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Cement Based Solidification/Stabilization Leaching Performances of Selected Heavy Metal Ions under Different pH Extractions

Basim A. Hussain
Environmental Engineering, Ministry of Science and Technology Directorate of Hazardous Wastes Treatment and Disposal, Baghdad, Iraq
basimsaidi@hotmail.com

Shahlaa E. Ebrahim
Environmental Engineering University of Baghdad, Environmental Engineer Department, Baghdad, Iraq
shahlaa.ebrahim@fulbrightmail.org

Abbas H. Sulaymon
Chemical Engineering, University of Baghdad, Environmental Engineer Department, Baghdad, Iraq. inas_abbas@yahoo.com

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Abstract- *Liquid to solid partitioning as a function of pH leaching Procedure LSP EPA method 1313 was carried out to test the effectiveness , performance and efficiency of the cement-based solidification / stabilization (S/S) of heavy metals contaminated sand samples using Ordinary Portland Cement OPC type A . Two cement based mix designs (7 and 25 %) have been applied to (S/S) sand contaminated samples with different heavy metal ions (Pb , Cu , Cr , and Cd) having the following concentrations (500 , 1500 and 3000 mg / kg). Fixed water to cement ratio of 0.45 was maintained for all the experiments. Effective retention levels for the heavy metal ions was achieved using a 25 % OPC mix ratio to (S/S) the contaminated samples even when the extraction solutions were of pH levels as low as 2. Leaching experiments showed that as the pH level of the extraction solution is reduces and as the OPC content in the (S/S) samples is reduced the more heavy metal ions that can leach out. Up to 80 % of chromium, cadmium, lead, and copper ions leachability can be prevented when higher cement content is introduced to the solidification / stabilization process under the same pH extraction. Acidic extraction effects and solubilized the Calcium – Silica – Hydrate (C-S-H) gel that is created by the OPC binder, which holds, and contain the heavy metal ions and thus results in more release of those ions into the extraction solutions. The alkaline environments provided by the cement binder are believed to have participated in the precipitation of several metal ions such as cadmium and lead io, leading to their less detection in the leaching extracts. Alkaline extraction experiments (pH 8-13) showed that the mobility of the metal ions under the same experimental conditions followed the order of pb> Cr > Cu > Cd in samples of various cement contents.*

Keywords- *Solidification / Stabilization; Heavy Metals; LSP; Leaching.*

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1. Introduction

Disposal of hazardous wastes in landfills is a worldwide environmental problem and the pollutants can leach into the surrounding environments causing a serious threat to life even longer after the source of pollution has been removed [1]. This is where solidification/ stabilization (S/S) comes as an effective technology of hazardous waste management. The technology works by converting the waste into a solid matrix, which allows for the ultimate disposal of the waste in a safe manner [2]. This remediation and treatment method is capable of reducing the mobility of the polluted contaminants so that they do not move through the environment. In many Parts of the world cement based (S/S), technology provides a very promising solution for the disposal and remediation of polluted soils with heavy metals. Several studies have shown that contaminated sites with inorganic pollutants can result in the leaching of those toxic substances to the surrounding environment. The release of this release of the contaminants into the environment has an adverse effect on the well-being of life and pose a potential danger to the hydrologic cycle and the food chain [3]. Various types of domestic, industrial and agricultural wastes such as garbage, sleds, solids, liquids, fertilizers and even nuclear wastes can much benefit from what immobilization technologies such as the cement-based solidification/stabilization can provide. In

