
The Role of pH on Mobilizing Lead Contaminated Solution

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Abstract -The role of pH on removal of metal contaminated solution was investigated by adding gradually drops of NaOH to lead solutions, the increase of the pH was observed and concentration of lead solution was measured by using ICP. The activated \ pulverised fly ash (PFA) was used as stabilizing material. The leaching behaviour of lead was investigated using 5 grams of the soil thoroughly mixed with 0.1g of the stabilising material in a polypropylene container to which 50ml of either deionised water; the mixture was shaken on a flat bed shaker for 2h, and then filtered using a what man No 542 filter paper. The lead concentration in the filtrate was determined by inductively coupled plasma-atomic emission spectrometry (ICP). The effect of adding PFA was a reduction in Pb released to an undetectable level at higher pH levels. Results from the analysis of X-ray diffraction on the soil samples retained on the filter paper showed the formation of lead sulphate and lead carbonate.

Keywords – ICP, Leaching Test: PFA, pH, Lead.

I. INTRODUCTION

The pH level is one of the most important chemical parameters influencing leaching of contaminants from waste material, and the pH of soil or contaminated material has a major influence on the solubility of contaminants by influencing the degree of ionization and subsequent overall charge Bone et al [2004]. In leaching experiments the pH is determined by a number of possible reactions such as production of CO₂ as a result of biological activity and dissolution of atmospheric CO₂, and many metals are known to leach more rapidly at extreme pH values [Van der Sloot et al., 1997; Jang Y et al [2002]; Townsend and Jang [2003]. Also CO₂ interacts with cementitious wastes when calcium in the waste reacts with the CO₂ to form calcite (CaCO₃) Pereira et al [2007]. Waste materials are produced in large volumes at coal-fired power plants; direct combustion by-products include fly-ash, bottom ash, and boiler slag and, in addition, there are the products of the desulphurisation of the flue gas. These materials have been shown to have certain advantageous properties for engineering, construction and manufacturing applications. [Vom Berg and Feuerborn 2005].

There are many reasons to increase the amount of fly ash being utilized, which are: firstly, disposal costs are minimized; secondly less area is required for disposal, thus enabling other uses of the land and decreasing disposal permitting requirements; thirdly, there may be financial returns from the sale of the by-product or at least an offset of the processing and disposal costs; and fourthly, the by-products can replace some scarce or expensive natural resources, [Ahmaruzzaman 2010].

Fly ash, or pulverised fuel ash (PFA) as it is known in the UK, is a by-product of coal-fired power generation and has been used for a wide range of applications for over 50 years. For example, Wang and Hongwei [2006], Weng and Huang [2004], Alinnora, [2007] and Pehlivan and Cetin [2008] have all shown that PFA may be used in wastewater treatment, particularly for adsorption, because of its major chemical components, such as alumina, silica, ferric oxide, calcium oxide, magnesium oxide, and carbon, and its physical properties, such as porosity,

particle-size distribution, and specific surface area. However, Gatima et al [2005] has pointed out that it is important to consider the source of the PFA, as certain sources may contain toxic elements (especially Cd, Cu and Pb), defeating the primary purpose of amelioration.

II. MATERIAL AND METHODS

The oxide composition of the uncontaminated soil and PFA is presented in Table 1. The water content of the soil was 13.49%.

Table 1. Chemical composition (by mass %) for PFA and uncontaminated soil used in these investigations.

Compound	pH	CaO	Al ₂ O ₃	SiO ₂	MgO	P ₂ O ₅	SO ₃	K ₂ O	TiO ₂	Fe ₂ O ₃	Na ₂ O	BaO
Fly Ash	0.1g of PFA + 50ml DI water =9.5	2.09	26.01	49.2	1.5	0.24	0.35	3.45	0.94	9.16	1.18	0.15
Uncontaminated soil	0.1g of soil + 50ml DI water =6.9	0.12	2.89	93.6	0.13	0.02	0.06	1.72	0.08	0.65	0.21	0.03

Y₂O₃, V₂O₅, ZrO₂, Cr₂O₃, ZnO, Mn₃O₄ and SrO were not detected in the uncontaminated soil and were present to less than 0.06% in the fly ash solution.

The soil was synthetically contaminated by adding litre of solution containing 1000 mg/l of Pb prepared from Pb (NO₃)₂, to 0.5kg of soil in 2 L flask. The mixture was shaken for 24h, until equilibrium is reached. The supernatant was discarded, and the soil was dried in an oven at 40 oC for 72hrs before use. The leaching test was implemented and the lead in the final leachate were filtered and measured by the ICP similar to Hassan et al [2012].

