RFP-2856

Conf. 781101--23

MASTER

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ACKNOLWEDGMENTS

The authors wish to thank J. A. Hayden, C. T. Illsley, and F. J. Miner for their helpful suggestions; R. H. Schmunk for laboratory assistance on the vitrification process; Analytical Laboratory personnel for analyses; and Waste Management personnel for obtaining soil samples. This work was performed under U.S. D.O.E. Contract No. DE-AC04-76 DP03533.

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ABSTRACT

Waste management processes have been developed to reduce the volume of Rocky Flats soil contaminated with plutonium and americium and to prepare the contaminated fraction for terinal storage. The primary process consists of wet-screening. The secondary process uses attrition scrubbing and wet screening with additives. The tertiary process involves volume reduction of the contaminated fraction by calcination, or fixation by conversion to glass. The results of laboratory scale testing of the processes are described.

INTRODUCTION

In January 1964, an area of the Rocky Flats Plant was found to be contaminated with plutonium. This area had been used to store 220-litre drums of plutonium contaminated lathe coolant oil and carbon tetrachloride (CCl_4) since 1958. Many of the drums had corroded and leaked plutonium contaminated oil-CCl_4 into the soil. All drums were removed from the storage area and processed by January 1968.

The plutonium contamination level in the soil was found to range from 2000 to 300,000 dpm/100 cm^2 with a depth penetration of from 2 cm to at least 20 cm. By November 1969, the contaminated soil area was covered with approximately 8 cm of fill dirt, 15 cm of loose gravel and 8 cm of asphalt.

Preliminary decontamination studies indicated that mechanical sieving could reduce the volume of contaminated soil in a windblown soil sample. The highest plutonium and americium concentrations were associated with the smallest soil particles.

In 1976, a program was initiated to find methods for decontaminating the soil now covered by the asphalt pad. Soil samples were taken from six different locations beneath the asphalt pad. Plutonium decontamination studies were then conducted on a laboratory scale with the pad soil as well as with soil samples from the windblown areas. These studies involved techniques such as dry and wet screening, attribion scrubbing and calcination with and without glass-forming agents. This report summarizes these findings.

EXPERIMENTAL

Materials

Soil decontamination experiments were conducted on eight batches of plutonium contaminated soil. Two of these were windblown soils, while the other six batches were obtained from beneath the asphalt pad. The contaminated soil was shoveled into double-bagged, 20 litre polyethylene bags. These bags were then sealed, placed in 220-litre mild steel drums and shipped to the soil decontamination laboratory.

All chemicals used in the study were regaent grade.

Equipment and Procedures

Soil decontamination procedures included screening, scrubbing, and calcination with and without glass formers. Prior to performing these procedures, each of the eight soil samples (aproximately 4 kg each) was placed in a drying oven at 100°C for a period of five days. Each batch was then weighed and mixed for an eight-hour period on a twin shell blender, and sampled.

A sieve shaker was used to dry screen the soil. U. S. Standard sieves (20 cm diameter) were used with the shaker. The shaker provided a horizontal, circular motion interspersed with a series of tapping impulses; it was operated 10 minutes per screening operation. Screened soil fractions were weighed, mixed for one hour, then sampled.

A Tyler Model Rx-24 portable sieve shaker was modified for wet screening operations. Basically it consisted of a wash solution reservoir (4 litre bottle), a peristaltic pump operating at 20 ml/sec, a modified sieve lid, a modified bottom pan, and valves and tubing.

The attrition scrubbing experiments were conducted with the lab model Fagergren flotation machine. This device consists of three six-bladed stainless steel opposed-pitch turbine-type propellers on a stainless steel drive shaft. These operations were conducted with 100 and 200 grams of soil suspended in 150 and 200 ml of wash solution, respectively. The soil samples were taken from either the <4 mm, <2.4 mm, or <0.42 mm fractions. The soil mixture was poured into the 1 litre mixing tank and scrubbed at 900 rpm for 10 minutes. Upon completion of the scrubbing process, each soil fraction was wet screened.

Volume reduction experiments were conducted using aliquots of an oven-dried (100°C) soil. The samples were heated to 600°C, 800°C, 1000°C, 1200°C and 1400°C. Weight loss and bulk density measurements were used to estimate the volume reduction obtained by heating to high temperatures.

