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IMMOBILIZATION OF TRITIATED AQUEOUS WASTE IN POLYMER IMPREGNATED CONCRETE

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Abstract

Techniques have been developed at Brookhaven National Laboratory for the immobilization of high-level tritiated aqueous waste in polymer impregnated concrete (PIC). This paper discusses these techniques and reports on the rates of tritium release from PIC waste forms for both static leaching in distilled water and burial in test lysimeters at the Savannah River Plant (SRP).

Tritiated aqueous waste when mixed with dry hydraulic cement produces concrete in which the waste is chemically combined in the form of hydrated silicate and aluminate compounds. However, this concrete contains a network of interconnected porosity which is subject to water intrusion and subsequent tritium loss by leaching and exchange. In the production of polymer impregnated concrete, a soaking technique is employed in which styrene monomer containing a polymerization catalyst (2,2'-azobis-2-methylpropionitrile) permeates the porosity of the cured concrete. Subsequent to complete penetration of the concrete by styrene monomer, the casting is heated to approximately 50°C which induces polymerization *in situ*. The PIC that results is essentially impermeable while its strength, durability, and resistance to chemical attack have been greatly enhanced. The various techniques that have been developed for the production of PIC each employ soak impregnation but differ in the method which is used to produce the concrete casting. These methods include external mixing, in-drum tumbling, and injection mixing. With both external mixing and in-drum tumbling, a homogeneous cement casting is produced. Injection mixing, in which the waste is injected along the centerline of a container filled with dry cement, produces an inhomogeneous concrete where the waste loading is highest in the center of the waste form and decreases as the surfaces are approached. Soak impregnation of this concrete results in a polymer loading which is highest at the surfaces and decreases towards the centerline effectively encapsulating the waste.

A PIC waste form with a volume of 0.566 ft^3 and containing ten curies of tritium produced by an external mixing technique has been statically leach tested in distilled water. This specimen, with a density of

107.7 lbs/ft^3 and a polymer loading of 12.9%, was immersed in forty liters of distilled water such that all surfaces were exposed to the leachant. After 295 days of leaching, the tritium release from this sample was determined to be linear with time at a rate of 1.89×10^{-5} day^{-1}. This rate is projected to predict a complete tritium release from the waste form after 145 years with a maximum fraction of 4.49×10^{-2} of the initially contained tritium present in the environment after 17.7 years when decay is considered.

Four PIC waste forms, each with a volume of 0.566 ft^3 and containing ten curies of tritium were buried (without containers) in individual lysimeters at the Savannah River Plant. These PIC waste forms had an average density of 106.6 lb/ft^3 with a polymer loading of 16.5%. Each lysimeter consists of a steel tank 1.83 m in diameter and 3.05 m deep which is buried in the ground. Rain falling on the exposed soil at the lysimeter surface permeates the soil, contacts the PIC specimen and accumulates in a gravel layer on the sloping bottom of the lysimeter. A pump is used to collect the percolate water which is analyzed for its tritium content. These waste forms have been in burial for thirty-one weeks and have exhibited a linear tritium fraction release rate with time of 1.16×10^{-6} day^{-1} since the twentieth week. Projection of this rate predicts a complete tritium release after 2,370 years with a maximum fraction of the initially contained tritium of 2.76×10^{-3} present in the environment after 17.7 years.

Techniques have been developed at Brookhaven National Laboratory (BNL) for the immobilization of high-level tritiated aqueous waste in polymer impregnated concrete. This paper discusses these techniques and reports on the rate of tritium release from polymer impregnated concrete waste forms for both static leaching in distilled water and burial in test lysimeters at the Savannah River Plant (SRP).

Aqueous tritiated waste reacts with hydraulic cement to form hydrated silicate and aluminate compounds. Theoretically, portland cement can combine with 28% water by weight, although in practice this amount may be slightly lower due to cement impurities. High alumina cement can bind 57% water by weight, however, metastable hydrates are produced which may convert to lower hydrate forms on aging. The hydration reaction is rapid at early ages, but the rate decreases with time and may continue at a low rate for an indefinite period with some tritiated water present as residual or unreacted water. The cement concrete formed has an open pore structure as a result of the interconnected porosity formed during curing. This makes the concrete permeable to water and corrosive fluids and thereby susceptible to tritium loss by leaching and exchange. Styrene monomer can be used to impregnate the porosity, voids, and capillaries throughout the concrete monolith and is subsequently polymerized in situ. This results in a polymer impregnated concrete that is essentially impermeable while its strength, durability and resistance to chemical attack are significantly improved.

The process for producing polymer impregnated tritiated concrete (PITC) is illustrated schematically in Figure 1. Hydraulic cement, tritiated aqueous waste and an absorber, if desired, are combined in the proper proportions prior to mixing. The water to cement (w/c) ratio (and water to absorber ratio) should be carefully determined as excess tritiated water in the unbound state may be more easily leached or evaporated, In addition, a dry cement mix enhances the ease of subsequent monomer impregnation. The incorporation of adsorbers may allow a larger tritiated water content per unit waste form volume.

Mixing may be performed either in the solidification container or in-line. In-container mixing may take one of three forms, external agitation, tumbling/rolling or gravity mixing (injection). The external agitation method employs a mixing blade which is lowered into the drum and blends the waste with cement. In the tumbling/rolling method, a mixing weight is added in a cold area to a drum containing dry cement. A predetermined quantity of the aqueous waste is then added to the drum which is capped and transferred to a tumbling or rolling station where its contents are mixed. Both of these methods produce a homogeneous waste form. The gravity mixing or injector technique shown in Figure 2 employs a distribution tube which is inserted along the centerline of a drum containing dry cement which has been tamped by vibration. Tritiated aqueous waste is added to the cement through this tube (injector) until the waste reaches the external surfaces of the cement as evidenced by dampness. In practice, the quantity of waste would be predetermined. The injector is removed from the casting after waste addition has been completed. This process does not produce a homogeneous waste form. The resultant aqueous waste content is highest near the centerline of the waste form coincident with the injector and decreases as the surfaces are approached. The subsequent polymer distribution, however, is such that the polymer loading is highest near the surfaces of the waste form and decreases as the centerline is approached, although polymer is present throughout the composite, effectively encapsulating the waste. In-line mixing can be provided on either a batch or continuous basis. In this process, cement and waste are fed into a powered screw dynamic mixer at predetermined rates and the mixture is discharged directly into the solidification container.

After the tritiated concrete has been allowed to cure, it is impregnated with styrene monomer by a soak technique. Styrene monomer was chosen because of its low viscosity, excellent radiation stability and ease of polymerization. Styrene monomer containing 0.5 wt.% AIBN (2,2' - azobis - [2-methylpropionitrile]) or benzoyl peroxide, used as a low temperature polymerization catalyst, is introduced in a prescribed amount into the casting container and allowed to soak into the concrete. The time required for complete impregnation varies depending upon the concrete volume, density and composition but typically requires a few hours. Monomer loadings of approximately 15% by weight are typical. After the soak impregnation has been completed, the casting is heated to 50-70°C (depending on the catalyst employed) to induce polymerization which is completed within twenty-four hours. Higher temperatures decrease the required time for polymerization.

An end-over-end drum tumbling technique has been developed to produce PITC castings in 30 gallon steel drums containing a polyethylene liner. The thirty gallon drum can be filled to 80% capacity at a water to cement weight ratio of 0.22 and be thoroughly mixed by tumbling at 15-20 rpm for three to eight minutes. Portland type III cement is used because of its rapid curing properties. Mixing by the drum tumbling technique eliminates required equipment cleaning operations and also minimizes the possibility of contamination as mixing occurs in a closed drum. Since the drum also serves as the casting container, the necessity for transference operations is eliminated. Figure 3 shows an axially cut polymer impregnated concrete cast in a 30 gallon drum using the drum tumbling technique. Surface discolorations are due to oils used in the cutting procedure. Inspection indicated that styrene had penetrated the entire casting.

