

Use of alumina red mud for the stabilization of tailings and contaminated soils

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ABSTRACT

The objective of this study was to evaluate the effectiveness of treated with gypsum Alumina Red Mud (ARM) as stabilizing agent for the chemical immobilization of lead, zinc and cadmium in mine tailings and contaminated soil originating from the Montecatini site, in SW Sardinia, Italy. This site is a redundant mine district where intense exploitation of Pb-Zn ore has taken place since last century resulting in the production of huge quantities of mining wastes. Stabilisation was performed by mixing of contaminated soil or tailings with 0-25% w/w treated ARM, saturation of the mixture with water and curing under saturating conditions for one month. The geochemical stability of the mixtures and efficiency of stabilization were evaluated based on two criteria: a) the reduction of metals mobility, as determined by the US EPA TCLP, below the TCLP regulatory limits, and b) the decrease of Pb, Zn and Cd phytoavailability which was determined by applying leaching with EDTA solutions. Based on the experimental results it was indicated that treated ARM addition in contaminated soil resulted in a significant decrease of Pb, Zn and Cd concentration in the TCLP leachate. The EDTA phytoavailable fractions of these metals decreased significantly by increasing the stabilizing agent addition rate in contaminated soil, but it remained practically constant in the case of tailings.

1. INTRODUCTION

In-situ stabilization - immobilization techniques, which aim at converting the contaminants to

low solubility, mobility and bioavailability forms, are relatively simple and of low-cost. They involve mixing of the contaminated soil or waste *in-situ* with appropriate substances and curing for some time, in order for the reactions to proceed.

A number of substances including chemical reagents and organic and inorganic wastes were tested and applied as stabilizing agents for wastes and metal-laden soils (Kumpiene et al., 2008). Their applicability depends mainly on the chemistry and mineralogy of the contaminants in wastes and soils. The basic mechanisms for the immobilization of metals in wastes and contaminated soils are (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, sulphides, 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.

In the stabilisation systems the contaminants remain in the solid product, therefore if conditions are favouring, the reverse reaction may occur. Because some fixation mechanisms, such as sorption and even more ion exchange, are fundamentally reversible, monitoring for appropri-

ate length of time of stabilised soil or waste is required, in order to ensure that the mobility of toxic elements remains safely low.

In the Montevecchio mine district, located in SE Sardinia, Italy, exploitation of the Pb-Zn ore, which is the richest ore deposit of this type in Italy, has been practised for the last 150 years. Now being a redundant mining area, it has been left with an estimated volume of 15-20 Mm³ wastes which constitute a pollution source for the surrounding land, surface waters and human health (Fanfani, 1995). Soil survey results and geochemical studies on the river sediments in the Rio Montevecchio drainage basin, downstream of the Levante tailings dam revealed that an estimated volume of 2 Mm³ soils have been contaminated with Pb, Zn, Cd and As (Dessi et al., 1999a, b; Fanfani, 1995). Furthermore, Pb content in livestock fodder (oats) collected from the area was found to be as high as 600 ppm, suggesting that the contaminated soil in this site poses a major environmental risk. Based on the above, remediation of Montevecchio contaminated soil as well as flotation tailings was considered necessary.

There was a number of stabilising agents tested for the remediation of Montevecchio tailings and soils including calcium oxyphosphate, sewage sludge and fly ash (Stouraiti et al., 2001). The objective of this study was to evaluate the effectiveness of treated with gypsum Alumina Red Mud (ARM) as stabilising agent for the immobilization of heavy metals containing in Montevecchio tailings and contaminated soils.

2. MATERIALS AND METHODS

2.1 Sampling - Samples preparation

The Alumina Red Mud sample used as stabilizing agent was collected from the disposal basin of the Bayer plant owned by EURALLUMINA in Portoscuso, Cagliari, Sardinia. Due to the high initial pH of the Alumina Red Mud it was treated with 5% wt gypsum originated from the HF plant of FLUORSID located in Assemini, Cagliari Sardinia. The final paste pH of treated ARM was 11.7. Stabilization experiments were conducted on the following samples:

- Montevecchio tailings sample. It is a representative composite sample of the material

disposed of at the Levante tailings dam in the Montevecchio mining site.