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 µg/g	<0.004	791 µg/g

III. RESULTS AND DISCUSSION

The composition of PFA will vary with the quality of coal used and the operating conditions of the power station. In this study the composition of fly ash was determined by XRF; the main components were SiO₂ (about 50%) and Al₂O₃ (about 26%); the next three most common components in order were Fe₂O₃ (about 9%), K₂O (between 3 and 4%) and CaO (about 2 %), see Table 1. These results concur with those of e.g. Gatima et al [2005] who found that, typically, about 95-99% of fly ash consisted of oxides of Si, Al, Fe and Ca, and about 0.5 to 3.5% consisted of Na, P, K and S with the remainder composed of trace elements. Erol et al., [2005] suggest that the principal oxide constituents of PFA can be divided into those that are acidic (SiO₂, Al₂O₃ and TiO₂) and those that are basic (Fe₂O₃, MgO, CaO, Na₂O and K₂O). Gatima et al [2005] also used PFA for

amelioration of lead contaminated soils and achieved good results in reducing the levels of lead below the regulatory limit for soils contaminated with different lead compounds, included $PbNO_3$.

When PFA is added to water, the solution initially has a low pH as sulphate on the surfaces of the particles enters into solution as sulphuric acid. However, after a short time, calcium is leached into solution and the pH rises rapidly to 9-12. Typically, for PFA the pH is between 8 and 11, but for those ashes with a higher free calcium oxide content the pH can rise to 12. In fact, very little free calcium is required to achieve the higher pH. For PFA that has had most of the water soluble content washed out e.g. lagoon ash or pond ash, a significant proportion of the material that influences pH will have been removed and the pH is lower, typically around 9 [Lindon. et al 2003]. In this study after shaking for two hours in DI water the PFA solution was 9.5 (see Table 3). Pb^{2+} removal capacities have been related to the CaO contents of the fly ash, which would dissolve in water and so increase the pH number. However, the content of CaO in the fly ash is only 2 % (see Table 1). When 0.1g of PFA powder was mixed with 50 ml of DI water, the average pH was 9.5, see Table 3. Erol et al [2005] studied the four parameters which affected the removal of Pb from solution which are, contact time, fly ash composition, fly ash concentration and the pH of the solution, as might be expected, that the pH value increased with the increases in concentration of the PFA. And they reported that maximum removal of Pb at pH 6-7 with using varied samples of fly ash was between 0.075-3.5 g/l.

Fig. 1 shows the effect of increased pH on reduction of lead in the final leaching solution. At a pH number of about 6.5 the lead concentration was reduced to 0.5mg/l. From Fig. 1 it is obvious that fly ash on its own has no effect on the concentration of lead in the final solution, However, if even a small amount of NaOH (just a drop – 100 μ micron of a 2 mole solution of NaOH) is added with the 0.1g of PFA powder, the concentration of lead in the final leaching solution was substantially reduced.

The effect of adding PFA was a reduction in Pb released to an undetectable level at higher pH levels. At the lower pH levels (2.2 and 1.2) for the leaching fluid the reductions were only 8% and 5% respectively. PFA can only effective, stabilize material with higher pH leaching fluid such as DI water which has a pH value of 5.6. (see Table 4). Orhan et al, [1999] in agreement with this result and reported that a low pH value (2.5 ± 3), the hydrogen ions compete with heavy metal cations and the percentage removal of metals decline. At intermediate pH values (3 ± 6), the degree of removal mainly depends on the ionic size of the metal. Above pH 6, precipitation becomes dominant especially for Pb_2 ions.

Kim et.al [2006] carried out an investigation of formatted compounds as a result of adding PFA and adjusting the pH and concluded that the sample set was divided into alkaline and acidic samples based on the ability of the ash to buffer the pH of the acid leachants. Anhydrite was identified in the alkaline samples, while gypsum was the $CaSO_4$ mineral identified in the acidic samples.

