# Toxicity Characteristic Leaching Procedure for Health Assessment of Stabilized Plating Sludge Using Amendments

Amin Falamaki

**Abstract**

**Background:** The occurrence of heavy metals in the environment is of important concern due to their toxicity and health effects on humans, including cancer. Because metals have been extensively used for centuries in commerce, environmental contamination is widespread; moreover, exposure to metals and metal compounds continues to be a significant public health problem. Electroplating sludge contains heavy metals. Solidification/Stabilization can be used to avoid leaching of these metals to the environment. The aim of this study was evaluating the effectiveness of the application of dicalcium phosphate (DCP) and sodium tripolyphosphate (STPP) on Cd, Co, Cu, Ni, Pb and Zn immobilization in dewatered metal plating sludge.

**Methods:** The ratios of STPP and DCP per dry plating sludge were determined to be 0.1%, 0.2% and 0.5% by weight. Metal leaching from the solidified plating wastes was assessed using the toxicity characteristic leaching procedure (TCLP). The results showed that the concentration of metals in untreated sludge were appropriate to classify this sludge as a hazardous waste as described in The Code of Federal Regulations (CFR) 40 CFR 261.24.

**Results:** DCP and STPP lowered the concentration of metal in the effluent. Increasing DCP concentration from 0.1 to 0.5% decreases the contaminant concentration in the effluent. For Cd, Pb, Cu and Ni increasing the percentage of STPP in the sludge increases the contaminant's concentration resulting from TCLP extraction.

**Conclusion:** Immobilization of heavy metals was more effective through application of DCP rather than STPP. Moreover, it may minimize the potential risk of groundwater eutrophication connected with the application of highly soluble phosphate like STPP.

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## Introduction

Because of the toxicity to humans and plants, heavy metals (HMs) and metalloid contaminants released in the environment are of major concern worldwide. This toxicity is lethal even in trace quantities as metals have a great tendency to bioaccumulate.[1] Environmental exposure to HMs is a well-known risk factor for cancers.[2] The presence of these contaminants in our environment is increasingly due to industrial pollution of the atmosphere, waterways, soils and sediments.[1] Tons of these elements are released into atmosphere by burning of the fossil fuels, smelting and other processing techniques, which can be carried long distances and later deposited on vegetation and soil. Therefore, there are many sources of them. All are daily ingested by humans either through the air or through food, water and soil.[3] Metals have been extensively used for centuries in commerce; consequently, environmental contamination is widespread and exposure to metals and metal compounds continues to be a significant public health problem. This would be true for people consuming grain grown on cadmium-enriched soil, from either phosphate fertilizer or sewage sludge, for people consuming fish from mercury-enriched lakes, or for those consuming vegetables from a lead-smelting contaminated area.[4]

Cadmium (Cd) is a heavy metal which is toxic to humans, animals, and plants. Cadmium in edible stuff is dangerous for human health since it accumulates in the main parts of body, like the kidneys and lungs, and can lead to some diseases like cancer.[5] Long-term exposure to low levels of lead can profoundly affect a child's development and neurological function, including intelligence. Lead poisoning has been shown to contribute to mental retardation, poor academic performance, and juvenile delinquency.[3] Epidemiological studies have shown that exposure to nickel (Ni) compounds is associated with a variety of pulmonary adverse health effects, such as lung inflammation, fibrosis, emphysema and tumors.[6]

Contrary to organic molecules which can be metabolized or destroyed, metals can only be transformed from labile toxic forms to more inert insoluble and less bio-available forms to minimize their harmful effects on living organisms. Therefore, the remediation of the environment contaminated with metals may involve the following processes: concentration reduction of bioavailable metals in soil and/or waste and contaminant isolation to prevent the interaction of such metals with the environment.[7] The solubility of heavy metals is related to their mobility and bioavailability; thus, chemical amendments can reduce the solubility of heavy metal contaminants. The application of phosphate-based amendments to contaminated soils and wastes has been identified as an extremely effective in situ remediation method.[8]

