



DEPARTMENT OF THE ARMY
ST. LOUIS DISTRICT, CORPS OF ENGINEERS
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January 23, 1998

REPLY TO
ATTENTION OF:

Formerly Utilized Sites Remedial Action Program Project Office

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5L-13

SLDS Administrative Record 9810191053
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Mr. Larry Erickson
Missouri Dept. of Natural Resources
P. O. Box 176
Jefferson City, MO 65102

**SUBJECT: FINAL SAMPLING AND ANALYSIS PLAN FOR THE 50 SERIES
BUILDING CRUSHATE AT THE ST. LOUIS DOWNTOWN SITE (SEPTEMBER
1997)**

Dear Mr. Erickson:

Enclosed for your information is the Final Sampling and Analysis Plan for the 50 Series Building Crushate at the St. Louis Downtown Site (September 1997)

If you have any questions or comments, please contact me at (314) 524-6857.

Sincerely,

Louis A. Dell'Orco
Deputy Project Manager

jlmm
Enclosure

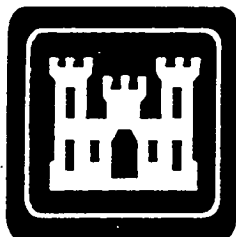
cc: Scott Honig (1)
Daniel Wall, EPA (1)
Robert Boland, Mallinckrodt (2)

USACE REVIEW DRAFT

SAMPLING AND ANALYSIS PLAN FOR THE 50 SERIES BUILDING CRUSHATE

ST. LOUIS, MISSOURI

NOVEMBER 1997



U.S. Army Corps of Engineers
St. Louis District Office
Formerly Utilized Sites Remedial Action Program

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ST. LOUIS, MISSOURI

NOVEMBER 1997

prepared by

U.S. Army Corps of Engineers, St. Louis District Office, Formerly Utilized Sites Remedial Action Program

with technical assistance from

Science Applications International Corporation ESC-FUSRAP
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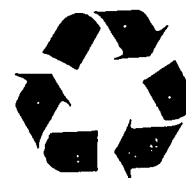


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1. INTRODUCTION

In 1974, the Atomic Energy Commission (AEC), a predecessor to the U.S. Department of Energy (DOE), instituted the Formerly Utilized Sites Remedial Action Program (FUSRAP). This program is now managed by DOE to identify, evaluate, and clean up or otherwise control sites where residual radioactivity remains from the early years of the nation's atomic energy program or from commercial radiological operations causing conditions that Congress has authorized DOE to remedy under FUSRAP. This sampling and analysis plan was written to guide the characterization of the debris from a remedial action under FUSRAP at the Mallinckrodt Chemical Company in St. Louis Missouri (Figure 1). These properties became impacted by radioactive materials as a result of activities in support of the Manhattan Engineer District (MED) during the development of atomic energy in the 1940s. The Mallinckrodt chemical facility received pitchblende uranium ore and processed it into uranium metal ingots.

2. BACKGROUND

The MED activities took place within Buildings 41A, 50, 51, 51A, 52, 52A, 501, and 502 at Plant 2, shown in Figure 2. During uranium processing operations, Plant 2 was used for digestion and treatment of triuranium octoxide (U_3O_8), ether extraction of pitchblende liquor, denitration, hydrogen reduction, and temporary storage of process residues. The plant was involved in uranium extraction from 1942 to 1945. Decontamination took place from 1948 to 1950. The plant was released for use with no radiological restrictions by the AEC in 1951 under guidelines accepted at that time.

Buildings 50, 51, 51A, 52, and 52A (hereafter referred to as the 50 series buildings) were used for ether extraction of uranyl nitrate and uranium oxide production. Building 50 was used as a utility area. Tanks installed in Building 50 stored liquids for use in Building 51. Incoming feeds and packaged products were stored there. It also served as a mechanical repair area and for other purposes as needed. In building 51, the black oxide was digested in nitric acid to form uranyl nitrate [$UO_2(NO_3)_2$] which was then purified by ether extraction. The uranyl nitrate was converted to uranium dioxide (UO_2) and then to uranium trioxide (UO_3) in Building 51A. It was then packaged and sent to Plant 4. Work supporting the MED and the AEC ceased in 1957.

