# CHARACTERIZATION OF PLUTONIUM CONTAMINATED SOILS FROM THE NEVADA TEST SITE IN SUPPORT OF EVALUATION OF REMEDIATION TECHNOLOGIES

Guilhermina Torrao[1], Robert Carlino[2], Steve L. Hoeffner[2] and James D. Navratil[1]
[1]Environmental Engineering and Science
[2]Clemson Environmental Technologies Laboratory
Clemson University
Clemson, SC 29634

## ABSTRACT

The removal of plutonium from Nevada Test Site (NTS) area soils has previously been attempted using various combinations of attrition scrubbing, size classification, gravity-based separation, flotation, air flotation, segmented gate, bioremediation, magnetic separation and vitrification. Results were less than encouraging, but the processes were not fully optimized. To support additional vendor treatability studies soil from the Clean Slate II site (located on the Tonopah Test Range, north of the NTS) were characterized and tested. These particular soils from the NTS are contaminated primarily with plutonium-239/240 and Am-241.

Soils were characterized for Pu-239/240, Am-241 and gross alpha. In addition, wet sieving and the subsequent characterization were performed on soils before and after attrition scrubbing to determine the particle size distribution and the distribution of Pu-239/240 and gross alpha as a function of particle size. Sequential extraction was performed on untreated soil to provide information about how tightly bound the plutonium was to the soil. Magnetic separation was performed to determine if this could be useful as part of a treatment approach.

The results indicate that about a 40% volume reduction of contaminated soil should be achievable by removing the >300 um size fraction of the soil. Attrition scrubbing does not effect particle size distribution, but does result in a slight shift of plutonium distribution to the fines. As such, attrition scrubbing may be able to slightly increase the ability to separate plutonium-contaminated particles from clean soil. This could add another 5-10% to the mass of the clean soil, bringing the total clean soil to 45-50%. Additional testing would be needed to determine the value of using attrition scrubbing as well as screening the soil through a sieve size slightly smaller than 300 um. Since only attrition scrubbing and wet sieving would be needed to attain this, it would be good to conduct this investigation. Magnetic separation did not work well. The sequential extraction studies indicated that a significant amount of plutonium was soluble in the "organic" and "resistant" extracts. As such chemical extraction based on these or similar extractants should also be considered as a possible treatment approach.

## INTRODUCTION

The removal of plutonium from Nevada Test Site (NTS) area soils has previously been attempted using various combinations of attrition, scrubbing, size classification, gravity-based separation, flotation, air flotation, segmented gate, bioremediation, magnetic separation, and vitrification (1). Results were less than encouraging, but the processes were not fully optimized. There is an opportunity for significant improvement through the utilization of more in depth studies.

To support additional vendor treatability studies six half-filled drums of soil from the Clean Slate II site [located on the Tonopah Test Range (TTR), see Figure 1] were delivered to the Clemson Environmental Technologies Laboratory (CETL). These particular soils from the NTS are contaminated primarily with plutonium-239/240 and Am-241. The soil was characterized to assist vendors in the design and optimization of their treatment processes and to indicate other possible treatment approaches.

## CHARACTERIZATION OF NTS CLEAN SLATE II SOIL

Characterization of the Clean Slates II soils included:

- Pu-239/240, Am-241 and gross alpha analysis
- Particle size distribution
- Pu-239/240 distribution as a function of particle size
- Attrition scrubbing
- Sequential extraction, and
- Magnetic separation.

Some additional information is provided for each of these below.

