



## CHEMICAL TREATMENT AND CEMENT FIXATION OF RADIOACTIVE WASTES

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The treatment of radioactive wastes is necessarily different from treatment of other industrial wastes because of the very nature of the material. The radioactive characteristics of the contaminants cannot be changed. Radioactive isotopes cannot be stabilized by oxidation as cyanides are oxidized to innocuous compounds; they cannot be reduced to less hazardous nuclides in the manner that hexavalent chromium is reduced to trivalent chromium. Only time has any effect on this kind of contamination. Because the contaminants cannot be destroyed, there are only two ways to handle these wastes—concentrate and contain or dilute and disperse. In the case of waste management at Los Alamos Scientific Laboratory (LASL), the former method has been chosen.

The "half-life" is the term used in the description of radioisotopes to indicate the rate of disintegration. It represents the length of time required to reduce the activity by one-half. This time varies from micro- or milliseconds for many fission products to 28 yr for strontium-90 and 30 yr for cesium-137, two of the more important contaminants, to 25,000 yr for plutonium 239, which is the principal contaminant at LASL, to 4.5 bil yr for natural uranium, which presents a very minor problem in water pollution.

There are three types of radiation emitted by unstable nuclides—alpha,

beta, and gamma. The alpha particles (actually helium nuclei) are relatively heavy and present no great external radiation problem because they do not penetrate even the thickness of a sheet of paper. The beta particle is a high-speed electron and is considerably more penetrating than the alpha particle. Gamma rays are similar to x-rays in having high energy and no mass, and they can pass through several feet of concrete. When wastes containing large concentrations of gamma emitters are processed, it is necessary to use high-density or thick concrete for protection from radiation. Fortunately, when this kind of waste is handled at LASL, the volume is generally quite small and relatively small shielded areas are required for control.

### Wastes Treated

The main contaminant at LASL is plutonium-239, an alpha emitter; hence, no shielding is necessary. However, there is another consideration related to exposures. Absorption of plutonium through the pulmonary tract is much more hazardous than through the alimentary tract. Control measures are therefore concerned with preventing plutonium particles from becoming airborne.

The liquid radioactive wastes at LASL are handled at two different plants. One plant handles a relatively large volume of low-level wastes generated in a variety of research laboratories and has been described previously (1). The other plant handles a relatively small volume of medium-level wastes discharged from a plutonium-process-

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ing facility and is the treatment plant discussed in this paper.

The wastestream results from an area in which research and development programs on plutonium are carried out. The group in this area synthesizes and fabricates well-characterized, pure plutonium fuel materials, including carbides, nitrides, and oxides as well as solid solutions of these with the corresponding uranium compound. The high-temperature thermodynamic, chemical, thermal, and physical properties of these materials are investigated. Electrorefined plutonium-238 is being prepared and evaluated for its use as a power source in life-support applications. The group also has the responsibility for the recovery and recycle of plutonium and the production and fabrication of plutonium metal, alloys, and compounds.

It should be pointed out that a major portion of the main wastestream

results from cleanup and decontamination procedures. The wastes are quite difficult to treat because many of the stable chemicals in the solution are used to complex plutonium in order to facilitate its removal from surfaces and materials. Because coprecipitation of plutonium with ferric hydroxide is the basis of the treatment process, complexing agents obviously create difficulties.

### Treatment Processes

As might be expected in a rapidly developing industry, the operations at the site producing these wastes have changed considerably over the past 25 yr. Original processes were modified and new processes were developed, with each improvement signaling a change in the volume and characteristics of the wastes. For uniformly efficient industrial waste processing,