- Montevecchio soil sample. It is also a composite sample that represents the soil horizons at the banks along the river flowing from the Levante tailings and is typical of the contaminated area in Montevecchio valley. This sample consists of (a) brownish clayey topsoil of 0.3-0.5 m average thickness, and (b) an overlying layer of flotation tailing muds, ocraceous which are disseminated outside the Levante tailings dam, of 0.3-1.2 m average thickness.

The composite samples were sieved to remove the coarse fraction (+2 mm) and the remaining -2 mm fractions were used as working samples for conducting characterization tests, analyses and stabilization experiments.

2.2 Environmental characterization

A detailed environmental characterization of the soil, tailings and ARM samples was carried out by applying conventional analytical techniques and standard and non-standard leaching tests. It included:

- Chemical analyses of the bulk samples following acid digestion and measurement of the ions concentration in solution by Atomic Absorption Spectrophotometry (A.A.S).
- Mineralogical analyses (X-ray diffraction and Scanning Electron Microscopy techniques).
- Particle size analysis.
- Toxicity Characteristic Leaching Procedure (US EPA TCLP, 1986) in order to determine the toxicity of the tailings and contaminated soil samples.
- 5-stage Sequential Extraction Procedure (SEP, Tessier et al., 1979) which provides valuable information on the chemical form of the contaminants. The 5 stages correspond to the exchangeable, carbonate, reducible (Fe-Mn oxides), oxidisable (organic compounds), and residual soil fractions. The soluble, exchangeable and carbonate fractions represent the readily available forms of the metals.
- Determination of the EDTA leachable fraction by leaching with EDTA (ethylenediaminetetraacetic acid, C₁₀H₁₆N₂O₈) - ammonium acetate solution (0.02 M Na₂-EDTA in 1N CH₃COONH₄ at pH 7). The EDTA extracts

of soils are associated with the plant available fraction of heavy metals (Misra and Pandey, 1976).

2.3 Stabilization procedure

Stabilization of the materials was carried out in laboratory scale by conducting pot experiments. A quantity of 600 g soil or tailings was thoroughly mixed with 0, 5, 10, 15, 20 or 25% w/w of treated ARM and placed into 1 L plastic pots. The weights in mixtures were calculated on dry basis for all the materials.

In order to promote the chemical reactions between the metal ions retained in the studied samples and ARM introduced in the mixture, the following procedure was applied: the pots were systematically hydrated with the appropriate volume of deionised water in order to obtain a sufficient but not excessive quantity of drainage water in the plate under the pot. The drainage water was recycled to the pot several times every day. When the excess water was depleted due to evaporative losses, a new quantity was added and the procedure was repeated several times a day. Therefore, the soil-additive mixtures were kept saturated in water for approximately one month.

Finally, the stabilisation efficiency was evaluated by applying chemical extraction tests including:

- Toxicity characterisation using the US EPA TCLP test.
- Determination of the bioavailable-phytotoxic fraction by leaching with EDTA.

EDTA extraction test was applied to estimate the phytoavailable fraction of Pb, Zn and Cd. The extraction solution consists of 0.02 M EDTA-2Na salt and 1N CH₃COONH₄ at pH 7.0. Ten (10) g of soil were mixed with 100 ml of extraction solution in 300 ml flask and the slurry was agitated for 1 h at 100 rpm. Following the filtration of the slurries, the metals in the leachates were analysed with flame atomic absorption spectroscopy. In general, the EDTA extracts of soils have been found to give an indication of the plant available fraction for Cd, Pb, Zn (Cu, Ni) (Quevauviller et al., 1996). However, it is widely accepted that EDTA overestimates the bioavailable fraction of pollutants.

3. RESULTS AND DISCUSSION

3.1 Environmental characterization

Based on particle size distribution of the Montevecchio contaminated soil sample, it is characterized as clay loam, where the fine fraction (-63 µm) is 56.9%. The paste pH of soil was found 6.8.

