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SOIL DECONTAMINATION AT ROCKY FLATS

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INTRODUCTION

Soil Contamination

During the last few years, many articles have appeared in newspapers and journals concerning radioactive contamination around Rocky Flats.[1,2] The amount of plutonium in the soil has been of particular interest. The Draft Environmental Impact Statement[3] on Rocky Flats lists the yearly alpha releases from the Plant since it was opened in 1952. The largest release was from "contaminated oil leakage." In 1958, a drum storage area was established on virgin ground just inside the present-day east gate to Rocky Flats. The drums contained cutting oil and carbon tetrachloride contaminated with plutonium and uranium cuttings from the machining of nuclear weapon components. Deterioration of and leakage from the drums was first observed in 1964. This leakage resulted in the soil being contaminated. In January of 1967, the last drums were added to the area. Shortly after this time, drum removal commenced and continued until all drums were removed by January 1968. The level of contamination in the soil was measured at this time. The results showed levels from 2,000 to 300,000 dpm/100 cm^2 and penetration depths of 3 to 20 cm. In April of 1969, a gravel cover of approximately 15 cm was applied and by July the area had been covered with a 7.5 cm asphalt pad.

DISCLAIMER

Form of Contamination

The plutonium at this site was originally in the form of plutonium metal from the machining process. In the environment, the plutonium metal oxidized to PuO_2. Actual PuO_2 particles have been identified in the cutting oil used for machining. The average diameter of these particles is 0.2 microns. Besides the particulate form of the plutonium in the soil, there exists also a dispersed form. The dispersed form of the plutonium will pass through a 0.01 micron pore filter. Up to 50% of the total contamination may have been in this form. As the barrels sat outside, hydrochloric acid was probably generated. This acid reacted with the plutonium giving a dissolved plutonium species. The exact nature of the dispersed form is not known. However, the plutonium is probably absorbed onto the clay or organic material in the soil or precipitated as Fe_2O_3-PuO_2 coatings on the mineral surfaces. When evaluating potential decontamination processes, both the particulate and dispersed forms of the plutonium must be considered.

Guidelines

The EPA has issued a guideline for maximum levels of radioactivity in soil. The level of 200 mCi/km^2 for plutonium in soil was calculated from a maximum permissible air concentration of respirable size dust assuming reasonable values for the soil density and mass loading. This is approximately 10 to 15 pCi/g or 20 to 30 dpm/g. Because of instrumental limitation during rapid survey of soil, DOE has indicated that soil containing less than 1,000 dpm/g does not have to be excavated, but can be left in place. However, if the soil is removed, it cannot be returned to the ground unless it is less than 30 dpm/g. Therefore, any process employed to decontaminate soil must reduce the level of contamination to below 30 dpm/g.

Alternative Solutions

The pad area is 113 m wide and 120 m long. Approximately 80 to 90 grams of plutonium are dispersed in 2×10^7 kg of soil beneath the pad. Water transport has not been observed under the pad since monitoring at the four corners began in 1969. Therefore, the contaminated soil is effectively isolated from the environment. In spite of this apparent stability, there was concern about long-term diffusion of plutonium from the site. Cost estimates to remove and ship the contaminated material were made and alternative solutions investigated. The present-day alternatives are as follows:

1) Stabilize in place.
2) Remove and transport all of the soil to a permanent disposal site.
3) Decontaminate.

The first alternative has been eliminated as a viable long-term solution because of the concern about diffusion. The second alternative has been used at Rocky Flats extensively during the last few years on small areas of contaminated soil. The decontamination alternative offers improved socio-political impact and will reduce any potential long-term effect. That is, the soil is actually being "cleaned up," not just moved to another site. Moreover, the decontamination option is also more economical. The actual cost to dig, package, and ship soil to a permanent disposal site in Nevada is $255 per 1,000 kg. Projected costs to decontaminate 90% of the soil and ship 10% is $123 per 1,000 kg. This second cost estimate includes manpower and chemicals, but excludes the initial capital cost of the processing facility. This cost was excluded because the process facility will be used only two years at Rocky Flats and then moved to other sites. The cost would increase proportionally if the decontamination was less than 90% effective.