Toxicity characteristic leaching procedure (TCLP) is a well-known index for assessment of the hazards of different metals according to US EPA SW-846 method 1311[9] to evaluate the toxicity of a substance. For example, Tang and colleagues, studied pre-treatment of tannery sludge with phosphoric acid (PA) and monobasiccalcium phosphate (MCP) as a potential heavy metal emission control option. This treatment was shown to effectively stabilize Pb and Cd in the tannery sludge. Pb and Cd leachability, as determined by TCLP leaching tests, decreased with increasing P amendment addition rate by 32.6% and 44.7% for PA treatment and 40.1% and 39.5% for MCP treatment, respectively.[10]

Mignardi and colleagues investigated the effectiveness of synthetic hydroxyapatite (HA) and natural phosphate rock (FAP) in immobilizing Cd, Cu, Pb, and Zn in mine waste soils. The phosphate treatment of the polluted soils significantly reduced the water solubility of the metals with a reduction percentage ranging generally from about 84% to 99%. The proposed immobilization mechanism involves both surface complexation of the heavy metals on the phosphate grains and partial dissolution of the phosphate amendments and precipitation of heavy metal-containing phosphates. Between the two amendments evaluated, HA was slightly more effective with respect to FAP in immobilizing heavy metals.[11]

Up to now, different investigations have been accomplished to show that phosphate-based amendments(specially including $PO^{4-}$) are useful for immobilizing heavy metals.[12, 13, 14] Some researchers used phosphate amendments to remediate the contaminated soil [e.g.,];[13, 15] some others investigated remediation of the sludge [e.g.][10, 16] and mine or other wastes [e.g.].[1, 8, 11] But solidification of plating sludge or waste using phosphate amendments is limited and only few researchers have investigated the stabilization of plating sludge by cement [e.g.].[17, 18] The aim of this study was to evaluate the effectiveness of the application of calcium monohydrogen phosphate and sodium tripolyphosphate amendments on Cd, Co, Cu, Ni, Pb and Zn immobilization in dewatered metal plating sludge.

## Materials and Methods

### *Phosphate Amendments*

Calcium monohydrogen phosphate (CMP) or dicalcium phosphate (CaHPO4) and sodium tripolyphosphate ($Na_5P_3O_{10}$) have been used as phosphate amendments in this study (2014). Dicalcium phosphate is usually found as the dihydrate, with the chemical formula of $CaHPO_4.2H_2O$, but it can be thermally converted to the anhydrous form. DCP is mainly used as a dietary supplement in prepared breakfast cereals, dog treats, enriched flour, and noodle products. It is also used as a tableting agent in some pharmaceutical preparations, including some products meant to eliminate body odor. Calcium monohydrogen phosphate is also found in some dietary calcium supplements (e.g. Bonexcin). It is used in poultry feed and also in some toothpaste as a tartar control agent.[19]

Sodium tripolyphosphate is the sodium salt of the polyphosphatepenta-anion, which is the conjugate base of triphosphoric acid. It is produced in large scale as a component of many domestic and industrial products, especially detergents. STPP is a white powder which is inexpensive. Soluble phosphate sources could provide an abundance of solution P and increase the efficiency of metal-phosphate mineral formation.[20] STPP is one of the soluble phosphate salts and its use to remediate HM-contaminated soils must be carefully studied, because of the secondary contamination problems. Due to the high solubility of these phosphates and the fact that phosphate is a nutrient, this technique can lead to eutrophication of groundwater and surface waters.[21] Moreover, sodium phosphates cause later problems in soils.[20] But using it to remediate hazardous wastes and then landfill them does not seems to be a problem.

*Sample Preparation*

Plating sludge was obtained in polyethylene bags from one of the plating industries at North West Shiraz, Fars province, Iran. Electroplating sludge contains heavy metals such as Cr, Sn, Zn, Cu, Ni, Mn, Pb, Cd and Ag.[22] As mentioned before, to avoid leaching of these HMs to the environment, two phosphate amendments were used. The ratios of the STPP and DCP per dry plating sludge were assigned to be 0.1%, 0.2% and 0.5% by weight in this study. The samples were kept in polyethylene bags and cured for 28 days. Then, the metals were extracted by the toxicity characteristic leaching procedure (TCLP) as defined by the U.S. EPA from non-stabilized and stabilized samples twice and the average value was reported.