The total content of Pb, Zn, Cd and Ba was found significantly higher than the available regulatory limits for soils, indicating that remediation of soil is required (Table 1). In addition, more than 80% of total Pb, 80% of Zn and 78% of Cd were accumulated in the fine fractions (-63 µm) raising the risk of aerial contamination to the surroundings.

Regarding heavy metal toxicity, Pb and Cd TCLP solubilities were found higher than the respective regulatory limits; therefore, the material was characterized as toxic (Table 2).

Table 1: Chemical analysis of materials used.

| Major elements (% wt.) | Tailings | Soil | ARM | Dutch intervention values |
|--------------------------------|----------|------|-------|---------------------------|
| SiO ₂ | 71 | 68 | ND | |
| Al ₂ O ₃ | 6.08 | 8.86 | 11.56 | |
| CaO | 0.15 | 0.84 | 10.1 | |
| MgO | 0.33 | 0.65 | 2.78 | |
| Fe ₂ O ₃ | 10.89 | 6.86 | 43.54 | |
| SO ₃ | BDL | 0.3 | ND | |
| LOI | 5.33 | 7.71 | ND | |
| <i>Trace elements (mg/kg)</i> | | | | |
| Pb | 2380 | 8900 | 144 | 530 |
| Zn | 5040 | 7900 | 306 | 720 |
| Cd | 34 | 50 | <5 | 12 |
| As | BDL | BDL | 50 | 55 |
| Ba | 4060 | 8600 | ND | 625 |
| Cu | 720 | 1600 | 134 | 190 |
| Mn | 3000 | 1160 | 360 | - |

BDL: Below Detection limit, ND: Not determined

Table 2: TCLP results of the tailings and soil samples and respective regulatory limits.

| Element | Tailings (mg/L) | Soils (mg/L) | TCLP regulatory limit (mg/L) |
|---------|-----------------|--------------|------------------------------|
| Pb | 5.7 | 57.3 | 5 |
| Zn | 13.3 | 83.1 | - |
| Cd | 0.42 | 1.1 | 1 |
| As | BDL | BDL | 5 |
| Ba | 2.6 | BDL | 100 |

The main and common minerals identified by XRD technique in all the particle size fractions were quartz (most abundant), clay minerals, illite/muscovite and kaolinite, and alkali feldspars (albite and microcline). Carbonate minerals, such as calcite, siderite and ankerite, were identified in the silt and clay fractions. Minor phases identified by optical microscopy and SEM/EDS analyses were galena (in the coarse grained fraction +1.18 mm), baryte, pyrite, arsenopyrite and goethite (secondary oxidation mineral of Fe-rich minerals). SEM/EDS compositional mapping of analyses revealed that, the carbonate minerals, clayey minerals as well as the Fe and Mn oxides are the major repositories for Pb, Zn and Cd.

From the five stage sequential extraction results, presented in Fig. 1a, it is indicated that the carbonate minerals (Ca-Mg-Fe carbonates and cerussite [PbCO₃]) as well as Fe-Mn oxides (corresponding to the reducible fraction) were the most important hosts of Pb (and Zn), which was in accordance with the SEM analyses results. Most of Cd was associated with exchangeable (39%), reducible (33%) and carbonate (19%) forms. The bioavailable (exchangeable and carbonate) fractions of Pb, Zn and Cd were found 47, 17 and 58% respectively.

In conclusion, the Montevecchio soils were considered as hazardous because they present (a) elevated concentrations of Pb, Zn and Cd, (b) high bioavailable fractions of these heavy metals, determined by the two initial stages of the SEP, and c) Pb and Cd solubilities above the EPA-TCLP regulatory limits. Because of the enhanced environmental risk, remediation of the contaminated soil is required.

3.1.2 Flotation tailings

Chemical assays showed that the total content of heavy metals Pb, Zn, Cd, Cu and Ba was several times higher than the Dutch soil intervention values (1993, Table 1). The particle size distribution analysis revealed that the material is characterised as sandy silt, where the fine fraction (<63 μm) was 41%. Moreover, chemical analysis of the six (6) different particle size fractions of the tailings sample (Xenidis et al., 1999) showed that 80% of Pb, 65% of Zn and 73% of Cd were accumulated in the fine fraction (<63 μm). The high proportion of the fine fractions as well as the increased metal accumulation in the fines raise the risk of aerial contamination emanating from the site.

