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Raman and XPS characterized cement stabilized lead contaminated soils and solutions

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---ABSTRACT--

Artificially lead (Pb) contaminated soil was stabilised with ordinary Portland cement(OPC) and the leaching behaviour of the element was investigated. A 5 grams sample of contaminated soil was thoroughly mixed with 0.1g of OPC, and The mixture containing 50 ml of leaching solution was shaken for 2hours, and then the solution was filtered using a Whatman Grade 540 . filter paper. The extent of lead leaching, with and without the addition of OPC, was determined after adjusting the solution pH between (1-12) .More than 90% of the lead was retained when the pH was 12.0. Results from the analysis of X-ray photoelectron spectroscopy and Raman , on the soil samples retained on the filter paper showed the formation of lead sulphate ,lead oxide and lead carbonate. which is in agreement with the analysis of X-ray diffraction and FTIR measurements .

KEYWORDS: *Raman,Leaching,Lead,XPS , Cement, Stabilization.*

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I. INTRODUCTION

The use of stabilization/solidification technology for the immobilization of heavy metals in contaminated lands with various additives including cement, lime and fly ash has been reported [1], ,[2]. Mickney et al [3] reported that the use of lime in contaminated soil reduces the solubility of toxic metals and also reduces the moisture content of the soil. 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] 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

Here we report on investigations in which Ordinary Portland cement has been used to stabilise lead contaminated soil.

II. MATERIALS AND METHODS

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

Table 1 The chemical composition (by mass%) of the cement and uncontaminated soil used in these investigations.

Component	Na_2O	MgO	Al_2O_3	SiO_2	TiO_2	SO_3	K_2O	CaO	Mn_3O_4	Fe_2O_3
OPC	0.35	0.85	4.86	19.25	0.53	0.44	0.53	62.8	2.33	2.33
Uncontaminated soil	0.20	0.13	2.89	93.6	0.08	0.06	1.72	0.12	0.01	0.65

The soil was synthetically contaminated by adding litre of solution containing1000 mg/l of Pb prepared from $Pb(NO_3)_2$, 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 °C for 72hrs before use. The leaching test was implemented and the lead in the final leachate were filtered and measured by the ICP see Hassan et al[4].

The total digestion test was conducted in 1g of contaminated soil with 5 ml of HNO_3, and 50 ml of water for 10min 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

Whilst taking the measurements using Raman instrumentation it was considered in this study to increase the concentration of lead in the soils or as solution to 20,000mg/l in order to enable the Raman instrument to detect the lead in the samples.

Raman microscopy was carried out using the Renishaw RM1000 NIR system workingrange at 785nm wavelength. The following parameters were used in order to collect data from the samples: x50 objective, 40 second scan time, 100% laser power.

Prior to analysis, the Raman instrument was calibrated using a silicon wafer, a spectrum of the silicon was collected in static mode with a 1 second scan time, using 100 % laser power. Grams software was used to collectthe spectra.

XPS measurements were made on a KRATOS AXIS 165 Ultra Photoelectron Spectrometer operated at 10KV and 15mA using the Al K(alpha) X-ray source (1486.6 eV). The takeoff angle was fixed at 90 degrees. The area corresponding to each acquisition was 400 µm in diameter. Each analysis consisted on a wide survey scan (pass energy 160eV, 1.0eV step size) and high-resolution scan (pass energy 20eV, 0.1eV step size) for Pb. The binding energies of the peaks were determined using the C 1s peak at 284.5 eV. The software CasaXPS 2.3.12 was used to fit the XPS spectra peaks.

III. RESULTS AND DISCUSSION

3-1 Raman Spectroscopic Analysis

Raman spectroscopy is sensitive to the presence of calcium carbonate; it thus offers a ready assessment of the extent of its presence in the samples and is a useful technique for finger-printing of the material. This is seen by comparing the two curves at uncontaminated soil spectra with lead contaminated soil spectra or lead contaminated soils and lime treated soils or lead contaminated solution and treated lead solution spectra, the procedure of conducting the measurement are described section two.

3.1.2 Raman Spectroscopic Analysis

The results of the measurements carried out on the OPC sample are shown in Figures1 and2.Raman spectroscopy is sensitive to the presence of the calcium carbonate; it thus offers a ready assessment of the extent of its presence in the samples and is a useful technique for finger-printing of the material Potgieter-Vermaak et al [2006]. This is seen by comparing the two curves in Figure 1 the one for 0.1gOPC in a solution of 50ml ofDI water, the other with lead added to the OPC in solution.

Figure 1 shows only one strong peak at 1040cm^{-1} which can be attributed to the lead-silicate-carbonate group, the gypsum present in the sample. The gypsum was identified as calcium sulphate dehydrate by the symmetric vibration of the sulphate ion observed at 1007cm^{-1}, as well as the anhydrite at 1023 cm^{-1}.KirkPatrick et al [1997], according to Table 3. the group present is lead silicate carbonate.