Table 3. Measured pH when 0.1g PFA powder was added to 50ml of DI water and to 50ml of 1000mg/l) $(PbNO_3)_2$ solution(n = 3).

sample	pH	M	Sd
50 ml of D.I water + 0.1g of PFA	9.45		
50 ml of D.I water +0.1 g of PFA	9.58	9.5	0.078
50 ml of D.I water + 0.1g of PFA	9.44		
1000mg/l solution of $PbNO_3$	3.54		

sample	pH	M	Sd
1000mg/l solution of PbNO ₃	3.55	3.5	0.005
1000mg/l solution of PbNO ₃	3.55		
50ml of 1000mg/l solution of PbNO ₃ + 50 ml of D.I water + 0.1g of PFA	4.78		
50ml of 1000mg/l solution of PbNO ₃ + 50 ml of D.I water + 0.1g of PFA	4.71	4.7	0.085
50ml of 1000mg/l solution of PbNO ₃ + 50 ml of D.I water + 0.1g of PFA	4.61		

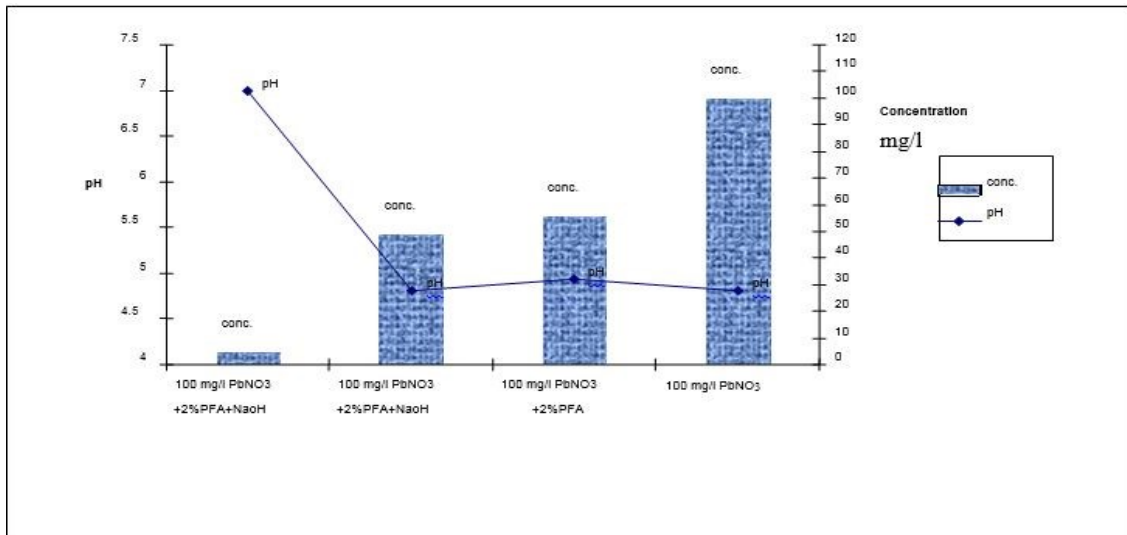


Fig. 1. Effect additions of NaOH and PFA on concentration of lead in solution.

According to Peng et al [2009] the pH value is a key parameter controlling heavy metal transfer behaviour in sediment. Normally, with pH decreasing in sediment, the competition between H⁺ and the dissolved metals for ligands (e.g. OH⁻, CO₃²⁻, SO₄²⁻, Cl⁻, S²⁻ and phosphates) becomes more and more important. It subsequently decreases the adsorption abilities and bioavailability of the metals, and then increases the mobility of heavy metals. Sometimes, with a small change in pH level, the percentage fixation of heavy metals on sediment particles may range from almost a 100% to none. According to Tingle et al. [1993] soils with pH < 4 do not have surface-bound Pb, whereas soils with pH > 4 do. With pH = 2.0 there was no detectable surface-bound Pb, and they concluded that with increasing pH, the amount of Pb adsorbed on surfaces increases due to the increasing negatively charged character of most mineral surfaces.

IV. EFFECT OF PFA

While performing the batch leaching test on soil contaminated with Pb (see Section 2.) in which 0.1g of PFA was added to the 5g soils and 50ml of DI water was added. The reduction of lead in the soil was from over 80µg/g with no PFA to nearly 0µg/g when 2% PFA was added, representing a reduction of about 95%. Figure 2 shows the effect of no PFA, 0.5%, 1.0%, 1.5% and 2.0% to the contaminated soil. Increasing the %PFA progressively reduced the lead remaining in the soil. This means that there is no retention of lead in the soil. Figure 2 shows the proportional reduction of lead in the soil with % PFA. The amount of lead in soil was 1000mg/l and maximum extraction was achieved by using a digest test 780 µg/g, (see section 2.1.). The extraction of Pb by using shaking test for two hours and DI water as leaching fluid is 80 µg/g. The 0.5% of PFA is equivalent to 0.25 g of PFA, which was the minimum amount of PFA used to assess reduction in Pb release. It