Although static leaching experiments have been performed using polymer impregnated concrete at BNL, people at the Savannah River Plant (SRP) were interested in how this material would perform in burial. Lysimeter testing at SRP was proposed. Polymer impregnated concrete specimens with a volume of one cubic foot containing one to ten curies of tritium were suggested. It was decided to use a five gallon screw top polyethylene carboy for casting the cement. Although the volume of the carboy is 0.67 ft^3, it represented a standard size container that was readily available. This size was acceptable to SRP. Because of the low rate of tritium release expected, ten curies of tritium were added to each specimen.

This specimen size was not compatible with the drum tumbling technique developed for large scale PITC composites. Instead, lysimeter specimens were mixed using a conventional dough type mixer (Blakeslee B-20) with a water to cement ratio of 0.22. Mixing in this manner produced a concrete of similar density to that obtained by drum tumbling. Since the impregnation and polymer loading of the PITC are dependent upon the density of the cement casting, the specimens prepared in this manner for lysimeter testing are believed to be representative of the product produced by drum tumbling.

Lysimeter specimens were prepared as follows. The amount of water necessary to provide a water to cement ratio of 0.22 for each casting was determined to which an additional two milliliters of tritiated water with a specific activity of 5,000 Ci/l was added to provide a total of ten curies for the specimen. This water was added to portland type III cement and mixed until a uniform consistancy was obtained after which the cement mix was transferred to a five gallon polyethylene carboy. Vibration was employed to provide proper packing of the mix. The carboy was sealed and placed into an oven at 40°C for five days to ensure complete curing of the cement. After removal from the oven, the casting was allowed to equilibrate to room temperature before styrene impregnation by the soak technique. The specimen was impregnated with styrene monomer containing 0.5 wt.% AIBN (2,2-azobis-[2-methylpropionitrile]) as a polymerization catalyst. After addition of the monomer, the carboy was sealed and the monomer allowed to soak into the concrete overnight. The carboy was then placed into an oven at 65°C over the weekend for polymerization of the monomer. Subsequent to the equilibration of the PITC to room temperature, the polyethylene carboy was sliced away. Four lysimeter test specimens each 27 cm in diameter by 28 cm high for a volume of 0.566 ft^3 were prepared by this technique. Formulational data for these specimens is shown in Table 1.

The four PITC specimens shipped to SRP were buried in individual lysimeters which are schematically described in Figure 4. Each lysimeter consists of a steel tank 1.83 m in diameter and 3.05 m deep which is buried in the ground with its open top approximately 15 cm above the soil surface. The PITC test specimens were buried without containers 1.2 m above the bottom of the lysimeter using soil excavated during emplacement of the steel tank. Rain falling on the exposed soil on the lysimeter surface permeates the soil, contacts the PITC specimen and accumulates in a gravel layer on the sloping bottom of the lysimeter. A pump is used to collect the percolate water. After the initial time required for soil saturation, percolate water was collected weekly. The four test lysimeters are denoted NE, SE, SW, NW, and contain respectively specimens 121-1, 121-2, 121-4, and 121-3. Figure 5 shows one of the specimens being lowered into its lysimeter.

The tritium concentration in the air above the lysimeter is also measured periodically. This requires the placement of a cover on the open top of the lysimeter for approximately twenty-four hours. Figure 6 shows the lysimeter with the top cover in place. Air is collected and passed through a Linde* 4A molecular sieve trap to retain tritium oxide and through a palladium coated Linde* 4A molecular sieve to collect elemental tritium that passed through the first trap.

Percolate water could not be removed from the lysimeters before the fourteenth week; prior to this time, soil in the lysimeter absorbed all incident rainfall. Figure 7 shows the total cumulative tritium release in the lysimeter percolate water for sixty-two weeks since burial after correction for the percolate tritium content from a control lysimeter. The cumulative rainfall after the first fourteen weeks is also shown in this figure. No tritium content in the air was noted for either the specimen or control lysimeters and as such, subsequent references to tritium release are understood to refer to tritium in the percolate water. The initial tritium releases are seen to be very low. This may be partially an artifact due to channeling of water down the sides of the lysimeter which otherwise might have been absorbed in the soil.

The tritium releases from the lysimeters have been averaged in Figure 8 and expressed as (cumulative fraction tritium release) x (V/S) where V is the specimen volume and S is its geometric surface area. The factor (V/S) is included so that the tritium release as expressed is independent of sample geometry and size for leach times which are short

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* Union Carbide Corporation, New York, New York

relative to total tritium release. The lysimeter test specimens exhibit a (V/S) ratio of 4.545 cm; for comparison, (V/S) for a thirty gallon drum is approximately 9.0 cm. Regression analysis of the average data obtained after the thirty-sixth week provides a linear least squares fit with a slope of 1.43×10^{-4} cm/day corresponding to a daily fraction tritium release rate of 3.15×10^{-5}. In Figure 9, this least squares fit is expressed as:

$$(\Sigma a_n/A_o)\ (V/S) = 5.23\times10^{-2}\ t\ (yr) - 3.58\times10^{-2},\ cm \qquad (1)$$

thus giving a slope expressed as cm/yr while the second term implies that this rate of release began after 250 days and no prior tritium release occurred. This projects a complete tritium release after 87.6 years. When this release is corrected for decay, it is seen that the maximum fraction of the initial contained tritium which appears in the environment is 7.2% after 17.7 years from the beginning of the initial tritium release.

The tritium releases projected have been for the lysimeter average with 0.566 ft^3 specimens (V/S = 4.545 cm) with no container. Figure 10 projects the cumulative tritium release corrected for decay for 30 gallon drum size waste forms (V/S = 9.0 cm) as a function of container lifetime. A fraction tritium release rate of 5.23×10^{-2} cm/yr is assumed. The maximum quantity of tritium present in the environment appears 17.7 years after container failure. This fraction of the initially contained tritium is 2.15×10^{-2}, 1.22×10^{-2}, 2.24×10^{-3}, and 1.33×10^{-4} for container lifetimes of 10, 20, 50, and 100 years.

A PITC specimen (without container) of the same dimensions and formulation as those in lysimeter testing at SRP is in static leaching in distilled water at BNL. This specimen which also contains ten curies of tritium had a density of 95.4 lbs/ft^3 prior to impregnation and 107.7 lbs/ft^3 afterwards for a polymer loading of 12.9%. The lower polymer loading in this specimen as compared to the lysimeter test specimens results from the higher initial density of the concrete (due to more vibratory tamping) and a minimization of polymer on the upper surface of the composite. Leach testing was performed by immersing the specimen without a container in 40 liters of distilled water such that all surfaces were exposed to the leachant. The leachant was not changed; one cm^3 was taken during sampling for analysis by liquid scintillation counting. The results after 386 days of leaching are shown in Figure 11. The rate of release is approximately linear with a slope of 3.18×10^{-2} cm/yr. A complete release after 143 years is projected as indicated in Figure 12. When corrected for decay, it becomes apparent that the maximum fraction of the initially contained tritium appearing in the environment is 4.55×10^{-2} after 17.7 years.

Acknowledgment

The efforts of E. Albenesius and R. Hawkins of the E.I. du Pont de Nemours & Company, Savannah River Plant, who were responsible for construction of the test lysimeters and analysis of lysimeter percolate waters are greatly appreciated.

TABLE 1

Formulational Data for PITC Specimens for Lysimeter Testing at SRP

Specimen Number	Formulation, Wt.% Cement	Formulation, Wt.% Water	HTO Content[(a)] ℓ/ft^3	Initial Mass, kg	Impregnated Mass, kg	Polymer Load, %[(b)]
121-1	82.0	18.0	7.44	23.4	27.3	16.7
121-2	82.0	18.0	7.47	23.5	27.4	16.6
121-3	82.0	18.0	7.47	23.5	27.3	16.2
121-4	82.0	18.0	7.47	23.5	27.4	16.2

(a) cylindrical specimens, 27 cm diameter x 28 cm height each containing ten curies of tritium.

