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## Treatment of Lead-Contaminated Soil at the Pantex Site

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AMARILLO NATIONAL RESOURCE CENTER FOR PLUTONIUM/  
A HIGHER EDUCATION CONSORTIUM

A Report on

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Submitted to the

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## *Abstract*

Lead is present in the soil at the Pantex site primarily as elemental lead, as in the bullets, in the vicinity of several firing ranges. If left without treatment, oxidation of elemental lead to the mobile lead ion,  $Pb^{+2}$ , may result in groundwater contamination and airborne lead particles.

A proposed treatment plan proposed would occur in three steps, which included removing bullet fragments from the soil, chemically treating the remaining soil, and finally, transferring the lead from the soil to the extractant solution, and then treating the liquid to re-precipitate the lead through pH balance.

We concluded that screening the soil with a No. 14 sieve, followed by mixing the

soil with 0.1 N nitric acid, is the most effective method for dissolving the lead. After conducting four separate soil washings, we noted that the pH of untreated soil was found to be 8.24; the alkaline soil naturally stabilized the lead, a factor that is purposefully countered by mixing the soil with a low pH extractant.

Our results indicate that screening the soil with a No. 14 sieve, followed by mixing the soil with 0.1 N nitric acid, can achieve the 90% reduction in the concentration of lead that is desired. We believe that the mixing time can be significantly reduced, thereby saving valuable time in full-scale operation. A mixing time that lengthens with each wash may be more effective and is presently being investigated.

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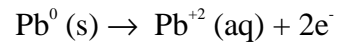
## 1. INTRODUCTION

The purpose of this ongoing project is to develop a treatment procedure for soil that has been contaminated with lead from ammunition at the Pantex site. The lead is present primarily as elemental lead, as in the bullets, in the vicinity of several firing ranges. If left without treatment, oxidation of elemental lead to the mobile lead ion,  $Pb^{+2}$ , may result in groundwater contamination and airborne lead particles.

The proposed treatment plan occurs in three steps. First, a physical separation of bullets and large bullet fragments is performed using sieves. This step is followed by a chemical treatment of the remaining soil to dissolve the smaller lead fragments and any lead, which has adsorbed to soil particles. After transferring the lead from the soil to the extractant solution, the liquid will be separately treated to re-precipitate the lead through pH adjustment. The initial screening is an essential step of the process because using chemical treatment to oxidize the elemental lead in full bullets would be cost prohibitive. On the basis of the sieve analysis (documented in a previous report), the contaminated soil is screened with a No. 14 sieve prior to the chemical treatment.

The goal of the chemical treatment is to dissolve the lead from the solid phase into an aqueous solution. After the initial screening, lead in the remaining soil is present as elemental lead, as small bullet fragments, and oxidized lead that has adsorbed to soil particles

or formed lead precipitates. We believe that the overwhelming majority is present as elemental lead. Nevertheless, the proposed treatment must provide a mechanism for the removal of both the elemental and oxidized lead. This removal is accomplished by washing the contaminated soil with a solution of 0.1 N nitric acid (pH=1). Nitric acid is an effective solvent for lead since it forms the water-soluble lead nitrate (McLeroy, 1994); the low pH is necessary to leave the lead in a soluble form. As the nitric acid is reduced to nitrogen gas, it oxidizes the elemental lead as shown in the following half reaction.



Removal of the oxidized lead is achieved through several mechanisms. Lead is removed from the soil by ion exchange since the negatively charged soil surface sites have a greater affinity for hydrogen ions than for lead ions (Cline and Reed, 1995). Removal also occurs through the low pH enhanced desorption of lead ions from the soil particles so as to achieve equilibrium with the surrounding solution (Wang and Benoit, 1996). In addition, the solubility of lead precipitates in the soil increases with the addition of a low pH extractant solution (Van Benschoten, et al., 1997). For these reasons, a low pH solution of nitric acid was selected as the extractant solution for washing the contaminated soil.

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## 2. PROCEDURE

The soil washing procedure consists of a series of steps that can be repeated as often as is necessary to accomplish the desired lead removal. Soil from the most heavily used firing range at the Pantex site, the multiple-use range, was collected and stored at 4°C. Before initiating the washing procedure, the soil was screened with a No. 14 sieve. The bullets, large bullet fragments, and other debris collected on the sieve were discarded; the soil passing through the sieve was used for the chemical treatment.

Prior to washing the soil, the solids content, pH, and concentration of lead in the soil are measured. The solids content of the soil is determined by drying approximately ten grams of soil for one hour at 102°C and calculating the percent difference from the original mass. Next, the pH of the soil is measured according to ASTM D4972-95a. The concentration of lead in the soil is measured using a Perkin-Elmer 2380 flame atomic absorption spectrophotometer (Standard Method 3111 B). The soil samples are first digested using hot nitric acid (ASTM D5198-92). This procedure calls for digesting five grams of a thoroughly mixed sample. However, the mass of soil used in the digestion has to be normalized in order to compare the lead concentrations of soil samples with varying moisture contents. Thus, five grams of solids, as opposed to five grams of the moist soil, were used in the digestion.