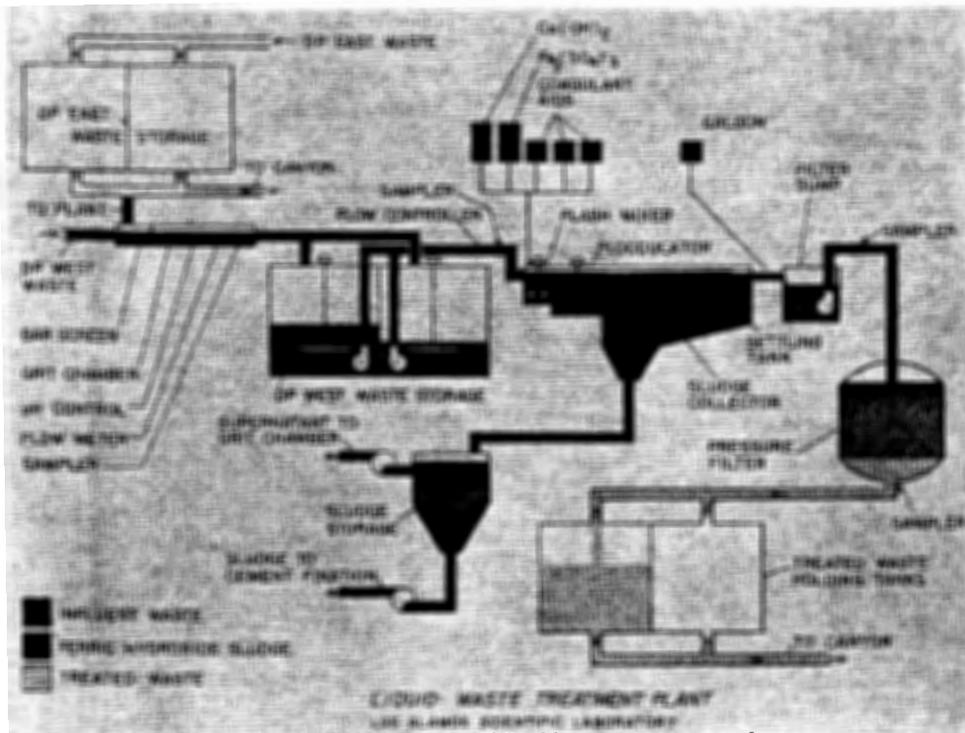


FIGURE 1.—Schematic diagram of liquid waste treatment plant, Los Alamos Scientific Laboratory.

the single most important consideration is an awareness of variations in plant operations. Fortunately, throughout this period the waste-management group has been able to maintain a very good liaison with the waste-producing group, and timely adjustments in waste-treatment procedures have been effected. Segregation and separate treatment of small volumes of waste that are incompatible with the main waste stream simplify the entire operation. Wastes ideally suited for treatment by evaporation usually are not processed economically by ion exchange; wastes easily incinerated generally are difficult to treat chemically. Acceptable changes in the main waste stream, with adequate advance information, can often be accommodated by minor modifications in the treatment process with little or no loss in efficiency.

#### Continuous Stream

A schematic of the process used at the site for treatment of the continuously flowing main waste stream is shown in Figure 1. The design data are presented in Table I. The wastes are collected from five buildings into a 4-in. (10.2-cm) mild steel pipe and are transported to one of two influent holding tanks with a capacity of 29,000 gal (110,000 l) each. Raw feed pumps lift the waste to a flash mixer where ferric sulfate, lime, and coagulant aids are added. The waste then flows to a flocculator and on to the settling tank; settled effluent is pumped through a pressure filter into the final holding tanks. The pressure filter, rather than a gravity filter, is used because the two existing 15,000-gal (56,780-l) steel tanks for containing the plant final effluent are at an elevation higher than the settling tank.

The filter sump located between the settling tank and the pressure filter permits backwashing of the filter with settled effluent while the plant is in operation. Backwash water is trans-

TABLE I.—Design Data for Continuous Stream Process

Variable	Value
Design treating rate (gpm)	125
Raw waste (normal) storage capacity (gal)	60,000
Acid batch waste (gal)	825
Alkaline batch waste (gal)	1,740
Flash mixer detention time (min)	1
Flocculator detention time (min)	30
Settling tank detention time (min)	140
Settling tank surface settling rate (gpd/sq ft)	918
Weir loading (gpd/ft)	6,400
Filter loading (gpm/sq ft)	2.8
Filter head loss (psi)	8 (clean) to 22
Wash water (% of flow)	7.5
Average length filter run (hr)	22
Sludge storage capacity (gal)	4,300
Solids in raw sludge (%)	Approx. 15
Total solids, raw waste, average (mg/l)	2,000

Note: Gal  $\times$  3.785 = l; gpd/sq ft  $\times$  40.7 = l/day/sq m; gpd/ft  $\times$  12.4 = l/day/m; psi  $\times$  0.0703 = kg/sq cm.

ferred to the influent holding tanks and is treated with the raw wastes.

The data shown in Table II indicate that the procedure used is very efficient in removal of plutonium from the wastes.