(b) $$\text{polymer load \%} = \frac{\text{impregnated mass} - \text{initial mass}}{\text{initial mass}} \times 100$$

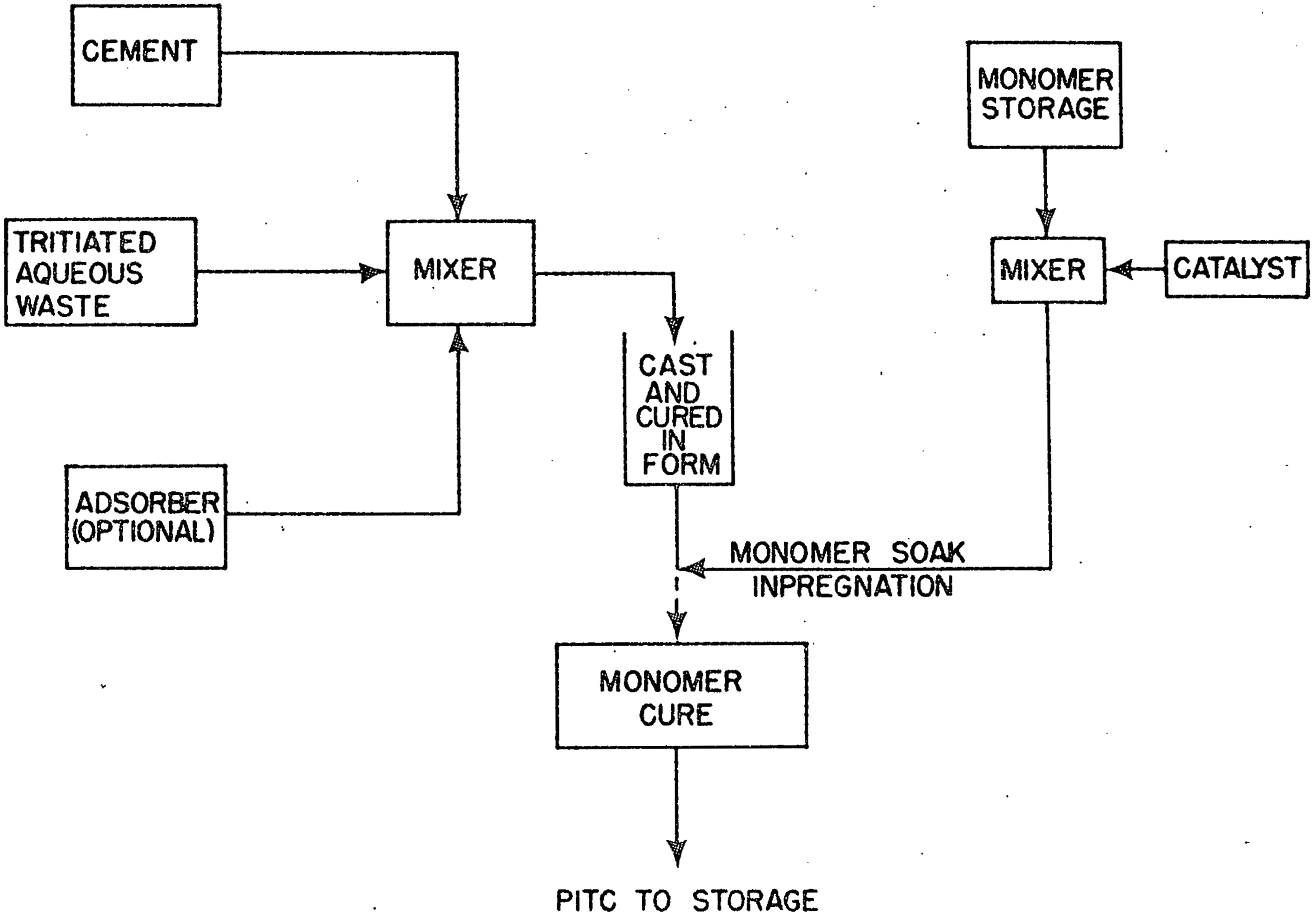

Figure 1. Conceptual Process for the Fixation of Tritiated Aqueous Waste in Polymer Impregnated Tritiated Concrete (PITC).

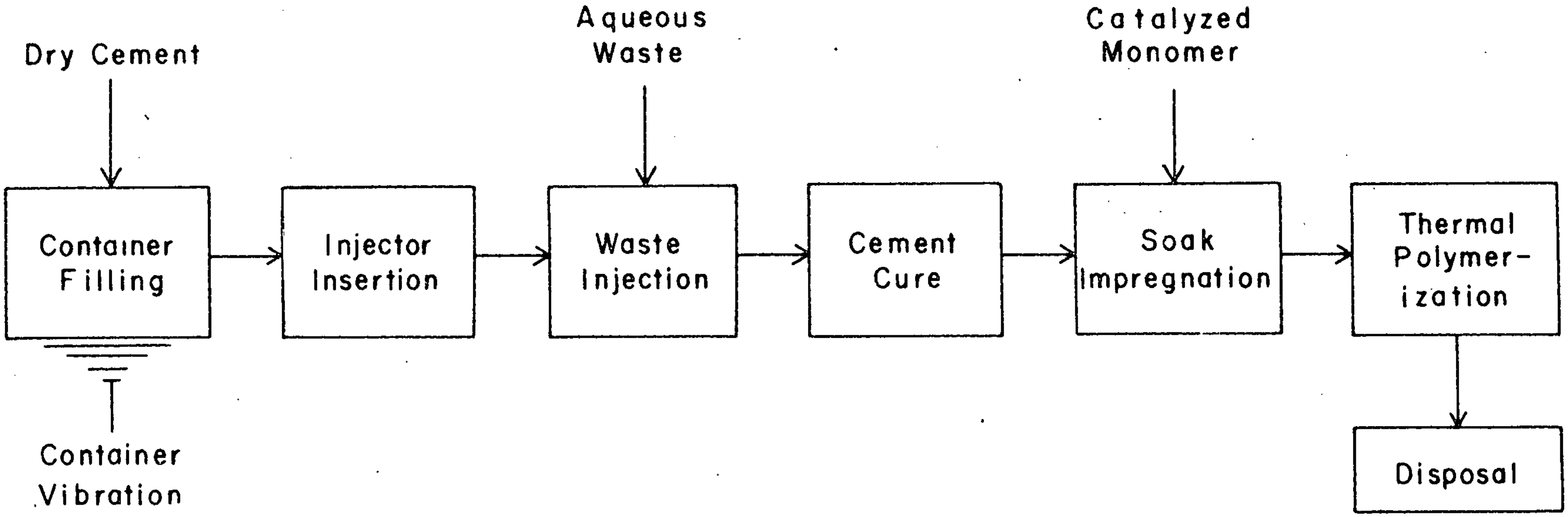

Figure 2. Conceptual Process for the Fixation of Tritiated Aqueous Waste in Polymer Impregnated Tritiated Concrete by the Injection Technique.