Additional experiments were done to demonstrate the feasibility of fixing contaminated soil by heating with glass forming agents commonly used in radioactive waste fixation. Soil was used in place of SiO_2. The materials were intimately mixed, then heated to temperatures ranging from 1250 to 1450°C and poured into graphite molds. The resulting waste forms were annealed ~~in~~ at 500°C for three hours, then slowly cooled to ambient temperature. The volume of the resulting waste form was compared to the original soil volume of oven-dried (100^{o}C) soil.

Soil samples and washes were analyzed radiometrically for ^{241}Am and ^{239}Pu.

RESULTS AND DISCUSSION

The analytical results of the excavated soil samples are shown in Table I. The sampling depth shows the soil removal depth required to reach soil reading $\leq$250 dpm/g. There is an estimated 14.5 tons of contaminated soil under the asphalt pad.

Elemental analyses on three of the soils showed that the elemental composition of the soils is similar. Wet screen analyses of samples P4 and P5 show a soil particle distribution that is log normal from 5.0 to 0.07 mm (Figure 1). The mass mean diameter is ~10 mm. The average plutonium and americium concentrations in the six pad samples are shown in Table II. The actinide content is associated with the smaller soil fractions. The plutonium particles found in and around the pad area have a mean size of about 0.2 μm. The maximum size of plutonium particle found was about 2 μm.

Primary Soil Decontamination Process

The wet and dry screening experiments described above were used to develop a primary soil decontamination process. The data (Table II) show that dry-screening did not decontaminate the larger fraction (>4 mm contains ~60% of the mass) to the desired activity level of <25 dpm/g. However, wet-screening successfully removed the contamination from the >4 mm fraction to a value below 5 dpm/g (plutonium and americium). The wet-screening also

FIGURE 1 PARTICLE SIZE DISTRIBUTION OF WET-SCREENING SOILS P-4 and P-5.