Figure 2 shows the Raman spectra of soil contaminated with lead, and soil contaminated with lead that had been subsequently treated with 0.1g OPC powder. The figure shows very similar peaks, except at 1000-1050cm^{-1} where the contaminated soil sample shows a strong peak, which is due to the lead silicate carbonate group according to [KirkPatrick et al 1997] andGibbs et al [2010] is $2PbCO_3.Pb(OH)_2$. The lead had reacted with the silicon and carbonate present in the soil. The v_1 and v_4 vibrations of the carbonate were observed at 1084cm^{-1} and 712cm^{-1} respectively, and the lattice vibration at 280 cm^{-1} is due to Ca-O, Portlandite.

Kirkpatrick et al [1997] are in general agreement with these results. There was the agreement on peaks of 462 cm^{-1} where he reportedthat internal deformations of Si-O,tetrahedra(O-Si-O bending) between 430-540 cm^{-1}. Alsofrom comparison of the two spectra it is obvious that there are not nearly as many peaks as obtained by FTIR or XRD. See Hassan et al 2014.This is be attributed to the lower laser efficiency.

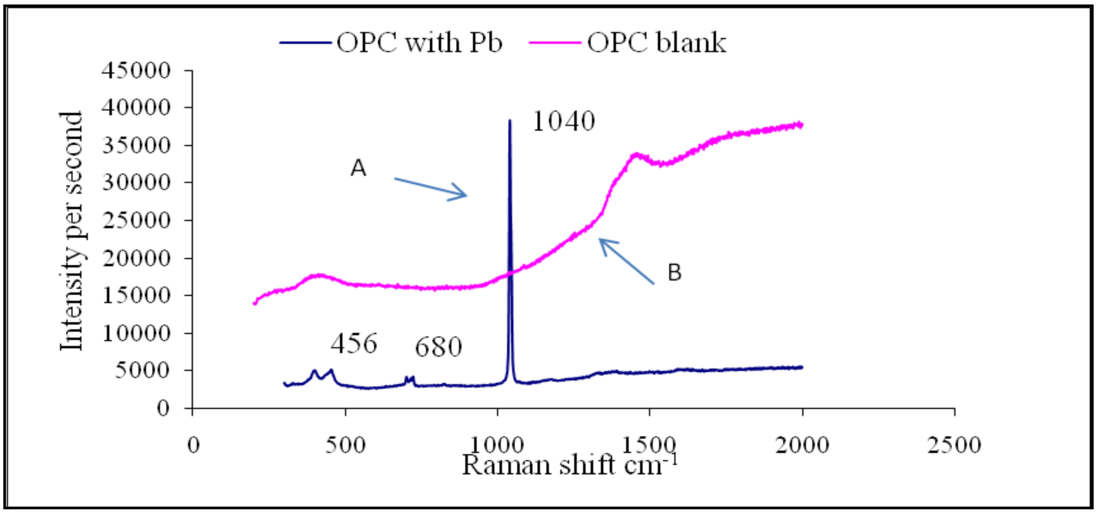


Figure 1 Raman spectra for: (A) - 0.1g of OPC in 50ml of lead solution, strength of lead solution 20g/l, (B) – 0.1g of OPC in 50ml DI water.

The spectra of the calcium aluminate phases on the other hand, were comparable and seemed to be independent of laser excitation wavelength. The major Raman peaks were identified at 456 cm^{-1} and 680cm^{-1} and 1040 cm^{-1}. According to Bersania et al [2008]plumbonacrite - Pb10(CO$_3$)6O(OH) - gives peaks at 1047cm^{-1} and 460cm-1, and the peaks at 450cm^{-1} and 680cm^{-1} are due to PbSO$_4$ and lead carbonate.