### Pu-239/240

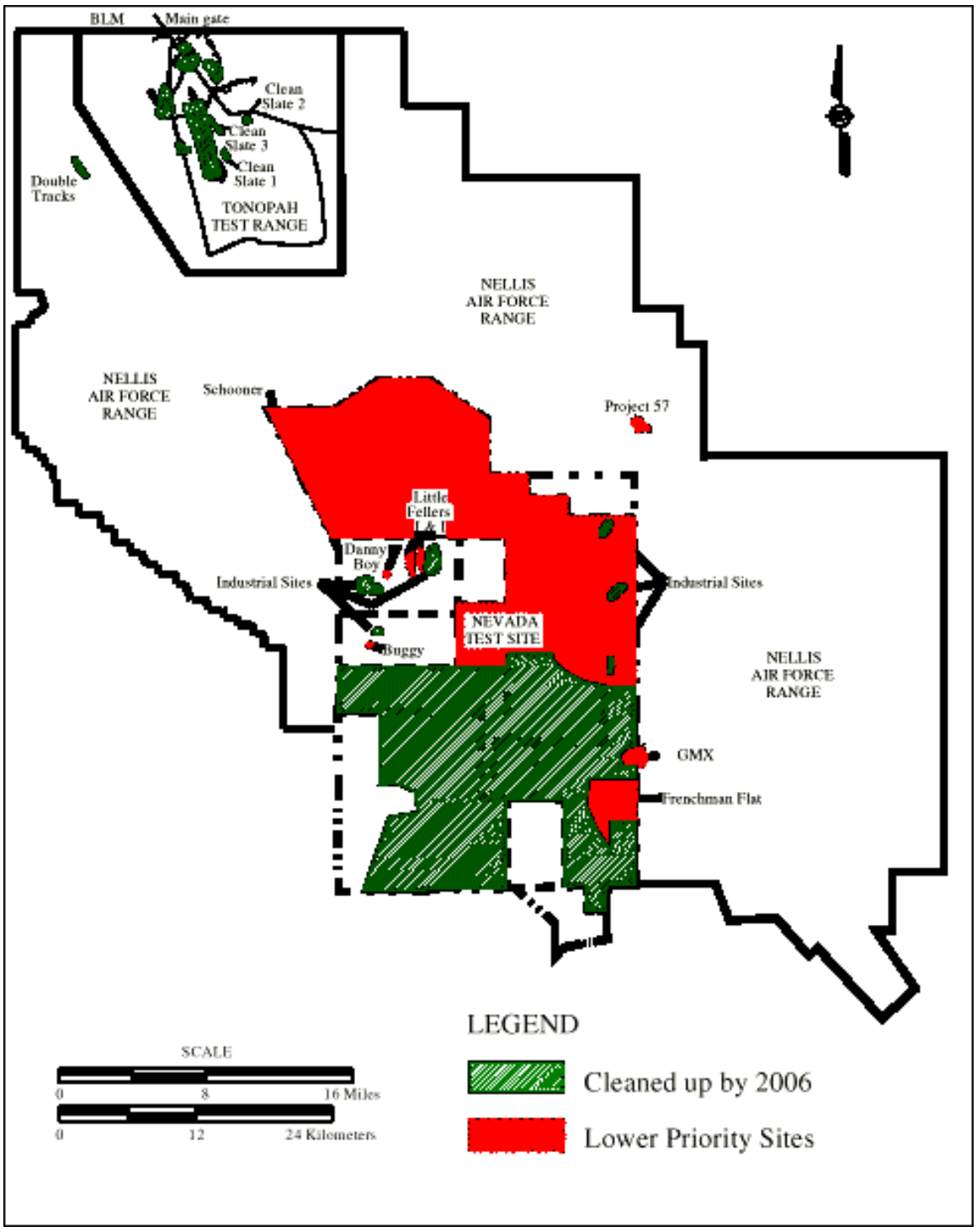
The amount of Pu-239/240 in the soils was determined by alpha spectroscopy. Soils were digested using HCL/$HNO_3$/HF. The rigorous digestion using HF was required to effect complete dissolution of the plutonium from the soil. The Pu-239/240 is isolated using anion exchange and cerium fluoride co-precipitation. Prepared samples were counted on EG&G Ortec Alpha Spectroscopy System and results were analyzed using Maestro for Windows software, Ver. 5.30.

### Am-241

The amount of Am-241 in the soils was determined by gamma spectroscopy. No sample preparation was required. Samples were counted on Genie 2000 Spectroscopy System using a low-energy germanium detector.

### Gross Alpha Analysis

The amount of gross alpha in the samples was determined by taking a portion of the acid digestate from the Pu-239/240 analysis (prior to any radiochemical separation). The aliquot was placed on a planchette, dried and counted on Canberra Alpha Beta System HT-1000 using a gas flow proportional counter.




| | | |
|---|---|---|
| NTS | GMX | Area 5 |
| | Plutonium Valley | Area 11 |
| | Project 57 | Area 13 |
| TTR | Clean Slates II | Area 52 |
| | Clean Slates III | |

Figure 1. Location of Safety Shot Sites (2)

**Particle Size Distribution**
TTR soil (125 grams) was allowed to soak overnight in about 500 mL of a 40g/L solution of sodium hexametaphosphate (a dispersant). The soil was then placed on a stack of sieves (300, 150, 75 and 38 micrometers), the sieves were placed on a Fritsch Instrument sieve shaker, a 3-nozzle spray head was attached to the top sieve and the sample was wet sieved for 15 minutes using a nominal volume of 2 liters of DI water.

**Pu-239/240 distribution as a function of particle size**
The different size fractions from the wet sieving were dried and weighed. The samples were digested to determine the amount of Pu-239/240 present in each of the size fractions.

**Attrition Scrubbing**
50 grams of soil were slurried with 200 mL of 40-g/L sodium hexametaphosphate solution. The slurry was then subjected to attrition scrubbing using a Denver Instruments Model 061873400011. Particle size and plutonium distribution as a function of particle size was measured before and after attrition scrubbing.

**Sequential Extraction**
This technique uses a series of increasingly aggressive extractants similar to those recommended by NIST (3). Typically the elements that are soluble in the select extractants, shown in Table I, are thought to be exchangeable, carbonates, reducible, organic or resistant. These descriptors provide a useful way to look at how tightly and in what fashion the contaminants are bound to the soil matrix. The sequential extraction process also may provide an indication of potential treatment technology approaches.