*TCLP Procedure*

TCLP is commonly used to determine whether the waste is hazardous and if a treated waste meets the treatment standards for land disposal. This test provides useful information on the potential leachability of metals in the sludge and bottom ash.[10]

The leaching test was conducted according to US EPA SW-846 toxicity characteristics leaching procedure (TCLP) test method 1311 to evaluate the leaching behaviors of Cd, Co, Cu, Ni, Pb and Zn from the untreated and the amended sludge.[19] Extracting solution no. 2 of the TCLP was used in the leaching test. A 5.7-mlaliquot of glacial acetic acid was diluted to 1.0 L with reagent water. The pH of the extracting solution was 2.88±0.01. A 20-ml extracting solution was added to a 50-ml polycarbon at the centrifuge tube containing 1,000 g of the tested soil. The tube was sealed with a cap and placed on an end-over-end shaker at 30±2 r/min for 18 h at 25 °C. After extraction, separation of the supernatant was done through centrifuging (J2-21, Beckman, USA) at 3000 r/min for 10 min. Atomic absorption spectrometry apparatus was used to determine the concentration of metals in the extracted solution samples.

*Testing Program*

Table 1 presents the experimental program TCLP tests for this research. A preliminary test (T1), in which phosphate additives were not present was conducted to find out the amount of the extracted metals. As shown in this table for Test T1, the concentration of cadmium and lead in untreated sludge was appropriate to classify this sludge as a hazardous waste. It is remarkable that according to US EPA, the maximum allowable concentrations of cadmium and lead in the sludge by TCLP (in ppm) must be less than 1 and 5 mg/kg, respectively.[19]

In order to find out the effect of the stabilizer concentration and optimum amount, Tests T2, T3 and T4 were conducted with 0.1, 0.2 and 0.5% DCP by weight of the dry sludge, respectively. The same concentrations of STPP were used in Tests T5 through T7 to compare the effectiveness of DCP and STPP.

## Results

The results of the leaching tests for Cd, Pb, Co, Cu, Ni and Zn are presented in Figure 1 through Figure 2, respectively. In these Figures, the concentration of a metal in the extracted leachate is plotted versus the percentage of the phosphate amendments. Some common results obtained from these figures are as follows:

1) As a main result, all the Figures demonstrate that both DCP and STPP used in this study lowered the Cd, Pb, Co, Cu, Ni, and Zn concentrations in the effluent resulting from TCLP experiments.

2) For a certain metal, all the Figures show that increasing DCP concentration from 0.1 to 0.5%

**Table 1:** TCLP tests conducted in this study

| Experiment | Test Symbol | Amendment | Amendment/Dry soil (% by weight) | Measured Contaminant by TCLP (ppm) | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | Cd | Pb | Co | Cu | Ni | Zn |
| T1 | Un-Sludge | - | 0 | 6.59 | 5.11 | 3.05 | 3.13 | 4.73 | 2.85 |
| T2 | DCP 0.1% | DCP | 0.1 | 0.76 | 2.04 | 2.11 | 1.59 | 1.39 | 1.05 |
| T3 | DCP 0.2% | DCP | 0.2 | 0.38 | 1.91 | 1.81 | 1.47 | 0.93 | 0.23 |
| T4 | DCP 0.5% | DCP | 0.5 | 0.25 | 1.83 | 1.76 | 1.41 | 0.80 | 0.23 |
| T5 | STPP 0.1% | STPP | 0.1 | 0.20 | 1.90 | 1.90 | 1.50 | 0.84 | 2.85 |
| T6 | STPP 0.2% | STPP | 0.2 | 0.14 | 1.84 | 1.76 | 1.38 | 1.77 | 2.70 |
| T7 | STPP 0.5% | STPP | 0.5 | 0.32 | 2.19 | 1.76 | 1.78 | 2.10 | 1.55 |