was observed during measurement of the pH at the end of the shaking batch test that the pH level of the final filtered solution increased as the %PFA increased (see Table 4). Kumpiene et al [2007] used PFA to mobilize the Cu and Pb and achieved 95 and 99% reduction of Pb. Erol et al [2005] reported that the amounts of PFA required to remove Cu²⁺ and Pb²⁺ were found to vary between 0.2–10g/l and 0.075–3.5g/l, respectively. Moon and Dermatas [2007] used 25% PFA (total solid weight) to treat as and Pb contaminated soils by S/S, the pH levels were 5.5 - 6.5. Ciccu et al [2003] reported that a small amount of PFA in the ratio 10: 0.75 ratio of soil: PFA reduced the leaching rate of heavy metals, below the regulation limit.

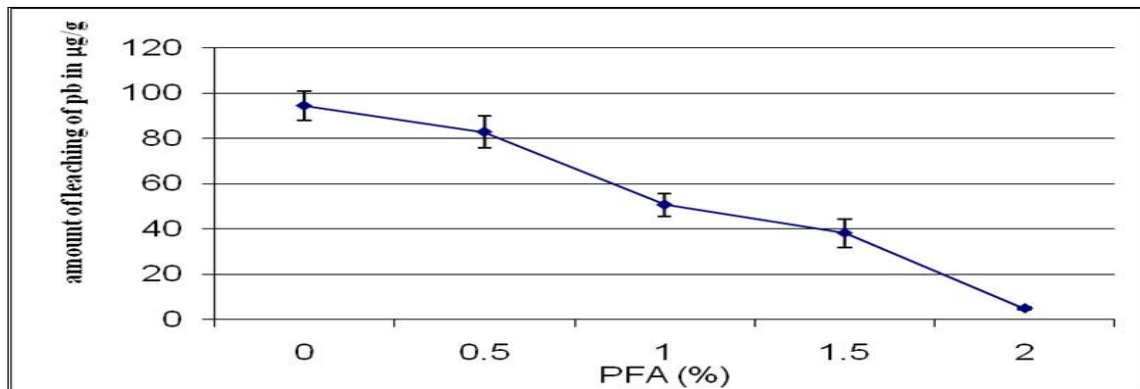


Fig. 2. Effect of adding different concentrations of PFA to lead-contaminated soil, followed by leaching with 50 ml of deionised water (n = 3).

Table 4 Effect of PFA on lead contaminated soils and subsequent release of other elements.

Sample	Pb (µg/g)	Mg (µg/g)	Ca (µg/g)	Na (µg/g)	K (µg/g)	pH
Pb contaminated soil + Deionised water	34.0	22.3	140.7	ND	13	4.95
Pb contaminated soil + Deionised water	33.5	17.1	136.8	ND	17.2	5.54
Pb contaminated soil + Deionised water	39.0	15.3	129.9	ND	23	5.66
Mean	36.1	17.9	139.4	ND	14.4	5.2
Sd	3.1	3.06	22		2.06	
Pb contaminated soil+ 0.1g of PFA + Deionised water	ND	17.1	188.7	15.1	19.3	6.21
Pb contaminated soil+ 0.1g of PFA+ Deionised water	ND	15	176.1	14.1	25.5	6.28
Pb contaminated soil + 0.1g of PFA+ Deionised water	ND	15.4	176.4	13.4	18.2	6.07
Mean		15.8	180.4	14.2	21	6.18
Sd		1.1	7.18	0.85	3.93	0.1

ND = none detected, NM = not measured

Table 5 Effect of PFA on release of lead with three leaching fluids and consequent release of Ca , Mg , Na and K.