The 50 series buildings were demolished in the late summer of 1996. Masonry rubble from the building demolition was processed through a rock crusher in order to reduce the volume and to apply volumetric criteria to the crushed masonry (crushate). Samples of the crushate were taken as the material emerged from the crusher. The crushate, consisting of finely ground brick and other masonry, was mounded in a pile approximately 50 feet long by 20 feet wide and 5-6 feet in height. The pile, located in a fenced area between Mallinckrodt and the Levee, is covered with a tarp.

LIST OF ACRONYMS AND ABBREVIATIONS

AEC	U.S. Atomic Energy Commission
BNI	Bechtel National, Incorporated
DOE	U.S. Department of Energy
EPA	Environmental Protection Agency
FUSRAP	Formerly Used Sites Remedial Action Program
IVC	Independent Verification Contractor
pCi/g	picocurie per gram
QC	Quality Control
SAIC	Science Applications International Corporation
TCLP	Toxic Characteristic Leaching Procedure
UO ₂	uranium dioxide
UO ₃	uranium trioxide
U ₃ O ₈	triuranium octoxide
UO ₂ (NO ₃) ₂	uranyl nitrate

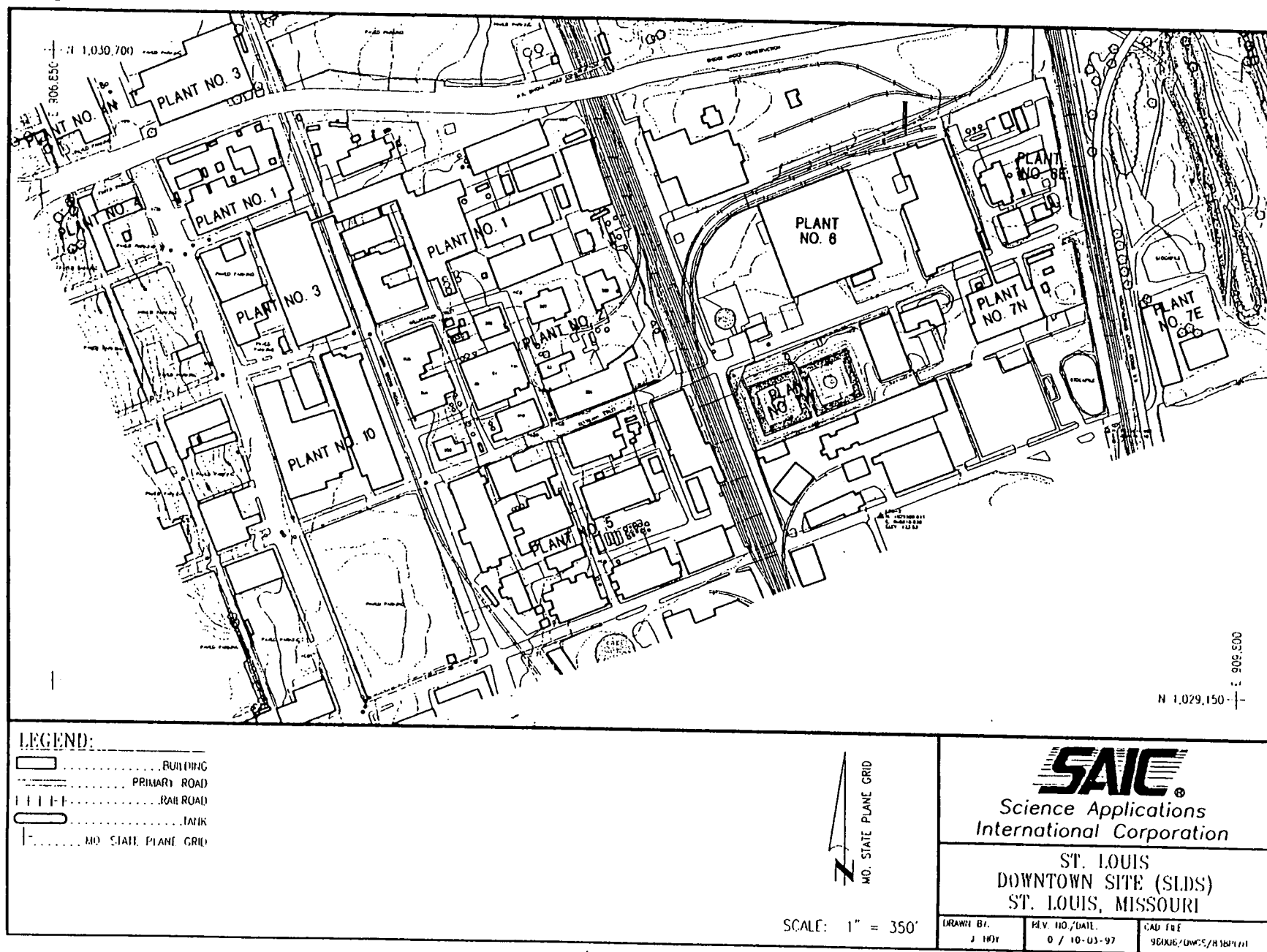


Figure 1. Mallinckrodt Chemical Plants

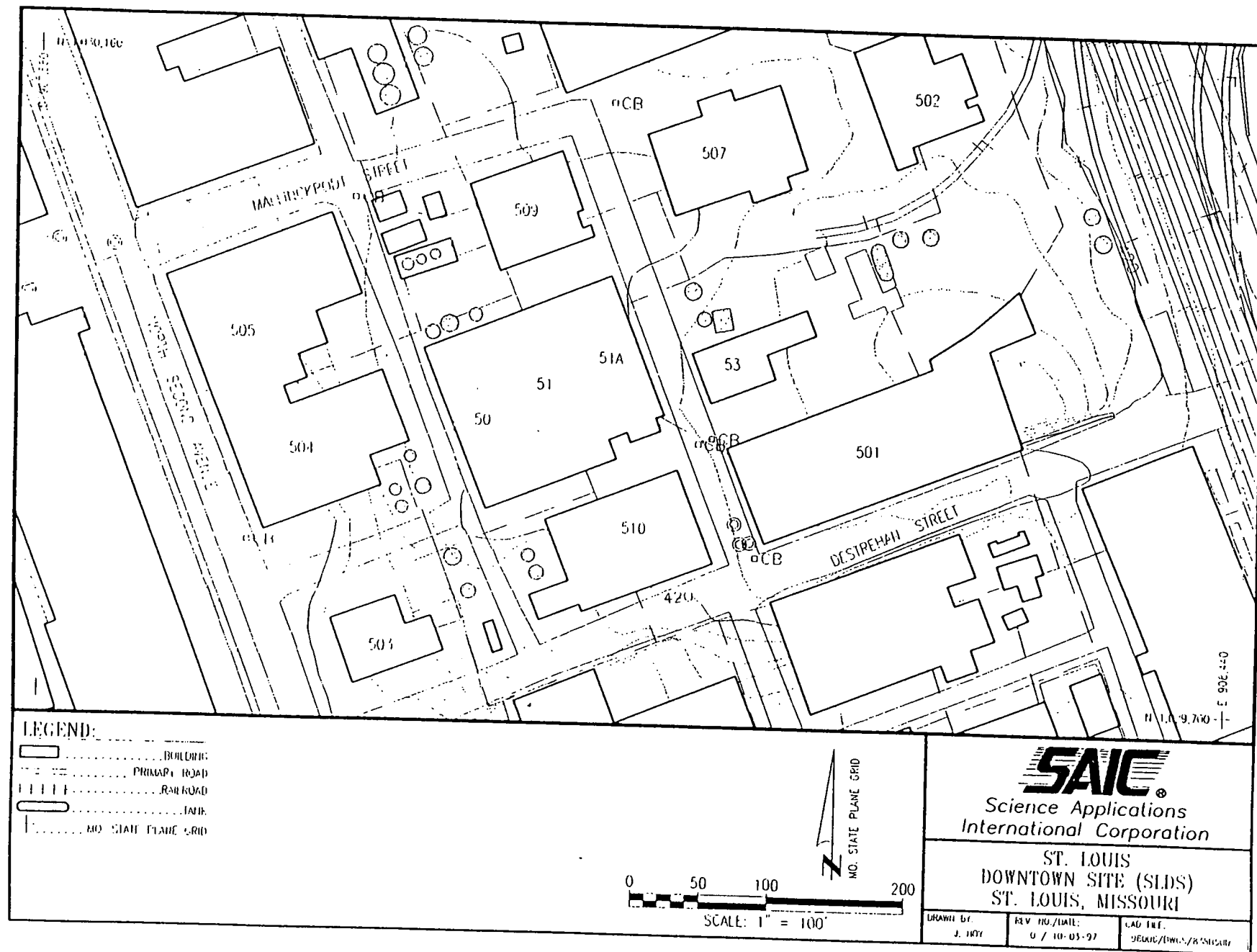


Figure 2. Plant 2 at Mallinckrodt

3. PURPOSE

