XPS and Raman Characterized Lime Stabilized Lead Contaminated Soil

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ABSTRACT

Artificially lead (Pb) contaminated soil was stabilised with hydrated lime and the leaching behaviour of the element was investigated. A 5 grams' sample of contaminated soil was thoroughly mixed with 0.1g of lime, 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 lime, 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, lime, stabilization. XPS

1- 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 hydrated lime has been used to stabilise lead contaminated soil.

2-Materials and Methods

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

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

Component	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	SO_3	K_2O	CaO	TiO_2	Mn_3O_4	Fe_2O_3	ZnO	SrO	BaO
Hydrated lime	0.13	0.22	0.13	0.83	0.04	0.09	ND	60.1	0.01	0.05	0.05	0.01	0.07	0.01
Uncontaminated soil	0.20	0.13	2.89	93.6	0.02	0.06	1.72	0.12	0.08	0.01	0.65	0.01	ND	0.03

The soil was synthetically contaminated by adding litre of solution containing 1000 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 working range 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 collect the 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 Casa XPS 2.3.12 was used to fit the XPS spectra peaks.

3-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.

In Figure 1 the peak at 1045 cm^{-1} show the presence of lead in the contaminated soils, spectra in B line, peak at 1045 cm^{-1} belongs to lead contaminated soils, since it is not present in blank soils. The soils were contaminated with 20, 000 mg/l of lead solution in order to enable the Raman instrumental to   detect the lead in the samples, as it had low detection limit.

In Figure 2, lime treated lead contaminated soil, not many peaks were observed by Raman, this may be attributed to curing effects, that it was not physical binding between the contaminated soils and the lime stabilizer. The only peak is at 455 cm^{-1} which was, present also in contaminated soils, there is only a small peak under close to 200 cm^{-1} which it might be attributed to Ca-O vibration, according to Kirk.et al [1997] that would suggest presence of Pb-CaO.

In Figure 3, for 0.1g lime in 50ml of deionised water, the other with 0.1 g of lime added to lead solution. This is seen by comparing the two curves in Figure 3, the one for lime in a solution of de-ionised water The lead solution was 20 000 mg/l to enable the Raman to detect the lead in the samples. (see figure 3).

The main peaks in stabilized solutions (see Fig.3) are 390, 701, 1045 cm^{-1}, which is According to [Kirkpatrick. and Yarger.l997], (see Table 3), is assigned to Ca-O, symmetrical stretching of silicate tetrahedral carbonate group) and silicate groups.

Those peaks are referred to lead formation in treated samples, which can be referred to Pb-Ca-O or Pb-SO$_3$, Pb-Ca-SO$_4$ which are the same compounds confirmed by other techniques' FTIR, and XRD. see Hassan et al 2013. in Figure 4.7 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 [Kirkpatrick and Yarger.l997] also according to Gibbs et al [2010] it is 2PbCO3.Pb(OH)$_2$. The lead had reacted with the silica 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 280cm^{-1} is due to Ca-O.

Figure 1 Raman spectra on lead contaminated soil, (A)-uncontaminated soil, (B)-lead contaminated soil
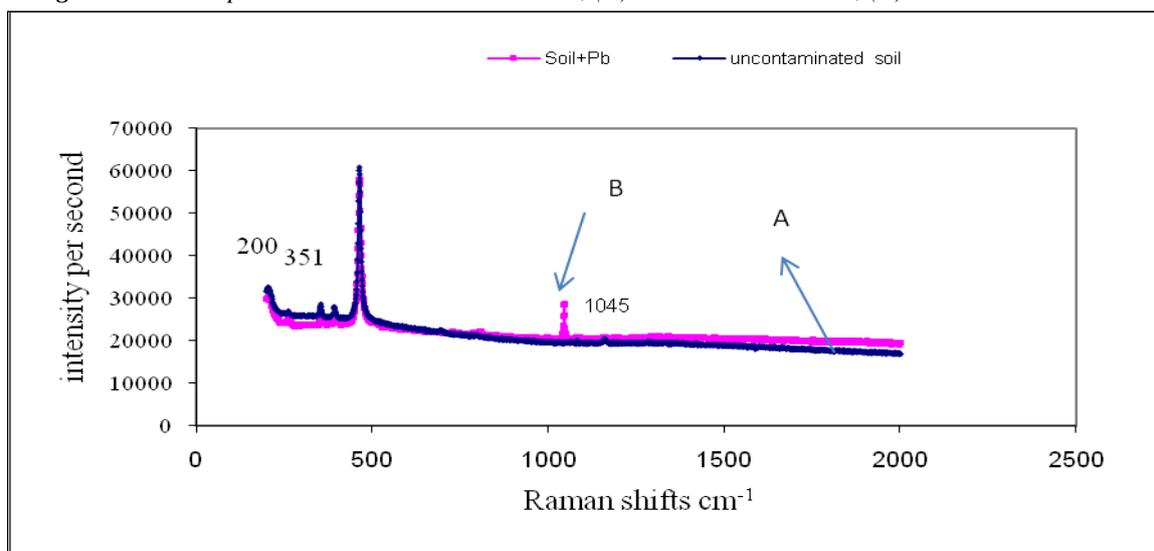

