than 10% w/w.

The 5-stage sequential extraction results (Figure 9) indicated that the exchangeable Pb fraction, which in the untreated sample was 7.2%, decreased to zero at a

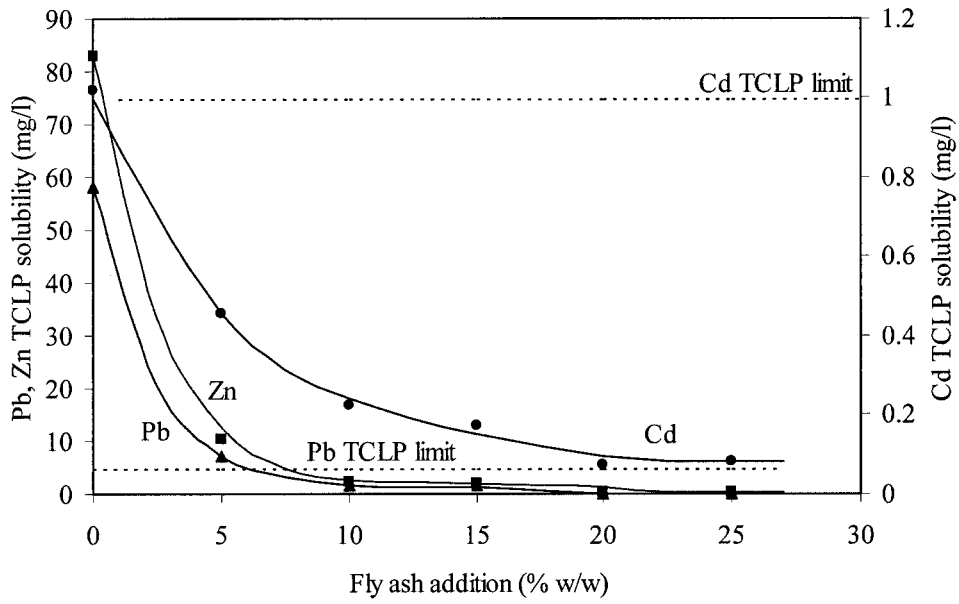


Figure 7. Lead, zinc and cadmium TCLP solubilities vs fly ash addition rate (soil sample).

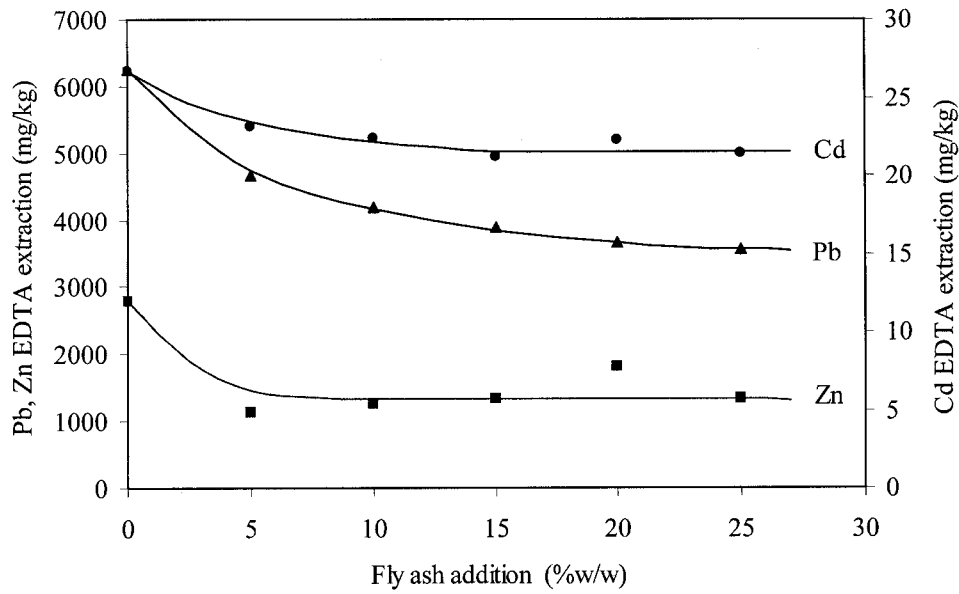


Figure 8. Lead, zinc and cadmium extraction using EDTA solution vs fly ash addition rate (soil sample).