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2412-0758/University of Technology-Iraq, Baghdad, Iraq

stabilization, the waste is detoxified through destruction or fixation of the contaminants present in the waste. Meanwhile, solidification improves the physical characteristics of the waste form [4]. The United States Environmental Protection Agency (EPA) considers the (S/S) technology a key treatment option for Resource Conservation and Recovery Act (RCRA) and Comprehensive Environmental Response Compensation and Liability Act (CERCLA) listed industrial hazardous wastes and contaminated sites [5]. (S/S) technologies have proven to have an effective leachability reduction for inorganic contaminated soils [6]. Soils and sediments polluted with inorganic contaminates could be treated by cement-based Solidification / Stabilization (S/S) technology. The toxic consistencies could be fixed and contained through a number of mechanisms such as Sorption (Physical and chemical adsorption), Complexation, and Precipitation [7]. In cement-based solidification/stabilization, the water-Cement reactions formulate three main products: Hydrated Calcium Silicates (C2SHx, C3S2 Hx) Known by calcium Silicate Hydrate gels (C-S-H), Hydrated Calcium aluminates (C3AHx, C4AHx) and Hydrated Lime Ca(OH). Because of those reactions, the cement particles bind the adjacent grains together and form aharden skeleton matrix. This matrix enclosed the soil particles. Moreover, the cement hydration process results in a raise in the pore water pH due to the dissociation of the hydrated lime. The strong based solution formed directly reacts with the soil silica and soil alumina strong acid. This reaction will gradually produce insoluble compounds (Secondary Cementations product) that play a big role in the stabilization of soil.

This study focuses on the cement based (S/S) process and the leaching characteristics under different pH extractions of five selected heavy metal ions (Cd, Cr, Cu, and Pb).

2. Experimental Work

The main objectives of this study include:

- Studying the mobility of selected heavy metal ions from cement based solidified / stabilized contaminated sand samples under different pH extractions .
- To determine the effectiveness of the cement-based treatment on the leachability characteristics of the (S/S) products.
- Analyzing the effects of the extraction solution pH and heavy metal ion type and concentration on the leaching potentials from cement based (S/S) matrixes.

3. Materials and Method

Sand samples from a barrow bit located at the city of KARBALA in the southern part of Iraq were collected to represent the contaminated media with the selected heavy metal ions. The sand media is classified as type sand and has the sieve analysis and characteristics shown in Figure 1 and Table 1 respectively. Synthetic heavy metal ions were prepared from standard metal salts using the standard weight equivalent procedure [8] and were then added to pre-weighted amounts of sand samples to obtain a contamination heavy metal ion to sand concentrations of (500, 1500 and 3000 mg/kg) The contaminated sand samples were then mixed with Ordinary Portland Cement OPC Type I of characteristics shown in Table 2 at two different mix designs (7 and 25 %) using an 0.45 water to cement ratio. The mixtures were then cast in plastic PVC molds of 5 cm in diameter and 10 cm in height and left of 28 days curing. Solidification/Stabilization was performed according to the ordinary cement paste mixing procedure ASTM C305.

The leaching characteristics and performance of Cement - based (S/S) specimens under different pH extractions were tested using the Liquid to Solid Portioning as a function of pH LSP standard leaching test procedures (EPA Method 1313). The experiments included samples of four heavy metal ions (Pb, Cd, Cr, and Cu) at three contamination loads (500, 1500, 3000 mg/ kg) and two cement based by weight mixed designs (7 and 25 %). Table 3 shows the experimental design used in this study. LSP leaching (EPA test Method 1313) as a function of pH was applied to express and evaluate the leachability characteristics of the cement-based solidified/stabilized samples. The LSP leaching tests can determine the mobility of inorganic analyses present in solid or solidified wastes under different pH extractions. The test is carried out by using extraction fluids of various pH levels, as shown in Table 5. After Specimens curing period, the samples were crushed, sieved to pass 9.5 mm mesh. A weight of 20-gram specimen was then taken and mixed with the 200 ml extraction solution of different pH as shown in Table 4, and then agitated top to bottom for 18 hours at 30 rpm (Rounds per minute. After the agitation period, the nine extraction bottles which represent extraction of nine pH levels (2 , 4, 5.5, 7, 8, 9, 10, 11 and 13) were left to settle, the solid was separated from the extraction fluids, and finally the extraction fluids were collected, filtered and taken for laboratory analysis.