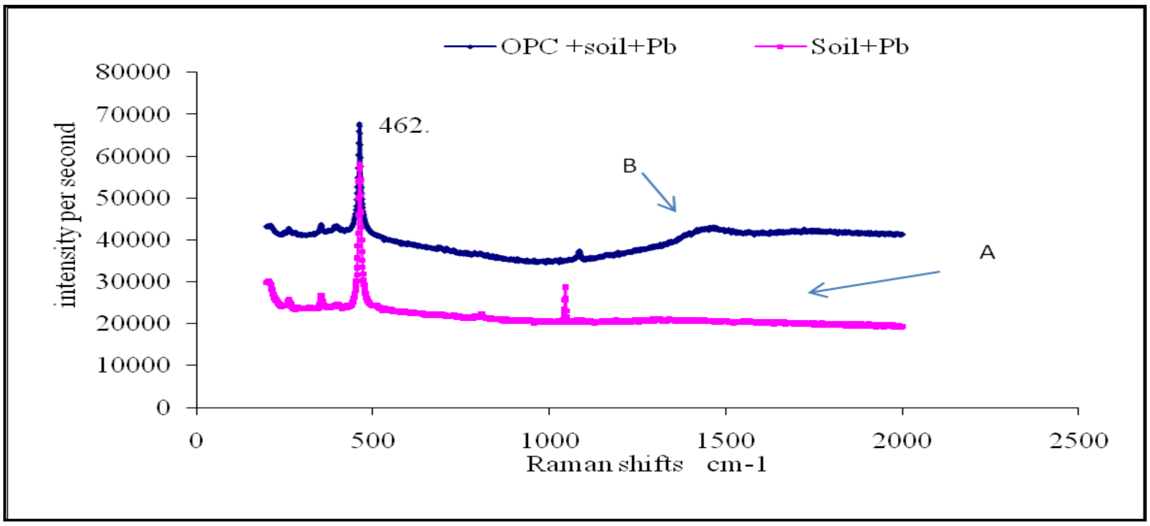


Figure 2 Raman spectra for: (A) - soil of mass 5g contaminated with 20,000mg/l of lead , (B)– as A but treated with 0.1 g of OPC

Table 3 Ramanfrequencies of the principal bands in hydrated Portland cement (after KirkPatrick et al 1997)

Band	**Origin**	**Lead contaminated soil treated with OPC in this study**	**OPC stabilized Pb solution in this study**
200-400cm^{-1}	Ca-O vibration		320-360cm^{-1} = Ca-O = Portlandite
430-540cm^{-1}	Internal deformations of si-O,tetrahedra(O-si-Obending)	462 cm^{-1}	430-540 cm^{-1}
600-700cm^{-1}	silicate group		
800-1100cm^{-1}	symmetrical stretching of silicate tetrahedral carbonate group) Symmetrical stretching (SS) of Si-O tetrahedral.	1044 cm^{-1}	976cm^{-1} (Si-OH) Pb, Si, Ca
3000-4000cm^{-1}	OH vibration		

3.2. X-ray photoelectron spectroscopy

3.2.1 Introduction

X-ray photoelectron spectroscopy XPS is widely used to investigate binding mechanisms of metal ions in cementitious materials Scheidegger et al,[2006] because it allows relatively straight-forward analysis of the near-surface of materials. It can offer significant micro-chemical information on material surfaces and is widely usedHulya et al, [2007]. Recent advances in XPS instrumentation have now made it possible to analyse small samples with improved spatial resolution and to make use of the so-called “imaging” XPS, where energies can be imaged with a spatial resolution of down to 3μm [James et al 2008]. The results of XPS imaging of the energy of the lead so-called 4f peak are shown in Figure 3.and 4. This peak is in fact of very small amplitude, and with the unaided eye is hardly discernible over the background.

3.2.2 XPS Contaminated Solution and OPC treated solution.

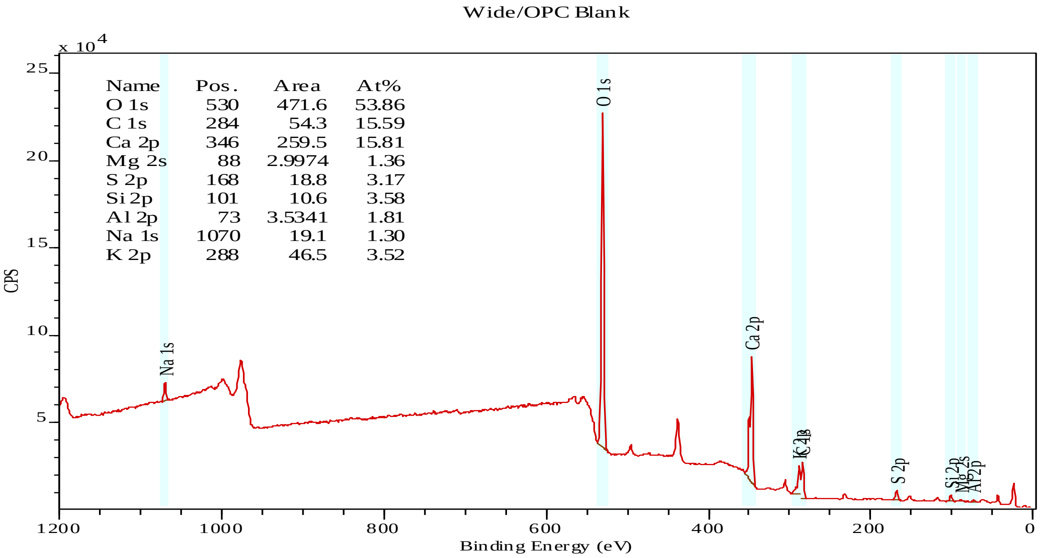
Figures 3to 6 were obtained by using XPS on OPC and 0.1 g OPC stabilized Pb solution. Figure 5 shows a wide XPS scan on which can be seen a small peak which was identified as lead 4f. The lead 4f peak is, in fact, naturally shaped as a “doublet” (i.e., has two main peaks separated by 4.7eV) positioned at 138eV with an area 0.844 % occupied of the samples, and is the smallest of the peaks listed. Each of the two peaks of the doublet was further made up of separate peaks arising from the various chemical states of lead that were present.