Plutonium is one of the most toxic radionuclides known to man. The maximum permissible amount of plutonium-239 that one can have in his body is about 0.65  $\mu$ g, and that of plutonium-238, which is also now present in the waste stream, is about 1/300 of that amount. The volume occupied by this mass of plutonium-238 is equivalent to that of half a red blood cell.

#### Batch Wastes

In addition to the waste stream described above, a variety of other wastes that are classified as "batch-type" arrive at the plant. Some are transmitted via 1.5-in. (3.8-cm) stainless steel industrial waste lines and are

TABLE II.—Typical Characteristics, Treatment Plant Operation

Treatment Rate (gpm)	Chemical Dosage (mg/l)						Radioactivity* Gross $\alpha$ (c/ml)			Efficiency (%)		
	Lime	Ferri-Floc	Cal-gon	Coagulant Aids			Raw Feed (in 1,000's)	Settling Tank Effluent	Filter Effluent	Raw Feed Through Settling Tank	Settling Tank Through Filter	Over-all
				Sepa-ran	A-10	C-31						
93	101	88	7.4	1.3	—	24.0	160	1,670	175	98.96	89.52	99.89
86	65	82	—	1.7	4.4	—	916	11,870	423	98.70	96.43	99.95
58	413	115	—	2.8	2.2	—	495	850	73	99.83	91.41	99.99
81	255	108	—	1.9	1.7	6.8	376	3,560	130	99.05	96.35	99.97
76	222	153	6.1	3.8	3.1	—	1,566	6,880	1,400	99.56	79.65	99.91
77	222	68	8.3	2.5	2.8	—	2,794	3,910	100	99.86	97.44	99.99+
83	446	108	10.7	2.2	—	16.2	2,545	21,170	700	99.17	96.69	99.97
89	209	89	5.1	1.1	—	—	703	3,190	248	99.55	92.23	99.96
81	437	115	1.2	1.1	7.3	4.0	346	1,840	133	99.47	92.77	99.96
77	462	113	3.8	1.2	3.6	—	234	2,628	92	98.88	96.50	99.96
65	395	90	2.3	1.3	—	4.5	94	200	20	99.79	90.00	99.98
64	329	84	1.5	1.4	—	9.2	493	730	77	99.85	89.45	99.98

$$\frac{c/m/l}{1.1 \times 10^6} = \mu\text{Ci/l}$$

MPC for  $^{239}\text{Pu}$  =  $5 \times 10^{-6}$   $\mu\text{Ci/ml}$  for 168-hr week. See Title 10 Part 20, *Federal Register*, December 22, 1965.

Note: Gpm  $\times$  3.785 = l/min.

collected in special stainless steel or concrete holding tanks at the plant; others are delivered in 270-gal (1,000-l) stainless steel tank trailers. Assorted wastes in polyethylene or glass bottles, 100 ml to 9 l, all enclosed in stainless steel cans, are often received for treatment. Though volumes are small in comparison to the normal waste flow,

a high percentage of the operator's and the laboratory's time is consumed in the receipt, treatment, disposal, and analyses of these wastes.

#### Cement Fixation

The waste demanding the most effort and time is a high solids-content, highly acidic solution, which is delivered in 270-gal (1,000-l) tank trailers. The radioactivity is of an intermediate level, averaging approximately 1 mg/l of americium-241 and 1 mg/l of plutonium-239. Table III indicates monthly volume and radioactivity data for this type of waste for the period of July 1968 through June 1969. After neutralization, the solids concentration is about 30 percent, most of which is sodium nitrate.

Management of this waste includes neutralization with 50 percent sodium hydroxide, mixing with cement in a pug mill, and pumping to deep pits on the site.

Figure 2 is a schematic diagram of the system, and Figure 3 is a picture of the pug mill during operation with the

TABLE III.—Americium Waste

Month	Volume (gal)	Americium (g)	Plutonium (g)
Jan. 1968	1,056	3.876	4.140
Aug.	1,607	3.530	5.823
Sept.	1,738	8.678	13.532
Oct.	1,497	5.457	10.918
Nov.	1,331	2.895	5.491
Dec.	1,790	5.110	8.513
Jan. 1969	1,327	3.658	5.104
Feb.	2,057	4.711	11.232
Mar.	1,564	3.889	13.022
Apr.	1,695	7.673	7.085
May	1,632	4.056	5.943
June	1,522	5.167	8.187
Totals	18,816	58.700	98.990
Average	1,568	4.892	8.249

Note: Gal  $\times$  3.785 = l.