Next, approximately ninety grams of soil are added to a 1000 mL polypropylene centrifuge bottle. Polypropylene was chosen for its resistance to strong acids. The

extractant is prepared by titrating nitric acid into distilled water until pH=1 is measured. The volume of extractant needed is calculated based on a liquid to solid ratio of 10:1 (volume to mass). As with the nitric acid digestion procedure, the mass of solids, not the moist soil, is used in this calculation. Once the extractant is added to the centrifuge bottle, the bottle is capped and sealed with Teflon tape. The centrifuge bottle is swirled by hand to wet the sample and then placed in a tumbling box. The tumbling box mixes the samples by rotating the bottles 360 degrees end-over-end at six rpm for a predetermined period, which has been varied from two to twenty-two hours. The mixing is temporarily stopped after approximately two hours, and the bottles are opened to release excess nitrogen gas; afterwards, the bottles are re-sealed and the mixing resumes.

After mixing the samples, they are centrifuged at 6,000 rpm for twenty minutes (International Equipment Company, Model K centrifuge, rotor radius = 16 cm) to separate the solids from the liquids. The liquid portion is pipetted out of the centrifuge bottle and its pH is measured (ASTM D1293-95). The concentration of lead in the liquid is measured using a Perkin-Elmer 2380 flame atomic absorption spectrophotometer (Standard Method 3111 B). The soil left in the centrifuge bottle is mixed by hand with a metal spatula. As previously described, the solids content, pH, and concentration of lead in the soil are measured. The soil washing procedure can be repeated as many times as necessary until a satisfactory residual lead concentration is reached.

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### 3. RESULTS

Several preliminary experiments were conducted which compared extractant solutions (HCl, HNO<sub>3</sub>), extractant concentrations (pH=1, 2), and initial sieve size for screening (No. 10, 14). These results are not discussed in this report. However, on the basis of these early experiments, it has been concluded that screening the soil with a No. 14 sieve, followed by mixing the soil with 0.1 N nitric acid, is the most effective method for dissolving the lead. The results from the three experiments described in this section were derived using these parameters.

The first experiment consisted of six consecutive soil washings; in other words, the soil that remained in the centrifuge bottle after the first solid-liquid separation was mixed with a freshly prepared extractant solution and placed on the tumbling box for another twenty-two hours. This procedure was repeated a total of six times. Since some of the soil must be removed after each solid-liquid separation for the pH test and nitric acid digestion, the mass of soil in the centrifuge bottle, and the corresponding extractant volume, decrease with each soil wash. This loss was accounted for in all calculations.

Table 1 lists the cumulative percent lead removal as well as the pH and lead concentration in both the solid and liquid fractions after the samples were centrifuged. The results show the average of four identical experiments. Note that the pH of the untreated soil is 8.24. Since the rate and extent of lead mobility are pH dependent (Ganguly, et al., 1998), the alkaline soil naturally stabilizes the lead, a factor that is purposefully countered by mixing the soil with a low pH extractant. At the conclusion of the first soil wash, the pH of

the soil had been decreased to 4.97. After six soil washes, the pH of the soil had been further decreased to 1.83, which indicates that the buffering capacity of the soil was diminishing. A similar trend may be observed in the pH of the liquid decanted after the sample was centrifuged. During the first twenty-two hours of mixing, the liquid pH increases from 1.00 to 4.42. However, the buffering capacity of the soil is reduced with each additional wash, and the increase in the liquid pH likewise diminishes with each wash. This is an important parameter to monitor because the solubilization of lead is pH dependent; therefore, both the solid and liquid pH are recorded after every wash.

The lead results are the primary interest in this research. The untreated soil contained an average of 16,780 mg lead/kg soil. The most significant decrease in the lead concentration (84%) occurred during the first three washes. In the final three washes, an additional 14% of the original lead was removed. This trend should be expected since lead in the soil is present in many forms (elemental, ion exchangeable, organically bound, precipitated, and adsorbed) which are bound to the soil matrix in varying degrees. After six washes, 270 mg lead/kg soil remained; thus, 98% of the lead had been transferred from the soil to the liquid. These results indicate that the degree of lead removal can be adjusted by altering the number of consecutive washes.