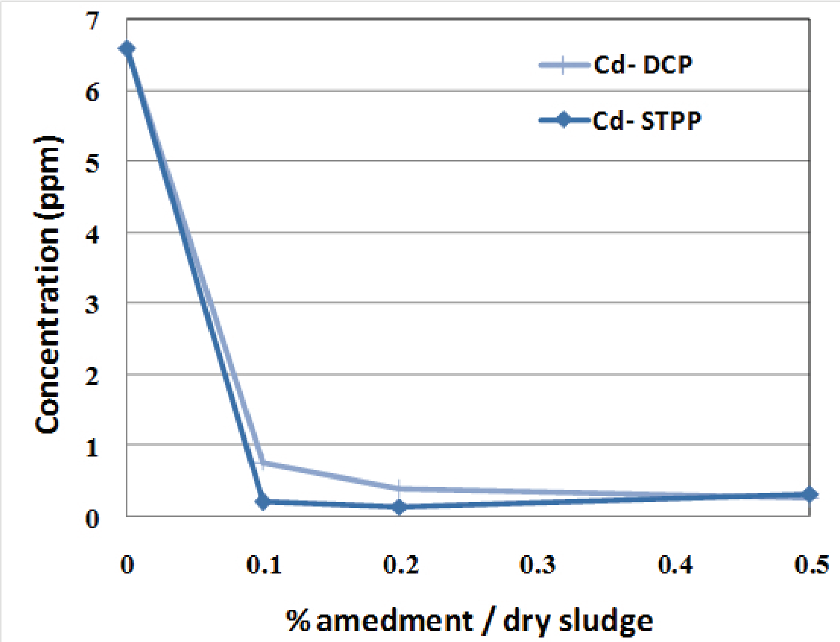


**Figure 1:** Adding DCP and STPP to the sludge lowered the Cd concentrations in the effluent resulting from TCLP experiments.

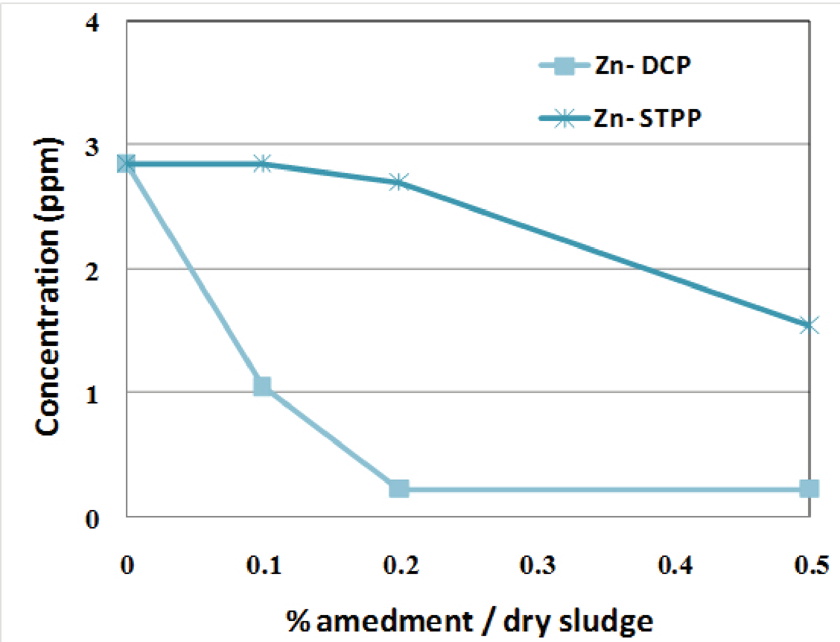


**Figure 2:** Adding DCP and STPP to the sludge lowered the Zn concentrations in the effluent resulting from TCLP experiments.

decreases the contaminant concentration in the effluent resulting from TCLP experiments. However, it is remarked that the rate of this decrease is lower for Cd and Pb compared to the others.

3) For a certain metal, the Figures (Except for Zn) showed that using 0.1% STPP stabilized more contaminants (decreases more contaminant concentration resulting from TCLP extraction) compared to 0.1 % DCP.

4) For Cd, Pb, Cu and Ni (Figures 1, 3, 4 and 5), increasing the percentage of STPP in the sludge increases contaminant concentration resulting from TCLP extraction, i.e. a decrease in stabilizing efficiency.

According to Figure 1, using 0.1%, 0.2% and 0.5% DCP decreases the leachability of Cd in stabilizing the plating sludge from 6.6 mg/kg to 0.7, 0.3 and 0.2 ppm, respectively. In addition, it decreased to 0.20, 0.14 and 0.32 ppm when the sludge was treated with 0.1%, 0.2% and 0.5% STPP. The same results and behavior are seen in Figures 3 through 5 for Pb, Co, Cu and Ni, respectively.

