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TRITIUM STORAGE DEVELOPMENT

PROGRESS REPORT NO. 9
JULY-SEPTEMBER 1976

Prepared for the
NUCLEAR FUEL CYCLE AND PRODUCTION DIVISION
UNITED STATES ENERGY RESEARCH AND DEVELOPMENT ADMINISTRATION
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PROCESS TECHNOLOGY DIVISION
DEPARTMENT OF APPLIED SCIENCE

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TRITIUM STORAGE DEVELOPMENT

PROGRESS REPORT NO. 9
JULY-SEPTEMBER 1976

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SUMMARY

Lysimeter testing of the polymer impregnated tritiated concrete (PITC) specimens at the Savannah River Plant has continued. After thirty-one weeks, a constant average tritium fraction release rate of 1.16×10^{-6} day^{-1} was reached in the percolate water with no measurable release into the air. Data from this experiment projected to long-term tritium releases estimate that a complete tritium release from the PITC will require 2,370 years and that the maximum fraction of the initially contained tritium present in the environment will be 2.76×10^{-3} after 17.7 years. A duplicate PITC specimen is in static leaching in distilled water. After 295 days, a constant tritium fraction release rate of 1.89×10^{-5} day^{-1} was determined for this specimen.

Development of the injector technique for PITC production has proceeded with the fabrication of a large-scale 27 gallon PITC casting. This casting was sectioned longitudinally and examined for its physical appearance, integrity, and polymer distribution.

A representative of Monsanto Mound Laboratory spent one week at Brookhaven National Laboratory for PITC production technology transfer.

I. LYSIMETER TESTING OF LARGE-SCALE POLYMER IMPREGNATED TRITIATED CONCRETE (PITC) SPECIMENS AT THE SAVANNAH RIVER PLANT (SRP)

A. Specimen Preparation

SRP suggested that specimens containing one to ten curies of tritium would provide adequate detectibility in lysimeter testing and that a specimen size of one cubic foot would be convenient. Because of the low rate of tritium release expected in the lysimeter testing of PITC, ten curies of tritium were added to each specimen. The specimens were prepared in five gallon (0.67 ft^3) screw-top polyethylene carboys. These containers represented a standard size that was easily obtainable; this size was acceptable to SRP.

The size of the specimen and its container were not compatible with the end-over-end drum tumbling technique(1) being developed for large-scale PITC composites. It was determined that a conventional dough type mixer (Blakeslee model B-20) when used with a water to cement ratio of 0.22 produced a product of similar density as that obtained by end-over-end tumbling with the same water to cement ratio. Since the resultant polymer loading in a homogeneous cement casting using soak impregnation is dependent upon the initial density, the PITC specimens produced by this method are representative of the product produced by end-over-end tumbling.

The amount of water necessary to give a water to cement ratio of 0.22 for each cement casting was determined. Two millileters of tritiated water with a specific activity of 5 Ci/ml were added to this water to provide a tritium content of ten curies for each specimen. The water was added to portland type III cement and mixed until a uniform consistancy was obtained. The cement mix was transferred to a five gallon polyethylene carboy which was vibrated to provide proper packing of the mix. The carboy was sealed and placed in an oven for five days at 40°C to ensure complete curing of the cement.

After removal from the oven, the casting was allowed to equilibrate to room temperature before polymer impregnation. The soak impregnation technique developed at BNL was employed, in which sufficient monomer is introduced into the void space above the specimen in its container and allowed to soak into the concrete. 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 containing the tritiated concrete 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 polymer impregnated tritiated concrete specimens were prepared by this technique.

Table 1 lists the formulational data for the four PITC specimens sent to SRP for lysimeter testing. Each specimen contained ten curies of tritium. The specimen geometry is cylindrical with approximate dimensions of 27 cm diameter x 28 cm for a composite volume of 0.566 ft^3. The tritiated concrete had a density of 91.5±0.3 lb/ft^3. Impregnation produced PITC specimens with a density of 106.6±0.2 lb/ft^3 and a polymer loading of 16.5±0.3%.