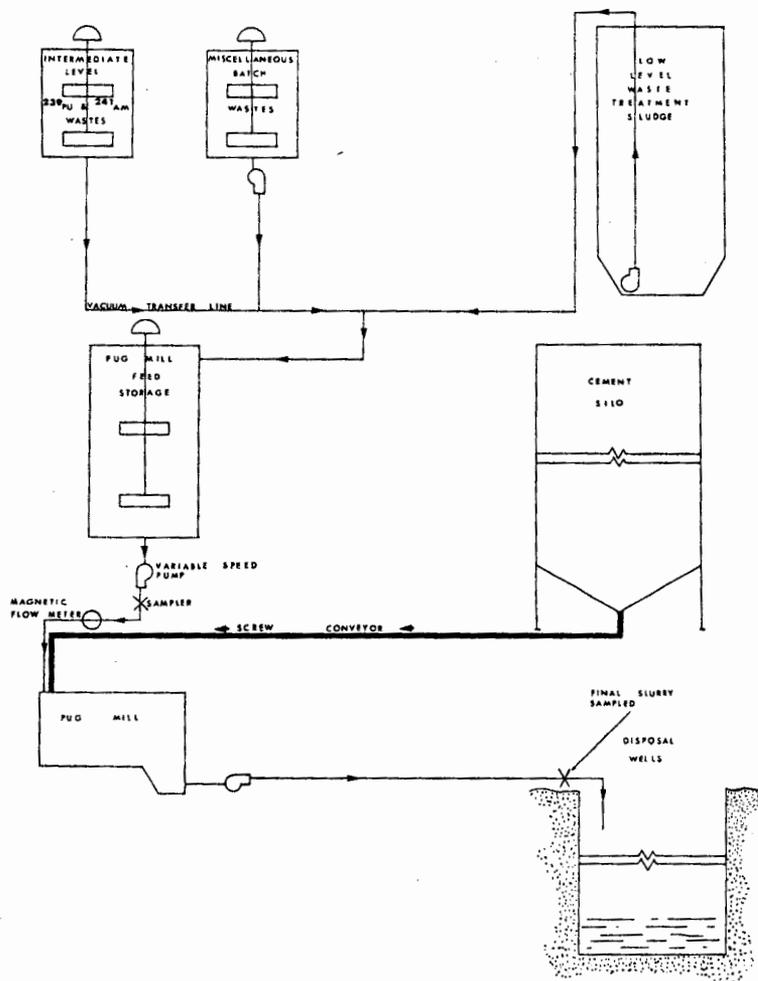


FIGURE 2.—Schematic diagram of continuous process for cement fixation of radioactive slurries.

cover removed to show the interior. As shown in Figure 2, sludges accumulated from chemical treatment of the main waste stream are also added to the pug mill feed for disposal.

When tank trailer loads of the americium are delivered to the site, the contents are first transferred by vacuum to a stainless steel storage tank; increments are removed from the storage tank by vacuum to a mixer-equipped, water-cooled neutralization tank. A 50 percent sodium hydroxide solution is used for neutralization of the 5 to 8 *N* acid waste. After the mixture has

cooled sufficiently, it is transferred by vacuum to a steel feed-storage tank. Transfer by vacuum is practiced whenever possible because spills of this hazardous material are extremely difficult to clean up. Vacuum transfer is a "fail-safe" procedure.

The pug mill is a large, horizontal, rubber-lined mixer with a number of separate paddles that mix and move the contents from an inlet at one end to an outlet at the other. Cement is added at the rate of about 130 lb/min (59 kg/min), and the liquid waste is pumped into the mill at a rate of about

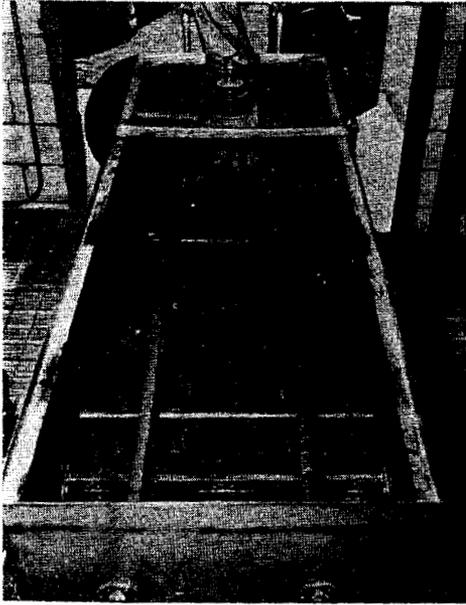


FIGURE 3.—Interior of pug mill during operation.