Table I. Summary of Extractants Used for Sequential Extraction

| Description | Extractant |
|---|---|
| Exchangeable | 0.4 M Mg Cl2 |
| Carbonates | 1 M NH4Ac |
| Reducible | 0.04 M NH2OH*HCl in 25% HAc |
| Organic Matter | 5 parts 30% H2O2 and 3 parts 0.02 M HNO3 |
| Resistant | 8 M HNO3 |

Note: All extractions were performed at 50 C, for 4 hours.

TTR soil (12 grams) was soaked in 15 mL of DI water overnight. Next, 180 mL of the extractant of interest was added to the sample. The sample was placed in a water shaker bath and allowed to react for 4 hours. After each extraction step the sample was centrifuged at 3000 rpm for 25 minutes. The supernatant was transferred into a beaker and the residual soil was rinsed twice, centrifuging each time. The rinses were combined with the supernatant, which was then analyzed for plutonium. The residual soil was carried to the next step of the sequential extraction process.

**Magnetic Separation**

Magnetic separation was used in this research to determine the amount of magnetic plutonium particles in the soil and/or the amount of plutonium associated with the ferromagnetic soil particles. Fifty gram samples of Clean Slate II were placed in polyethylene bottles (125 mL) with two 0.5 Tesla magnets attached to the outside of the bottles. Then 50 mL of distilled water was added. The soil mixture was shaken softly to allow the soil to pass through the magnet field, and eventually the soil magnetic particles became attached to walls of the bottle at the location of the magnetic force. The samples were rinsed seven times with distilled water to remove the non-magnetic particles, thereby improving the magnetic separation efficiency. The magnetic and non-magnetic fractions were dried and weighed and then analyzed for gross alpha. Magnetic separation was also performed on dry soil without the use of water.

**RESULTS AND DISCUSSION**

A summary of the CETL characterization of the Clean Slate II soil is provided below. The soil was characterized to assist vendors in the design and optimization of their treatment processes and to possibly indicate what other treatment approaches might prove useful

**Amount of Pu-239/240**

Preliminary analyses were performed to determine the relative amounts of radioactivity present on each of the six drums from the Clean Slate II Site. These data indicated only minor differences between the drums. Drum #1 was selected and the soil in this drum was homogenized by placing the drum on a drum tumbler. The drum was tumbled overnight.

The amount of plutonium in this blended soil was measured in 2- and 20-gram aliquots. Different aliquot sizes were used to determine if the soil might be inhomogeneous on the smaller 2-gram scale. A total of 6 samples were taken for each aliquot size. These numerous analyses were also performed to determine if there appeared to be any hot particles in the soil. The average amount of Pu-239/240 in the untreated soil from Drum #1 of the Clean Slate II Site was determined to be 1100 pCi/g (see Table II). No significant difference in activity or in analytical variability as a function of sample size was observed. These data are in good agreement with Bechtel Nevada anticipated results, around 1200 pCi/g, which was based on historical data.

**Pu-239/240 Variability as Function of Sample Size**

There does not appear to be any difference in variability of results for Pu-239/240 for initial aliquot or samples sizes of either 2 or 20 grams (see Table II). This would imply that there is a similar level of homogeneity in 2 or 20 grams of the soil. The range for each of the sample sets is also shown. No significant hot spots were indicated in these analyses.

Table II Amount of Pu-239 Present in Clean Slate II Soil

| Replicate Number | Pu-239, pCi/g | |
|---|---|---|
| | 2 gram sample size | 20 gram sample size |
| 1 | 1250 | 1140 |
| 2 | 979 | 915 |
| 3 | 813 | 1261 |
| 4 | 1043 | 1098 |
| 5 | 1279 | 1371 |
| 6 | 1154 | 888 |
| Average +/- SD | 1086 +/- 177 | 1112 +/- 189 |
| %RSD | 16.3 | 17.0 |
| Range | 813 - 1279 | 888 – 1371 |
| Overall Average +/- SD | 1099 +/- 175 (RSD = 16.0%) | |

**Gamma Spec Comparison**

Table III compares the amount of Am-241 measured by NTS, CETL and a commercial laboratory, General Engineering Laboratories (GEL). NTS measurements were made on the complete half-filled 55-gallon drums. The CETL and GEL measurements were made on laboratory scale samples (750 grams or less). Overall agreement is very good, with the exception of one outlier from GEL.

