Leaching Batch Test and XRD Characterized OPC Treated Lead Contaminated Soil

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Abstract — The metal leaching behaviour of synthetically prepared contaminated soil containing 792 μg/g lead was investigated after the addition of cement. The leaching behaviour of lead was investigated using 5 grams of the soil thoroughly mixed with 0.1g of the stabilizing material in a polypropylene container to which 50ml of either deionized water, 0.01M HNO3 or 0.1M HNO3 was added. The mixture was shaken on a flat bed shaker for 2h, and then filtered using a Whatman No 542 filter paper. The lead concentration in the filtrate was determined by inductively coupled plasma-atomic emission spectrometry. When deionised water or 0.1M HNO3 was used, the concentration of lead in the leachate was less than 1% of the added lead in the soil. In similar experiments with 0.1M HNO3 lead retention in the presence of Portland cement was 90%. Results from the analysis of X-ray diffraction measurements on soil samples retained on the filter paper showed the formation of lead sulphate and lead carbonate when Portland cement is used to stabilize the lead contaminated soil.

Index Terms — ICP, Leaching, lead, Shaking test.

I. INTRODUCTION

Stabilization/solidification (S/S) technology has been widely applied to immobilize heavy metals in contaminated soils, sediments, and sludge with additives such as cement, lime, and fly ash [1], [2]. The US Environmental Protection Agency (USEPA) recognizes cementitious solidification as the “best demonstrated available technology (BDAT)” for land disposal of most toxic elements. Alkaline matrices such as Ca(OH)₂ and cement are commonly used in waste conditioning because they are inexpensive, readily incorporate wet wastes and their alkalinity reduces the solubility of many inorganic toxic or hazardous metals. U.S. Department of Energy [3] performed experiments in an effort to quantitatively define the waste form performance response to the four binding constituents (i.e. Portland cement, fly ash, blast furnace slag, clays), also The GGBFS which is a 100% recycled material, using significantly less energy at reduced levels of CO₂ emissions during production as compared to Portland cement [4], [5].

Pb is the most common contaminant in the environment and has chronic toxicity. Pb contamination has been found in 604 out of 1221 superfund sites on the National Priorities List (NPL). There have been intensive studies about Pb immobilization mechanisms in S/S-treated wastes [2]. Heavy metals may enter the human body through food, water, air, or absorption through the skin. Human exposure could be through their use in agriculture and in manufacturing, pharmaceutical, industrial, or residential settings. Industrial exposure is a common route of exposure for adults while ingestion is the most common route of exposure in children [6].

The aim of this study to investigate the effect of incorporating Portland cement to stabilize lead contaminated soil by using the digestion test and the batch leaching test to determine the optimum conditions.

II. EXPERIMENTATION

The soil used for this investigation was obtained from an urban soil from a quarry in South Yorkshire, UK. It was sieved according BS 932-1/2 for 5 mm. Prior to artificial contamination, the pH, particle size, water content and initial Pb content in each clean soil sample were determined. The particle size was determined by using the sieving shaker and XRD characterized OPC cement. The US Environmental Protection Agency (USEPA) recognizes cementitious solidification as the “best demonstrated available technology (BDAT)” for land disposal of most toxic elements. Alkaline matrices such as Ca(OH)₂ and cement are commonly used in waste conditioning because they are inexpensive, readily incorporate wet wastes and their alkalinity reduces the solubility of many inorganic toxic or hazardous metals. U.S. Department of Energy [3] performed experiments in an effort to quantitatively define the waste form performance response to the four binding constituents (i.e. Portland cement, fly ash, blast furnace slag, clays), also The GGBFS which is a 100% recycled material, using significantly less energy at reduced levels of CO₂ emissions during production as compared to Portland cement [4], [5].

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| Soil | OPC | Oxide |
|------|-----|-------|
| 93.62 | 19.25 | SiO₂ |
| 0.65 | 2.33 | Fe₂O₃ |
| 2.89 | 4.86 | Al₂O₃ |
| 0.08 | 0.53 | TiO₂ |
| 0.12 | 62.8 | CaO |
| 0.13 | 0.85 | MgO |
| 0.06 | 0.44 | SO₃ |
| 1.72 | 0.53 | K₂O |
| 0.21 | 0.35 | Na₂O |
| 0.01 | 2.33 | MnO₂ |

The soils were artificially contaminated in the laboratory. The contaminant was introduced in the soils on the basis of solution of heavy metals derived from the salts of Pb(NO₃)₂ which was equivalent to 1000 mg/l of Pb (i.e. 1 L of Pb solution added to 0.5 kg of soils in a 2 liter glass flask) and constantly shaken for 24h in the platform shaker, until it reached the equilibrium. Subsequently the soils were dried in an oven at 40 °C; the dry soil was prepared for further investigation. The total digestion test was conducted in 1g of contaminated soil with 5 ml of HNO₃, and 50 ml of water.
for 10 min duration on a hotplate, where the maximum extraction of Pb was achieved. The properties of the contaminated and non-contaminated soil are given in Table 2.