The purpose of this sampling and analysis project is to determine whether the crushate in the pile exceeds DOE criteria for use at the site as clean fill. The criteria for release of the crushate for use as fill can be found in DOE Order 5400.5 which limits concentrations in soil to less than 5 picocuries per gram (pCi/g) above background for Ra-226 or Th-230 (whichever is higher) in the first 15 cm (6 in) and less than 15 pCi/g above background in deeper soil averaged over 15 cm intervals. The criteria for the Th-232/Ra-228 parent-progeny pair is identical to the Th-230/Ra-226 pair. A site specific criterion of 50 pCi/g above background has been developed for U-238.

In order to accomplish this purpose, this sampling and analysis plan has been developed to determine how many samples would be required to demonstrate with a high degree of confidence whether the crushate meets the criteria and to describe how the samples will be taken and analyzed.

4. PREVIOUS CHARACTERIZATION RESULTS

Analytical results from the grab samples collected during the crushing operation are shown in Table 1. All of the samples collected from the crusher outlet were analyzed with gamma spectrometry, however the Th-230 results were below gamma spectrometry minimum detectable activity. The analyses were repeated for Th-230 and Th-232 using alpha spectrometry. For Th-230, both the detection limit and the standard deviation were significantly lower in the alpha spectrometry analyses, thus the alpha spectrometry results are shown in Table 1 for Th-230 and "U" (for nondetected) is shown in the duplicate results for samples without duplicate alpha spectrometry results. The gamma spectrometry analyses had a lower detection limit and standard deviation for Th-232 than the alpha spectrometry analysis, thus the Th-232 results shown in Table 1 are the gamma spectrometry results. Table 1 also presents the results from background brick and soil samples. The results labeled background brick are for two samples taken from bricks, collected from the rubble pile before it was crushed, which scanned at near background levels with a handheld radiation detector. The background soil results were taken from the Remedial Investigation Report for the St. Louis Site (BNI 1994).

None of the results exceeded the DOE surface soil criteria of 5 pCi/g for Ra-226, Th-230, and Th-232 and only U-235 and U-238 were outside of the range of values that could be expected to represent background concentrations. Although uranium exceeded background in all samples, concentrations were well below the site-specific uranium guidelines.