The paste pH was found weakly acidic presenting values around 5.8. According to the US EPA TCLP test, the material was characterized as toxic because it exhibited high Pb solubility (5.7 mg/l), above the TCLP regulatory limit, while Cd and Ba solubility was well below the respective regulatory limits. Arsenic solubility was found below detection limit (Table 2).

The main minerals of the tailing sample identified by XRD technique were quartz, muscovite/illite, siderite and plagioclase. Minor phases containing the heavy metals found by optical microscopy and SEM analysis are anglesite, baryte, gypsum, pyrite, lepidocrocite/goethite,

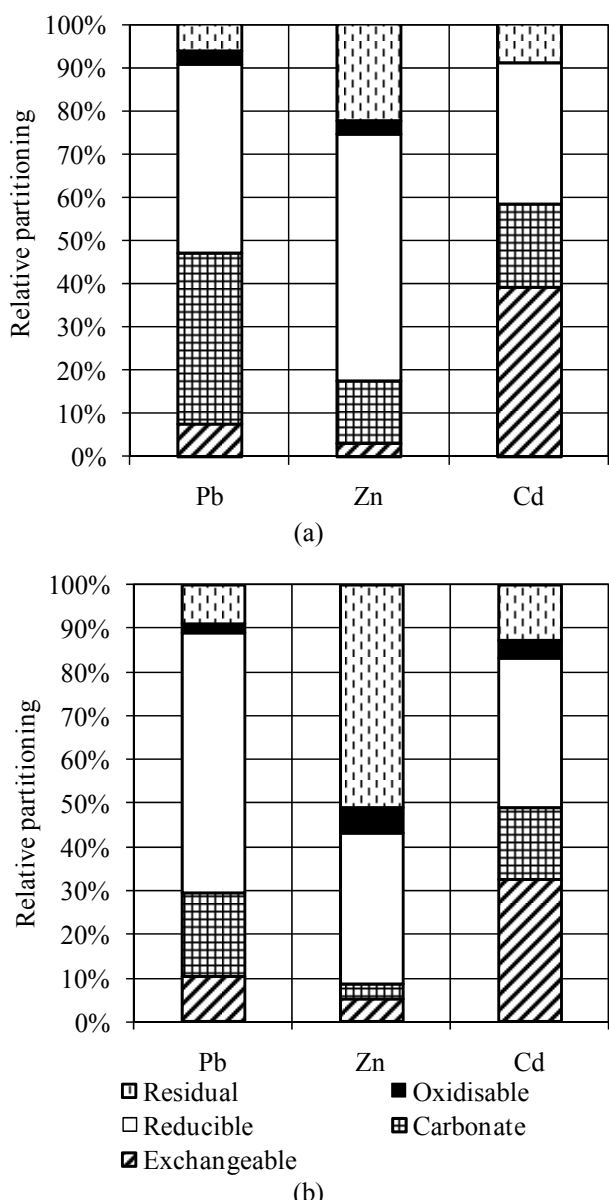


Figure 1: 5-stage Sequential Extraction Procedure results of (a) contaminated soil, and (b) tailings samples.

galena, chalcopyrite and arsenopyrite. Extensive replacement of sulfides and Fe-oxides by goethite was common and widespread, as seen by optical microscopy. Heavy metals were mainly hosted in the Fe-Mn- oxides and hydrated oxides. More specifically, significant amounts of Pb were found in anglesite, baryte and commonly in limonites which also were the common repositories for Zn and Mn.

Metal speciation results from Sequential Extraction Procedure indicated that 60% of total Pb content in this sample reside in reducible Fe-Mn oxides, such as limonite ($\text{FeOOH}\cdot x\text{H}_2\text{O}$) while 19% and 10% were extracted during the carbonate and exchangeable stages respectively (Fig. 1b). Zinc was mainly extracted during the reducible (51%) and residual (35%) stages, while Cd was almost equally associated with the exchangeable and reducible forms (34%) and less with the carbonate form (16%). The respective bioavailable fractions of Pb, Zn and Cd which were determined by the first two extracts, were 30%, 9% and 49%.