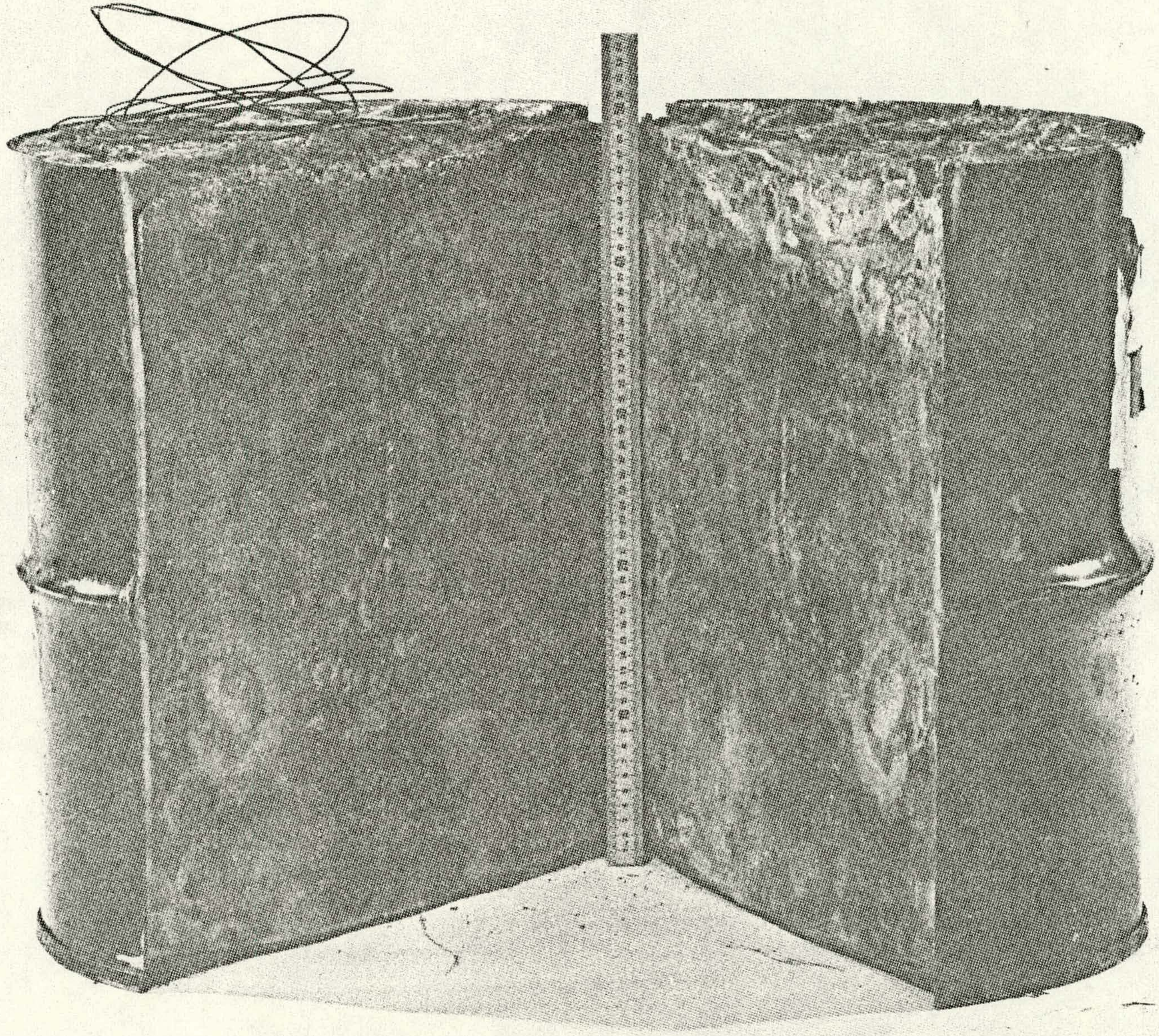

Figure 3. Axial Section of a Thirty-Gallon PITC Casting Made by the Drum Tumbling Technique.

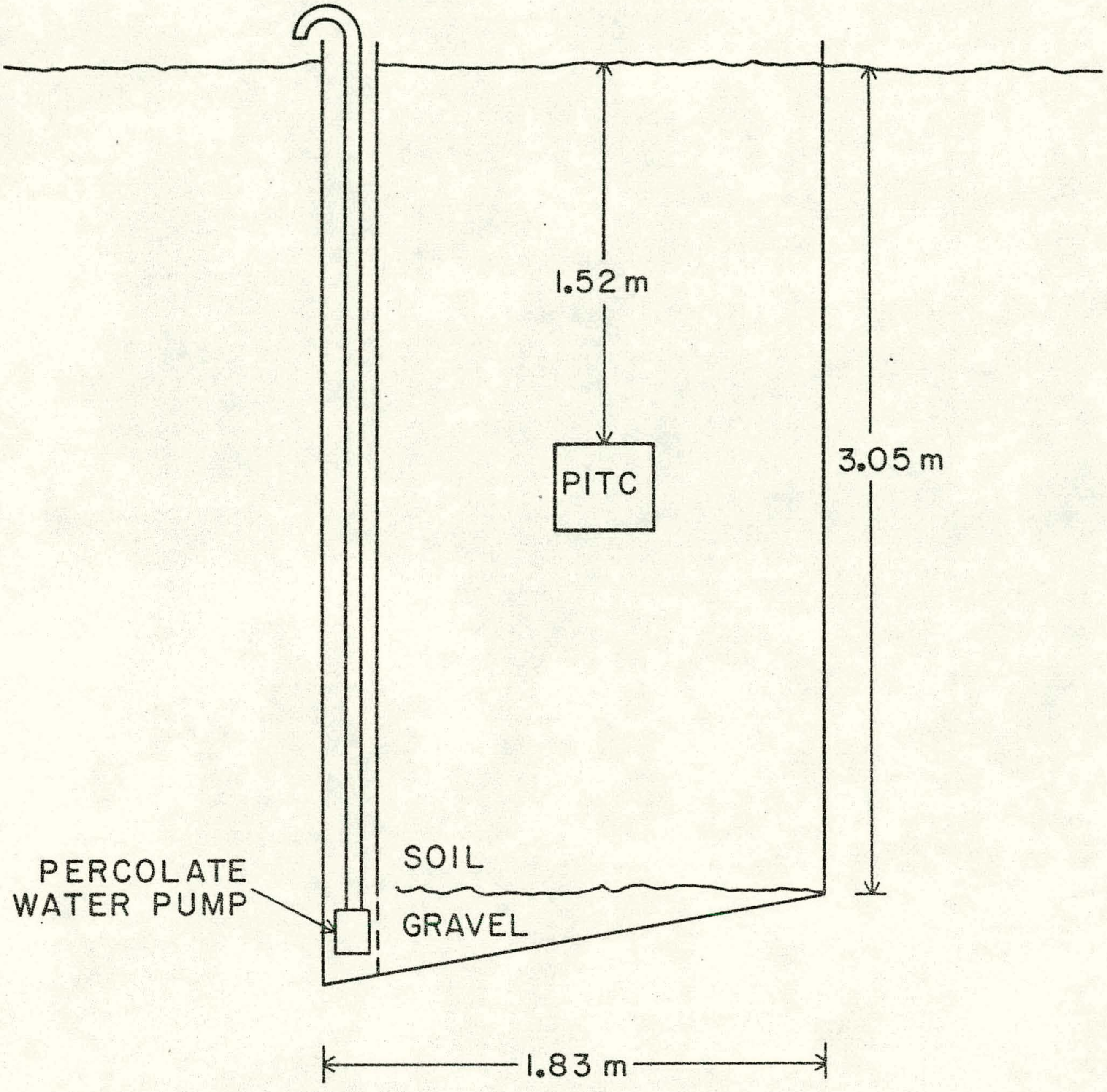

Figure 4. Schematic Drawing of a SRP Test Lysimeter.