Sample	Leaching fluid	pH	Pb (µg/g)	Ca (µg/g)	Mg (µg/g)	Na (µg/g)	K (µg/g)
5g of Pb contaminated soil	50ml D.I water	5.4	37.6	140	19	5.4	17
0.1g of PFA + 5g Pb contaminated soil		6.2	0	180	17	14.1	21

5g of Pb contaminated soil	50ml 0.01M HNO ₃	2.2	744	2400	270	4.0	19.6
0.1g of PFA + 5g of Pb contaminated soil			622	2800	370	29	29
5g Pb contaminated soil	50ml 0.1M HNO ₃	1.2	858	2600	280	5.0	22.1
0.1g of PFA + 5g of Pb contaminated soil			786	3500	330	23.8	41

V. X-RAY DIFFRACTION INVESTIGATION (XRD)

In regard to the Cambridge XRD database [<http://www.cds.dl.ac.uk>] and according to Dorsam et al [2008] who reported the formation of Pb₂(Al₂Si₂O₉) on the surface of PFA and the formation of melanotekite-Pb₂(Fe₂Si₂O₉) - [PBCN] at 56.3 theta, which is also in agreement with the results obtained in this work. See Fig.3, the PBCN is the number of the dimensions in the space group of crystal.

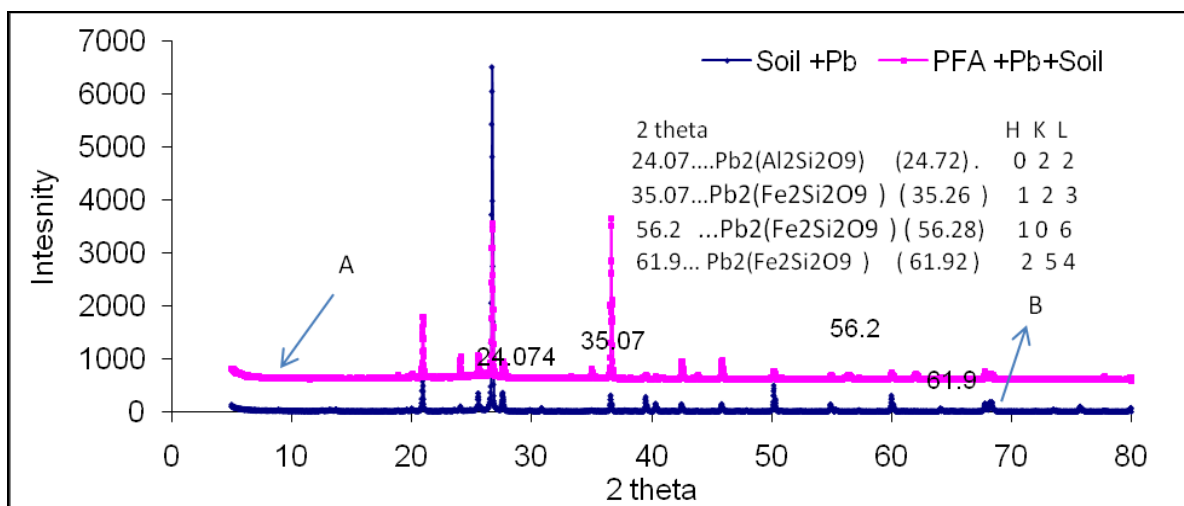


Fig. 3. XRD investigation for soil contaminated with Pb and contaminated soil after treatment with PFA; A-line, spectrum for contaminated soil treated with PFA, and B-line, spectrum for lead contaminated soil.

VI. CONCLUSION

The pH at 6 and above will results full of reduction on metal concentration in the final solution.

The participation of metal on surface of the solution was obvious, the role of pH not only the driven factor for reduction of lead concentration in the final contaminated solution.

The XRD suggest main the compounds which are formed by PFA and interact with the Pb solution are, Pb₂(Al₂Si₂O₉) on the surface of PFA and the formation of melanotekite-Pb₂(Fe₂Si₂O₉)-[PBCN].

When adding 2% of PFA to treat 5 g of lead contaminated soils, there was a reduction of 99 % in the lead in the elute solution with increase of the pH in the final solution to 6.2.