Figure 2 Raman spectra on lead contaminated soil and Lime treated soil, (A) .Lime treated contaminated soils, (B).lead contaminated soils
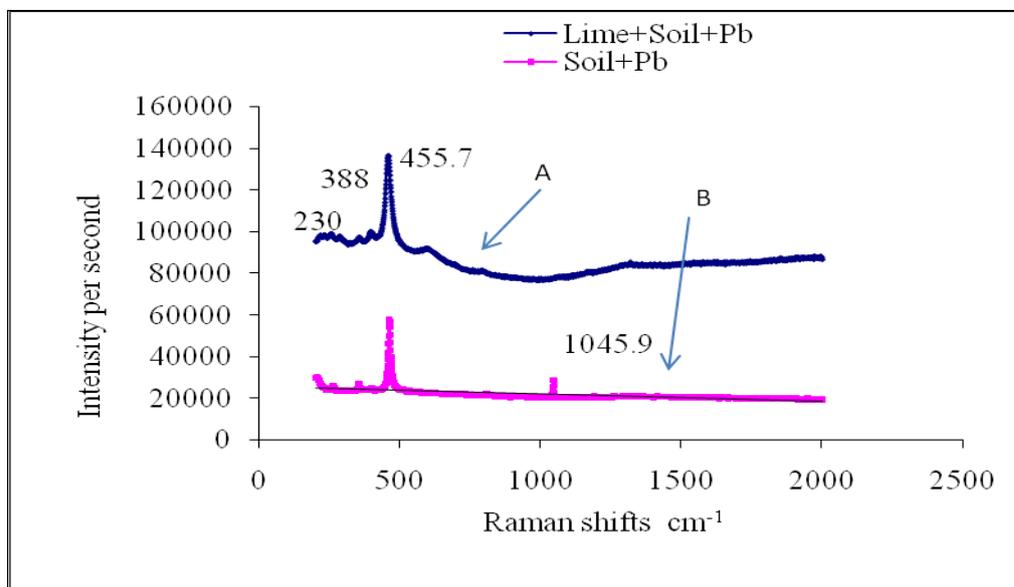
Figure 3 Raman spectra on Lime stabilized lead solution, (A)- blank lime ,1g of lime in 50ml of deionised water (B)- 0.1g of lime stabilized Pb solution
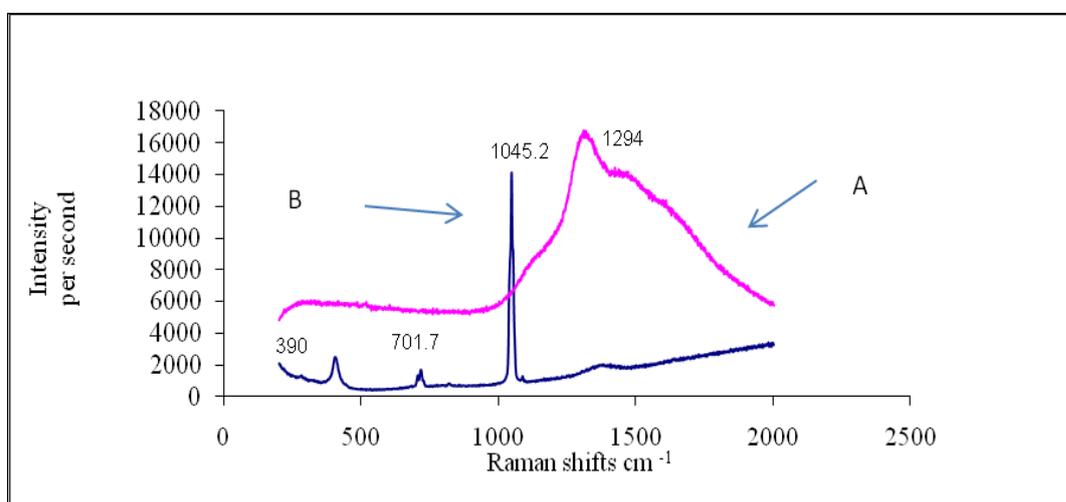