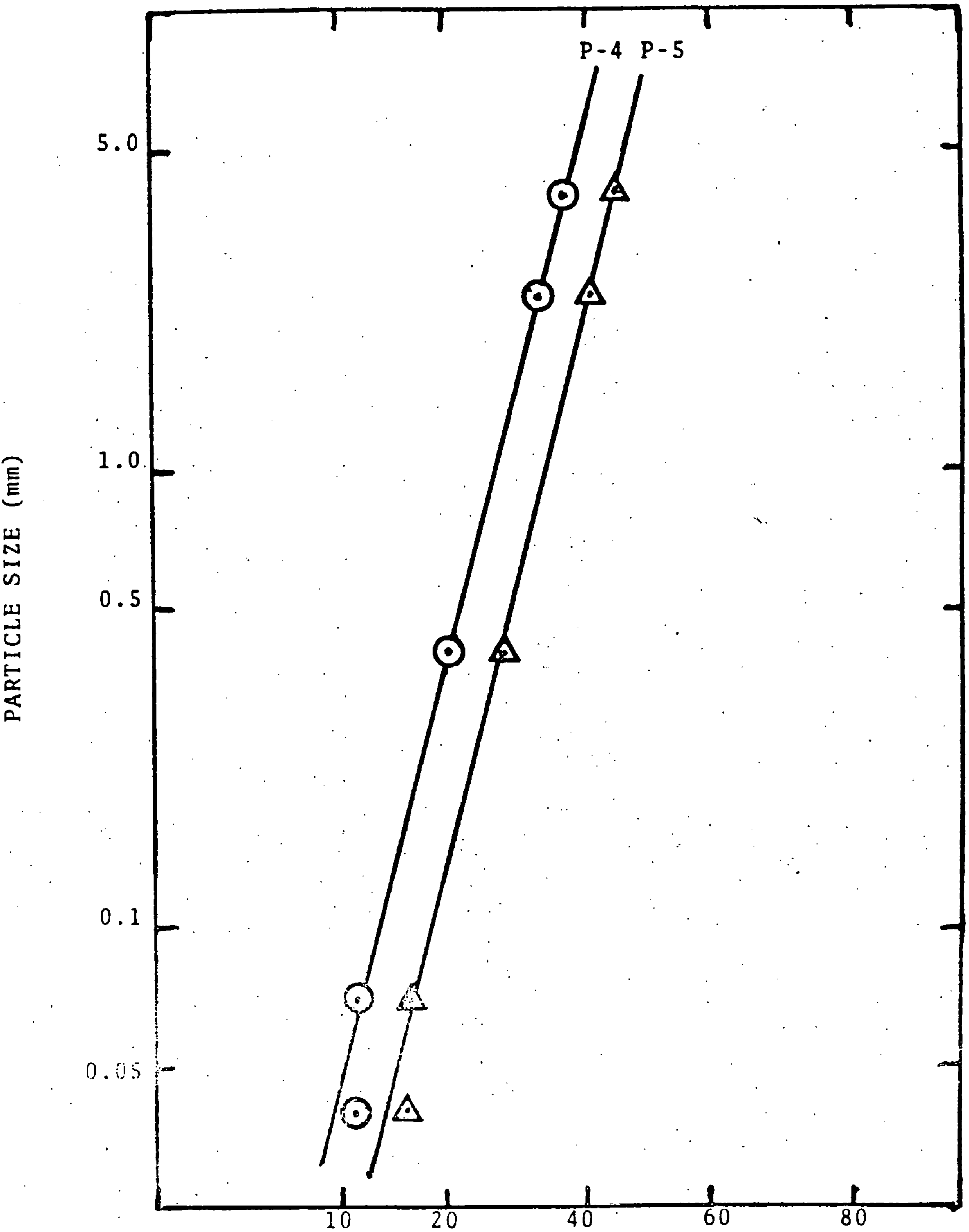

TABLE I

ANALYTICAL RESULTS OF EXCAVATED SOIL SAMPLES

Sample	Actinide Content dpm/g Pu	Actinide Content dpm/g Am	Sampling Depth from Top of Pad, cm
A	1,200	330	--
B	11,900	1,400	--
P-1	940	620	46
P-2	1,400	1,100	61
P-3	8,000	1,000	56
P-4	45,000	4,200	66
P-5	14,000	4,100	61
P-6	17,000	5,000	61

TABLE II

AVERAGE DRY AND WET-SCREENING RESULTS OF THE SIX PAD SOIL SAMPLES

Dry-Screening	4.0 mm	4.0 to 2.4 mm	2.4 to 0.42 mm	0.42 mm
Weight%	60	4	12	24
Pu(dpm/g)	240	1,400	3,100	29,000
Am(dpm/g)	150	270	560	4,100
Wet-Screening				
Weight %	61	4	11	24
Pu(dpm/g)	<5	120	670	27,000
Am(dpm/g)	<5	24	160	4,500

substantially reduced the plutonium and americium contamination level in the 4 to 2.4 mm fraction.

The proposed primary process is shown in Figure 2. It utilizes a wet-screening operation to separate the contaminated fines from the larger particulates (>2.4 mm) fo the soil. The average wet-screening data in Table II show that the >2.4 mm fractions contain <12 dpm/g Pu and <6 dpm/g Am representing 65 wt% of the dried soil. Screening water was easily filtered through filter paper to reduce the plutonium and americium concentration below 5 dpm/ml.

Secondary Soil Decontamination Process

Currently the candidate secondary decontamination process comprises attrition scrubbing followed by additional wet-screening. Figure 3 outlines the conceptual flowsheet and includes data for the attrition scrubbing wet-screening process.

Additional tests were done with various reagents added to the process water to aid in dispersing and decontaminating the soil. A composite sample consisting of weighted portions of the six pad samples was attrition scrubbed for 10 minutes and wet-screened with the reagent solutions. The reagents that appeared to best improve the decontamination of soil compared to water alone were 10 wt% calgon, 0.1 $\underline{M}$ citric acid, and 0.1 M oxalic acid; results are shown in Table III. These results show that attrition scrubbing