### TABLE 2: PROPERTIES OF THE SOILS

| Parameters | Uncontaminated soil | Contaminated soil |
|------------|---------------------|-------------------|
| pH         | 6.94                | 5.65              |
| particle size | 5mm                | 4mm               |
| water content % | 13.49 %           | 1.5 %             |
| lead in ug/g | <0.004             | 791 ug/g          |

**A. The Batch Test**

The batch test was conducted in different conditions before selecting the most suitable conditions. However, the most effective factors are the ratio of S/L, duration, pH leaching fluid, the solid / liquid 1:10 S/L, which was equivalent to 5g of solid to 50 ml of deionised water (DI) or HNO₃. The ratio of 1:10 was selected carefully with the following standard of Modified NRA test for U.K superseded with EN 14457-2, after many trials on different parameters.

### III. RESULTS AND DISCUSSION

Table 1 present these results in ug/g with respect to the volume of liquid and the mass of the soil using the simple digestion test for 1 g of soil with particle size 600um. The average value of Pb leached out is 791 ug/g of soil.

**A. Effect of Leaching Fluid**

Many researcher including [7]; and [8]; adopted the digestion test methods to determine the maximum available of metals in soil [8] has used the digestion test method to determine the total phosphors in soil with 5 different reagent included NaCO₃, fusion, HClO₄ + HNO₃, HF + HClO₃ or NaOBr oxidation methods., also [9] has used the digestion test to determine trace metals in fly ash by HCl as solution with different concentration and combination of HCl and HNO₃. There was no need to use any of methods by other authors because the added lead was not lightly bound and therefore could be released by addition concentrated nitric acid. the simple digestion test shows the maximum amount of release of Pb is greater than batch test extraction by 5 times, that digestion test can estimate the amount of the metal binding in the particle of contaminated soil. In present of acid and high temperature the Pb will be dissolve and more soluble which caused high release of Ca, in Table 3 different leaching fluid with differ values of pH, A decrease in the pH causes an increase in leaching as shown in Table 3 and Table 4.

### TABLE 3: LEACHING OF Pb WITH DIFFERENT FLUID MEDIUMS

| Leaching Fluid | Concentration of Pb (ug/g) | pH | Ratio | duration in hour |
|----------------|---------------------------|----|-------|-----------------|
| Deionised water | 37.8                      | 5.4 | 1:10  | 2               |
| 0.1M HNO₃      | 858                       | 1.2 | 1:10  | 2               |
| 0.01M HNO₃     | 744                       | 2.2 | 1:10  | 2               |
| Rain water     | 5.28                      | 7.2 | 1:10  | 2               |

### B. Effect of Stabilizing Material

The leaching of untreated soil was 37.8 ug/g by deionised water at pH 5.4 with 0.01HNO₃ pH 2.1 was 744 ug/g. Other tests were conducted by using 0.1HNO₃ solution of pH 1.1 which showed greater release of Pb than using deionised water or acidified water of pH 2.1. This shows the effects of pH values. A decrease in the pH causes an increase in leaching as shown in Table 4. This is in agreement with results reported by [2] who examined the TLCP extraction fluid and DI water with a pH of 5.1 and 7.68 respectively. This could be attributed to metal precipitation as hydroxides [2].