B. Lysimeter Testing at SRP

The four PITC specimens shipped to SRP were buried without containers in individual lysimeters as shown in Figure 1. Each lysimeter consists of a steel tank 1.83 m in diameter and 3.05 m deep which was buried in the ground with its open top approximately 15 cm above the soil surface. The PITC specimen was buried 1.5 m below the soil surface and approximately 1.2 m above the bottom of the lysimeter using SRP soil excavated during placement of the steel tank. Rain falling on the exposed soil at 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 with volume and tritium concentration data compiled.

The tritium concentration in the air above the lysimeter was also measured periodically. This required the placement of a cover on the open top of the lysimeter for approximately 24 hours. Figure 2 shows the lysimeter

TABLE 1

Formulational Data for PITC Specimens for Lysimeter Testing at SRP

Specimen Number	Formulation, Wt.% Cement	Formulation, Wt.% Water	HTO Content ℓ/ft^3	Initial Mass, kg	Impregnated Mass, kg	Polymer Load, %
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	16.6

Each specimen contains ten (10) curies of tritium.

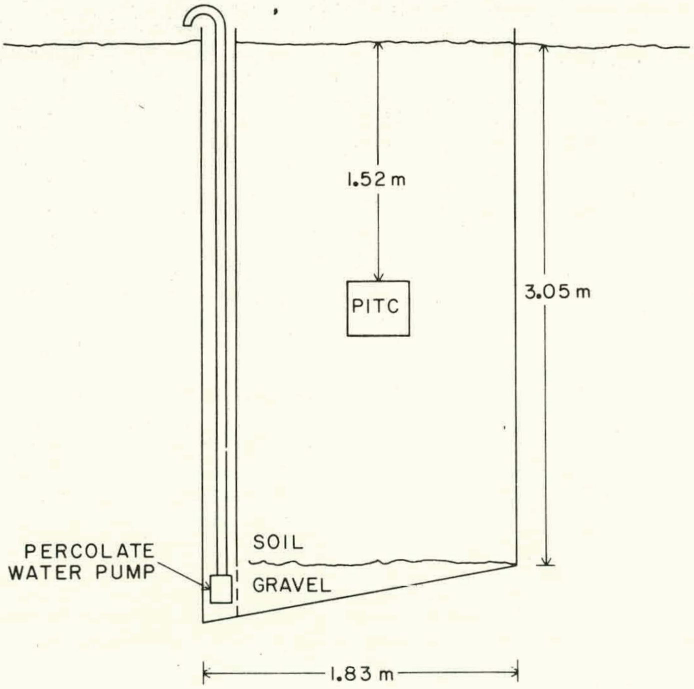

Figure 1. SRP test lysimeter for measurement of the rate of tritium release from polymer impregnated tritiated concrete (PITC).