Figure 2. Conceptual Primary Process

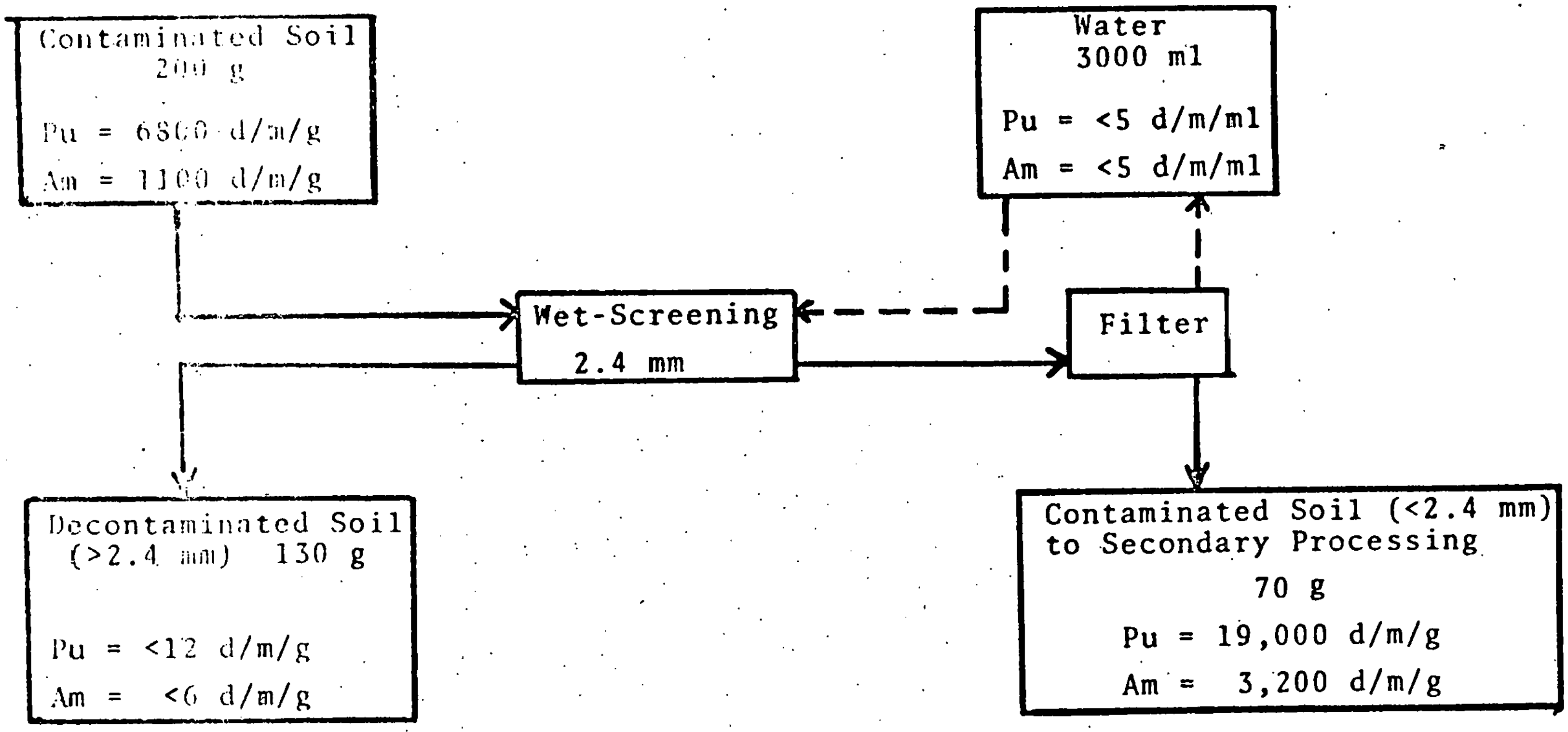

Figure 3 Candidate Secondary Processes

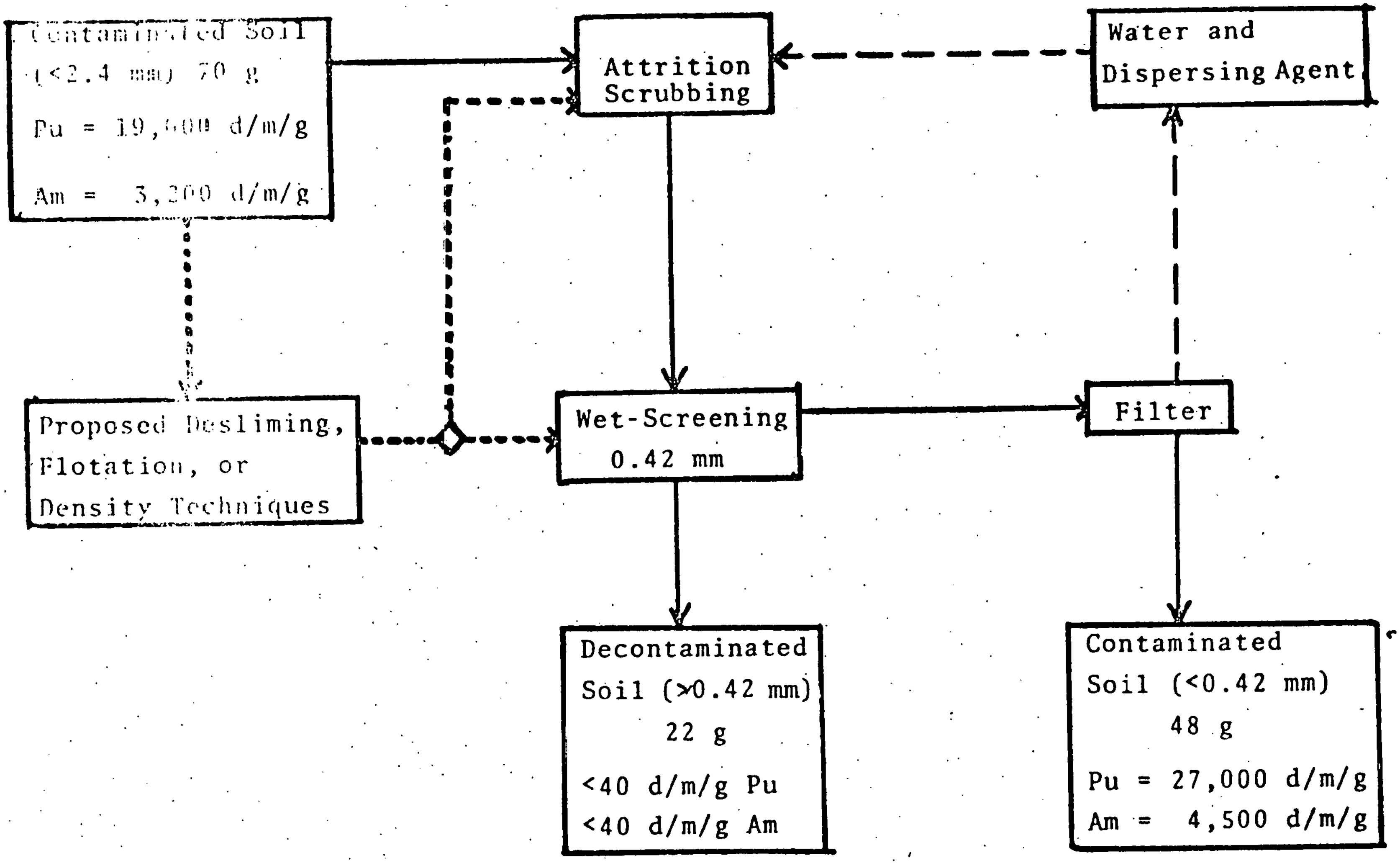

TABLE III

ATTRITION SCRUBBING AND WET-SCREENING A COMPOSITE SOIL WITH VARIOUS SOLUTIONS

	4.0 to 0.42 mm Fraction		
Solution	Wt%	Pu[b] (dpm/g)	Am[b] (dpm/g)
Distilled Water[a]	97	740	120
Distilled Water	80	125	28
Hot Distilled Water (~80°C)	80	180	35
Calgon 10 wt%	80	66	15
Citric Acid 0.1M	--	160	32
Oxalic Acid 0.1M	79	68	21

[a] No attrition scrub

[b] Actinide in composite soil: Pu= 3.7×10^3 dpm/g; Am= 6.3×10^2 dpm/g

reduces the concentration of plutonium and americium in the 2.4 - 0.42 mm size f~~un~~raction as well as reducing the size of the soil particles. Recycle of these solutions after filtering to remove actinide to <5 dpm/ml is also possible; 10 wt% calgon in particular shows promise for recycling without loss in decontamination effectiveness.