6 to 9 gpm (23 to 34 l/min). The rate of feed of both liquid and cement may be adjusted easily to maintain a good mix. The pug mill is sealed during operation, and air is withdrawn to maintain a less-than-atmospheric pressure to prevent the escape of radioactivity to the area around the mill. The exhaust air is passed through high-efficiency filters, which have a removal efficiency of 99.98 percent (DOP test—0.3- $\mu$ -diam particle). The paste is discharged into the hopper of a positive-displacement pump that pumps it approximately 150 ft (46 m) through a 2.5-in. (6.4-cm) diam line to the receiving pits. The pits are 8 ft (2.4 m) in diameter and vary in depth from 15 to 65 ft (4.6 to 19.8 m), with most of them of the deeper type.

To determine the extent of migration of radioactivity from the disposal pits, 2-in. (5.1-cm) diam holes are drilled adjacent to them. To date, no movement of radioactivity through the tuff formation has been detected.

During a run, samples of the paste are collected for determination of com-

pressive strength and leachability. The test cylinders for compressive strength are cured underwater for 28 days before testing. Compressive strength has varied from about 800 psi to 3,500 psi (56 to 246 kg/sq cm).

The leach samples are collected in bottles of about 75 ml capacity. The samples are allowed to set, volume and weight are determined after removal from the bottle, and the block is immersed in a measured volume of water. Periodically the water is removed, analyzed for radioactivity, and replaced with fresh water. Records are maintained on the quantity of radioactivity that has leached from the block. None of the samples, including some from an old drum tumbler operation that have been leaching for more than 9 yr, has lost as much as 1 percent of its radioactivity to date.

The pug mill continuous cement fixation process described above is a recent development and, to our knowledge, is the only one in operation. The method used previously at LASL was to put the cement into a 55-gal (208-l) drum, add 9 lb (4.1 kg) ground exfoliated vermiculite and about 20 gal (76 l) of waste and mix in a drum tumbler for about 15 min. This method, described elsewhere (2), was time consuming, laborious, and expensive, with materials costs high because of the use of 55-gal (208-l) drums. The sludges from chemical treatment of the main waste stream were treated separately by dewatering on a vacuum filter, packaging in 55-gal (208-l) drums, and transporting to a burial site. The continuous method has decreased the cost of treatment of the americium waste and plant sludges from approximately \$24,000/yr to \$6,000/yr. Although the proximity to a disposal area is fortuitous and results in a large saving in transportation costs, the continuous cement mix method could be advantageous where the final disposal area is more remote because of the possible use of inexpensive con-

tainers or reusable forms for containing the cement paste.

#### Other Wastes

Table IV lists a variety of other wastes received for disposal. The distillate waste, though it contains moderately high concentrations of uranium-235, is normally routed into the main waste receiving tanks for treatment with the low-level alpha wastes. The KOH waste, on the basis of its plutonium-239 content, could be treated with the normal waste, but its fluoride content is very high. Because the treatment plant does not remove fluorides efficiently, this waste is received into a special concrete storage tank. For treatment and disposal, it is included with wastes that are mixed with cement in the pug mill operation. The Am-Pu solutions and the uranium-235 solutions are normally alkaline and are undesirable in the main flow stream because of chlorides, fluorides, and high levels of radioactivity. They are therefore added to the feed solutions for disposal through the pug mill. The nitric acid solutions and miscellaneous wastes are either treated through the pug mill operation or added to the normal influent flow, depending on their degrees of radioactivity. The alcohol waste, contaminated with plutonium-239, is added to cement and vermiculite in 55-gal (208-l) steel drums, mixed by tumbling, and sent to the solid wastes burial area.

Oils and miscellaneous organic solutions are mixed with kerosene as necessary and incinerated in standard "salamander" gravity burners. Tests have shown that essentially all the radioactivity is retained in the ash residue. The ash is removed periodically, mixed with cement, and sent to burial.