In Figure 4 which shows the binding energy for uncontaminated OPC, no distinct peaks were found in the region of 138eV, the lead 4f peak, as there was no Pb present in the specimen.

On Figure 3. the peak Ca2p is seen at 346eV and had a 15.8 %of area. On Figure 5 the Ca2p was at 346eV but with a smaller area, 12.1%. This decrease in area was due to the presence of Pb in the specimenthat ion exchange reaction may occurred between the Ca and Pb ions.

This is confirmed by Figure 6, which shows the binding energy over the range 130-148eV. The peaks at 137eV and 139eV were attributed to the lead 4f peak. According to international XPS data base the two peaks are due to the presence of $PbCO_3$ and PbOH. Tingle et al [1993] reported presented of Pb CO_3 at 138.3 eV. Mollah and Cock [1992] and James et al [2008] support this suggestion, which is consistent with the results obtained from the other investigative techniques used in this study, e.g.XRD and FTIR, the leaching tests, and ESEM. All of which shows the presence of lead in samples.

Rha et al [2000]has reported that lead ions concentrate on the surface of slag and precipitate into salts such as carbonates, hydroxides, and sulphates. Because Pb salts have extremely low solubility, it was likely to work as a barrier between slag particle and water. For this reasonthe presence of lead ions retard the initial hydration of slag.



Name	Pos.	Area	At%
O 1s	530	471.6	53.86
C 1s	284	54.3	15.59
Ca 2p	346	259.5	15.81
Mg 2s	88	2.9974	1.36
S 2p	168	18.8	3.17
Si 2p	101	10.6	3.58
Al 2p	73	3.5341	1.81
Na 1s	1070	19.1	1.30
K 2p	288	46.5	3.52

Figure 3. Wide scan of XPS spectra for OPC powder blank sample, no lead

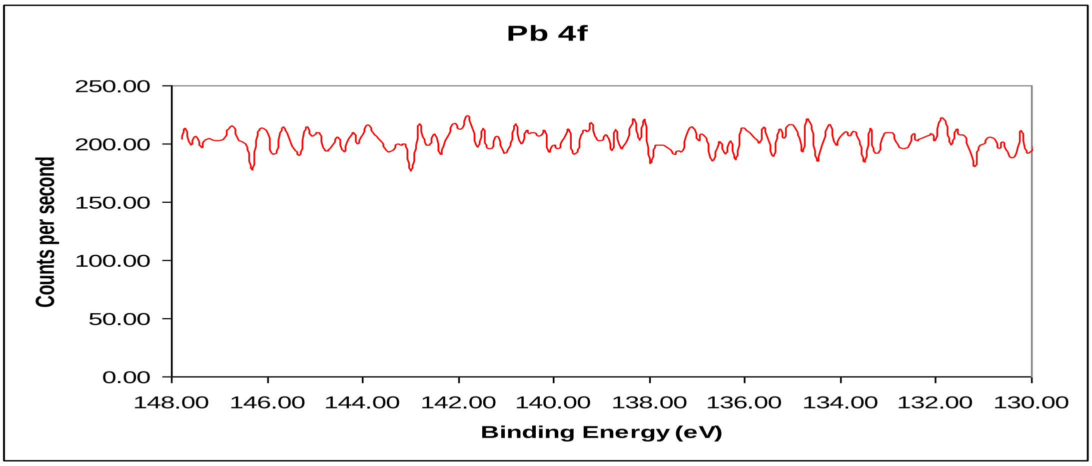
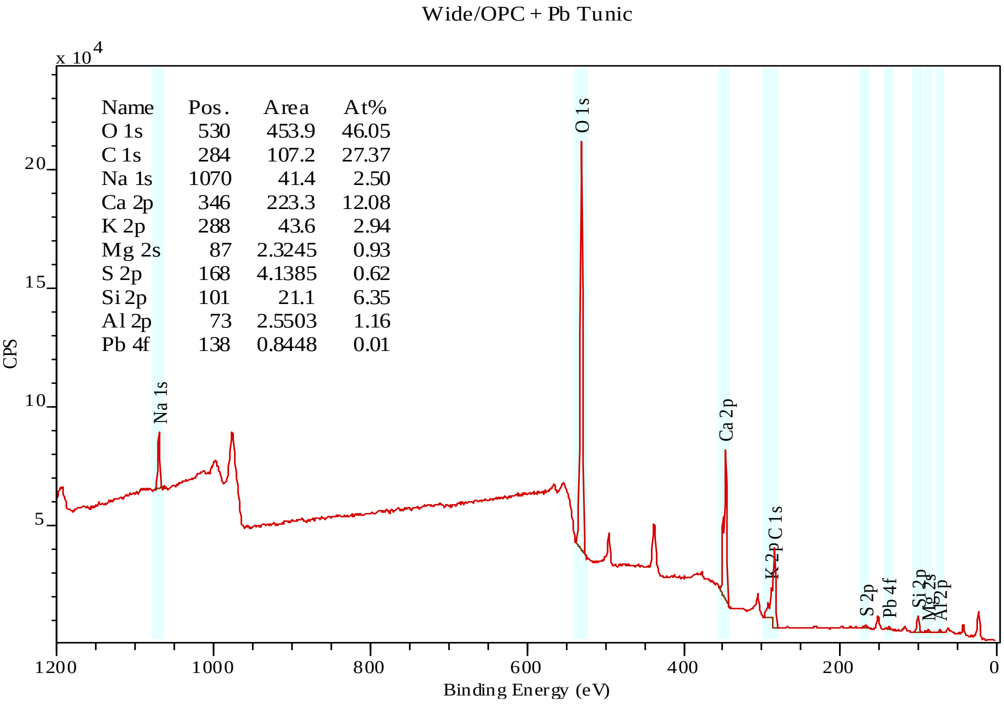