Table 1. Results from Crusher Outlet Sampling (pCi/g)

Sample No.	Ra-226	Th-232	Th-230	U-235	U-238
1167E009	0.73 ±0.07	0.60 ±0.08	1.32 ±0.58 ^a	0.26 ±0.04	3.66 ±1.03
1167E009D	0.75 ±0.07	0.63 ±0.08	1.37 ±0.58 ^a	0.25 ±0.04	4.17 ±1.17
1167E010	0.80 ±0.09	0.50 ±0.09	3.88 ±1.25 ^a	0.32 ±0.06	5.13 ±1.49
1167E010D	0.69 ±0.08	0.57 ±0.09	U	0.36 ±0.06	5.51 ±1.70
1167E011	0.87 ±0.09	0.76 ±0.11	1.90 ±0.78 ^a	0.60 ±0.08	10.48 ±1.98
1167E011D	0.87 ±0.09	0.69 ±0.11	U	0.59 ±0.08	11.15 ±2.16
1167E012D	0.73 ±0.08	0.45 ±0.09	U	0.37 ±0.06	6.27 ±1.70
1167E012	0.67 ±0.11	0.48 ±0.12	1.95 ±0.83 ^a	0.50 ±0.11	9.29 ±2.16
1167E013	1.01 ±0.14	0.71 ±0.18	1.54 ±0.65 ^a	0.91 ±0.15	18.03 ±3.12
BACKGROUND BRICK					
116B014	1.43 ±0.13	1.18 ±0.18	3.48 ±1.23 ^a	0.17 ±0.07	1.78 ±0.79
116B014D	1.36 ±0.13	1.39 ±0.19	U	0.16 ±0.07	1.10 ±0.75
BACKGROUND SOIL (BNI 1994)					
	0.9	1.0	1.3	0.05	1.1
The suffix "D" after the sample number indicates a duplicate analysis. U denotes non-detected. ^a Results from alpha spectrometry					

5. METHODOLOGY

The sampling methodology presented in this section is based on the following assumptions:

- The pile is homogeneous with respect to the concentrations of radioisotopes and the homogeneity is uniform over time.
- The release criterion is that the sum of the ratios of the individual isotopes to their respective criteria is less than one. The criteria for the individual isotopes are 50 pCi/g for U-238, 5 pCi/g for Ra-226 or Th-230, whichever is higher, and 5 pCi/g for Th-232.
- Although process knowledge does not suggest the material would contain hazardous constituents as a result of the uranium processing operations, Plant 2 was built by Mallinckrodt prior to the

MED work and continued to be used subsequent to uranium processing activities. Consequently, 1 sample will be acquired for toxic characteristic leaching procedure (TCLP) metals analysis.

- The concentrations of metals and radionuclides in the crushate pile have a normal distribution.

5.1 Determination of Sample Size

The data shown in Table 1 were used to calculate an estimate of the variability in the radionuclide concentration in the pile to establish the number of samples that would need to be taken to determine the average concentration of the pile with 95% confidence. The number of samples required was calculated using the method presented in EPA's *Methods for Evaluating the Attainment of Cleanup Standards Volume 1: Soils and Solid Media* (EPA 1989). The governing equation for determining the sample size is given by EPA 1989 as

$$n_d = \sigma^2 \left\{ \frac{z_{1-\beta} + z_{1-\alpha}}{C_s - \mu_1} \right\}^2 \quad (1)$$

where:

n_d is the desired sample size for the statistical calculations;

σ is an estimate of the standard deviation;

$z_{1-\beta}$ and $z_{1-\alpha}$ are the critical values for the normal distribution with probabilities of $1-\alpha$ and $1-\beta$;

α is the false positive rate for the statistical test. The false positive rate is the probability that the area will be declared clean when it is actually dirty. For this project, α has been set equal to .05;

β is the false negative rate for the statistical test. The false negative rate is the probability that the area will be declared dirty when it is actually clean and the true mean is μ_1 . The sample size n_d is selected so that the statistical procedure has a false negative rate of β at μ_1 . β was set equal to .20 for this project;

C_s is the cleanup standard;

μ_1 is the value of μ under the alternative hypothesis for which a specified false negative rate is to be controlled ($\mu_1 < \mu$); and

μ is the "true" but unknown mean concentration across the sample area, the population mean.