Because of the projected savings of the decontamination alternative, a soils decontamination project was initiated. The objective of the project is to develop and demonstrate decontamination processes to concentrate or remove actinides associated with contaminated soils at Rocky Flats. The bulk of the soil would be returned to its natural environment, while the remaining small fraction would be packaged for shipment. Approximately nine man-years of effort were expended in FY-1979. The ultimate goal of the project is the construction of a $5-7 million mobile process facility.

EXPERIMENTAL AND RESULTS

Laboratory Studies

Several soil conditions exist at Rocky Flats that are advantageous to decontamination processes:

> 1) The soil is very rocky, 2) the contamination exists on the surface of the minerals, and 3) the surface-contaminated soil contains only approximately 20% clay and organic matter. A typical soil profile in the Rocky Flats area contains three distinct horizons. The dark top soil layer is usually 15 to 25 cm thick. This horizon is usually followed by a rocky zone rich in limonite and hematite-coated minerals. This zone runs from 25 to 40 cm in depth, but is missing under the pad. Finally, a layer of tan bentonite clay is

observed. This layer varies in thickness and is located at a depth of 40 to 75 cm below the surface. The plutonium contamination does not penetrate the clay layer. The total cover over the Rocky Flats area consists of this rocky alluvial material.

Because of this rocky material, a physical scrubbing process is very effective. Four such processes have been investigated:

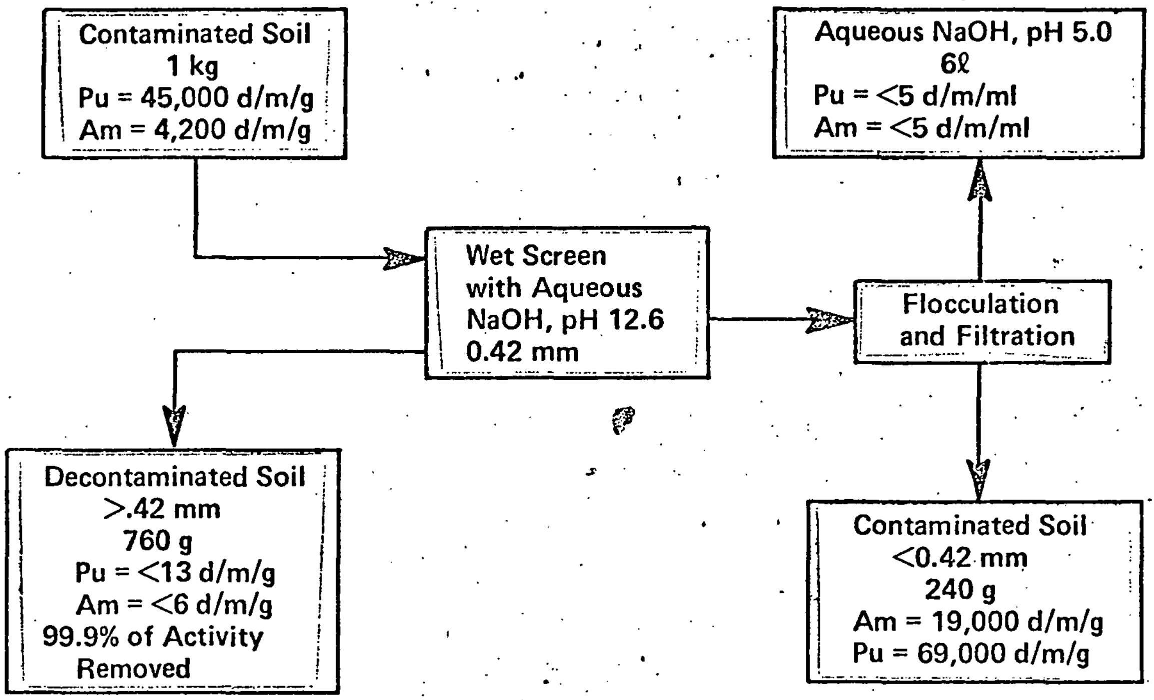
1) Wet screening at high pH.
2) Attrition scrubbing with Calgon® at elevated pH.
3) Attrition scrubbing at low pH.
4) Cationic flotation of clays.