Table III. Comparison of Am-241
Measured Using Gamma Spectroscopy, pCi/g

| Impacted Soil | NTS (Measured in drum) | CETL (Measured in lab) | GEL (Measured in lab) |
|---|---|---|---|
| Drum 1 | 108 | 70<br>70 | 62<br>249<br>137<br>120 |
| Drum 2 | 77 | 72 | --- |
| Drum 3 | 65 | 77 | --- |
| Drum 4 | 72 | 72 | --- |
| Drum 5 | 71 | 66 | --- |
| Drum 6 | 79 | 68 | --- |

**Pu-Am Ratio**

The ratio of plutonium to americium, as determined by analyses at CETL, is summarized in Table IV. The ratio varies from 11.5 to 17.3, with an average of 14.7. This average value is similar to the value of 12 that Nevada expected to see, based on historical data (4). Notice that there is a significant fluctuation in this ratio. As such, use of the Am-241 value (as determined by gamma spectroscopy) to estimate the amount of plutonium-239/240 would at best provide a crude approximation. Because of the poor correlation, CETL will use Am-241 analyses only to provide a rough indication of the amount of Pu-239/240. Gross Alpha will be more routinely used to provide process feedback (see next paragraph), and Pu-239/240 analysis will be used to provide definitive data.

Table IV. Pu-239/Am-241 Ratio for Untreated Clean Slate II Soil

| | Pu-239, pCi/g | Am-241, pCi/g | Pu-239/Am-241 |
|---|---|---|---|
| DW-6-17 | 1140.5 | 78.6 | 14.5 |
| DW-6-18 | 914.8 | 73.6 | 12.4 |
| DW-6-19 | 1261.0 | 72.9 | 17.3 |
| DW-6-20 | 1098.4 | 71.3 | 15.4 |
| DW-6-21 | 1371.4 | 79.7 | 17.2 |
| DW-6-22 | 888.4 | 77.5 | 11.5 |
| | | | |
| Average | 1112.4 | 75.6 | 14.7 |

**Pu-Gross Alpha Correlation**

Good correlation is obtained between Pu-239/240 and gross alpha (see Figure 2). Typically the gross alpha numbers are slightly higher than the Pu-239/240. An average ratio of 1.2 is obtained for the Gross Alpha/Pu-239/240 data presented in the figure. This indicates that about 85% of the total alpha activity is Pu-239/240. It is reasonable that the gross alpha is higher, since Am-241 and other alpha emitters may be present. The good correlation indicates that gross alpha can be used to provide a reasonable indication of the amount of Pu-239/240.

**Size Distribution**

The particle size distribution of the Impacted Drum #1 soil is shown in Figure 3. Three soils aliquots were wet sieved. The results for each are shown on the graph. The data indicate that 35-40% of the soil is larger than 300 um.

**Plutonium Activity as a Function of Particle Size**

A total of four aliquots of blended soil from Drum #1 of the plutonium contaminated soils from the Clean Slate II site were wet sieved. All separations were performed identically. Although there were some differences, a typical distribution of plutonium as a function of particle size is shown in Figure 4. Results of all four aliquots are summarized in Tables V, VI and VII.

Table V. Particle Size Distribution of Clean Slate II Soil, % Mass in Each Fraction. Shown for 4 Replicates.

| | Replicate | | | |
|---|---|---|---|---|
| Particle Size, Microns | 1 | 2 | 3 | 4 |
| >300 | 39.8 | 39.3 | 37.7 | 36.0 |
| 150-300 | 14.8 | 20.5 | 21.0 | 20.5 |
| 75-150 | 22.6 | 24.5 | 24.1 | 23.6 |
| 38-75 | 6.6 | 6.2 | 9.4 | 8.3 |
| <38 | 8.6 | 6.8 | 6.7 | 9.4 |