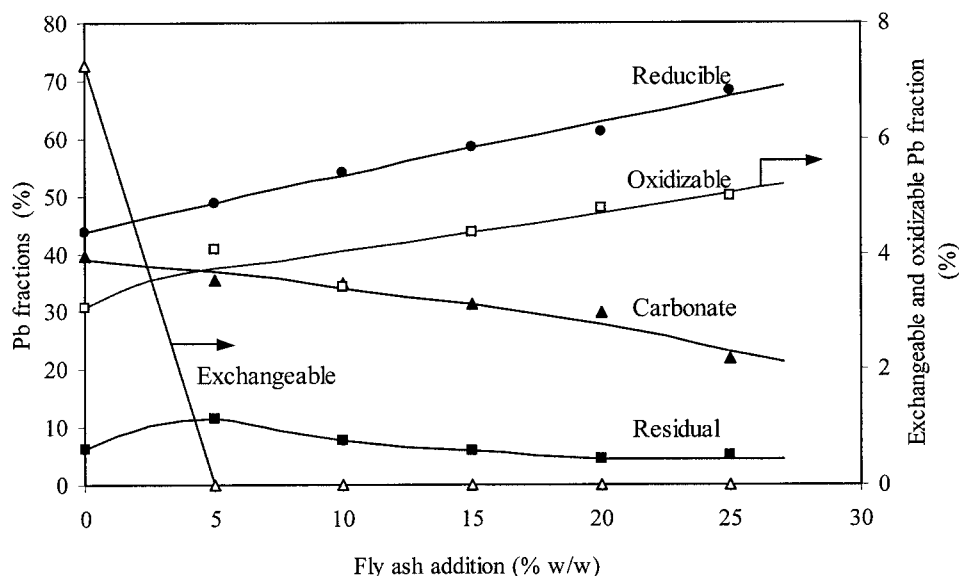


Figure 9. Distribution of Pb in the five fractions of the sequential extraction technique as a function of fly ash addition rate (soil sample).

fly ash content of 5% w/w. At the same time, the reducible and residual fractions evenly increased by approximately the same total percentage. Furthermore, the carbonate fraction was reduced from 40% at the untreated sample to approximately 22% at a fly ash content of 25% w/w, whereas the reducible fraction of Pb increased progressively with the fly ash addition rate from 44 to 68%. The oxidizable Pb fraction increased in a linear fashion from 3 to 5% as the fly ash dose was increased from 0 to 25% w/w.

The Zn exchangeable fraction, which was initially 2.7%, decreased to 0.22 at 5% w/w fly ash addition with a similar increase in the residual fraction (Table III); this suggests that, as in the case of tailings, the amount of Zn associated with the exchangeable forms was dissolved and subsequently bound to the hydrated fly ash compounds. The carbonate, reducible and oxidizable fractions of zinc in the untreated and treated samples remained almost constant at around 14, 56 and 3%, respectively.

The Cd exchangeable fraction was decreased from 39 to 13% at 25% fly ash addition while the carbonate and reducible fractions increased by 20 and 6%, respectively. The oxidizable and residual fractions remained almost constant. No significant changes in Cd speciation were observed at fly ash contents greater than 15% w/w.

Results from the 5-stage sequential extraction procedure performed on both samples indicated that most of the easily dissolved Pb (i.e., Pb associated with exchangeable and carbonate forms) after treatment with fly ash was extracted in the

reducible fraction denoting that Pb was adsorbed on the surface of the oxides and hydroxides. Furthermore, a part of the easily dissolved Pb after treatment was associated with the residual fractions suggesting that it was dissolved and subsequently bound to the hydrated fly ash compounds. Almost all the easily dissolved Zn in both samples was extracted with the residual fraction, indicating that it was bound with the emanating fly ash compounds. Although Pb and Zn exchangeable fractions were reduced to almost zero in both samples tested at 5% w/w fly ash addition rate, the exchangeable fraction of Cd remained at significant levels (approximately 15%) even at the highest fly ash addition rates applied. The amount of Cd dissolved during the treatment was adsorbed on the surface of oxides and hydroxides and extracted during the reducible stage.

Based on the above, the reaction mechanisms and consequently the short- and long-term performance of a potential stabilization scheme depend on the contaminant as well as the fly ash addition rate. They are associated with the increase of pH, adsorption of contaminants on the iron oxides and hydroxides, as well as binding of the contaminants to the hydrated fly ash compounds.

4. Conclusions

Detailed environmental characterization of the Monteverchio tailings and contaminated soil revealed that these materials are hazardous because they presented high concentrations of Pb, Zn and Cd, high bioavailable fractions of these heavy metals, and TCLP solubilities of Pb and Cd above the respective regulatory limits.

A significant decrease in the TCLP solubilities of the heavy metals in fly ash amended soil or tailings samples was effected. The minimum fly ash addition required to reduce the Pb TCLP solubility below the respective regulatory limit was 5 and 10% w/w for Monteverchio tailings and soil, respectively. At the same fly ash contents, Cd solubility also was reduced below the respective regulatory limit, while Zn solubility decreased from 23.5 to 21 and from 87.5 to 2.2 mg L⁻¹ for tailings and soil samples, respectively. Furthermore, fly ash addition resulted in significant reductions in the EDTA extractable fractions of Pb, Zn and Cd. The results of the sequential extraction procedure performed on both samples suggested that most of the easily dissolved Pb, Zn and Cd after treatment with fly ash were extracted either in the reducible or in the residual fraction, denoting that these metals were adsorbed on the surface of the oxides and hydroxides or bound to the hydrated fly ash compounds.

Based on the above information, a remediation scheme was proposed for the Monteverchio tailings and soils involving fly ash application at rates of 5 and 10% w/w, respectively. However, although fly ash addition resulted in a significant decrease of contaminants leachability and availability due to the increase of pH, adsorption on the oxides and hydroxides surfaces and binding with the hydrated fly ash compounds, long term experiments are required before accepting it as

a stabilizing agent for the remediation of the Montevecchio oxidic tailings and contaminated soils.

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