It is also important to discuss the applicable federal regulations and the extent to which they affect the desired end point. If the contaminated soil is excavated and sent to a secure landfill, the land disposal restrictions

**Table 1:** Soil Washing with Twenty-Two Hour Mixing Period

	Original Soil	Wash #1	Wash #2	Wash #3	Wash #4	Wash #5	Wash #6
Soil pH	8.24	4.97	4.27	2.54	2.50	2.11	1.83
Liquid pH	--	4.42	3.44	1.69	1.14	1.07	1.14
Soil Pb (mg/kg)	16,790	13,790	9,360	2,660	1,130	530	270
Liquid Pb (mg/L)	--	270	510	600	180	30	20
Lead Removal	--	18%	44%	84%	93%	97%	98%

(LDR) for soil finalized on May 26, 1998, require a 90% reduction in the concentration of hazardous constituents (Federal Register, 1998). The extremely high concentration of lead present in the soil will undoubtedly classify the excavated material as a hazardous waste; therefore, the concentration of lead in the soil must be reduced by at least 90%. A reduction of 93% of the lead was accomplished by the end the fourth wash.

A second experiment was performed to determine whether the twenty-two hour mixing time could be reduced to facilitate faster remediation in the field. Six identical batch experiments (same soil mass and extractant volume) were started simultaneously. As time progressed through the mixing stage, the centrifuge bottles were removed one at a time at logarithmic intervals (0.5, 1, 2, 4, 8, and 22 hours). After performing the solid-liquid separation for each bottle, the concentration of lead and pH were measured. The results from this procedure reveal the amount of lead removed as time progressed through the first wash, as opposed to the previous experiment which only showed the lead removal after the wash had been completed (22 hours). Table 2 lists the pH and lead concentration in both the

solid and liquid fractions after the samples were centrifuged. It is useful to compare the soil pH to the soil Pb concentrations. Most of the lead removal (approximately 40%) occurs in the first two hours; the liquid pH at the end of this time period is 2.07. Since lead removal is a function of pH, this experiment demonstrates that most lead removal occurs when the pH is below 2.0. It should also be noted that there is significant variability in the measured soil lead concentrations. Similar variation has been observed in previous experiments and is likely due to the inherent difficulty in obtaining a homogenous soil sample for digestion. The lead concentration in the liquid has very little variation and is a better indicator of the point at which lead removal tapers off.

Due to these results, a third experiment was conducted in which the mixing time for each consecutive soil wash was reduced to two hours. This time period was selected because most of the lead removal in the previous experiment occurred in the first two hours when the pH was below 2.0. Table 3 shows the average results obtained from three identical experiments. A total of four consecutive soil washes were performed.

**Table 2: Lead Removal Versus Time During the Initial Wash**

Time (hours)	0	0.5	1	2	4	8	22
Soil pH	7.20	6.23	5.98	5.88	5.66	5.54	5.24
Liquid pH	--	1.53	1.72	2.07	2.56	3.01	3.54
Soil Pb (mg/kg)	15,060	9,220	9,780	8,940	6,720	9,780	7,830
Liquid Pb (mg/L)	--	510	540	570	580	570	570

**Table 3: Soil Washing with Two-Hour Mixing Period**

	Original Soil	Wash #1	Wash #2	Wash #3	Wash #4
Soil pH	8.10	4.64	3.61	2.13	1.88
Liquid pH	--	2.68	1.55	1.06	1.00
Soil Pb (mg/kg)	16,930	13,930	11,350	7,130	3,320
Liquid Pb (mg/L)	--	370	310	150	80
Lead Removal	--	18%	33%	58%	80%

After the first two-hour wash, 18% of the lead was removed. This is the same amount of lead removed in the twenty-two hour wash. This confirms the conclusion of the previous experiment and indicates that the first wash can be reduced from twenty-two to two hours with no significant decrease in performance. However, in all subsequent washes, the lead removal in the two-hour experiment was less than the removal in the twenty-two hour

experiment. For example, after four washes, 80% lead removal was attained in the two-hour experiment, while 93% of the lead was removed in the 22-hour experiment. Even though the pH in the two-hour washes stayed in a range (1.00 to 2.68) that is favorable to solubilization of lead, the removal was not as high as expected because there was not enough time for solubilization to occur as in the longer experiment.

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#### **4. CONCLUSIONS**

These results indicate that screening the soil with a No. 14 sieve, followed by mixing the soil with 0.1 N nitric acid, can achieve the 90% reduction in the concentration of lead that is desired. The solid-liquid separation and mixing procedure have been well defined and can be scaled up to field level. Furthermore, the procedure to remove lead from the firing range target area has been developed and

tested, and it has achieved lead levels acceptable under the federal Land Disposal Restrictions. Even though the objective for this phase of the research has been completed, it is believed that the mixing time can be significantly reduced, thereby saving valuable time in full-scale operation. A mixing time that lengthens with each wash may be more effective and is presently being investigated.

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