Table 3 Raman frequencies of the principle band in hydrate Portland cement [after KirkPatrick 1997] compared with results in this study

Band Cm⁻¹	Origin	Lead contaminated soil treated with lime in this stu	Lime stabilized Pb Solution in this study

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200-400	Ca-O vibration	351	390
430-540	Internal deformations of Si-O, tetrahedra (O-si-Obending)	455.7	
600-700	silicate Group		701.7
800-1100	symmetrical stretching of silicate tetrahedral carbonat group) Symmetrical stretching (SS) of Si-O tetrahedra	1045.9	1045
3000-4000	OH vibration		

3-2.1 XPS investigation for lead contaminated solution

The XPS provides extra powerful information on characterisation the samples of lime treated lead solution. In Fig.4 a wide scan of XPS spectra on blank lime with deionised water shows no lead peaks in the spectra and demonstrates the elements that make the lime which are Ca, K, O in comparison with a wide scan of XPS for lime stabilised lead solution (see Fig.5).

In this spectra the Pb4f were clearly presented in the specimen and positioned at 138 eV, which is only attributed to Pb 4f.

In comparing with spectra of blank lime in Fig 4. the amount of Ca was higher due to none lead in blank lime. The explanation of low Ca2p in   Fig 5, is the replacement of Pb ion to Ca ion which is attributed to ion exchange reaction between the Ca and Pb in presence of water. However, according to the XPS spectra standard database, which generally provide sufficient data for the determination of chemical states for uncomplicated (i.e. single peak) spectra, the main formation of lead compounds Pb4f are given to $PbCO_3$ and PbO, see Fig.6. However, according to James et al [2008]. The binding energy at 138 eV and the doublet 141 eV are assigned to PbO, or Pb SO_3.

The FTIR and XRD are in supporting of these results, see Hassan et al 20013.

In addition, Daeik et al [2009]   observed that Pb 4f $_{7/2}$ and $_{5/2}$ doublet were observed at 140 and 145 eV and insufficient to distinguish PbO from PbO_2 or $PbSO_3$, or even $PbSO_4$ and concluded that the survey scan is sufficient to distinguish metallic lead from the oxidized forms .