According to Figure 3, Pb in the sludge was measured about 5 ppm and using both amendments

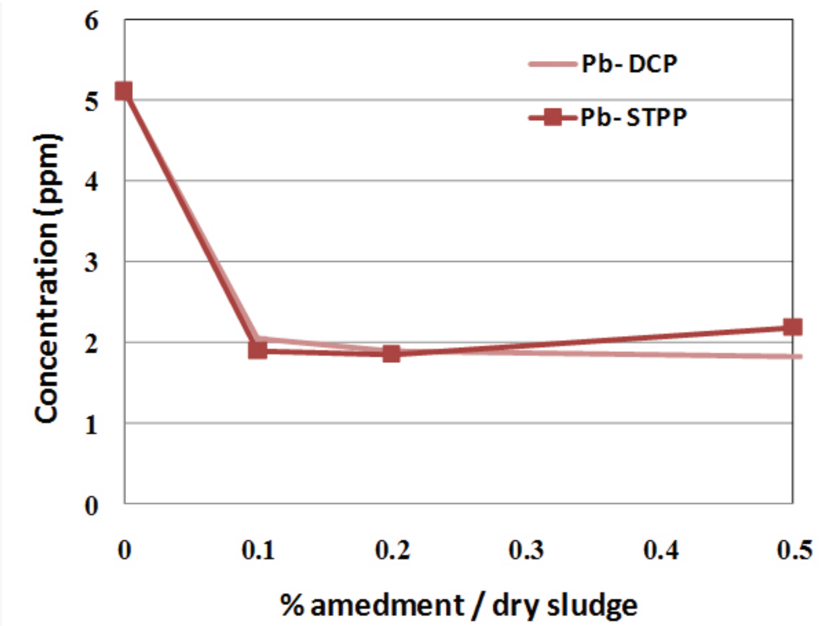


**Figure 3:** Adding DCP and STPP to the sludge lowered the Pb concentrations in the effluent resulting from TCLP experiments.

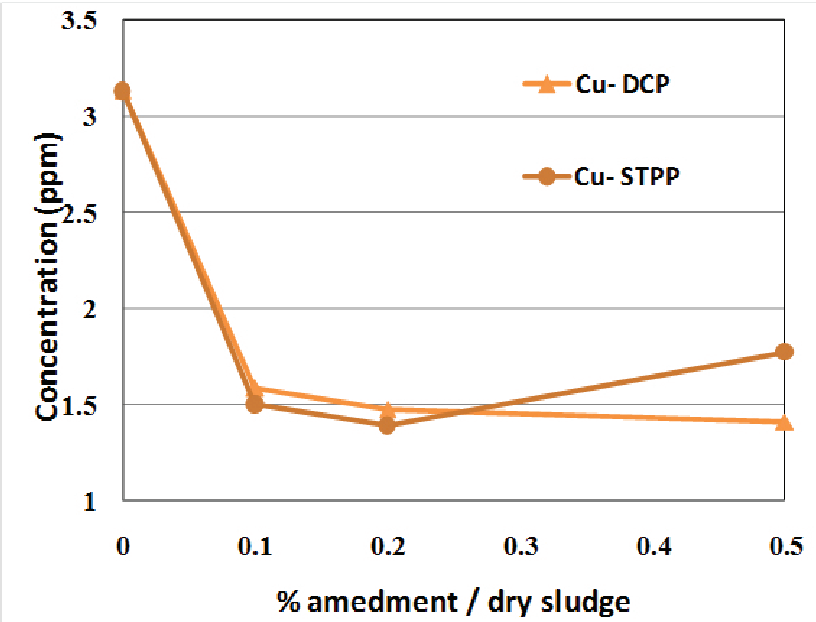


**Figure 4:** Adding DCP and STPP to the sludge lowered the Cu concentrations in the effluent resulting from TCLP experiments.

causes the leachability to reduce about 2 ppm. For Co presented in Figure 6, the amendments less than 2% is less effective; however, using more than 2% reduces the extracted Co dramatically. Increasing STPP concentration increased Cu and Ni in the effluent, significantly (Figures 4 and 5), and the optimum percentage for DCP and STPP was 2 and 1%, respectively.

Figure 2 shows that DCP can decrease the concentration of Zn from 2.9 in the untreated sludge to lower than 0.25, while STPP could not immobilize Zn.