Wet Screening. The first process is a simple wet screening process with the pH adjusted to 11 with NaOH. Both the Na^+ and the OH^- ions help disperse the clay particles. In fact, a colloidal suspension is formed. This suspension is due to the hydroxide ions attaching to the surface of the clay, creating negatively charged particles which repel each other. Details of one run are shown in Figure 1. The +35 mesh (greater than 420 micron) fraction of soil is decontaminated to less than 30 dpm/g. Typically, this material represents 60 to 70 wt % of the soil and can be returned to the environment. The remaining 30 to 40 wt % is radioactive and would be packaged and shipped for permanent disposal.

Attrition Scrubbing at High pH. Calgon solutions at high pH also effectively decontaminate soil. The soil is scrubbed in a rotary-type attrition scrubber (jar mill) four times. The fine material is decanted each time. In a typical experiment, 1 kg of soil is scrubbed with 1,000 ml of solution for 5 to 7 minutes. The fines are decanted removing most of the contamination. The scrub is repeated three more times with 250 ml of solution each time. A total of 99.9% of the activity is removed with the fine fraction. This fraction represents about 20 wt % of the total soil. The remaining 80 wt % is below the EPA guideline and can be returned to the environment.

Two processes are taking place that decontaminate the soil. One process is the physical grinding action due to the large rocks present in the soil. The tumbling action in the jar mill actually grinds away the outer surface of the particles. The second process is the dispersion of the clay and the fines being generated by the high pH Calgon solution. The two processes work together to decontaminate the soil.

If an additional blender-type scrub is incorporated in the process, the amount of material decontaminated can be increased. The material less than 4 mm is scrubbed at 800 rpm in a special



WET SCREENING AT HIGH pH

container. This process imparts a high shear to the particles thus liberating more of the contamination into the fine fraction. The outer surfaces of the particles are also effectively removed.

Attrition Scrubbing at Low pH. Attrition scrubbing at low pH employs the same process as attrition scrubbing at high pH except that the scrubbing solution has been changed. An aqueous solution of 2% HNO_3, 0.2% HF, 2% pine oil, and 5% Calgon is most effective. The soil is scrubbed five times in the rotary-type scrubber: three times for seven minutes each and two times for one minute. After each wash, the fines are removed. The first wash removes 88.1% of the contamination, while the second, third, and fourth washes remove 7.1, 3.5, and 1.3% of the contamination respectively. A typical experiment decontaminated 84% of the soil to less than 5 dpm/g. Originally, the soil contained 45,000 dpm/g.

The acid attacks the surface of minerals and aids in the grinding process. Smaller sized particles are scrubbed effectively, thereby increasing the total amount of soil that is decontaminated. Using the acid scrub solution, approximately 2% of the decontaminated material is less than 200 mesh (74 microns) in size.

When an acid solution is used in scrubbing, no colloidal suspension is observed. However, some of the plutonium does dissolve. This plutonium must be removed from the water so it can be recycled. The removal can be accomplished by: 1) Coprecipitation of the plutonium with $BaSO_4$ or $Fe(OH)_3$, or 2) adsorption by the hydroxide form of an anion exchange column. The ion exchange process is actually a precipitation of $Pu(OH)_4$ on the resin in the column.

In some experiments, the larger material (-5 +35 mesh) did not decontaminate to an acceptable level. However, by removing the magnetic fraction, the level was reduced to less than 30 dpm/g. Close examination of the magnetic fraction revealed that all the contamination was contained in several small particles. These particles could have been pieces of the rusted drums.

Cationic Flotation. The fourth decontamination process takes advantage of the anionic surface of the clay particles. A cationic flotation agent such as an amine can be used to float the clay material in a conventional flotation process. By adding a quartz suppressor, the soil can be scrubbed at a high speed (greater than 1,000 rpm). Usually at such high speeds, the larger rocks are abraded extensively, causing an increase in the weight of the fine fraction. However, with the addition of the suppressor, these abraded particles will not float with the clay fraction. Further research would be needed on this method.

Methods to extract the plutonium from the fine clay fraction are also being considered. These processes include leaching with ceric solutions in HNO_3 and contact leaching with HF, HNO_3, and Na_2CO_3 solutions.