μ_1 was set equal to the mean of the data set for each radionuclide. The mean was chosen as the best approximation available to date of the true value of the mean.

was also used to calculate the number of samples required to characterize the pile. The method used for verification of remedial actions by DOE's IVC is based on the formula given in Cochran (1977);

$$n_0 = \frac{t^2 \times s^2}{d^2} \quad (3)$$

where:

n_0 is the sample size uncorrected for population size;

t is the student t value;

s^2 is the estimate of variance, pCi/g (equivalent to σ^2 in eq. 1); and

d is the absolute acceptable error, pCi/g.

The confirmation unit used by the IVC is a 10 m by 10 m (100 m²) grid. The sampling approach uses 2.5 cm diameter cores. There are over 200,000 possible sample locations within the 10 m × 10 m grid and if $n \leq 50$, then 200,000 represents an infinite population for all practical purposes and no adjustment to n_0 is required. The pile, which is 15.2 m (50 ft) long by 6.1 m (20 ft) wide, has an area of approximately 93 m², essentially equivalent to the IVC's confirmation unit.

The t value is set equal to 2.6 for 99% confidence and the acceptable error is set at 1. Under these conditions, if an infinite number of sites are cleaned up to an average concentration of 4 pCi/g, an average of 1 in 100 would be accepted as below the 5 pCi/g criterion when it actually exceeds the criterion. This methodology was adopted with the modification that, because the criterion for U-238 is ten times the criteria for thorium and radium, the acceptable error for U-238 should also be ten times the acceptable error for thorium and radium. These calculations indicate the number of samples required is:

Ra-226: 0.11

Th-232: 0.10

Th-230: 7.3

U-238: 2.1

Thus, the desired sample size is 8 samples.

5.2 Sample Collection

Soil sampling activities will be performed in accordance with BNI Instruction Guide 14501-191-IG-041, *Instruction Guide for Soil Sampling Activities* (BNI 1996a), except that certain exceptions to the procedures should be made as appropriate due to the nature of the material. For example, the procedure calls for geologic logging. It should be sufficient, given the known origin of the crushate pile, to briefly describe the material and note any non-homogeneities encountered during sampling.

A hand auger will be used for collecting the samples. The location of the samples will be determined by dividing the pile into ten sections and taking 1-500 ml sample in the center of each section, compositing the sample through the entire depth of the pile. In addition, the pile will be scanned for gamma emissions and 1-500 ml sample will be collected from each of the two locations

The estimate of the standard deviation was obtained from the available samples in Table 1 using the formula:

$$\sigma = \sqrt{\frac{\sum_{i=1}^n x_i^2 - \frac{\left(\sum_{i=1}^n x_i\right)^2}{n}}{n-1}} \quad (2)$$

where:

n is the number of samples in the data set; and
 x_i is the value of the i^{th} data point.

σ^2 was calculated using only the values in Table 1 designated as samples. The duplicate values were ignored in the calculations. The number of samples required for $\alpha=.05$, $\beta=.2$ was calculated to be one sample, as shown in Table 2.