Figure 4. Detailed XPS analysis of the spectrum for OPC powder over the region of the lead 4f spectral line, on lead in blank sample



Name	Pos.	Area	At%
O 1s	530	453.9	46.05
C 1s	284	107.2	27.37
Na 1s	1070	41.4	2.50
Ca 2p	346	223.3	12.08
K 2p	288	43.6	2.94
Mg 2s	87	2.3245	0.93
S 2p	168	4.1385	0.62
Si 2p	101	21.1	6.35
Al 2p	73	2.5503	1.16
Pb 4f	138	0.8448	0.01

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Figure 5 Wide scan of XPS spectra for cement matrix containing a stabilized Pb solution.

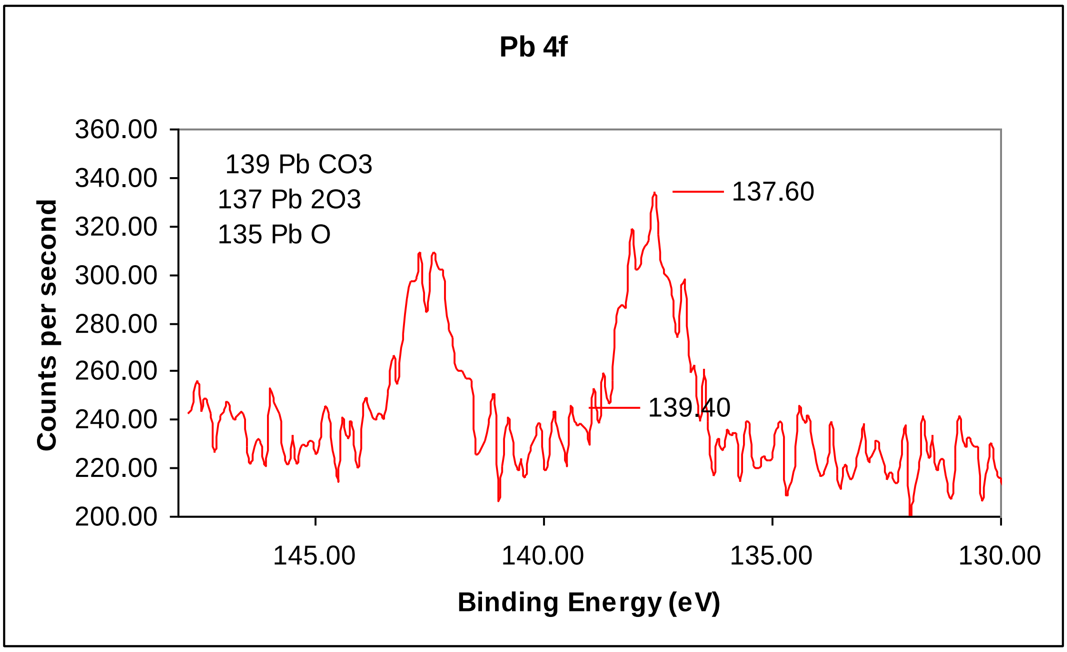
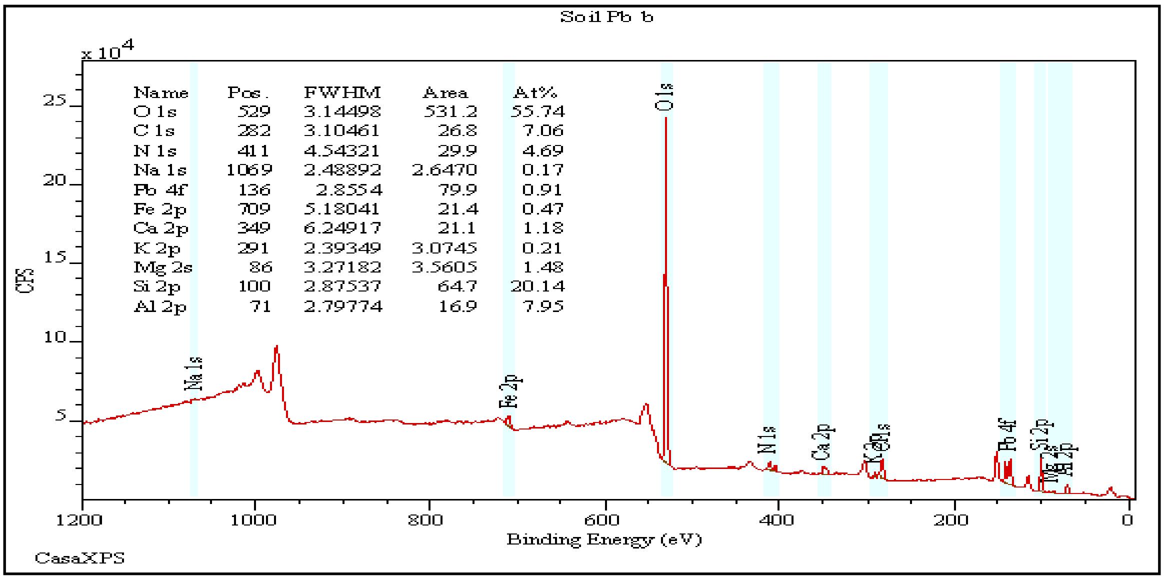