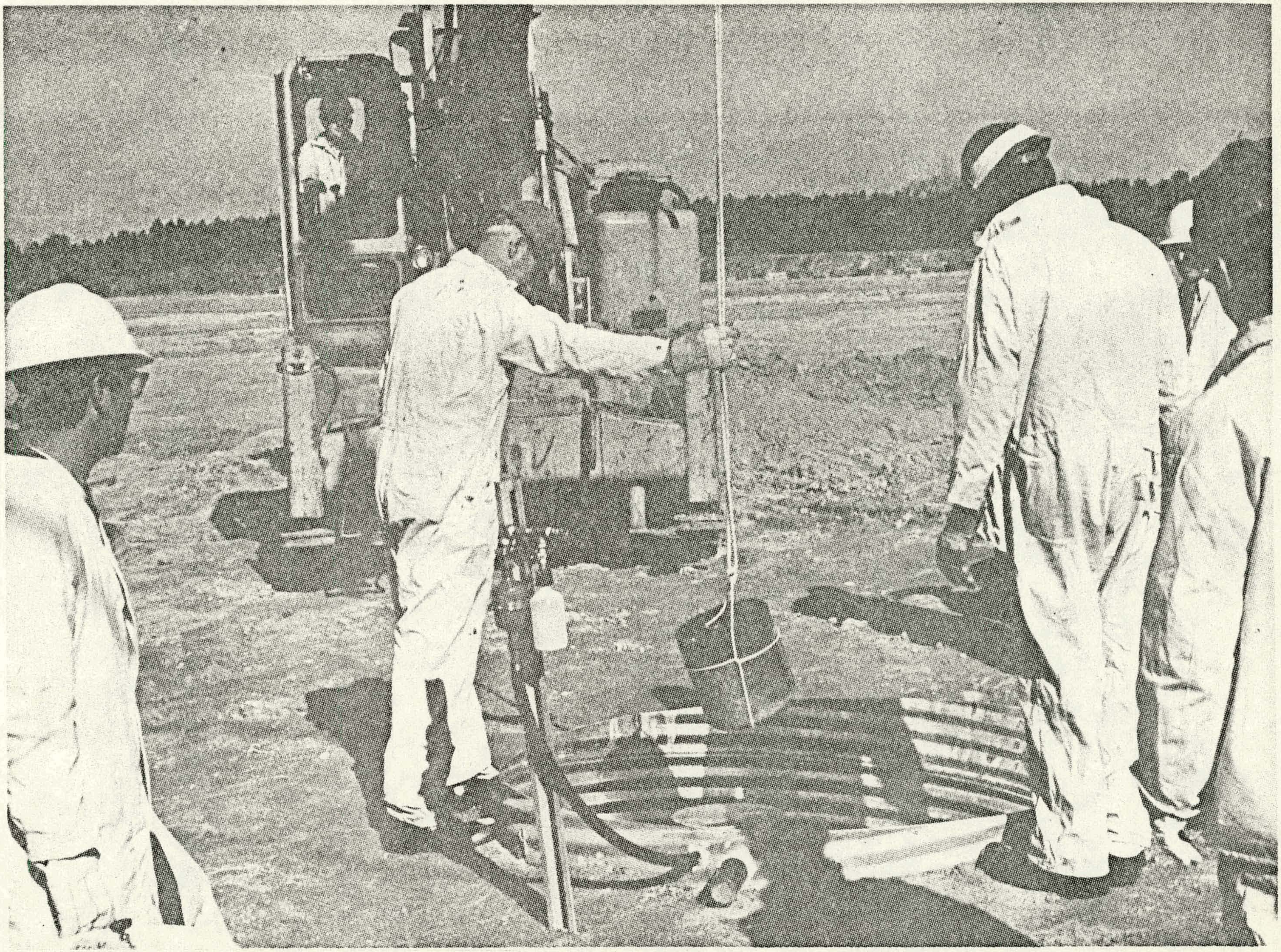

Figure 5. Lowering a PITC Specimen into the Test Lysimeter.

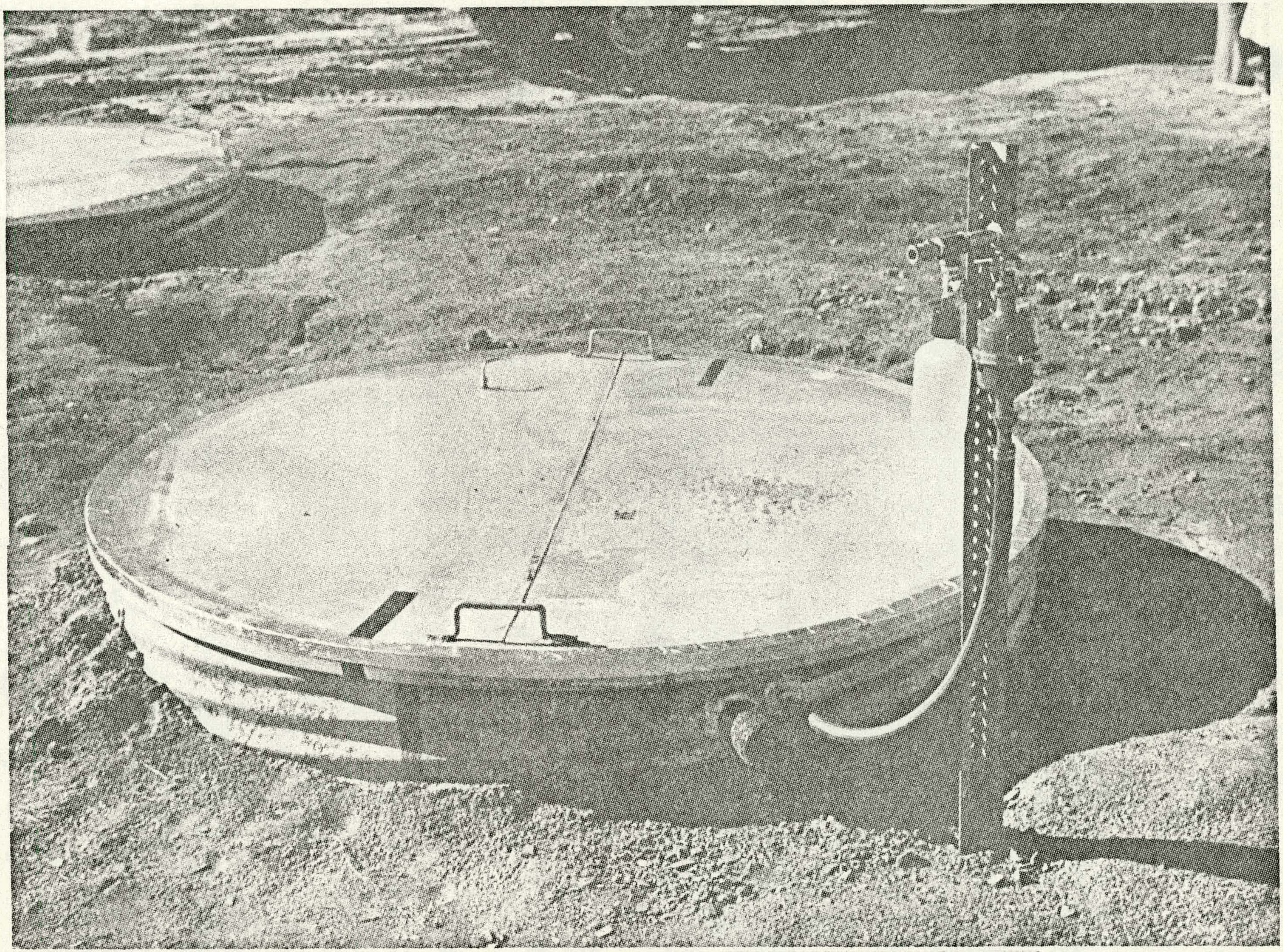

Figure 6. Lysimeter with Air Collection Cover in Place.