### TABLE 4: EFFECT OF STABILIZING MATERIAL ON LEACHING OF Pb

| Leaching fluid | sample | Pb ug/g | pH | Ca ug/g | Mg ug/g | Na ug/g | K ug/g |
|----------------|--------|---------|----|---------|---------|---------|--------|
| Deionised water | Contaminated soil | OPC+ | 37.6 | 5.4 | 180 | 19 | 5.4 | 17 |
|                | OPC+ | 0 | 12.2 | 2000 | 0 | 13 | 82 |
| 0.1M HNO₃ | OPC+ | 858 | 1.2 | 2600 | 280 | 5 | 22.1 |
| 0.01M HNO₃ | OPC+ | 597 | 44882 | 403 | 37 | 102 |
|              | OPC+ | 744 | 2.2 | 2400 | 270 | 4 | 19.6 |

**C. Leaching Time**

The investigation of the leaching time effect was conducting by run the leaching test under the same conditions with more time of contact between the leaching fluid and the contaminated soil. The release after 8 hours of contact was measured by ICP. Fig. 1 shows the leaching of Pb at different leaching times. The leaching of Pb was high at 2 h an then at 8hours of shaking using a platform shaker with constant speed rotary of 300 r.p.m. as the time progresses (after 8 hours) the leaching of Pb is decreased. This is shown in Fig. 1 [10], [11], [12] has reported similar trend using same parameters with leaching test on ash with water and acid.

![Fig. 1 Effect of leaching time on release of Pb.](image)

**D. Effect of L/S Ratio**

An increased L/S ratio generally increased the amounts of water-soluble metals found for the contaminated soil with Pb. The calculations of release were based on 5 g of soil and proportional amount of deionized water. Fig. 2 shows the release of Pb with solid to liquid (L/S) of 1:5 to 1: 40 L/S. The liquid used is deionized water (DI) with pH of 5.6. The
results show that large amount of liquid causes large release of Pb. Similar trends were reported elsewhere [11]-[13].

The solubility equilibrium for the metal compounds can be represented by the limiting factor. The limiting factor is the L/S ratio needed to be optimized in order to get the correct result. The concentration increased as the L/S ratio was raised from 5:1 to 10:1. A further increase of L/S ratio caused a sharp decrease in Pb concentration, falling eventually to an undetectable level at L/S ratio of 60:1. The lead (Pb) existed as the Pb-hydroxide complexes under relatively highly alkaline conditions when the L/S is less than 20:1. Higher Pb concentration at L/S 20:1 can be attributed to the exposure of the waste to higher absolute level of acidity, thereby leading to a faster release of Pb during the leaching period. The concentration of Pb decreased because the pH decreased to values where Pb was less soluble. Therefore, at L/S ratios of 10:1 and 20:1 the leachate pH was dominated by the alkalinity of the waste, but as the L/S ratio increased. [14] has an agreement with these results and reported that at low L/S is more soluble for low L/S mainly as a consequence of the pH and Ca evolution.

![Graph showing amount of leaching of Pb at different L/S ratios.](image)

**Fig. 2. Amount of leaching of Pb at different L/S ratios.**

**IV. XRD INVESTIGATIONS**

About 95% of all solid materials can be described as crystalline. When X-rays interact with a crystalline substance (Phase), one gets a diffraction pattern. The X-ray diffraction pattern of a pure substance is, therefore, like a fingerprint of the substance. The powder diffraction method is thus ideally suited for characterization and identification of polycrystalline phases. With regard to some authors and reviewers as [15], [16], today about 50,000 inorganic and 25,000 organic single component, crystalline phases and diffraction patterns have been collected and stored on magnetic or optical media as standards. The main use of powder diffraction is to identify components in a sample by a search/match procedure. Furthermore, the areas under the peak are related to the amount of each phase present in the sample. As there is proof of precipitation of the metals on the surface of the beaker and the filter, it was useful to characterize the sort of chemical structure of the metals on the surface. Theoretically it has been reported that in many cases hydroxide compounds occur on the surface. However due to the lack of using XPS to identify the metals formula, using XRD was quite useful to recognize the shape of metals. The XRD was run for two hours to examine the contaminated OPC Pb with disk of KBr against the blank sample which is OPC with no contaminant of Pb. The graphs and the tools of analysis suggest that PbCO3 or PbOH may have formed on the surface, as most of the composition of Pb is CaCO3 which is the main calcite shape as figured out with XRF. The main composition of OPC 60% of OPC is CaCO3.

![Graph showing XRD spectra for OPC and Pb contaminated OPC.](image)

**Fig. 3. The XRD spectra for OPC and Pb contaminated OPC.**

**V. CONCLUSIONS**

1. The contact time and ratio of L/S is an important factor in the leaching experiment included in the filtration.
2. The pH plays a major role in the remediation process.
3. The minimum amount that can be used for mobilization of the metals is 0.1 g of cement. Which equivalent to 5% of total weight.
4. The compounds which are formed by OPC and interact with the Pb solution are PbSiO3, PbSO4, PbCO3. OPC with PFA interact with the Pb solution and the compound formed is Pb2O(CO3).

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