Figure 2 (a, b, c and d) show the cement based solidified/Stabilized heavy metal contaminated samples, experimental apparatus and extraction bottles and the agitation extraction devise used respectively.

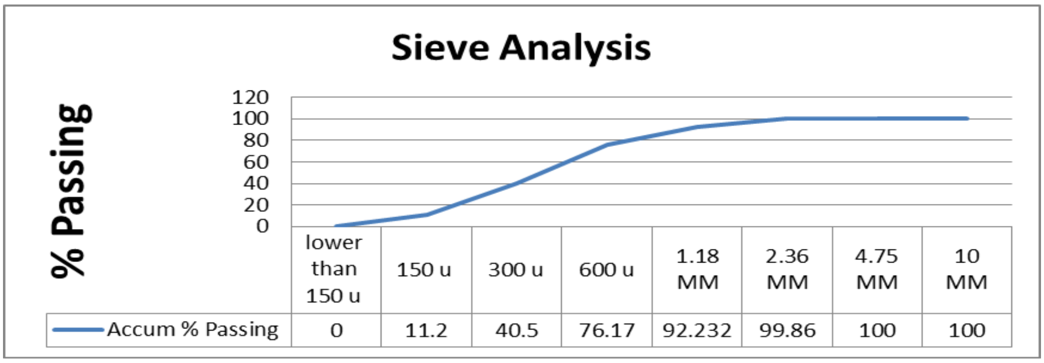

Figure (1) Sieve analysis for the sand used in the study

Table 1: Sand characteristic

Parameter	Characteristics
Texture	Sandy
pH	8.2
SO_3	< 0.5
Total Organic Carbon (%)	1.5
Organic Matter (%)	1.8
Bulk Density (Kg/M3)	1400
Surface Area (M2/g)	3.7
Moister Content (%)	2.28

Table 2: Cement Chemical Specifications

Content	Result
Alumnae Total Content %	6.42
Magnesium Oxide Concentration %	3.13
Sulfate content SO_3 %	2.38
Total non-dissolved materials %	1.02
Loss due to ignition %	3.65
Tar total Content %	0.96

Table 3: Experimental Matrix

Heavy Metal Ion type	Ion Concentration in sand Sample Mg/Kg	Mix Design	EPA 1313 Liquid-to –solid portioning Test
Cd	500 mg/Kg	M1,M2,M3	*
	1500 mg/Kg	M1,M2,M3	*
	3000 mg /kg	M1,M2,M3	*
Cu	500 mg/Kg	M1,M2,M3	*
	1500 mg/Kg	M1,M2,M3	*
	3000 mg /kg	M1,M2,M3	*
Cr	500 mg/Kg	M1,M2,M3	*
	1500 mg/Kg	M1,M2,M3	*
	3000 mg /kg	M1,M2,M3	*
Pb	500 mg/Kg	M1,M2,M3	*
	1500 mg/Kg	M1,M2,M3	*
	3000 mg /kg	M1,M2,M3	*

Table 4: Acid and Base Titration Schedule for LSP pH function leaching test

Bottle No.	Targeted Extract pH	Volume of 2N HNO_3 added ml	Volume of 1N KOH added ml	Sample moister Volume ml	Volume of reagent water added ml
TO1	13.0	-	19	2	179
TO2	12.0	-	13	2	185
TO3	10.5	-	6.3	2	192
TO4	9.0	-	2.5	2	196
TO5	8.0	-	1.5	2	197
TO6	Neutral	-	-	2	198
TO7	5.5	1.4	-	2	197
TO8	4.0	8.5	-	2	190
TO9	2.0	26	-	2	172
Control 1	-	-	-	-	200
Control 2	-	26	-	-	174
Control 3	-	-	19	-	181