For a better understanding of the above-mentioned results, Figures 7 and 8 reveal the relative reduction in contaminant concentration for different metals versus the percentage of amendment are plotted. Relative reduction in contaminant concentration is calculated by dividing the difference between metal concentrations extracted from untreated and treated sludge by the metal concentrations extracted from the untreated sludge. Figure 7 shows that increasing the concentration of DCP enhances the efficiency of stabilization for all metals. The rate of efficiency decreases for more than 2% DCP. Therefore, the optimum percent for stabilizing may be between 0.1 to 0.2% for DCP. Contrary to DCP, increasing STPP concentration does not warranty the efficiency and may decrease it according to Figure 8.

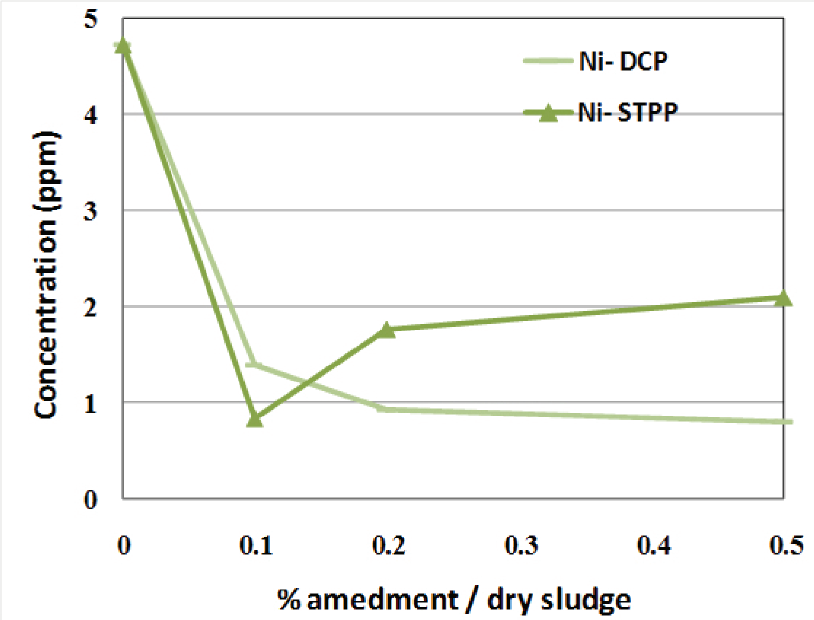


**Figure 5:** Adding DCP and STPP to the sludge lowered the Ni concentrations in the effluent resulting from TCLP experiments.

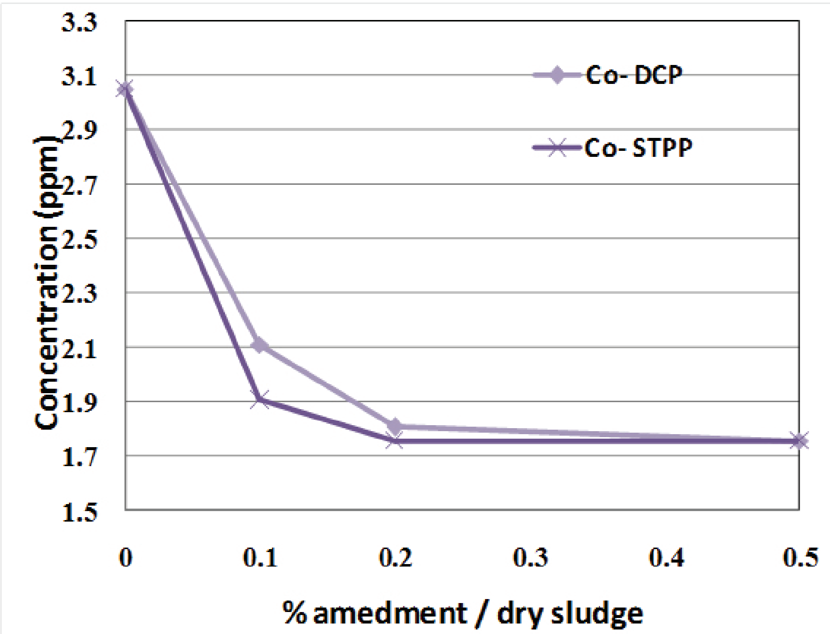


**Figure 6:** Adding DCP and STPP to the sludge lowered the Co concentrations in the effluent resulting from TCLP experiments.