Figure 4. *Wide scan of XPS spectra of lime blank (deionised water and lime)*
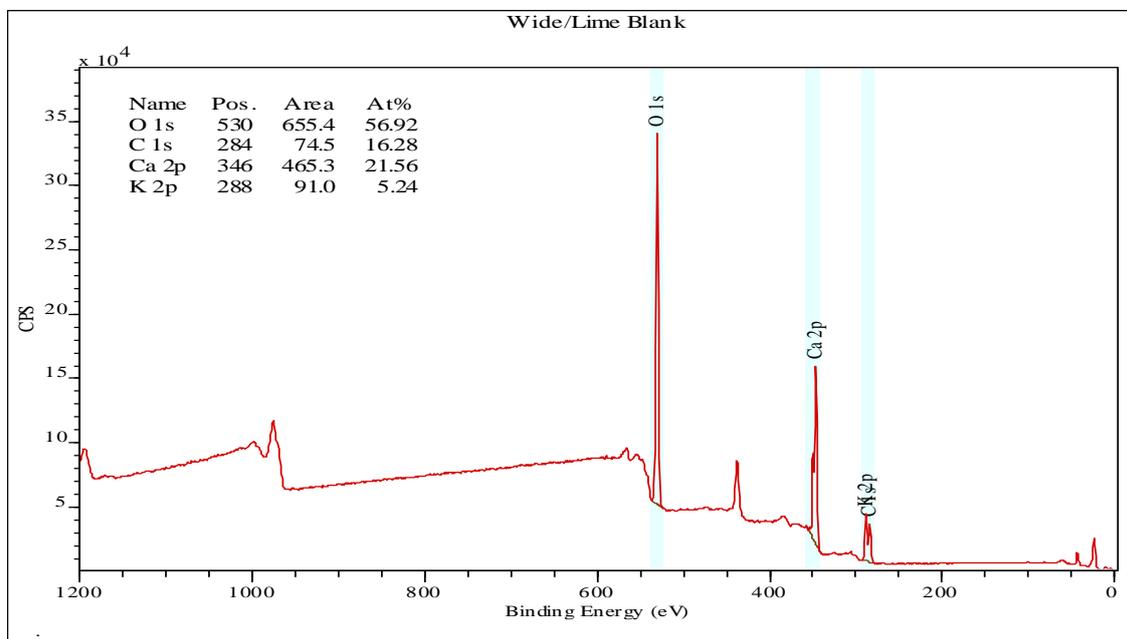
Figure 5 XPS wide scan spectra for 0.1 g of lime stabilized 50ml of 20,000 mg/lead solution
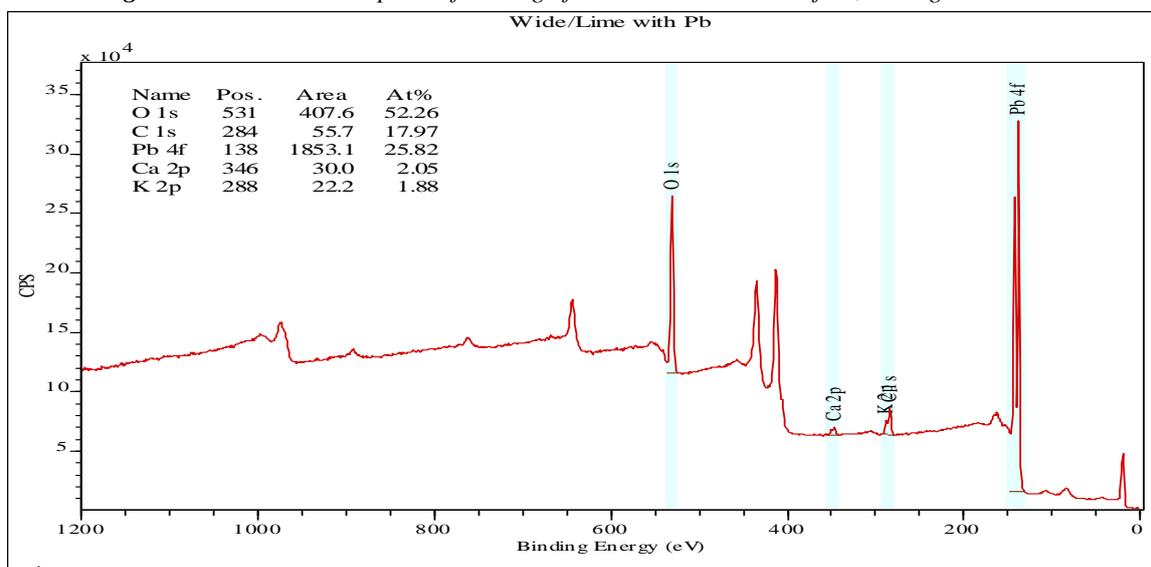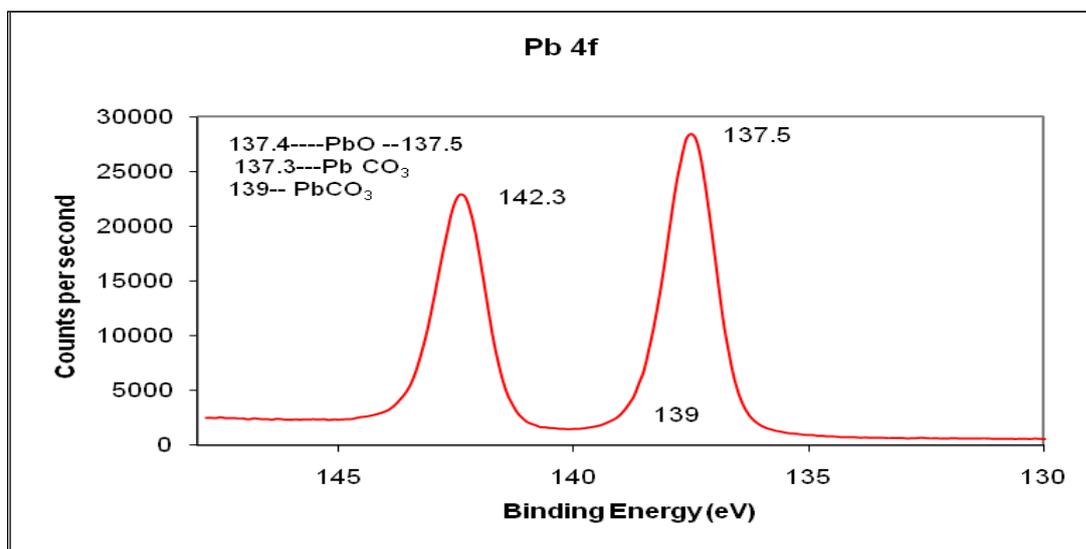
Figure 6 Detailed XPS analysis of the spectrum for lime treated lead contaminated solution, over the region of the lead 4f spectral line