Figure 6 Detailed XPS analysis of the spectrum for OPC stabilized lead contaminated solution, over the region of the lead 4f spectral line

3.2.3.XPS contaminated soils and cement treated soil results

The Fig. 7presents wide scan of lead contaminated soil, untreated, it shows clearly position of lead Pb4f at 136 eV occupied about 0.91 at %. The most of the elements were O 1 s, Si2p, and Na1s, which account, 55, 20, 4 % respectively while Ca2p only account 1.18. See Figure 7 and 8. However the peaks 136 eV are assigned to Pb4f7 according to XPS international data base. And 141 eV assigned to Pb4f5. In classification to the chemical state for those peaks and relaying on James et .al, [2008] the 137 eV and the doublet 141 eV are assigned to Pb O. Or Pb SO_3. Similarly the Fig. 9 show the wide scan of treated contaminated soil with 0.1g cement, comparing with none treated sample see Fig. 7 The Ca2p occupied 10% , the Pb occupied 0.74 % reduced from 0.91% in none treated soil. And Si to 13% from 20 % in none treated samples, the Pb 4f at peaks 136 doublet 141.2, in regard to James, et al. [2008] are assigned to $PbSO_3$, $PbSO_4$ which are similar in agreement with results obtained by XRD and FTIR**.** See Hassan..et al [2014] The shifting in binding energy in Fig11.Distribution of lead Peaks over region of Pb4f spectra's is referred to different types of lead in Pb4f region that $Pb4f_{7/21}$ and $Pb4f_{5/21}$ and which are multi-compounds of lead , such as Pb, PbO, $PbSO_x$.



Name	Pos.	FWHM	Area	At%
O 1s	529	3.14498	531.2	55.74
C 1s	282	3.10461	26.8	7.06
N 1s	411	4.54321	29.9	4.69
Na 1s	1069	2.48892	2.6470	0.17
Pb 4f	136	2.8554	79.9	0.91
Fe 2p	709	5.18041	21.4	0.47
Ca 2p	349	6.24917	21.1	1.18
K 2p	291	2.39349	3.0745	0.21
Mg 2s	86	3.27182	3.5605	1.48
Si 2p	100	2.87537	64.7	20.14
Al 2p	71	2.79774	16.9	7.95