It is observed from these figures that using DCP and STPP can reduce leachability of Cd from sludge about 88% to 98%, however, STPP is a little more effective. Cd immobilization may be related to the ion exchange and complexation mechanisms, suggesting that the process results in formation of Cd-containing phosphates.[11, 23] Similar fixation mechanisms have been also proposed for Zn.[24, 25]

The extractable concentrations of Pb in the DCP and STPP treated the sludge decreased by about 60-64% and 57-63%, respectively (Figures 7 and 8). Similar results were also found by Theodoratos and colleagues and Tang and colleagues when they stated the treatment with MCP stabilized Pb and Cd effectively.[10, 26] Formation of chloropyromorphite (or hydroxypyromorphite) through the dissolution/precipitation mechanism is suggested for Pb fixation[27, 28] although some studies also reported the participation of surface mechanisms in the overall immobilization of Pb.[25]

The extractable concentrations of Cu in the treated sludge decreased about 44% to 55%. For the immobilization of Cu, Sugiyama and colleagues reported that the main mechanism was dissolution/precipitation[29] whereas Cao and colleagues concluded that the surface adsorption was the main fixation process.[30]

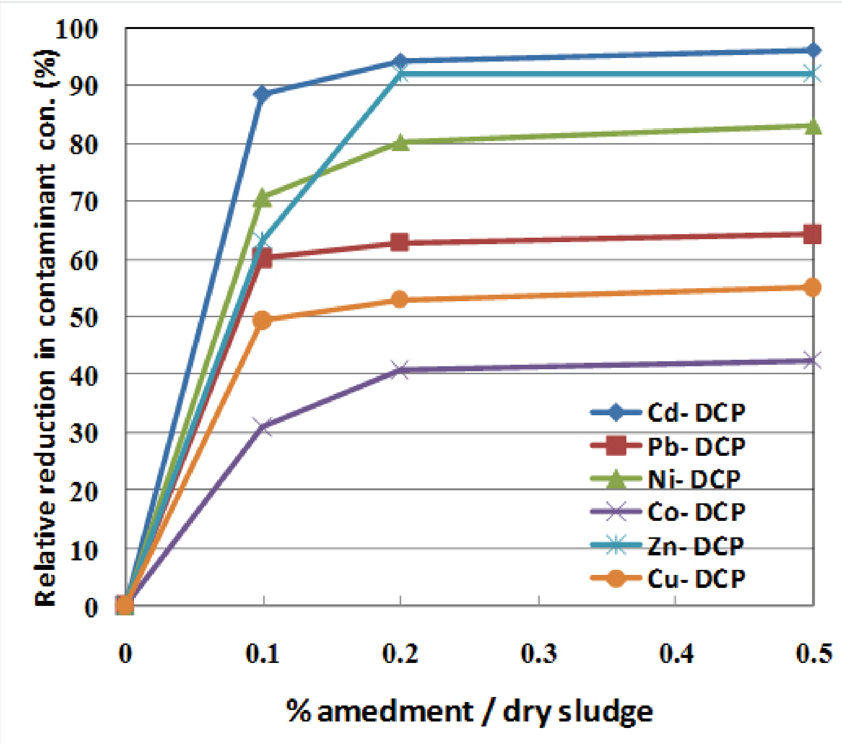


**Figure 7:** Increasing the concentration of DCP effects on the stabilization and enhancement of the efficiency for all metals