3-2.2 XPS investigation of lead contaminated soils and treated soils

Figure 7 presents a wide scan of lead contaminated soil; it shows clearly the position of lead Pb4f at binding energy peak 136 eV, occupied about 0.91. The majority of elements were O 1 s, Si2p, and Na1s, which occupied 55, 20 and 4 %, respectively. While Ca2p only accounts for 1.18 %. (see Figure 8 and 9).

However, the peaks 136 eV are assigned to Pb4f7 according to XPS international data base, and 141 eV is assigned to Pb4f5. In classification to the chemical state for those peaks and relaying to James,.et al [2008] and [Tyczkowski and Pietrzyk.1998] the 137 eV and the doublet 141 eV are assigned to PbO, PbO_2 or $PbSO_3$.

Similarly, Fig. 10 shows the wide scan of contaminated soil treated with 0.1g lime, compared with untreated sample (see Fig, 8).

The Pb occupied 0.55 % reduced from 0.91% in untreated soil. Ca2p occupied 0.50% and Si to 23% from 20.14 % in untreated samples, the Pb 4f at doublet peaks 136.5 and 141.3 (see

Fig.11), however in regard to James et al [2008] these peaks are assigned to $PbSO_3$ and $PbSO_4$.

Also many other compounds of lead are present (see Fig. 11) which are in agreement with the results obtained by XRD and FTIR. (See Hassan et al 2013). The multi-peaks in Fig.11 shows that many compounds were formed in the region of Pb4f, those compounds are for Pb at the region of BE from 138.2 eV to 144 eV, such as $Pb4f_{7/21}$ and $Pb4f_{5/21}$, $Pb4f_{7/22}$ and $Pb4f_{5/22}$