Figure 7.XPS wide scan of lead contaminated soil

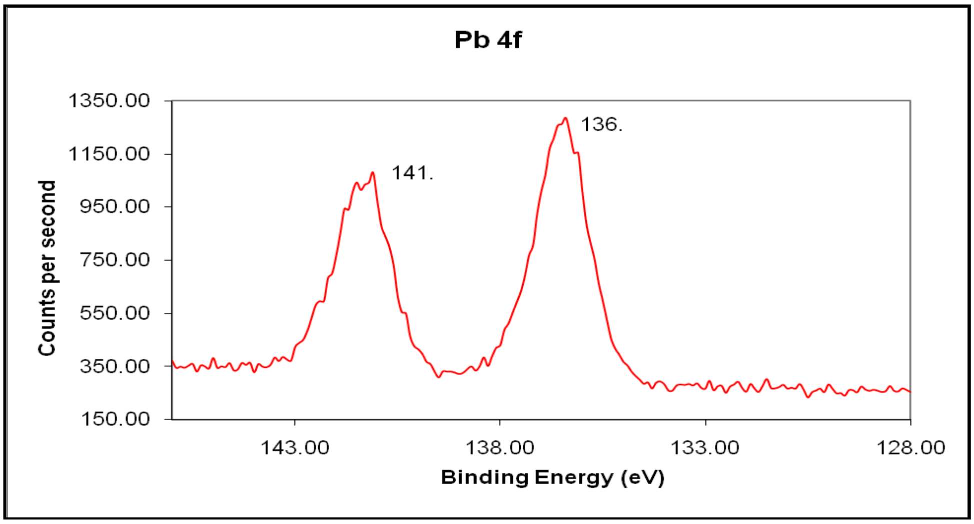
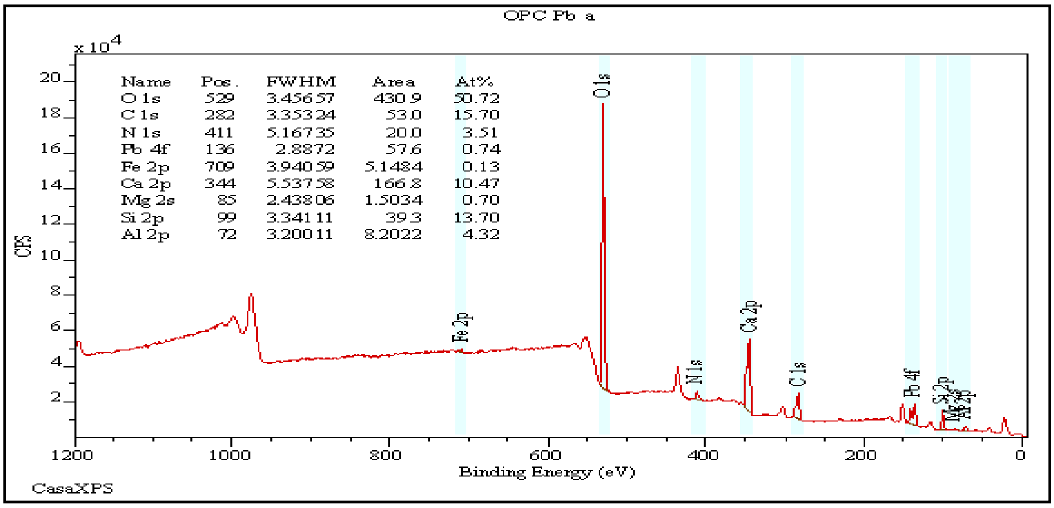


Figure 8. DetailedXPS analysis of the spectrum for lead contaminated soil, over the region of the lead 4f spectral line



Name	Pos.	FWHM	Area	At%
O 1s	529	3.45657	430.9	50.72
C 1s	282	3.35324	53.0	15.70
N 1s	411	5.16735	20.0	3.51
Pb 4f	136	2.8872	57.6	0.74
Fe 2p	709	3.94059	5.1484	0.13
Ca 2p	344	5.53758	166.8	10.47
Mg 2s	85	2.43806	1.5034	0.70
Si 2p	99	3.34111	39.3	13.70
Al 2p	72	3.20011	8.2022	4.32

Figure 9.XPS wide scan spectra of 0.1 g of cement a stabilized 5 g of Pb contaminated soil.

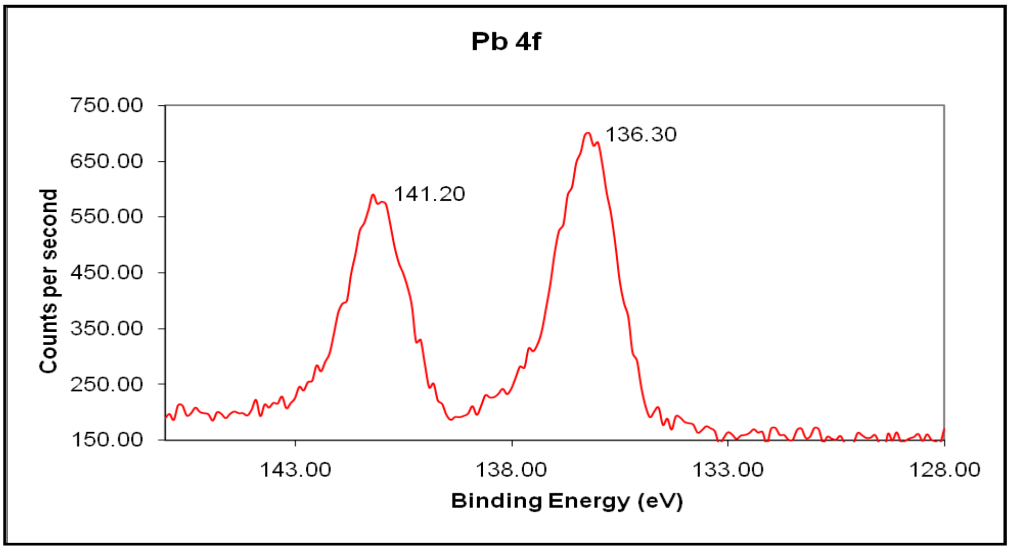


Figure10 Detailed XPS analysis of the spectrum for cement treated lead contaminated soil, over the region of the lead 4f spectral line