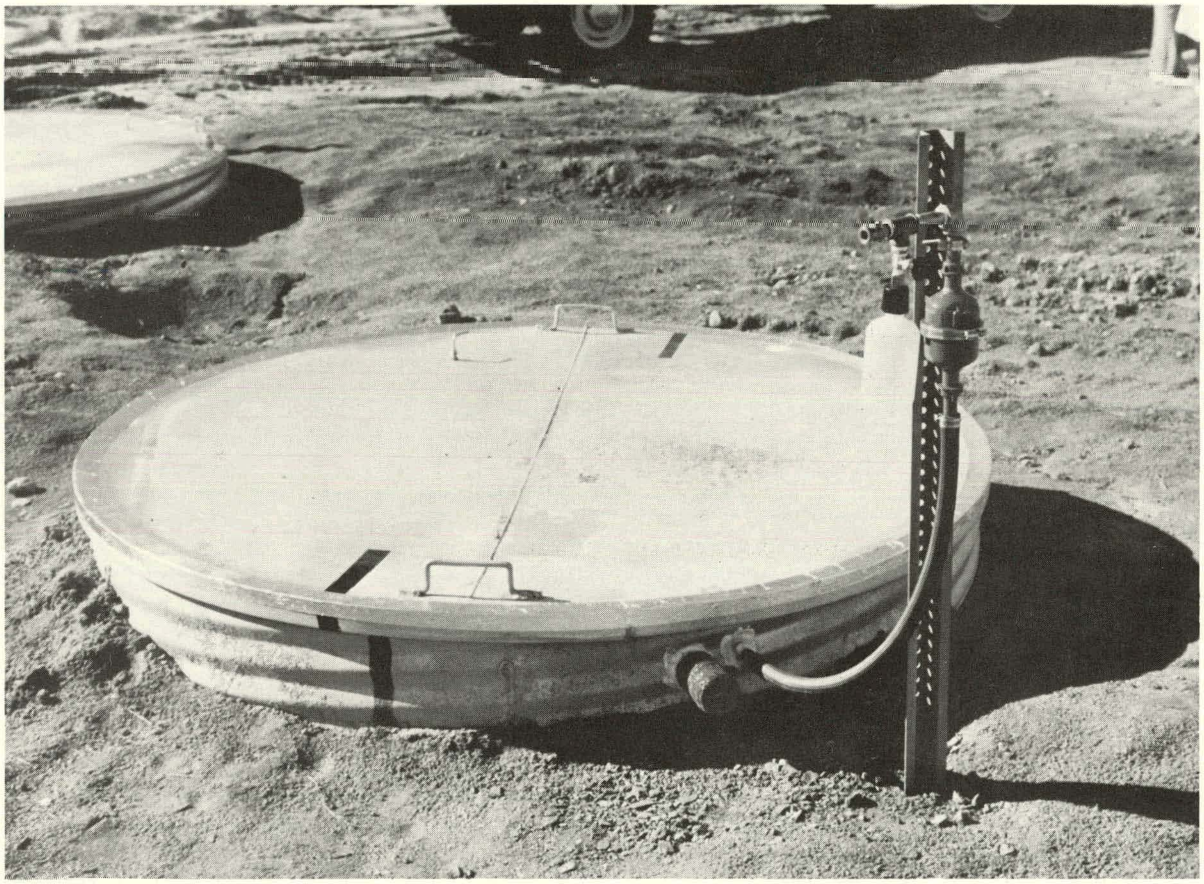

Figure 2. Lysimeter with top cover in place for air sampling.

with the top cover in place. Air was collected and passed first through a Linde* 4A molecular sieve trap to retain tritium oxide (HTO) and then through palladium coated Linde 4A molecular sieve to collect elemental tritium (HT) that passed through the first trap.

The four test lysimeters are denoted NE, SE, SW, and NW according to their compass position and contain respectively specimens 121-1, 121-2, 121-4, and 121-3. The specimens were each set in a nylon sling, wrapped in a polyethylene bag, and placed into a 30 gallon drum for shipment to SRP. Vermiculite was poured into the space between the drum and the polyethylene bag containing the sample. An air sampling valve and pressure gauge were mounted on the drum head, however, no pressurization occurred. Figure 3 shows one of the PITC specimens being lowered into its lysimeter. After it was placed in the lysimeter, the nylon sling was removed, and the specimen was then covered with soil. Additional soil is added if settling occurs in the lysimeter.

Percolate water could not be removed from the lysimeters before the fourteenth week; prior to this time all rainfall was absorbed by the lysimeter soil. The cumulative tritium (as HTO) and cumulative percolate water removed from the control lysimeter as a function of time are shown in Figure 4. Both of these parameters vary directly with the cumulative rainfall at the SRP burial site which is given in Figure 5. The tritium (as HTO) removed from the control lysimeter during weekly sampling is treated as background and is subtracted from the tritium release (as HTO) measured in the corresponding sample lysimeter percolate waters. No tritium content in the air above the lysimeter was noted for either the control or sample lysimeters and as such, subsequent references to tritium release are understood to refer to tritium in the percolate water as HTO. Figures 6-9 give the cumulative tritium releases (less control) and cumulative percolate water for the NE, SE, SW, and NW sample lysimeters respectively for thirty-one weeks since burial. The composite of the sample lysimeter tritium releases with the time since burial shown in Figure 10 indicates a relatively wide range of tritium release. A cumulative tritium release of

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* Union Carbide Corp., N.Y., N.Y.