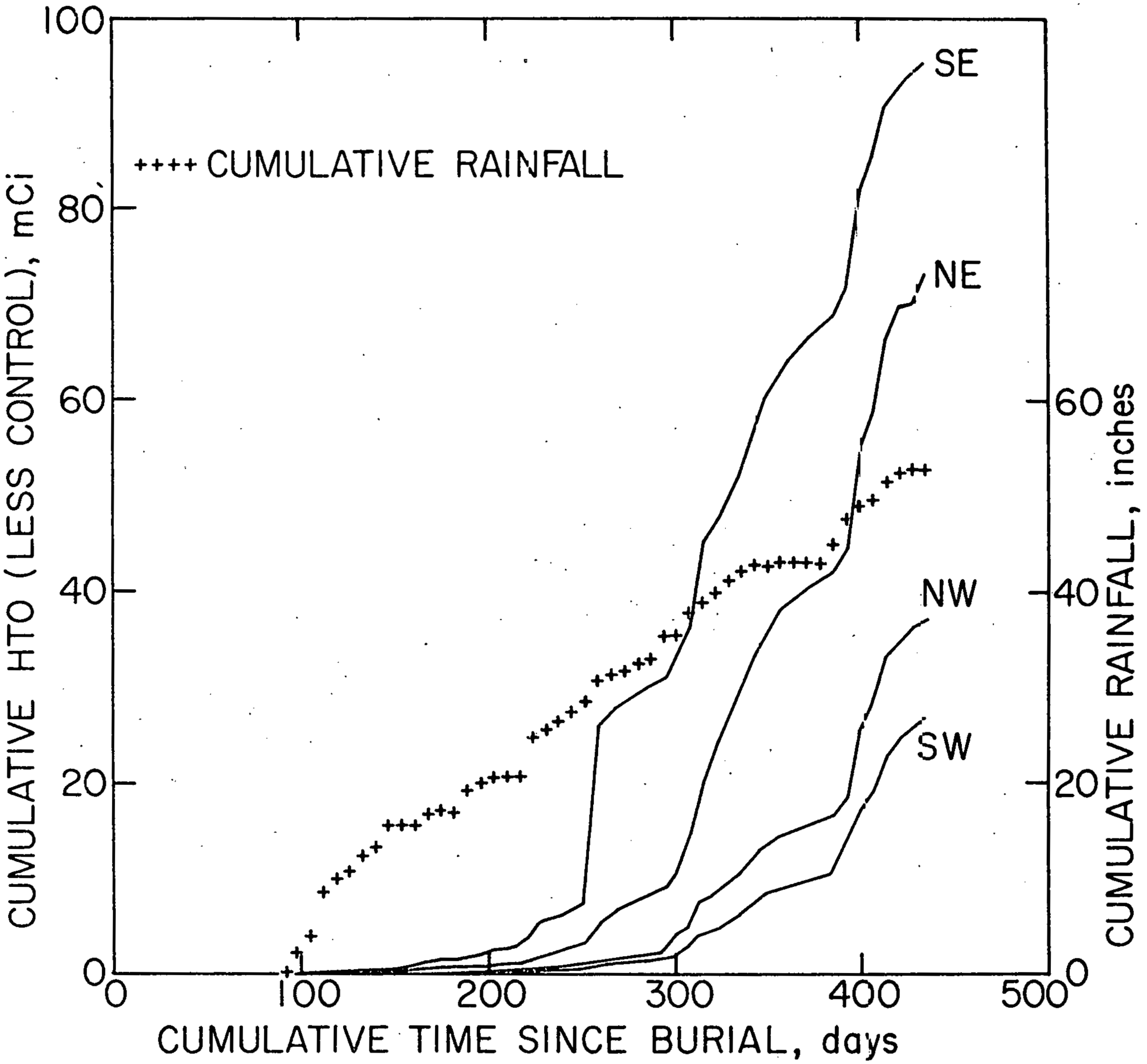

Figure 7. Cumulative Tritium Release and Rainfall for the SRP Lysimeters.

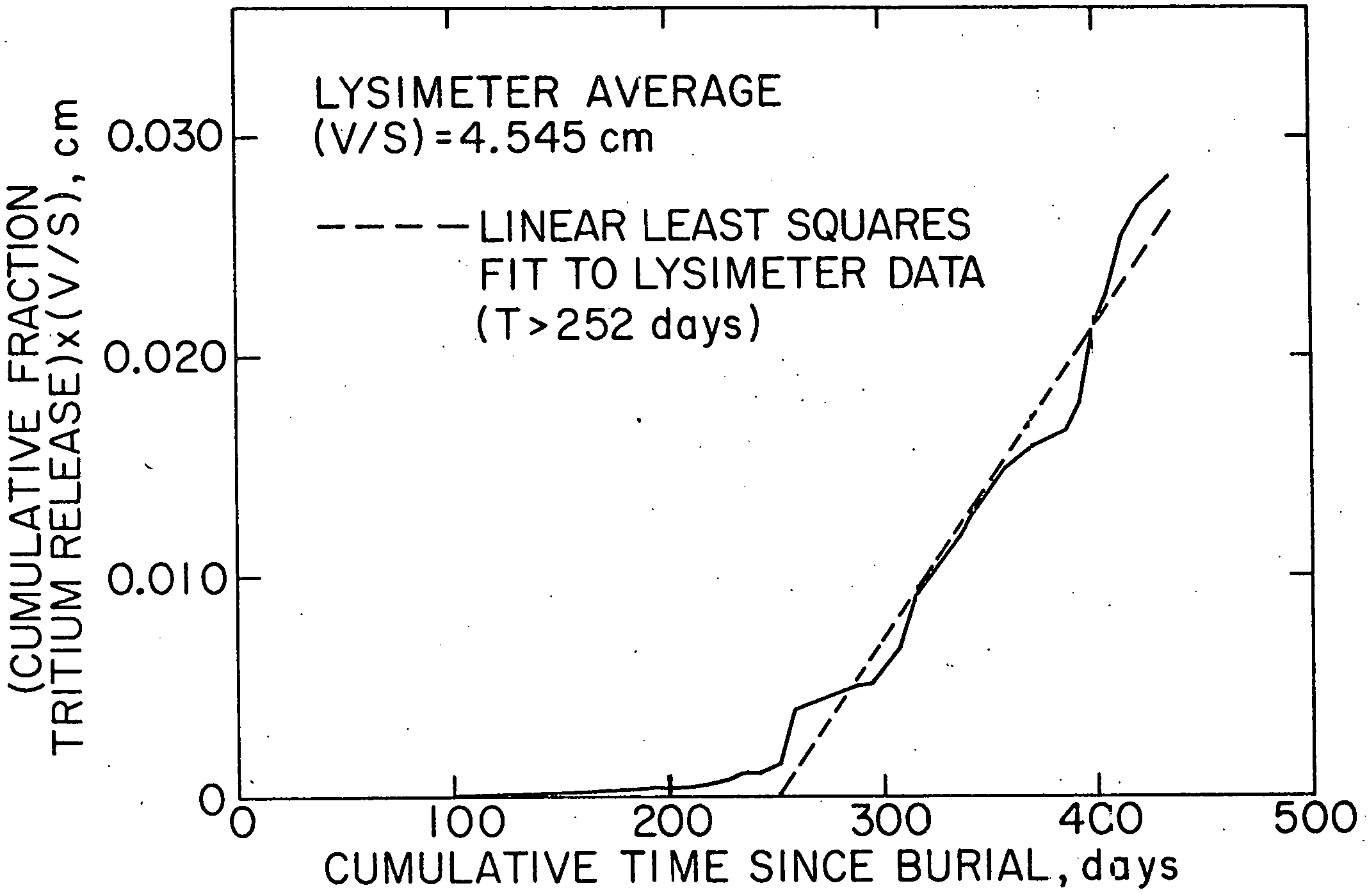

Figure 8. (Cumulative Fraction Tritium Release)X(V/S) Versus Time Since Burial, Lysimeter Average.