Tertiary Soil Decontamination Process

Successful application of a primary and secondary decontamination process may reduce the volume of soil to be shipped to an off-site respository by 75 to 80%. Introduction of a tertiary process could further reduce shipping volume. Acid leach techniques are routinely used in plutonium recovery processes to recover plutonium from residues. However the large scale application of a leaching technique is not considered to be economically feasible for soil. Other techniques such as magnetic separation are being considered and tested at present. Eventually some volume of highly contaminated soil will remain which will require either additional treatment for actinide recovery or storage.

Experiments in which the soil was simply heated were also done. Heating was expected to do two things: destroy organic materials which might "cement" or complex actinide to the soil particle and thus prevent decontamination; and reduce the volume by driving off moisture and destroying organic material. The results of heating soil at various temperatures are shown in Table IV. A maximum volume reduction of 26% was attained at $1000^{\circ}C$. At $1200^{\circ}C$, the volume decrease was 17% and the soil had sintered into a mass which would require crushing

TABLE IV

VOLUME REDUCTION OF SOIL BY CALCINATION

Temperature (°C)	Vol. Change, %
100	*
600	- 1.8
800	-19
1000	-26
1200	-17
1400	+40

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*The starting soil had been dried at 100°C.

for it to flow again. At 1400^{0}C, the soil had fused into a glassy but highly porous mass which was 40% greater in volume than the original soil mass. Vitrifying by heating alone would require temperatures greater than the 1500^{0}C attainable in our muffle furnace.

Heating the soil at temperatures >100^{0}C undoubtedly did destroy organic material, but it also made the PuO_2 less soluble; actinide recovery was not enhanced by heating.

Although volume reduction is improved by heating the soil, dispersibility is increased since organic material and moisture are removed. The product is a fine dust which flows easily. Since this would prove to be a problem if containers were breached, and since storage of dispersible fines may not even be permitted in waste repositories, additional experiments were done to demonstrate fixation of soil. Unlike the experiments described previously, this has been done only with clean soil at RFP.

The results of soil vitrification are shown in Table V. Soil was used in place of SiO_2 and glass forming and modifying agents were added as shown. As expected, those mixtures with large amounts of Group I element oxides and no ZnO and Al_2O_3 melted most easily and gave the best waste forms. Those with Al_2O_3 and ZnO still had particulates in the glass melt after 1 hour at the pouring temperature. Vitrification gave little or no increase in waste volume compared to the original volume of soil dried at 100^{0}C.

TABLE V

WASTE VOLUME INCREASE FROM VITRIFICATION

Mix	Soil	M_2O	B_2O_3	TiO_2	CaO	ZnO	Al_2O_3	Temp. (^{o}C)[a]	ΔV(%)[b]
I	52.5	22.5[c]	10	10	5	--	--	1250	2
II	52	13.5[d]	19.5	4.5	3	7.5	--	1400	7
III	52.5	22.5[e]	10	10	5	--	--	1250	0
IV	56	9.0[f]	14	3	3	5	10	1450	6

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[a] Temperature at which melt was poured.

[b] Compared to original soil volume, dried at 100^{o}C.

[c] 18.5% Na_2O, 4% Li_2O.

[d] 7.5% Na_2O, 4% K_2O.

[e] Na_2O only.

[f] 5% Na_2O, 4% K_2O.

CONCLUSIONS

The test results indicate that dry-screening is not an effective means for decontaminating Rocky Flats soil. Wet-screening with water will decontaminate approximately 65% of the pad soil (the >2.4 mm fraction) to <12 dpm/g plutonium and <6 dpm/g americium. The activity in the fraction between 2.4 mm and 0.42 mm is reduced to an average of 670 dpm/g plutonium by wet-screening. Decontamination of the 2.4 to 0.42 mm fraction by attrition scrubbing is enhanced by the addition of reagents like Calgon and citric and oxalic acids; the plutonium and americium were both reduced to <40 dpm/g representing 11 wt% of the soil. Additional volume reduction can be obtained by calcining the contaminated fraction of the processed soil.

FUTURE WORK

The primary and secondary processes, wet-screening and attrition scrubbing, will be evaluated on a pilot plant scale. Additional methods to be evaluated comprise desliming, flotation, and density techniques. Additional tertiary process evaluation will be done, including physical and chemical methods for decontaminating or immobilizing the final contaminated soil fraction.