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REFERENCES

- [1] Ahmaruzzaman, M. (2010). A review on the utilization of fly ash. *Progress in Energy and Combustion Science*. Vol. 36: pp.327–363.
- [2] Alinnora, I.J. (2007) Adsorption of heavy metal ions from aqueous solution by fly ash. *Fuel*. J. Vol. 86. Issues 5-6: pp.853-857.
- [3] Bone, B.D, Barnard, L.H. and Boardman, D.I. (2004) Review of scientific literature on the use of stabilisation/solidification for the treatment of contaminated soil, solid waste, and sludges. *Science Report SC98003/SR2*. www.environment-agency.gov.uk. ISBN 1 844 323 196.
- [4] Ciccu, R., Ghiani, M., Serici, A., Fadda, S., Peretti, R. and Zucca, A. (2003) Heavy metal immobilization in the mining-contaminated soils using various industrial wastes, *Minerals Engineering*. Vol.16: pp.187–192.
- [5] Dorsam, G., Liebscher, A., Wunder, B. and Franz, G. (2008) Crystal structures of synthetic melanotekite (Pb₂Fe₂Si₂O₉), kentrolite (Pb₂Mn₂Si₂O₉), and the aluminium analogue (Pb₂Al₂Si₂O₉). *Mineralogical Society of America*, Vol.93; No. 4; pp.573-583.
- [6] Erol, M., Ku, S. and Ulubas, T. (2005) Removal of Cu²⁺ and Pb²⁺ in aqueous solutions by fly ash. *Energy Conversion and Management*. Vol. 46: pp. 1319-1331.
- [7] Gatima, E., Mwinyihija, M. and Killham, K. (2005) Assessment of pulverised fly ash (PFA) as an ameliorant of lead contaminated soils, *American J. of Env. Sci.* Vol.1 (3): pp230-238.
- [8] Hassan, M, Gardiner, PHE, Khatib, J M, Mangat, PS (2012) “Stabilisation of Lead Contaminated Soil using Portland Cement”, International Workshop on Earthquake and Sustainable Materials, Sakarya University, Faculty of Technology, Civil Engineering Department, Turkey, pages 157-167, ISBN: 978-975-7988-92-2.
- [9] Jang, Y., Townsend, T., Ward, M. and Bitton, G. (2002) Leaching of arsenic, chromium, and copper in a contaminated soil at a wood preserving site. *Bull. Environ. Contam. Toxicol.* Vol. 69 : pp. 808-816.
- [10] Kumpiene, K., Lagerkvist, A. and Maurice, C. (2007) Stabilization of Pb- and Cu-contaminated soil using coal fly ash and peat. *Environmental Pollution*. Vol. 145: pp.365-373.
- [11] Kim, Ann G. (2006) the effect of alkalinity of Class F PC fly ash on metal release. *Fuel*. Vol. 85: pp. 1403-1410.
- [12] Lindon, K.A., Searle, A., Weatherley, A.J.. (2003). The Environmental Impacts of using Fly Ash—the UK Producers’ Perspective, www.flyash.info/2003/20sear.pdf access date 10.9.2009.
- [13] Moon, D.H. and Dermatas, D. (2007) Arsenic and lead release from fly ash stabilized/ solidified soils under modified semi-dynamic leaching conditions, *J. Haz. Mat.* Vol.141: pp.388–394.
- [14] Pereira, C.F., Galiano, L., Rodriguez-Pinero, M.A. and Parapar, J.V. (2007) Long and short-term performance of a stabilized/solidified electric arc furnace dust. *J. Haz. Mat.* Vol.148: pp .701–707.
- [15] Pehlivan, E. and Cetin, S. (2008) Application of fly ash and activated carbon in the removal of Cu²⁺ and Ni²⁺ ions from aqueous solutions. *Energy Sources, Part A*. Vol.30:pp.1153–1165.
- [16] Peng, J-F., Song, Y-H., Yuan, P., Cui, X-Y. and Qiu, G-L. (2009) Review: The remediation of heavy metals contaminated sediment. *J. Haz. Mat.* Vol.161: pp.633–640.
- [17] Townsend, T. and Jang, Y-C. (2003) A guide to the use of leaching tests in solid waste management decision making. Florida Centre for Solid and Hazardous Waste Management, University of Florida Gainesville, Report #03-01(A).
- [18] Tingle, T., Borch, R., Hochella, M., Becker, C. and Walker, W. (1993) Characterization of lead on mineral surfaces in soils contaminated by mining and smelting. *Applied Surface Science*. Vol.72: pp. 301-306.
- [19] Vom Berg, W and Feuerborn, H.J, (2005) Present Situation and Perspectives of CCP Management in Europe in: 2005 world of coal ash conference proceeding, april 11-15, Lexington, ky
- [20] Van der Sloot, H.A., Heasman, L. and Quevauviller, P.H. (1997). Harmonization of leaching/extraction tests. *Studies in Environment Science*. Vol.70. Elsevier, Amsterdam, the Netherlands.
- [21] Wang, S. and Hongwei, W. (2006) Environmental benign utilisation of fly ash as low-cost adsorbents. *J. Haz. Mat.* Vol.136: pp. 482-501.

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