Figure 3. PITC specimen being lowered into lysimeter.

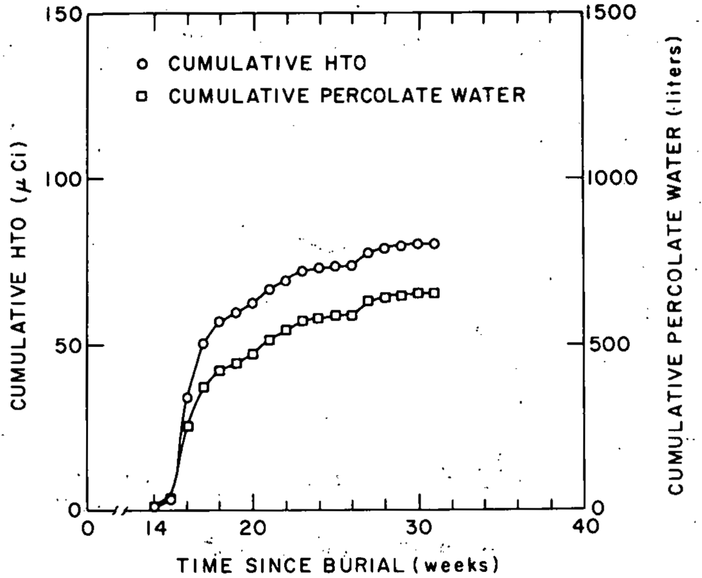


Figure 4. Cumulative tritium (as HTO) and cumulative percolate water collected versus time for the SRP control lysimeter.

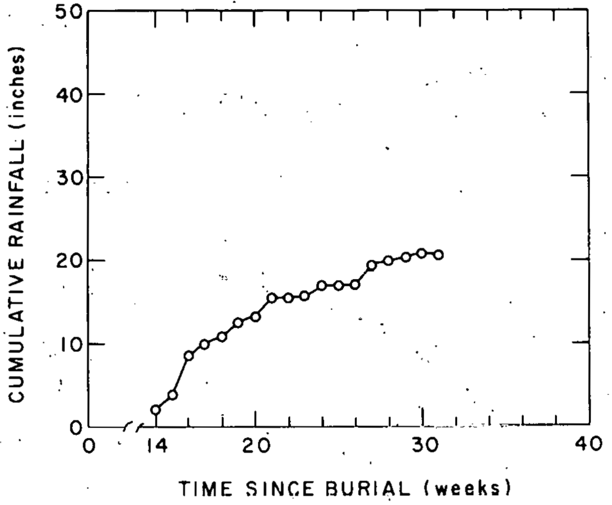


Figure 5. Cumulative rainfall versus time since burial at the SRP lysimeter site.