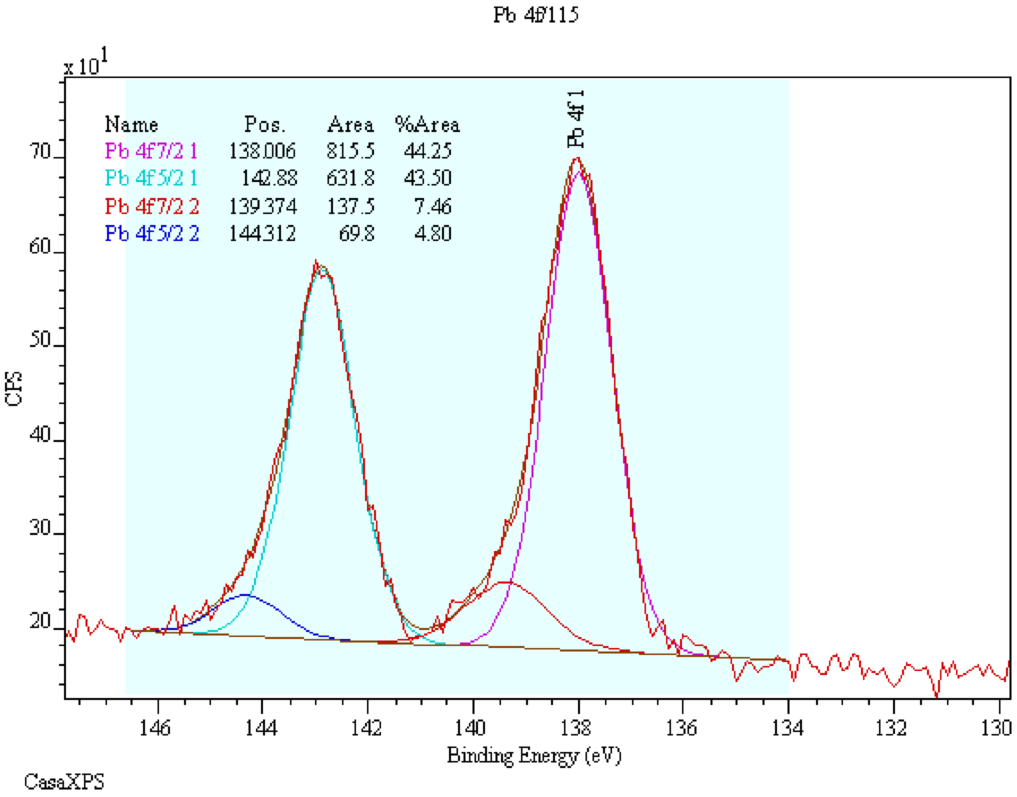


Figure11 Distributionof lead Peaks over region of Pb4f spectra

IV. CONCLUSIONS

The XPS results suggests the formation of $PbSO_3$ and $PbSO_4$.The Raman results; suggests formation of Pb-Ca-O or Pb-SO_3, Pb-Ca-SO_4.The FTIR results suggest the formation of $PbCO_3$ whereas the main compounds identified by the XRD formed in the presence of cement are: $PbSiO_3$, Pb_2SO_4, $PbCO_3$, $PbCO_3$ or $Pb(OH)_2$ **.**CaO, and $CaCO_3$, Ca $(OH)_{\mathbf{2}}$.

1. The compounds which are formed by OPC and interact with the Pb solution are $PbSiO_3$, Pb_2SO_4, $PbCO_3$.
2. The FTIR results suggest the formation of $PbCO_3$ whereas the main compounds identified by the XRD formed in the presence of OPC are: $PbSi_{O3}$, $P_{b2}SO_4$, $PbCO_3$, PbC_{O3} or $Pb(OH)_{\mathbf{2}}$ **.**CaO, lead sulphate, $P_{b2}(SO_4)$. $PbCO_3$, and Plumbonacrite, P_{b5} $O(CO_{3)3}$ $(OH)_2$-[P63CM].
3. $CaCO_3$, Ca $(OH)_{\mathbf{2}}$. The identification of compounds by XRD in OPC treated contaminated solution were more than OPC treated contaminated soils

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