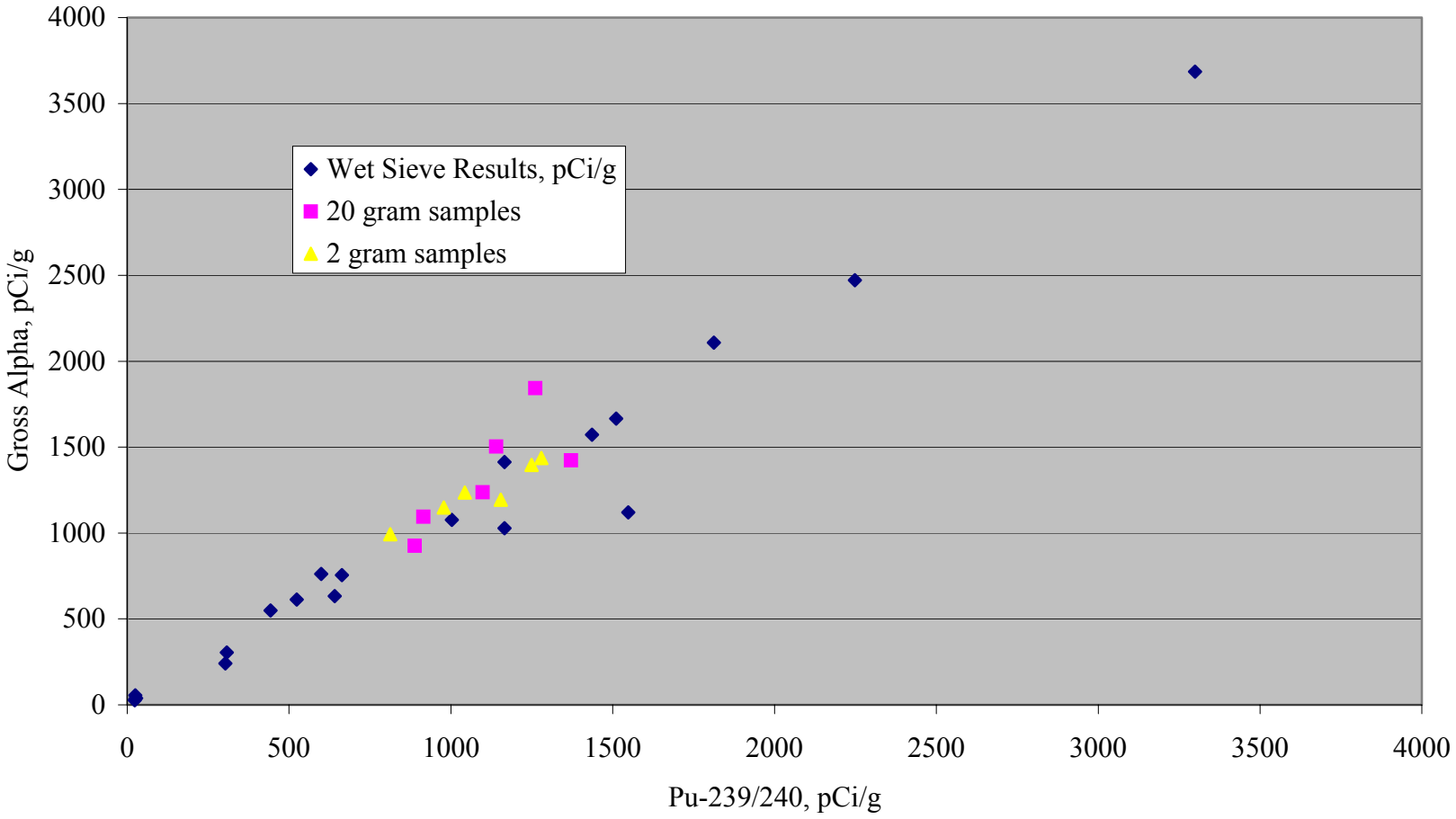



Figure 2. Correlation Between Pu-239/240 and Gross Alpha

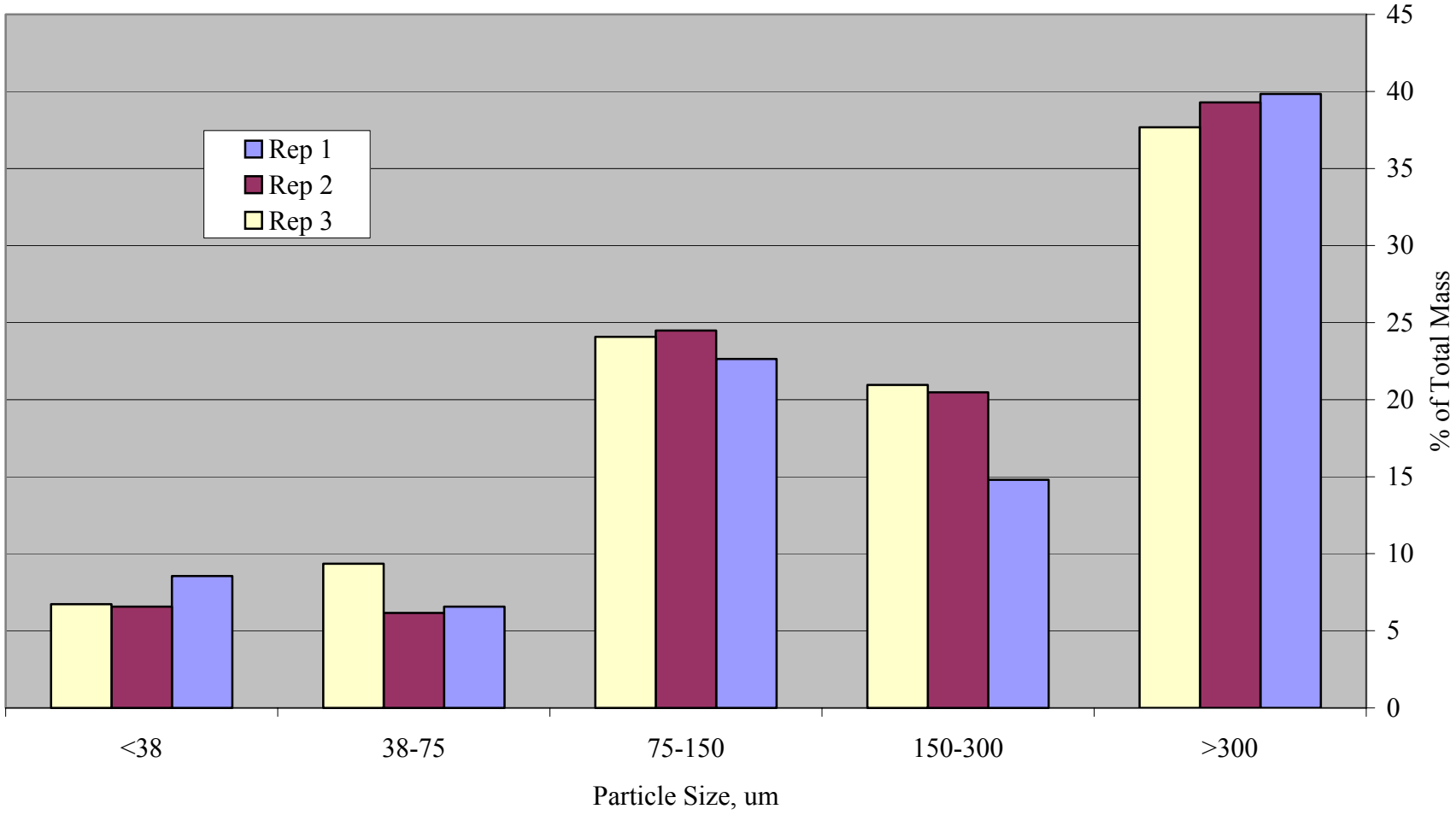



Figure 3. Size Distribution of Clean Slate II Soil, Drum #1