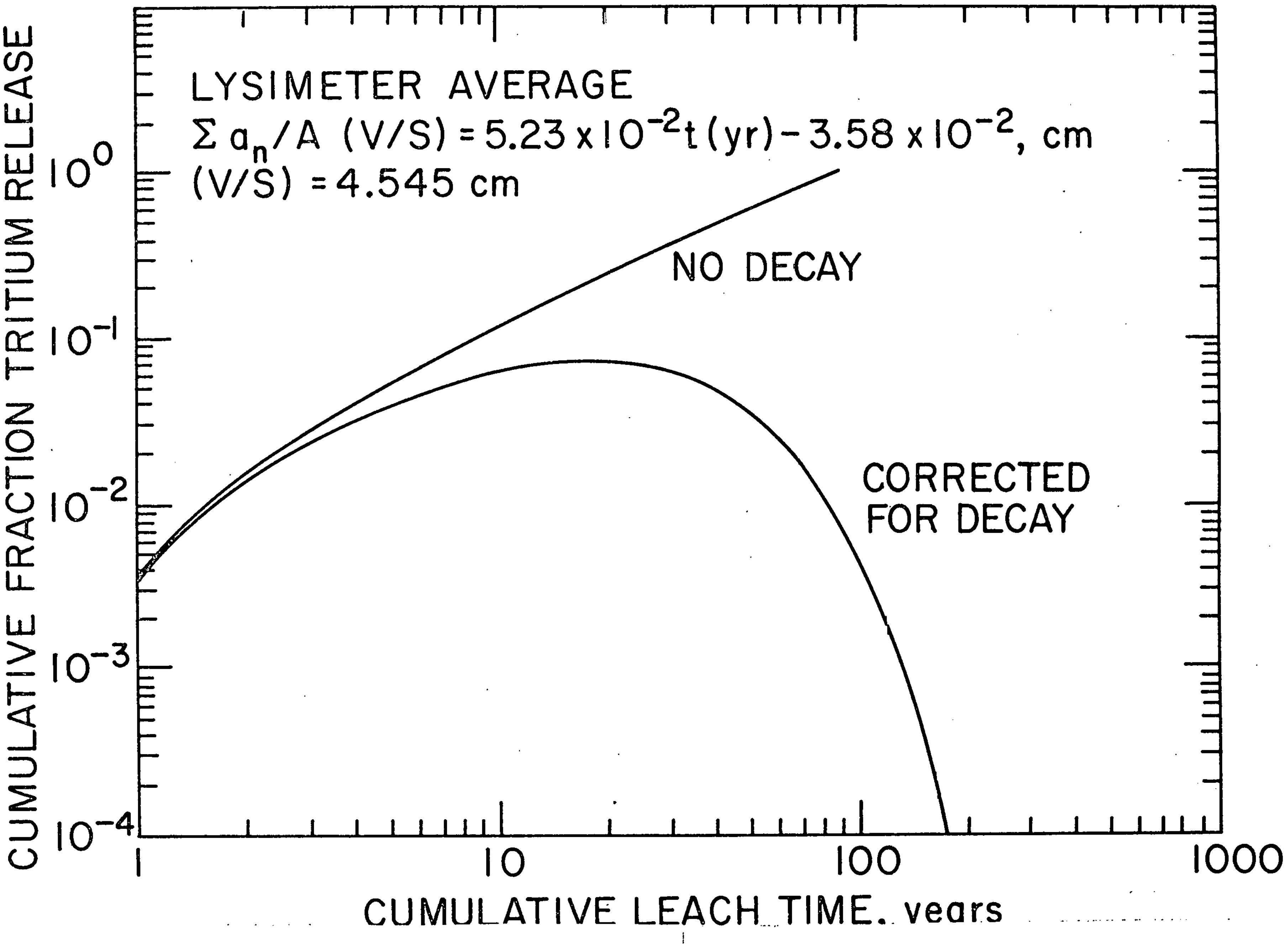

Figure 9. Projected Cumulative Fraction Tritium Release with Time, Based on the Test Lysimeter Average Rate of Release.

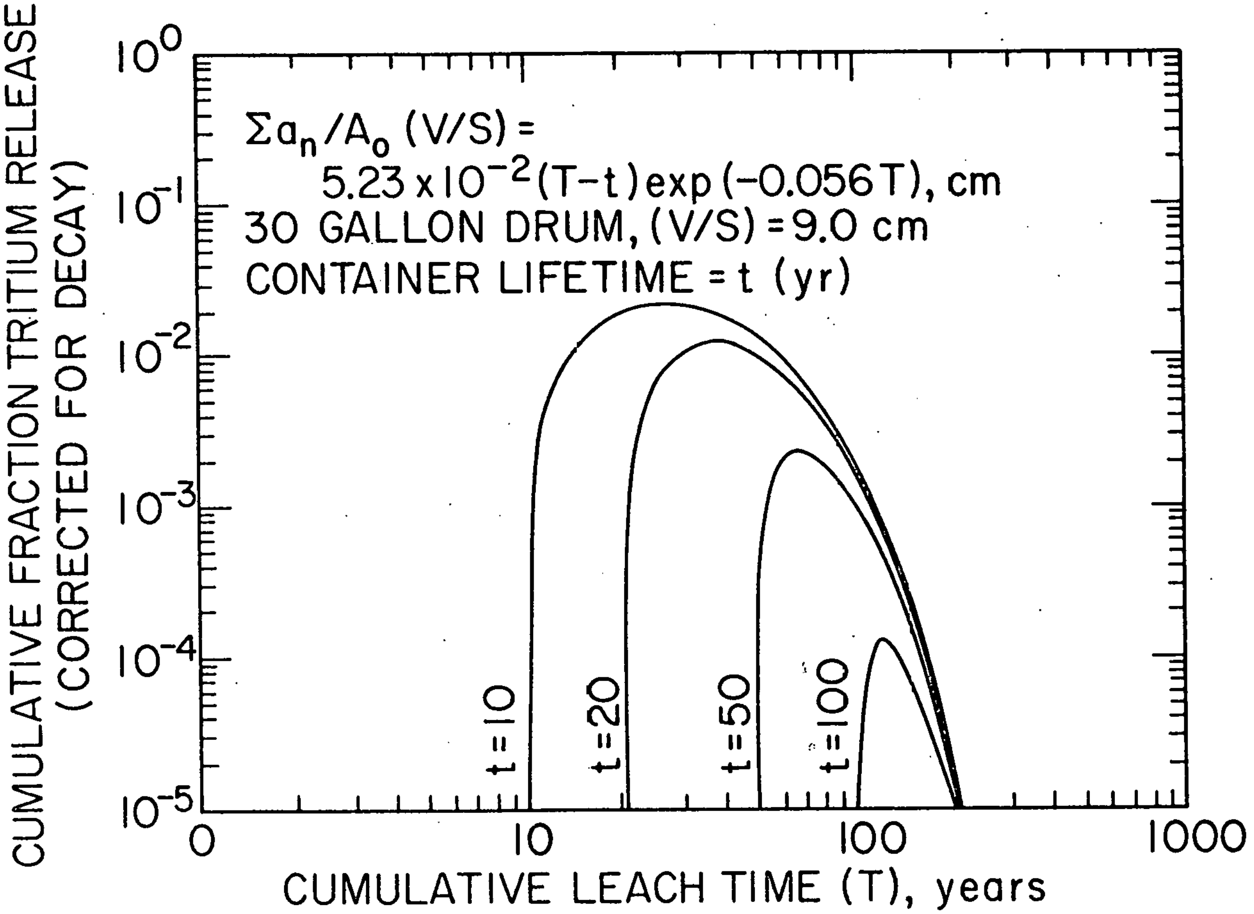

Figure 10. Projective Cumulative Fraction Tritium Release for PITC in Containers with Finite Lifetimes.