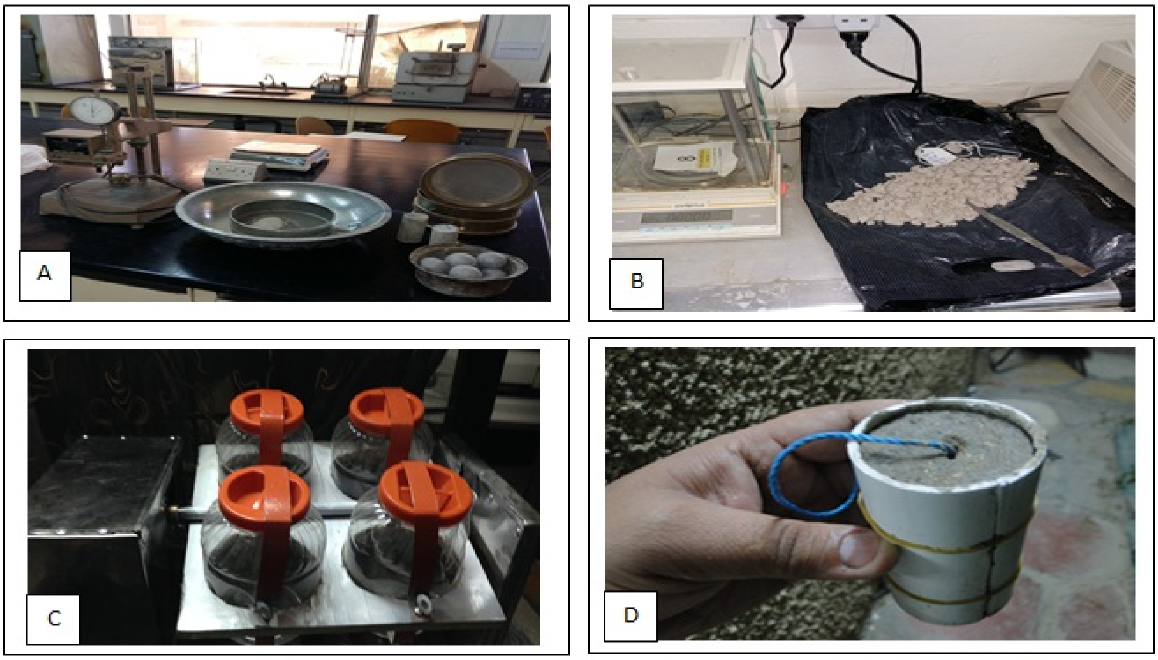

Figure 2: Experimental Procedure and apparatus, A) Specimen Preparation B) Crushing the Sample C) Agitation Process D) Sapling for Leaching Test

4. Results and Discussion

Liquid to solid portioning (LSP) as a function of pH leaching tests was carried after 28 days of curing of the cement-based solidification and stabilization of the heavy metal ions contaminated sand samples using EPA method 1313.

I. Chromium ions leachability

The results showed as in Figure 3 that up to (80%) of chromium ions leachability can be prevented by introducing more cement content to the (S/S) samples at all pH level extractions. The figures also show that when higher OPC ratios have used the gap in leachability between low, moderate, and high initial chromium contaminated samples is also reduced that for all the samples. Figure 3 also shows a study inclement of chromium ions leachability with respect to pH reduction of the extraction solution. It is expected that during the (S/S) process, the soluble chromium ions reacted with the calcium present in the cement and formed calcium chromate compounds in the form of CaCrO4. This compound then precipitates during the hydration stages of cement as chromate ions on the surface of the(C-S-H) gel matrix and thus lower concentrations of chromium ions detected in the leaching extracts. Omotoso et al. [9] in their study to fix chromium ions using cement found that during the hydration stage of cement chromium ions are precipitated in the form of complexes such as $Ca_2CrO_5.3H_2O$ and found in the cement matrix which results in lower detection of chromium ions in the leached extractions.