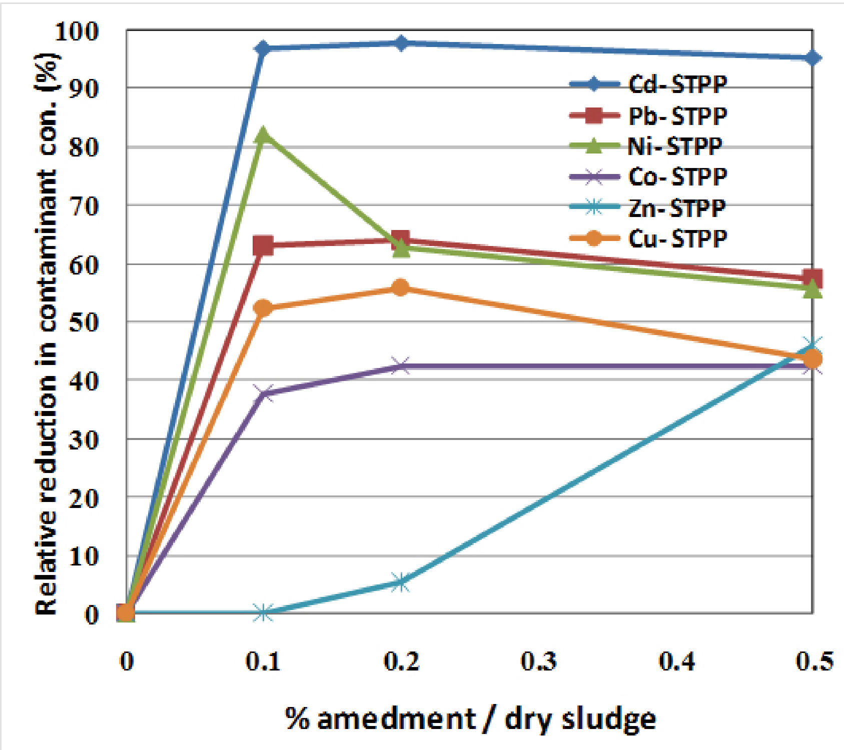


**Figure 8:** Increasing the concentration of STPP effects on the stabilization and enhancement of the efficiency for all metals

The application of 0.5 % DCP to the plating sludge reduced concentrations of Ni and Co about 83% and 42%, respectively (Figure 7). However, STPP could not immobilize the Co and Ni containing sludge effectively. Mignardi and colleagues reported that in contrast to other heavy metals, relatively limited information about Co and Ni immobilization by phosphate amendments exists. They showed that formation of complexes of the Co and Ni on the surface of phosphate grains and partial dissolution of the amendments and precipitation of these heavy metal-containing phosphates are the dominant immobilization mechanisms. Moreover, they suggested that the mineralogical composition of the mine waste soils may impact the effectiveness of metal immobilization.[25]

Zn was stabilized with DCP efficiently (more than 80% in Figure 7) while STPP at the best efficiency could stabilize less than 50 % of it. Tang and colleagues inferred that the increase of Zn solubility when mixed with soluble phosphate like phosphoric acid (PA) was attributed to the weak bonds of the surface complex mechanism between Zn and phosphate. Therefore, this may cause greater leachability of Zn in the treated sludge with STPP. The fixation mechanism of Cu and Zn involved both surface complexation and co-precipitation.[31] Ma and colleagues also proved that Cu and Zn reacted with dissolved P through precipitation of amorphous to poorly crystalline metal phosphates.[32] Thus, the DCP treatment had positive effects on Zn.

## Discussion

The results of previous studies suggested that metals having high water solubility pose a high potential risk to the local aquatic environments as metal water solubility is directly related to mobility and bioavailability of the metals.[25] HM toxicity to humans and plants is lethal even in trace quantities and metals have a great tendency to bioaccumulate. Environmental exposure to HMs is a well-known risk factor for cancers.

In the present study, the effectiveness of two phosphate treatments called DCP and STPP was tested in immobilizing Cd, Co, Cu, Ni, Pb and Zn in the plating sludge. The application of DCP amendment significantly reduced the water solubility of the metals through immobilization mechanisms involving surface complexation of the heavy metals on the phosphate grains and partial dissolution of the phosphate amendments and precipitation of heavy metal-containing phosphates.

Heavy metals immobilization was slightly more effective with respect to application of DCP. Moreover, it may minimize the potential risk of eutrophication connected with the application of highly soluble phosphate amendments. Modifications with highly soluble P may increase the risk of P-induced eutrophication.

Although the exact reaction mechanism responsible for the removal of metal ions by DCP remains unknown, previous research suggested that the reaction mechanisms for metal immobilization by phosphate minerals include: (a) ion exchange process; (b) surface complexation; (c) dissolution of the original phosphate minerals and precipitation of new metal phosphates; and, (d) substitution of Ca in phosphate by other metals during recrystallization (co-precipitation).[32]

**Conflict of Interest:** None declared.

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