Pilot Plant Studies

The attrition scrubbing process at high pH is the most feasible process to scale up. The process flow diagram shown in Figure 2 was generated based on the high pH scrub. A feed rate of 10 tons per hour (9,000 kg/hr) was selected for the full scale facility. The soil would pass through a 4-inch (10 cm) grizzly to eliminate the large rocks. The material would then enter a rotary Trommel scrubber. A screen attached to the end of the scrubber would separate out the material greater than 1/4 inch (6 mm). This fraction would be sent to landfill because it would contain less than 30 dpm/g. The fines material would then be washed and screened at 35 mesh (0.420 mm). The material greater than 0.420 mm would be sent to landfill. The fines fraction would be further processed using three stages of 1-inch (2.5 cm) liquid cyclones. The cyclones would separate the soils fractions at 10 µm. The smaller fraction would be packaged for shipment while the larger fraction would be decontaminated by further treatment. This process would provide a weight reduction of 88%. As the final plant must be mobile and self-contained, a water recycle system is shown on the diagram.

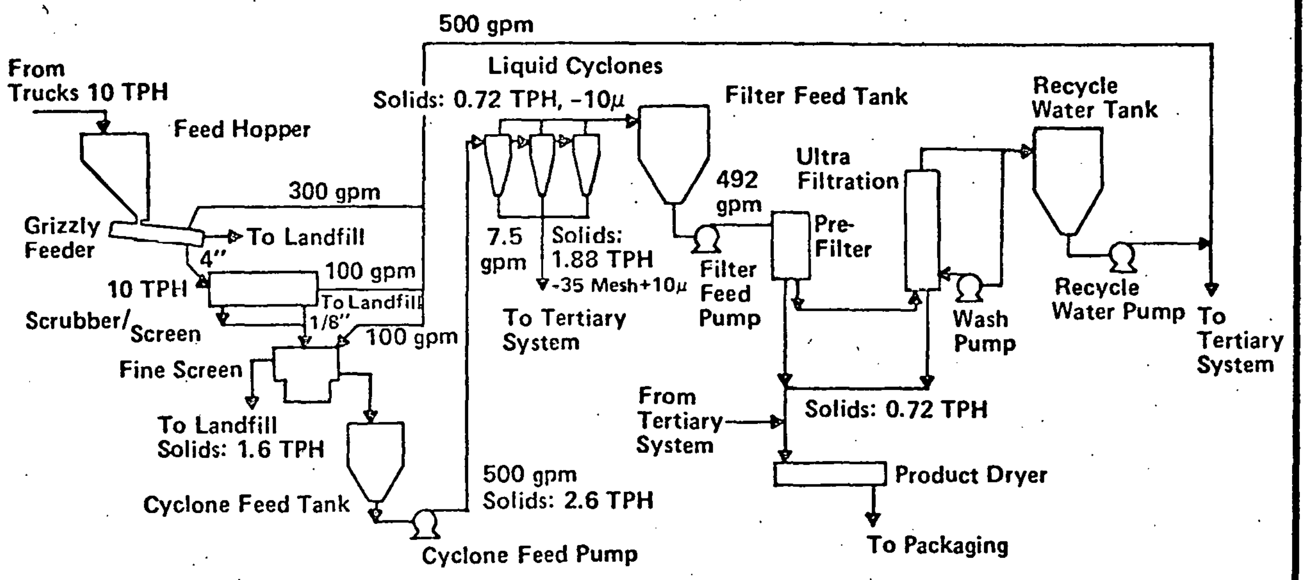
Results. Pilot Plant testing was performed on "cold" material fed at a rate of approximately 275 kg/hr. Testing on "hot" material was accomplished at a rate of 70 kg/hr. The mass balance for the cold test circuit is shown in Table I. Calculations showed that 4-inch (10 cm) cyclones were better suited for the desired flow rates. Three stages of cyclones were employed to separate the soil at 10 µm. However, as indicated in Table I, the underflow (the desired decontaminated product) still contained 17% of the minus 10 micron material.

If the cut is made at 400 mesh (37 micron) after two stages of cyclones, the underflow contains only 1.6% and 0.4% of the -38 micron and -10 micron material respectively. These numbers represent 0.36% and 0.086% respectively of the total mass. This cut is made very efficiently. Therefore, a separation could be made at 400 mesh (37 microns) instead of 10 microns. The weight reduction is lowered to 83.8%.