II. Cadmium ions leachability

Cadmium ions leachability under different pH extractions took the pattern seen in Figure 4. As soon as the pH value of the extraction solution dropped below (5) the cadmium ions concentrations in the leachate increased sharply. This increment may be related to the high solubility of Cd (OH) 2, which is the form of a compound that is created as soon as cadmium particles contact cement particles in the presence of water .This compound is then trapped within the cement pores and at pH levels below (5), the (C-S-H) gel and cement matrix are solubilized leading to the direct release of the compound and increasing its cadmium ions concentration in the extracting leaching effluent. Bishop [10], Cartledgeet et al. [11] in their study to investigate cadmium leachability potentials found out that cement based (S/S) process are very much affected by the pH level of the extraction solution and that low pH values can solubilize the cement matrix and lead to the release of the entrapped inorganic species. It was also found that alkaline environments (pH levels above (10) have helped in the precipitation of cadmium ion compounds and the lowest leached concentrations have been detected under such high pH extractions. Cement is capable of providing high alkaline environments, which can help in the precipitation of many inorganic compounds [12].

III. Lead ions leachability

Figure 5 shows that lead ions began to leach rapidly directly after pH levels below (7).

This indicates that lead as a compound is incorporated within the (C-S-H) matrix and as soon as this matrix is dissolved, the metal is released into the leachate solution. The leaching of lead was the lowest in those specimens in the pH range of (8.0–10.0). The leaching rate of lead ions increases as the pH levels of the extraction solutions decreases or increases beyond this pH range. Increment in OPC content in the (S/S) matrix had a great influence in reducing the leachability of lead ions under all pH extractions. Results show that using high cement percentage in preparing the (S/S) matrix can result in very low lead ion leachates even if the inertial concentrations of the ion are relatively high (3000 mg / kg). Rachana and Rubina [13] found out stated that cement based (S/S) of lead-contaminated sites could be a very attractive remediation approach.

IV. Copper ions leachability

Copper ions leachability behavior with respect to extraction solution pH took the patterns seen in Figure 6. At the extraction solution of (pH < 7), It was seen that the increment of copper ions concentrations in the final leachate was moderate when compared with the other metal ions investigated in this study. Results revealed that copper ions leached concentrations from cement based (S/S) systems were much lower than what was expected. This indicates that new reactions and formation of new species have taken place during the hydration and hardening process of cement bases metal ions admixture. The amount and nature of those species is a function of the proportion between the amount of copper ions present and the amount of cement used in the (S/S) process. Athanasios et al. [14] showed through XRD analysis cement based (S/S) matrixes that copper formulates species when mixed with cement. The results of this study have reviled that copper leachability in cement-based matrixes is related to cement content, metal ion concentration and the pH level of the extraction fluid.

5. Conclusions

Alkaline extraction experiments (pH 8-13) showed that the mobility of the metal ions under the same experimental conditions followed the order of pb> Cr> Cu> Cd in samples of various cement contents. The mobility of cadmium and Copper ions were very sensitive to pH, unlike the mobility of chromium lead ions, which were not affected as much. The leaching trend of the metal ions seems to be influenced by the manner that those metals incorporate within the cement matrix. The (OPC) content used in the (S/S) process had a direct effect on the extraction solution pH increasing it to levels much higher than the intended set out levels in the (LSP) extraction test. (LSP) leaching experiments showed that the lowest retention capacities and the highest leachate concentrations were attained at pH (2). Cementitious binders provide a strong alkaline internal environment through the presence of $Ca(OH)_2$. When a cement mortar is exposed to an acidic solution, the surface is eroded and exposed for more metal leaching.