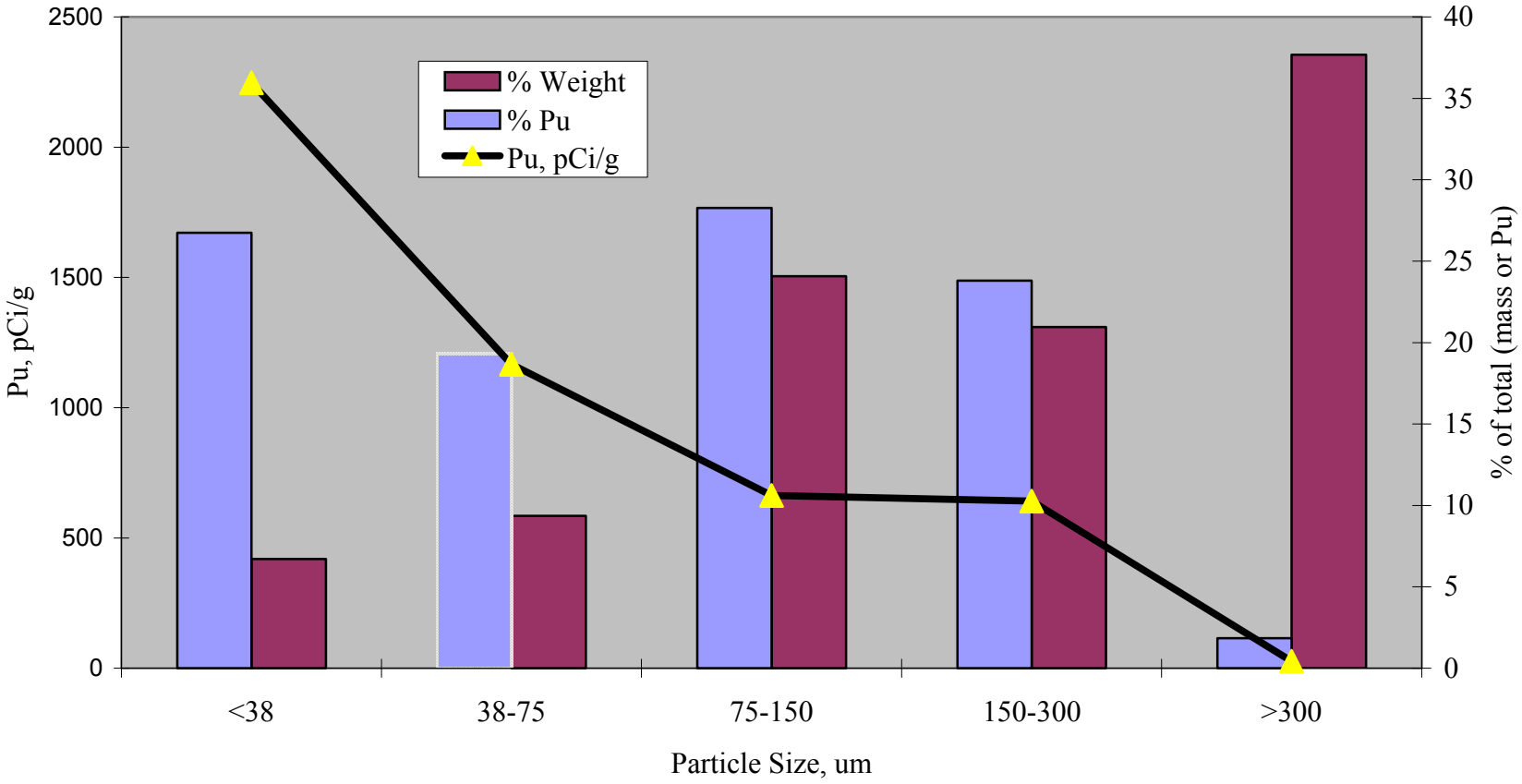



Figure 4. Pu as a function of soil size, Rep 3

Table VI. Plutonium Distribution in Clean Slate II Soil as a Function of Particle Size, pCi/g. Shown for 4 Replicates.