FUTURE WORK

Modifications

If the circuit were modified to cut at 100 mesh (149 microns),



PRIMARY & SECONDARY TREATMENT

TABLE I

Product	Pulp Density Weight (%)	Pulp Density Solids (%)	Particle Size Distribution -37μm (%)	Particle Size Distribution -10μm (%)
Grizzly				
Feed	100.0	100.0	100.0	100.0
+4 in. (10 cm) rock	15.0	100.0	0.0	0.0
-4 + 1-1/2 in. rock (100-38 mm)	25.0	100.0	0.0	0.0
	40.0	Removed by Grizzly, 60% Sent to Scrubber		
Scrubber				
Feed (-1-1/2 in.)	60.0	100.0	100.0	100.0
Discharge	60.0	63.0	100.0	100.0
-1-1/2 in. + 1/4 in.	26.5	70.0	.6	.4
	26.5	Removed by Screen on End of Scrubber, 33.5% Sent to Vibrating Screens		
Sweco Vibrating Screen				
Oversize (-1/4 in. +35M) (6-.42 mm)	10.9	77.3	.06	.04
Undersize (-35M) (-.42 mm)	22.6	8.5*	99.3	99.6
	10.9%	Removed, 22.6% Sent to Cyclones		
1st Stage Cyclone				
Overflow	15.1	18.0	91.1	92.6
Underflow	7.5	68.0	8.2	7.0
	15.1%	Sent to 3rd Stage, 7.5% Sent to 2nd Stage		
2nd Stage Cyclone				
Overflow	1.1	5.0	6.6	6.6
Underflow	6.4	71.0	1.6	0.4
	6.4%	Removed, 1.1% would be Treated Further		
3rd Stage Cyclone				
Overflow	10.0	9.5	0.0	75.6
Underflow	5.1	33.1	0.0	17.0

*This product was thickened to 25% solids prior to 1st stage cycloning.

the cyclones and screens could be replaced with spiral classifiers. This modification would result in a weight reduction of only 80% compared to 84% by the previous circuits. However, the advantages are numerous. Spiral (or screw) classifiers are almost maintenance free while cyclones are not. The spiral classifiers are also excellent dewatering devices leaving a product with a pulp density of 80% solids. Furthermore, the screen is eliminated making the circuit simpler. Spiral classifiers for a 10-ton per hour plant would have a spiral diameter of 16 inches (400 cm) with a total machine length of 12 ft (3.6 m). Four of these units operating in a counter-current configuration would make a very precise cut producing a clean product with a low moisture content.

Pilot Plant runs based on the circuit in Figure 2 using hot soil revealed that sometimes the -5 +35 mesh (4 to 0.42 mm) fraction contained over 100 dpm/g. This level is not acceptable. The probable cause of this situation is that the clay is lubricating the rocks in the Trommel scrubber and efficient grinding action is not being achieved. The solution is to simply deslime (remove the clay) the material prior to scrubbing. One method of achieving this removal is to have two Trommel scrubbers. The clay would be removed in the first scrubber, therefore allowing effective scrubbing action in the second scrubber.