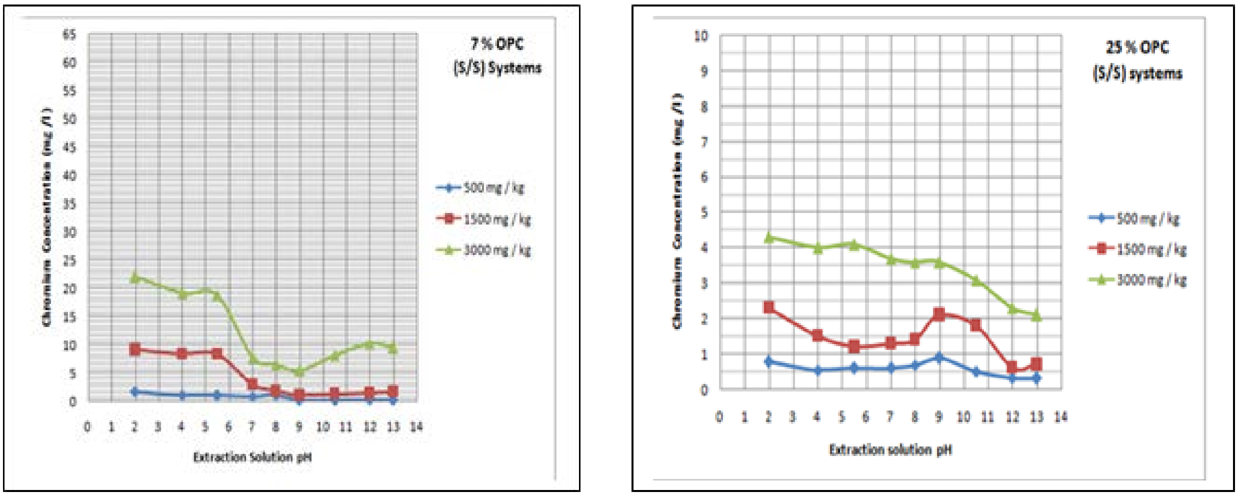

Figure 3: LSP As a function of pH chromium ions leaching from Cement-based S (S/S) samples.

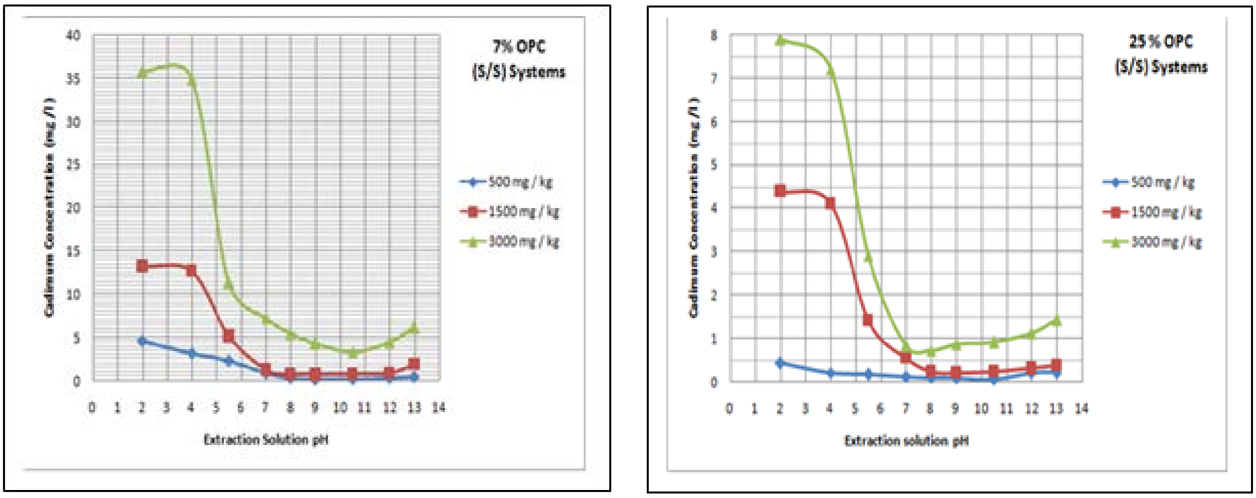

Figure 4: LSP As a function of pH cadmium ions leaching from Cement-based S (S/S) samples.