3.2 Stabilisation results

The efficiency of the additives in reducing metal solubility was evaluated mainly based on the TCLP results and supplemented by the EDTA test results.

The effect of ARM addition rate on Pb, Zn and Cd concentration in the TCLP leachates is shown in Figures 2, 3 and 4 respectively for contaminated soil and tailings. As seen in these figures, the TCLP solubility patterns displayed a

decreasing trend with the increase of applied ARM dose. The increase of ARM addition rate from 0 to 25% w/w resulted in a significant decrease of Pb TCLP solubility (Fig. 2) from 57.3 mg/l to 9 mg/l. However, even at the highest dose applied, the Pb concentration in the TCLP leachate still remained higher than the TCLP regulatory limit for Pb (5 mg/l).

Concerning tailings, the increase of ARM addition rate from 0 to 20% w/w resulted in an abrupt decrease of Pb concentration in the TCLP leachate from 5.7 mg/l to below detection limits (Fig. 2), whereas the reduction of Pb TCLP concentration below the respective regulatory limit (5 mg/l) was obtained at the mini-

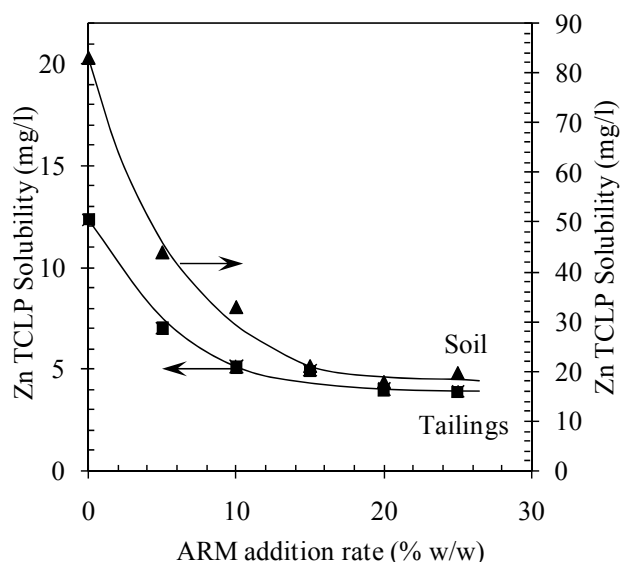


Figure 3: Zn concentration in the TCLP leachate vs. ARM addition rate.

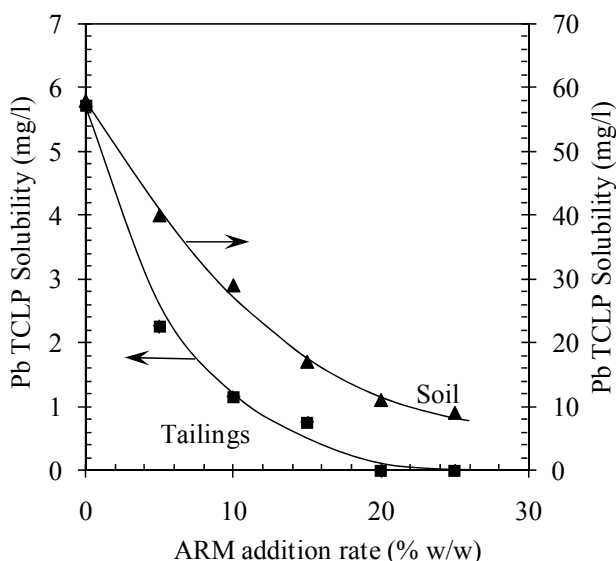


Figure 2: Pb concentration in the TCLP leachate vs. ARM addition rate.