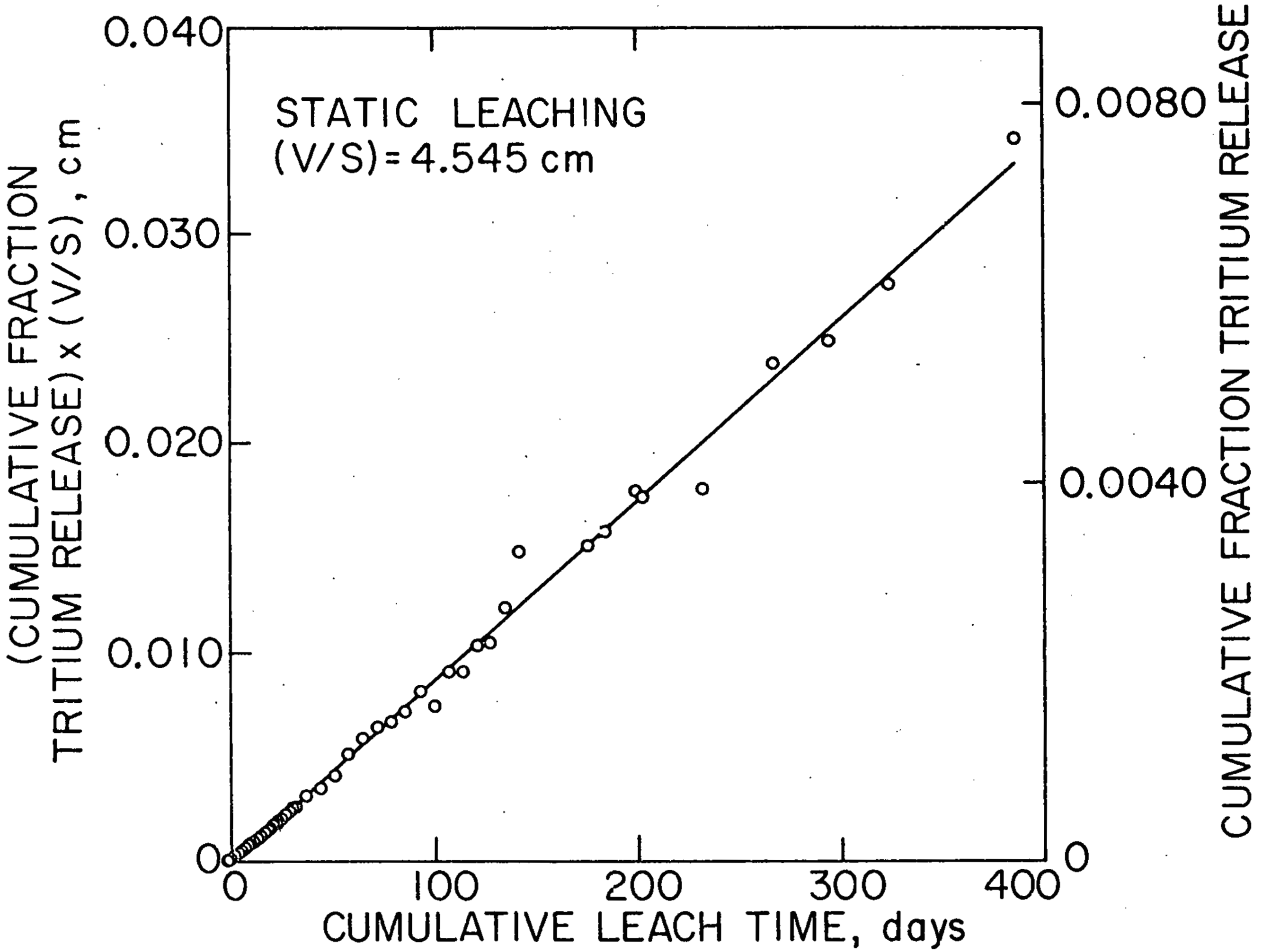

Figure 11. (Cumulative Fraction Tritium Release)X(V/S) Versus Leach Time for Static Leaching of the Lysimeter Test Duplicate Specimen.

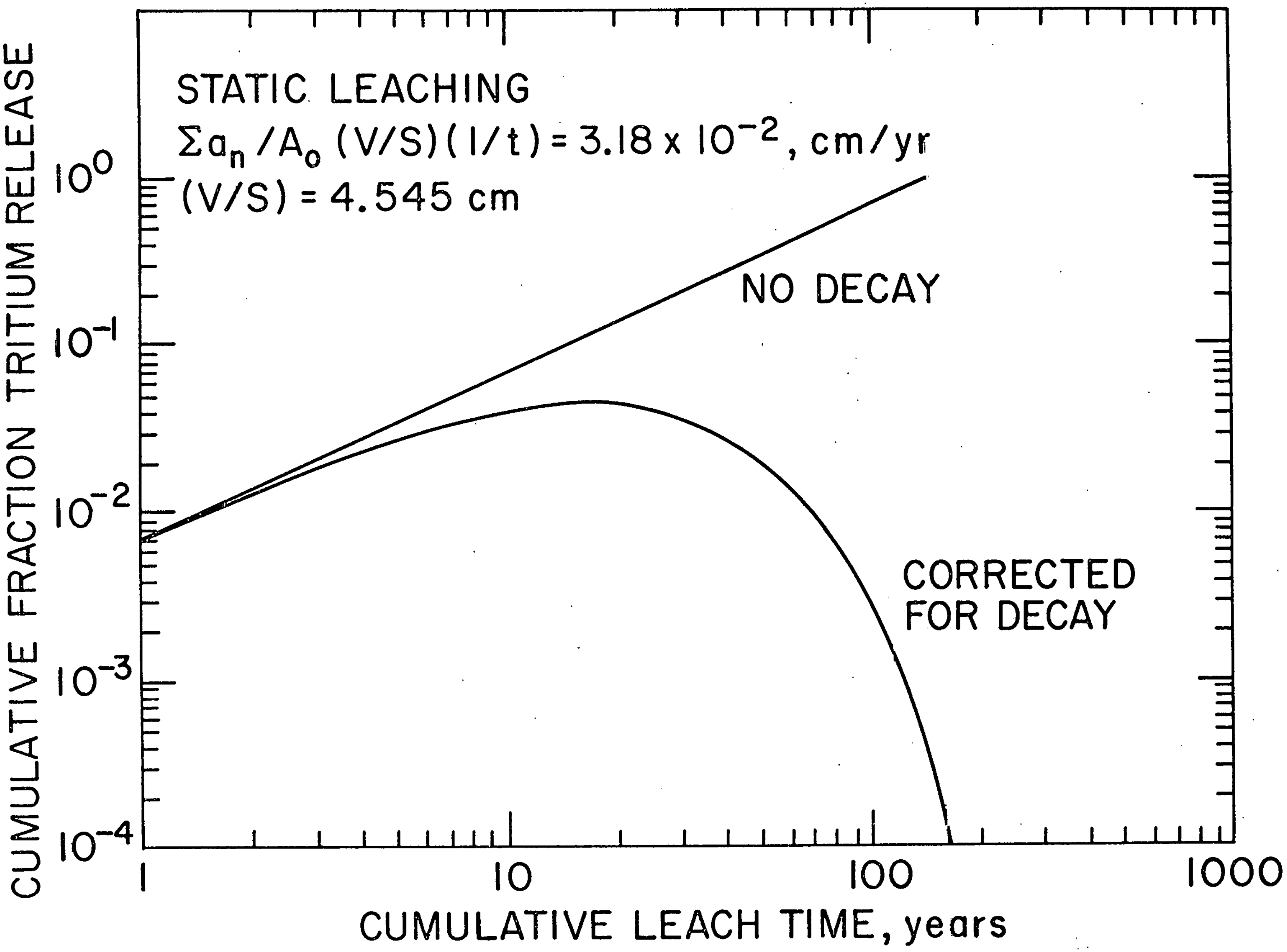

Figure 12. Projected Cumulative Fraction Tritium Release with Time for Static Leaching of the Lysimeter Test Duplicate Specimen.