"Strip" waste, resulting from reprocessing small amounts of spent uranium fuel, is an acid solution and contains both strontium-90 and cesium-137. It is processed chemically in

TABLE IV.—Batch Waste Volumes, Excluding Americium Wastes

Month	Am-Pu Solution (gal)	KOH (F) (gal)	Distillate (gal)	Strip (gal)	Solids CN-Asphalt	Alcohol (gal)	HNO <sub>3</sub> Solution (gal)	Oil (gal)	Lard-Veg Oil (gal)	<sup>235</sup> U Solution (gal)	Miscellaneous (gal)
Jan. 1968	79.3	300.1	1,003.9	158.5	—	—	—	—	—	—	—
Aug.	23.0	187.0	1,225.8	317.0	4 drums*	11.1	1.6	1.6	—	84.5	—
Sept.	83.5	150.1	1,262.8	475.5	—	—	0.5	—	6.3	42.2	—
Oct.	4.8	150.1	649.9	158.5	—	10.6	—	—	—	126.8	10.6
Nov.	95.6	300.1	612.9	158.5	—	10.6	—	—	—	5.0	3.8
Dec.	87.4	150.1	1,146.5	317.0	—	—	0.4	—	—	31.7	—
Jan. 1969	173.3	150.1	803.1	158.5	8 lb†	—	—	—	—	105.7	7.9
Feb.	160.4	300.1	1,262.8	158.5	5 lb†	10.6	—	—	—	10.6	2.4
Mar.	161.1	150.1	956.3	158.5	8 lb†	—	27.5	—	—	190.2	0.4
Apr.	89.6	150.1	766.1	158.5	6 lb†	10.6	2.4	—	—	158.5	—
May	111.7	300.1	1,569.2	317.0	—	10.6	—	—	—	179.6	—
June	95.4	150.1	1,283.9	158.5	—	—	—	—	—	127.1	5.7

\* CN<sup>-</sup> waste in asphalt; 55-gal (208-l) drums.

† Pu-contaminated solids.

Note: Gal × 3.785 = lb; lb × 0.454 = kg.

special batch-waste treatment tanks to precipitate both strontium and cesium by the addition of strontium nitrate, ferric chloride, tribasic sodium phosphate, nickelous sulfate, and copper ferrocyanide. Cesium is precipitated as a nickel ferrocyanide, and strontium is removed from solution as the phosphate. The entire mixture, after precipitation, is added to feed solutions for treatment through the pug mill system.

Infrequently, minor amounts of very toxic chemicals or solid wastes containing relatively large amounts of plutonium are delivered to the site for final disposal. These items have been placed in the pits at the site during pug mill operation to provide adequate concrete encasement.

#### Environmental Effects

The LASL policy has always been to discharge liquid wastes at less than 10 percent of the allowable concentration for drinking water as set by the International Committee on Radiation Protection. Although there is always the possibility of reconcentration by aquatic organisms, the wastes usually are discharged into dry canyons where there is little, if any, chance of reconcentration. The wastes disappear into the unsaturated alluvium and tuff within 0.25 to 2 miles (0.40 to 3.2 km) downstream of the outfall, depending on seasonal runoff. Extensive analyses have demonstrated that none of the contaminants reaches the Rio Grande, which is about 15 miles (24 km) away, nor has any contamination been discovered in the groundwater or springs surrounding the area.

The burial of solid wastes is another major concern in waste management. Because plutonium decays at a very slow rate, the burial grounds must be under surveillance for thousands of

years. Fortunately the water table is at least 1,000 ft (305 m) below the surface. Although the volcanic tuff on which Los Alamos is built has a low ion-exchange capacity (about 2 meq/100 g), the volume of tuff in 100 acres (40.5 ha), 1,000 ft (305 m) deep has a very large total capacity. It is unlikely that the plutonium would move into the groundwater because rainfall of only 15 in./yr (38.1 cm/yr) provides little transport.

An Environmental Studies Group at LASL concerns itself exclusively with monitoring the air and water in and around the LASL site. The work of this group is augmented by the United States Geological Survey, which has a continuing contract with the Atomic Energy Commission for test-well drilling and for water and soil sampling and testing.

Several thousand samples of air and water from the environs are analyzed each year for various contaminants. In the 25 yr of operation of the Laboratory, the average of these samples has indicated a concentration of radioactivity well below 10 percent of the maximum permissible concentration.

#### Acknowledgment

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