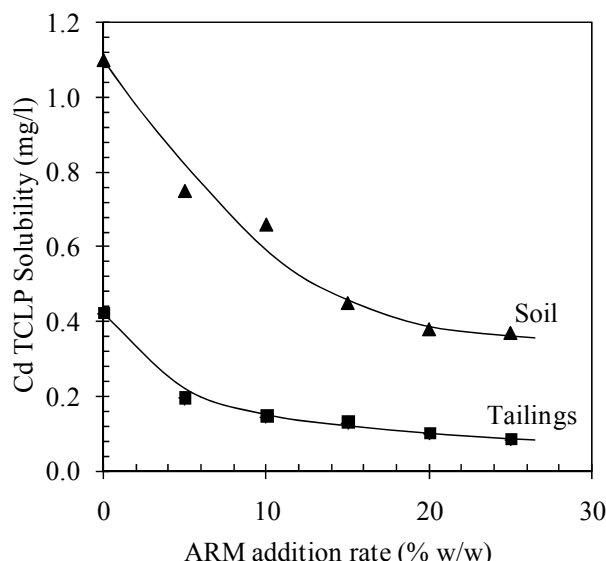


Figure 4: Cd concentration in the TCLP leachate vs. ARM addition rate.

imum ARM dose applied (5% w/w).

Zn leachability was also decreased from 83 to less than 20 mg/l for soils and from 13.3 to 3.9 mg/l for tailings with the increase of ARM addition rate from 0 to 25% w/w. Cd TCLP leachates concentration, which for the untreated soil sample was slightly above the regulatory limit (1 mg/l), was reduced below it at the minimum ARM dose applied (5% w/w). In the case of tailings, the Cd concentration in the leachates was also decreased from 0.42 to 0.085 mg/l with the increase of ARM addition rate from 0 to 25% w/w.

The results of Pb, Zn and Cd phytoavailability, as determined by the EDTA extraction test

are presented in Figures 5, 6 and 7 respectively. As seen in these figures, the addition of ARM resulted in a significant decrease of the phytoavailable fractions of Pb, Zn and Cd in contaminated soils. Pb EDTA phytoavailable fraction in contaminated soil was decreased from 6150 to 4820 mg/kg with the increase of ARM dose from 0 to 25%. The Zn and Cd phytoavailable fractions in contaminated soil were also decreased from 2380 to 2030 mg/kg and from 28.2 to 19.6 mg/kg respectively by increasing ARM addition rate from 0 to 25% w/w. Concerning tailings, it was indicated that by increasing ARM addition rate from 0 to 25% w/w, the EDTA extraction of Pb, Zn and Cd in tailings remained practically constant at average values of 750, 285 and 6.7 mg/kg respectively.

The reduction of heavy metals solubility determined either by applying TCLP or EDTA extraction test is attributed to the increase of pH due to ARM alkalinity and the adsorption in specific binding sites of mineral surfaces contained in ARM. According to the TCLP results, even at the highest ARM addition rate applied on contaminated soil, the concentration of Pb in the TCLP leachate was found above the respective regulatory limit of 5 mg/l. Based on this criterion, other additives have to be co-added into the mixture to further improve leaching characteristics of the mixture. On the other hand, the minimum ARM dose applied (5% w/w) was sufficient to reduce Pb and Zn TCLP leachates concentration below the respective regulatory

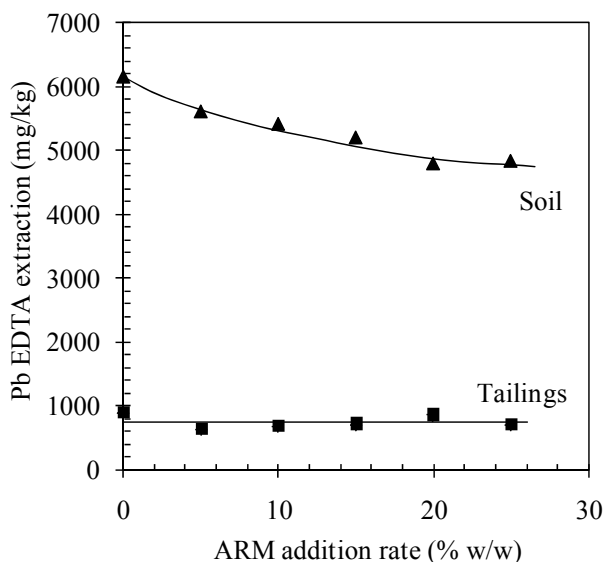


Figure 5: Extraction of Pb from contaminated soils and tailings with EDTA solution.