Figure 7 *Wide scan of XPS spectra of lead contaminated soil*
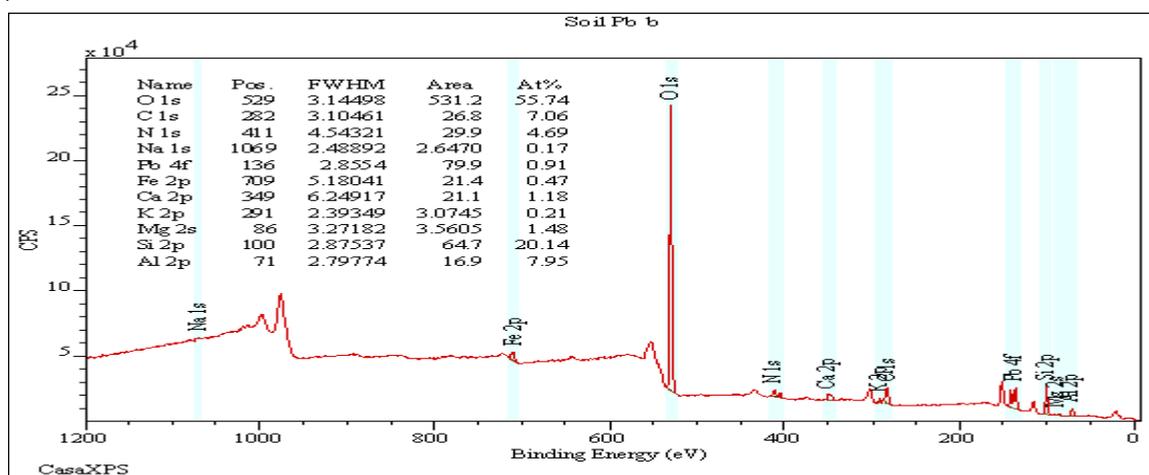
Figure 8 *Detailed XPS analysis of the spectrum for lead contaminated soil, over the region of the lead 4f spectral line*
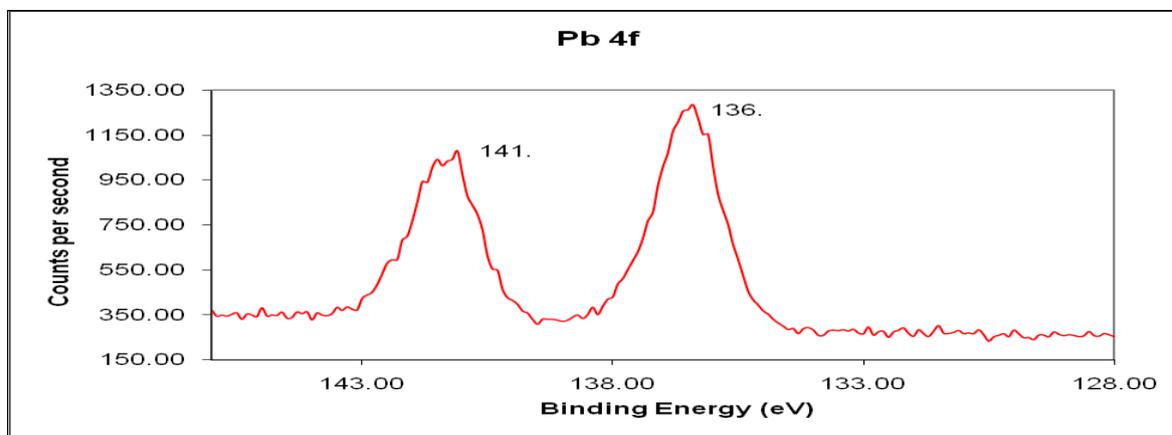
Figure 9 Wide scan of XPS spectra of 0.1 g of lime a stabilized 5 g of Pb contaminated soil, leached with 50 ml of deionised water
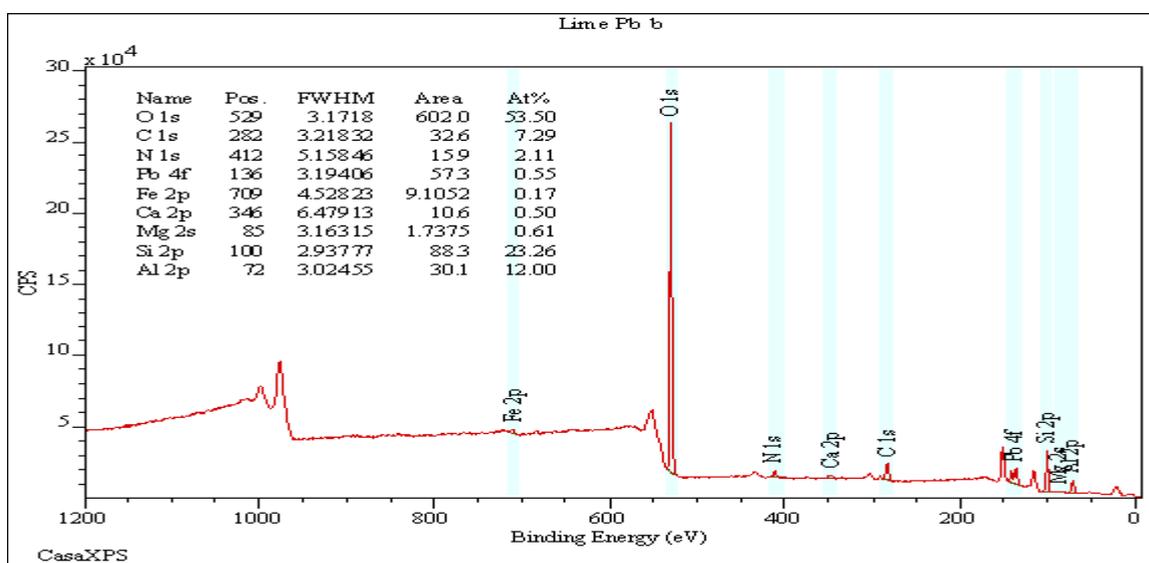
Figure 10 *Detailed XPS analysis of the spectrum for lime treated   lead contaminated soil, over the region of*