Table 2. Statistical Calculation of Required Sample Size

	Ra-226	Th-232	Th-230	U-235	U-238
Average	0.82	0.61	2.12	0.52	9.32
$(\sum x_i)^2/n$	3.329	1.861	22.430	1.342	434.126
σ^2	0.017	0.015	1.038	0.067	31.701
C_s	5	5	5		50
μ_i for $\alpha = .05$ $\beta = .2$	0.82	0.61	2.12		9.32
$z_{1-\alpha} = 1.645$ $z_{1-\beta} = .842$ $n_d =$	0.01	0.00	0.77		0.12

In addition to using statistically valid sampling methods to characterize the pile, a second objective of this plan is to ensure consistency with standard FUSRAP remediation verification methodology. Consequently, the method used by DOE's independent verification contractor (IVC)

section, compositing the sample through the entire depth of the pile. In addition, the pile will be scanned for gamma emissions and 1-500 ml sample will be collected from each of the two locations with the highest readings. Thus, a total of 12 samples will be collected from the pile. Results from the two biased samples will not be used in calculating the mean.

Samples should be labeled with a unique sample nomenclature. The composited radiological samples should be placed in 500 ml (1 pt) nalgene bottles. The TCLP sample can be composited from the material left over after compositing the ten radiological samples. This sample should be stored in a 500 ml (1 pt) amber glass bottle.

A field log book will be maintained and all field activity records will be kept in accordance with PI E2.9 *Control of Field Logbooks* (BNI 1996b).

The radiological samples should be analyzed for the following isotopes:

Analyte	Analytical Method	Detection Limit
Uranium-238	Gamma Spectroscopy	1 pCi/g
Radium-226	Gamma Spectroscopy	0.5 pCi/g
Thorium-232	Gamma Spectroscopy	0.5 pCi/g
Protactinium-231	Gamma Spectroscopy	1 pCi/g
Thorium-230	Alpha Spectroscopy	0.5 pCi/g
Actinium-227	Alpha Spectroscopy	0.5 pCi/g

Following analysis, the required number of samples will be recalculated by Science Applications International Corporation (SAIC) from the unbiased data using the Environmental Protection Agency (EPA) method outlined in Section 5.1. If the results indicate that more than ten samples are required, the additional samples should be obtained and analyzed following the procedures specified in this plan.

6. QUALITY CONTROL

Quality control (QC) samples will be used to assess data quality in terms of precision and accuracy and to verify that sampling procedures such as chain of custody, decontamination, packaging, and shipping are not introducing variables into the sampling chain, which could compromise the validity of the results. The following field and laboratory QC samples will be collected and analyzed.

6.1 Field QC Samples

Rinse Blanks: Analyte-free water will be used to rinse decontaminated sampling equipment and sampling accessories as a check that the decontamination procedure has been adequate and there is no cross contamination of samples occurring due to the equipment itself. The blank should be collected at the beginning of the day prior to the sampling event and that blank must accompany those samples that were taken that day.

6.2 Laboratory QC Samples

Method Blanks: In order to detect possible contamination of samples during sample preparation and/or analysis, method (or laboratory) blanks are used. The laboratory shall prepare and analyze method blanks at the frequency specified in the appropriate method or at a minimum frequency of one per batch, whichever is more frequent.

Laboratory Control Samples: Laboratory control samples, or method blank spikes, are used to determine the accuracy of the analytical method. These samples are generally used for metals analyses and are prepared at a frequency of one per batch.

Matrix Spikes and Matrix Duplicates: Matrix spike and matrix duplicate samples shall be used to quantitatively determine accuracy and precision. Accuracy is measured by how close the reported concentration value is to the "true" value. "True" value is established by spiking the matrix with known concentrations of analytes of concern. Precision is a measure of how reproducible the measurements are and is calculated from duplicate analysis. A minimum of one matrix spike and one matrix duplicate shall be performed per batch.

Preservatives and Holding Time: The samples will be preserved at 4°C prior to analysis. The holding time for all metals analyses except mercury is 180 days. The holding time for mercury is 28 days if collected in amber glass bottles.

7. REFERENCES

Bechtel National, Incorporated (BNI) 1994. *Remedial Investigation Report for the St. Louis Site*, DOE/OR/21949-280, Oak Ridge, Tennessee, January.

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