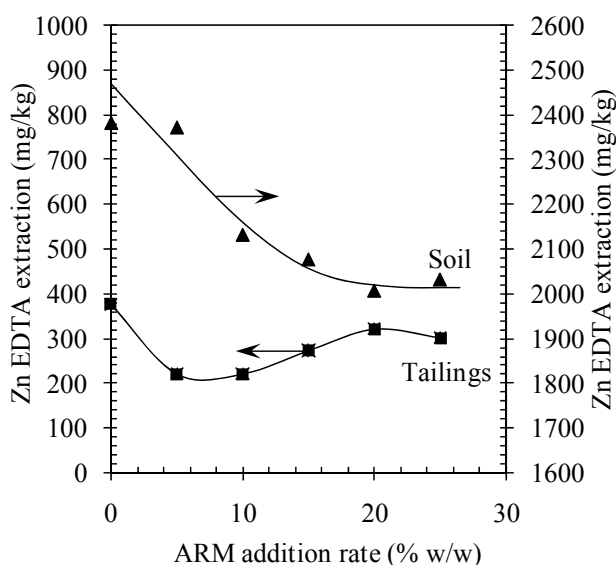


Figure 6: Extraction of Zn from contaminated soils and tailings with EDTA solution.

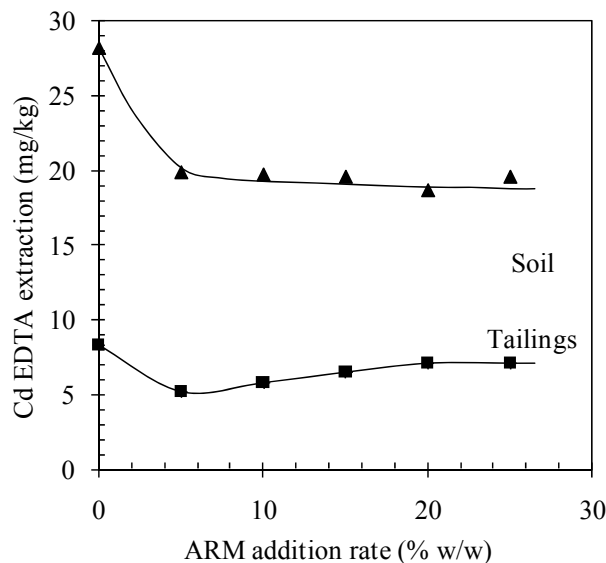


Figure 7: Extraction of Cd from contaminated soils and tailings with EDTA solution.

limits for all the remaining cases.

4. CONCLUSIONS

The Montevecchio soils and tailings are considered as hazardous since they present elevated heavy metals content, well above the Dutch intervention values, as well as high bioavailable fractions of these heavy metals as determined by the 5 stage sequential extraction procedure. Furthermore, either the Pb, or Pb and Cd concentration in the leachates of US EPA TCLP applied on tailings or contaminated soil respectively, were above the respective regulatory limits, whereas their phytoavailable fractions of Pb, Zn and Cd was also high. Due to the enhanced environmental risk, remediation of both sources of pollution is required.

Laboratory scale stabilization experiments carried out using treated with gypsum Alumina Red Mud as stabilizing agent indicated that addition of ARM improves immobilization of Pb, Zn and Cd in contaminated soils and tailings as proven by applying TCLP and/or EDTA extraction tests. Application of ARM on Montevecchio tailings at rates higher than 5% w/w was proven successful for the stabilization of Montevecchio tailings since it decreases Pb concentration in the TCLP leachates below the respective regulatory limit. However, this criterion has not been met in the case of Montevecchio soils, since Pb concentration in the TCLP leachates, although significantly decreased from 57 to 9 mg/L, it was still higher than the respective regulatory limit even at the highest dose applied.

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