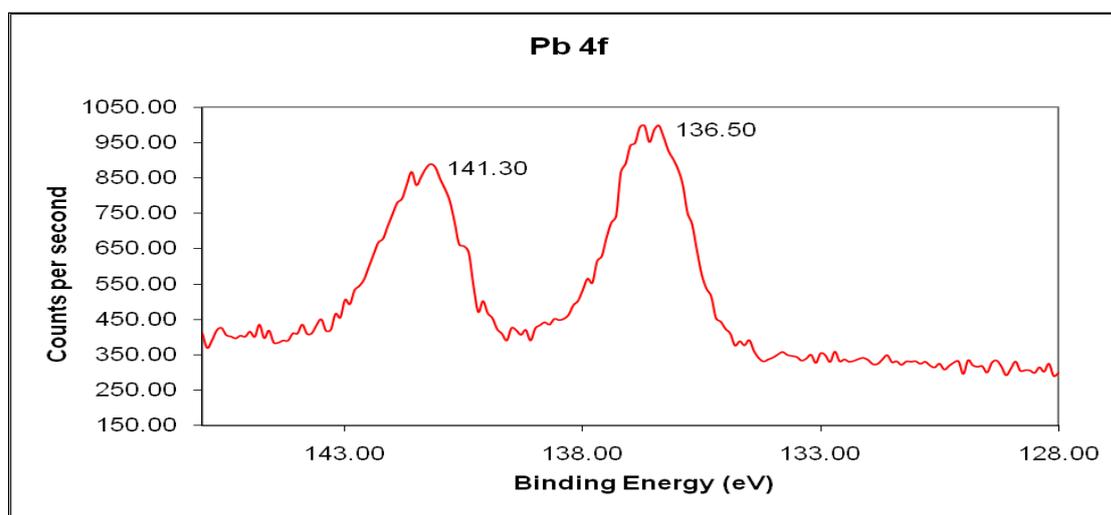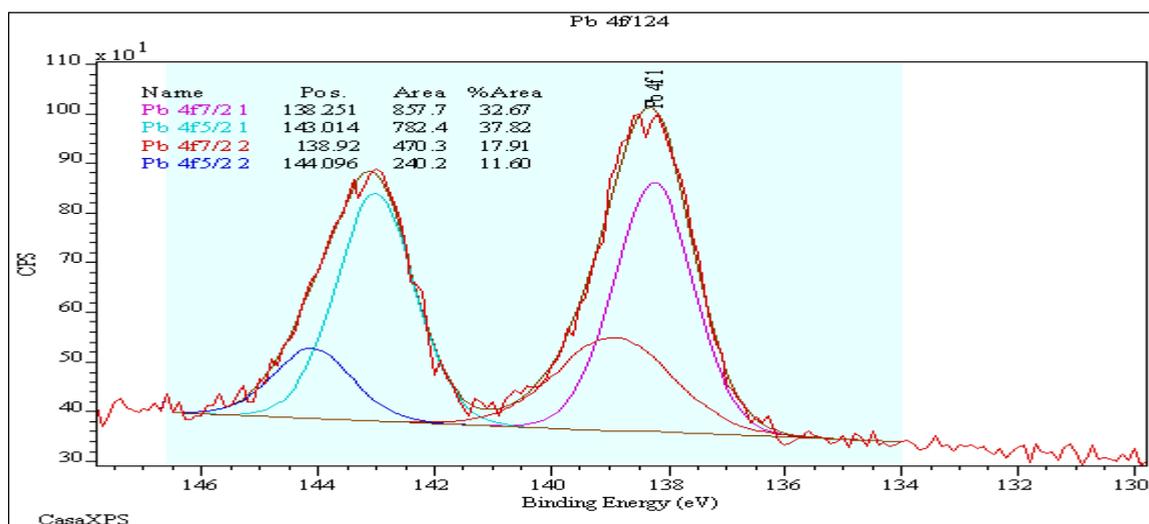*the lead 4f spectral line*

Figure 11 *Detailed XPS analysis of the spectrum for lime treated   lead contaminated soil, over the region of*
the lead 4f spectral line

5-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 lime are: $PbSiO_3$, Pb_2SO_4, $PbCO_3$, $PbCO_3$ or $Pb(OH)_2$. CaO, and $CaCO_3$, Ca $(OH)_2$.

Acknowledgements

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