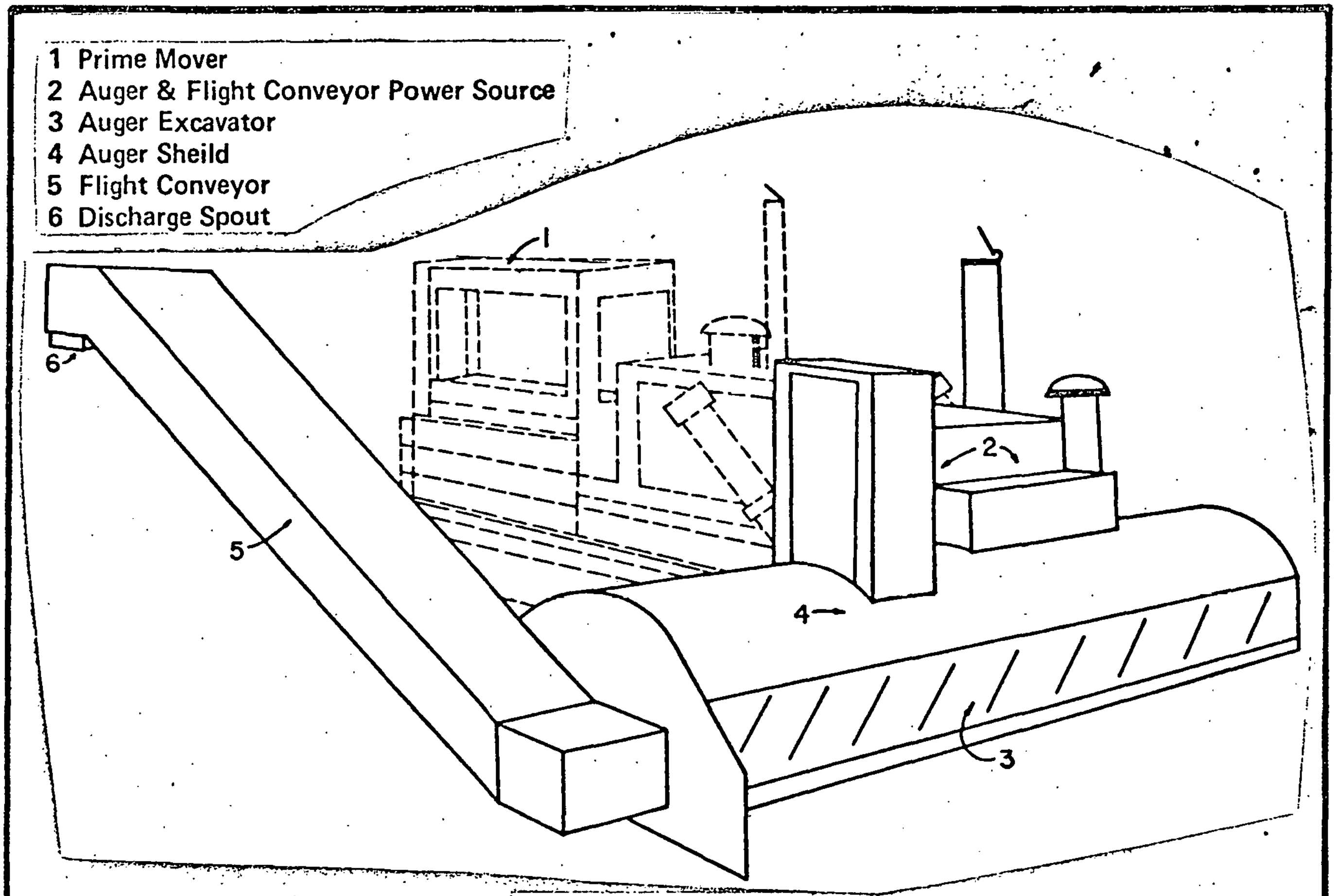
Further Research

Several areas need more research before final design criteria can be issued. These areas include water recycle and clay dewatering. Dissolved solids in the water must be controlled carefully if the water is to be continually recycled. The product that is to be packaged and shipped is the clay fraction. This clay is present in the water as a colloid; therefore, it must be flocculated. This flocculated clay then must be dewatered so that the volume to be shipped is minimized. Probably the best method to accomplish dewatering is with an automatic filter press. Such presses are relatively new, but have been shown to eliminate 20% more water than previous presses. The possibility of using a vacuum brick extruder is also being considered.

Research is also planned using the modified circuit with an acid solution. The acid solution was not selected originally because of its corrosive nature. However, tests indicate that the abrasion of the equipment by the rocks and not the corrosion by the solutions is the main factor in equipment wear.

The Total Concept

As previously mentioned, the total process must be mobile so that it can be moved from site to site. Conceptual designs have been generated for mounting the process in semi-trailers. Three



AUGER EXCAVATOR

trailers will probably be required: One containing the process equipment, one with two stages of HEPA air filteration, and one with water recycle and power generation equipment.

The total concept also involves excavating the contaminated soil. To accomplish this excavation, a dustless mining machine has been conceptually designed (Figure 3). This machine has many advantages over the typical front-end loader method generally used. One of the main advantages is that the rotary blade is continually against the face of the excavated bank; therefore, the contaminated soil is not exposed to the open. The machine is also very maneuverable, capable of being adjusted precisely (within ±2 inches). As the contaminated material is excavated, it is moved up the enclosed conveyor into a 20-ton dumpster. The dumpster is then moved to the process facility.

Other DOE Sites

Soils from four other Department of Energy sites are currently being evaluated: Hanford, INEL, LASL, and Mound. Preliminary decontamination tests are encouraging. Results will be available later this year.

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