| | Replicate | | | |
|---|---|---|---|---|
| Particle Size, Microns | 1 | 2 | 3 | 4 |
| >300 | 25 | 23 | 28 | 25 |
| 150-300 | 1166 | 303 | 641 | 443 |
| 75-150 | 599 | 308 | 663 | 524 |
| 38-75 | 1548 | 1003 | 1166 | 1511 |
| <38 | 1813 | 3299 | 2248 | 1436 |

Table VII. Plutonium Distribution in Clean Slate II Soil as a Function of Particle Size, % Total Pu. Shown for 4 Replicates.

| | Replicate | | | |
|---|---|---|---|---|
| Particle Size, Microns | 1 | 2 | 3 | 4 |
| >300 | 2 | 2 | 2 | 2 |
| 150-300 | 30 | 15 | 24 | 19 |
| 75-150 | 24 | 18 | 28 | 26 |
| 38-75 | 18 | 15 | 19 | 26 |
| <38 | 27 | 51 | 27 | 28 |

The data indicate very little plutonium activity (<100 pCi/g) in the >300 um fraction. Since 35-40% of the soil is greater than 300 um, the data indicate that size separation may be useful as part of a treatment process. All other size fractions contained significant amounts of plutonium activity. The data in Tables V, VI and VII also indicate that, although the soil has been blended, there is still some variation from sample to sample in plutonium distribution as a function of particle size.

**Attrition Scrubbing**

The effect of attrition scrubbing on particle size distribution is shown in Table IIX. The data indicate that effect of attrition scrubbing on particle size is minimal. At best there is a slight increase in the <38 um material. The effect of attrition scrubbing on distribution of plutonium activity is shown in Table IX. No additional plutonium activity in the <38 um material is produced by attrition scrubbing. There does, however, appear to be a shift in activity from the 150-300 um fraction to the 38-75 um fraction. But the concentration of plutonium in the 150-300 um fraction remains well above the 100-pCi/g target level.

**Sequential Extraction**

Plutonium contaminated soils from the Clean Slate II Site were subjected to sequential extraction. The results of the sequential extraction process applied to the untreated soil are shown in Table X. The data indicate that significant amounts of plutonium are soluble in the "organic" (HNO3/peroxide) and "resistant" (8 M HNO3) extracts. The solubility of plutonium in the HNO3/peroxide is somewhat surprising because historical data indicated

that the plutonium was present as plutonium dioxide and as fused plutonium silicate. These would usually be soluble in the resistant phase and any remaining residual phase.

Table IIX. Effect of Attrition Scrubbing on Particle Size Distribution,
% Mass in Each Fraction.
Results are the average of 3 samples.

| Particle Size, Microns | Without Scrubbing | With Scrubbing |
|---|---|---|
| >300 | 38.2 | 36.3 |
| 150-300 | 19.2 | 19.3 |
| 75-150 | 23.7 | 22.7 |
| `38-75 | 7.6 | 8.1 |
| <38 | 7.8 | 10.0 |

Table IX. Effect of Attrition Scrubbing on Plutonium Distribution,
% Total Pu in Each Fraction.

| Particle Size, Microns | Without Scrubbing | With Scrubbing |
|---|---|---|
| >300 | 2 | 2 |
| 150-300 | 24 | 16 |
| 75-150 | 26 | 27 |
| 38-75 | 21 | 27 |
| <38 | 27 | 28 |

Table X. Sequential Extraction of Clean Slate II Soil,
Soil Not Heated in Muffle Furnace Prior to Extractions

| | Percent of Total Pu-239 Activity | | |
|---|---|---|---|
| Sample I.D. | Rep 1 | Rep 2 | Rep 3 |
| Exchangeable | 0.56 | 1.14 | 1.68 |
| Carbonates | 0.92 | 1.17 | 0.56 |
| Reducible | 1.70 | 6.36 | 4.97 |
| Organic Matter | 69.12 | 17.15 | 48.59 |
| Resistant | 27.70 | 74.18 | 44.20 |

To determine if the plutonium was truly associated with an organic phase, a portion of the soil was also placed in a muffle furnace prior to extraction. Heating to 550 C destroys organic material that is present in the soil. The results are shown in Table XI. The total amount of activity leached by this process remained about the same, with or without the use of the muffle furnace. However, the distribution of activity did change. After pretreatment with the muffle furnace about 20% of the activity is soluble in the "reducible" extractant.