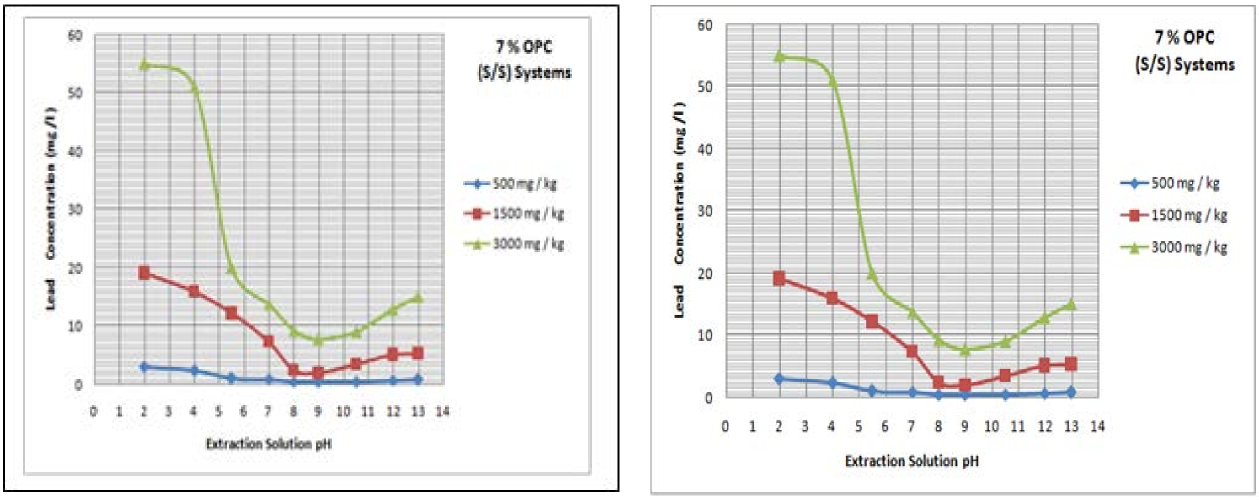

Figure 5: LSP As a function of pH Lead ions leaching from Cement-based S (S/S) samples.

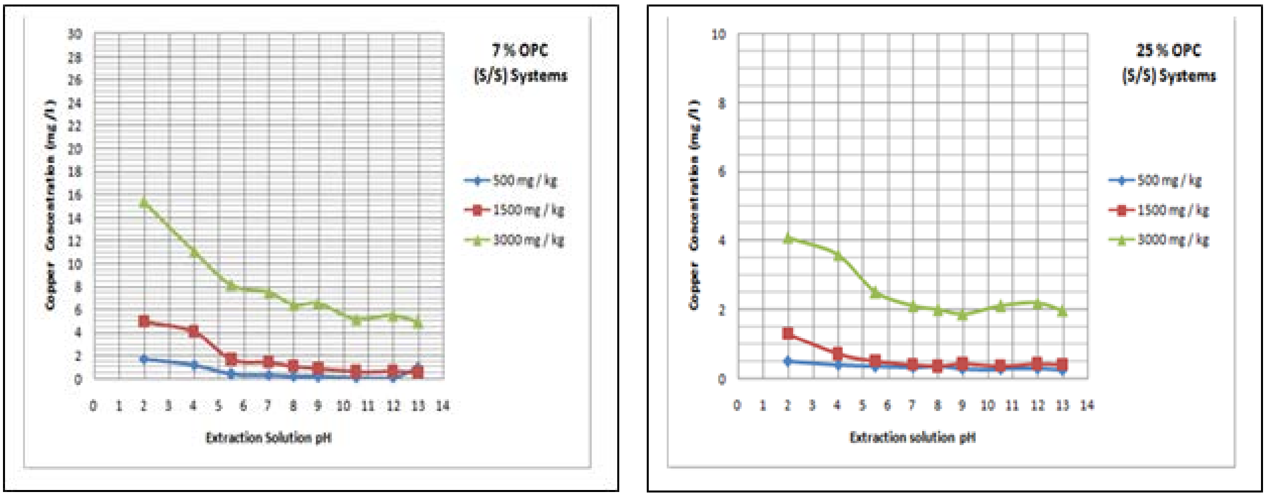

Figure 6: LSP As a function of pH Copper ions leaching from Cement-based S (S/S) samples.

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