The implications of this are uncertain, although perhaps the muffle furnace destroyed the organic matrix, oxidized some of the plutonium and made more of the plutonium available in the reducible phase.

Table XI. Sequential Extraction of Clean Slate II Soil,
Soil Heated in Muffle Furnace Prior to Extractions

| | Percent of Total Pu-239 Activity | | |
|---|---|---|---|
| Sample I.D. | Rep 1 | Rep 2 | Rep 3 |
| Exchangeable | 0.74 | 2.25 | 2.98 |
| Carbonates | 1.20 | 1.42 | 1.27 |
| Reducible | 24.03 | 15.25 | 24.23 |
| Organic Matter | 38.26 | 13.20 | 40.59 |
| Resistant | 35.77 | 67.88 | 30.94 |

**Magnetic Separation**

The results are show in Table XII. Magnetic separation was able to reduce the amount of activity in the soil from 1200 down to 600 pCi/g (for wet separation) and 750 pCi/g (for dry separation). However, both of these remain well above the 100-pCi/g target level. Both processes removed a similar portion of the activity (19% of the total activity), but the wet process was more efficient (6.1% of the soil contained 19% of the total activity) than the dry process (15.1% of the soil contained 19% of the total activity).

**CONCLUSIONS**

The soil from the Clean Slate II site has an average Pu-239/240 concentration of 1099 +/- 175 pCi/g. The analyses do not appear to depend on sample size and no hot particles were detected. The average ratio of Pu-239/240 to Am-241 was 14.7. This agrees reasonably well with the historical value of 12. There was significant variation in the Pu/Am ratio from sample to sample. As such, use of Am-241 to estimate the amount of Pu-239/240 should be used with caution. The average ratio of gross alpha to Pu-239/240 was 1.2. The variation from sample to sample was much less for this ratio. The use of gross alpha to estimate the amount of Pu-239/240 can be used with some confidence. But for definitive results, actual analysis of Pu-239/240 is recommended.

About a 40% volume reduction of contaminated soil can be achieved by removing the >300 um size fraction of the soil. Attrition scrubbing may allow a slightly smaller cutoff size for the clean material from >300 um down to 250 or 200 um. This could add another 5-10% to the mass of the clean soil, bringing the total clean soil to 45-50%. Since only attrition scrubbing and wet sieving would be needed to attain this reduction, it would be good to investigate this further. Future work should include looking at fractions between 150 and 300 um.

The sequential extraction work showed that significant amounts of plutonium were extracted from the soil using "organic" ($HNO_3$/peroxide) and "resistant" (8 M $HNO_3$) extracts. These or other similar reagents may prove useful in a soil washing treatment process. Separation of plutonium-contaminated particles from clean soil using the 0.5 Tesla magnets was poor and further research in this area is not warranted.

Table XII. Effect of Magnetic Separation on Removal of Alpha Activity From the Clean Slate II Soils

| Replicate Number | Magnetic Fraction | | | | Non-Magnetic Fraction |
|---|---|---|---|---|---|
| | Grams | Gross Alpha, pCi/g | % Alpha Activity Removed | % of Total Soil Mass | Average Gross Alpha, pCi/g |
| Wet Separation | | | | | |
| Rep 1 | 4.2 | 2779 | 17.7 | 8.3 | 606 |
| Rep 2 | 2.1 | 4286 | 14.2 | 4.3 | |
| Rep 3 | 3.4 | 8445 | 42.2 | 6.5 | |
| Rep 4 | 3.7 | 2452 | 14.2 | 7.6 | |
| Rep 5 | 4.1 | 4900 | 30.4 | 8.1 | |
| Rep 6 | 3.8 | 2701 | 15.6 | 7.5 | |
| Rep 7 | 2.9 | 1709 | 7.6 | 5.8 | |
| Rep 8 | 2.3 | 5264 | 18.5 | 4.6 | |
| Rep 9 | 2.0 | 1926 | 5.7 | 3.9 | |
| Rep 10 | 2.4 | 5571 | 19.7 | 4.6 | |
| Average | 3.1 | | 18.6 | | |
| SD | | | 10.7 | | |
| %RSD | | | 57.6 | | |
| | | | | | |
| Dry Separation | | | | | |
| Rep 1 | 8.0 | 1546 | 19.0 | 15.4 | 748 |
| Rep 2 | 7.7 | 1742 | 20.5 | 14.7 | |
| Rep 3 | 7.4 | 1292 | 14.4 | 13.7 | |
| Rep 4 | 7.0 | 2326 | 25.1 | 16.6 | |
| Rep 5 | 8.3 | 1444 | 18.4 | 15.3 | |
| Average | 7.7 | | 19.4 | | |
| SD | | | 3.9 | | |
| %RSD | | | 19.9 | | |

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