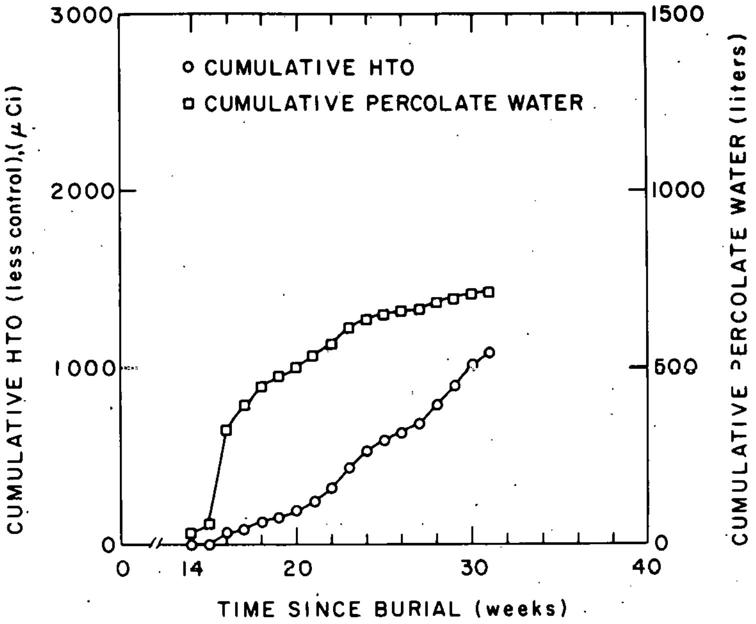


Figure 6. Cumulative tritium (as HTO) and cumulative percolate water collected versus time for the NE sample lysimeter.

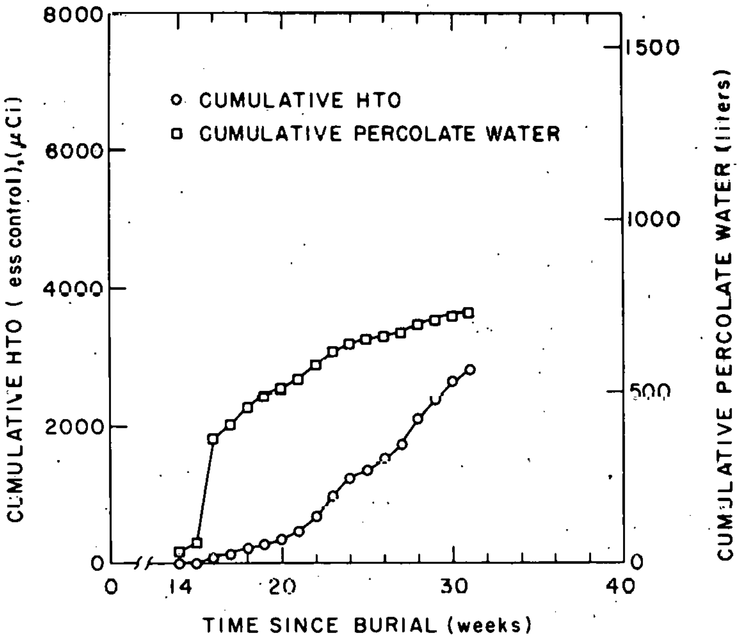


Figure 7. Cumulative tritium (as HTO) and cumulative percolate water collected versus time for the SE sample lysimeter.

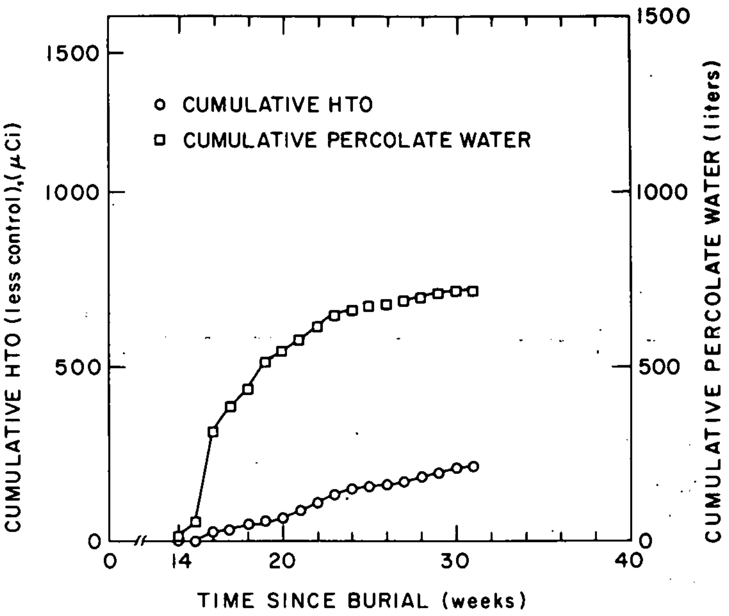


Figure 8. Cumulative tritium (as HTO) and cumulative percolate water collected versus time for the SW sample lysimeter.

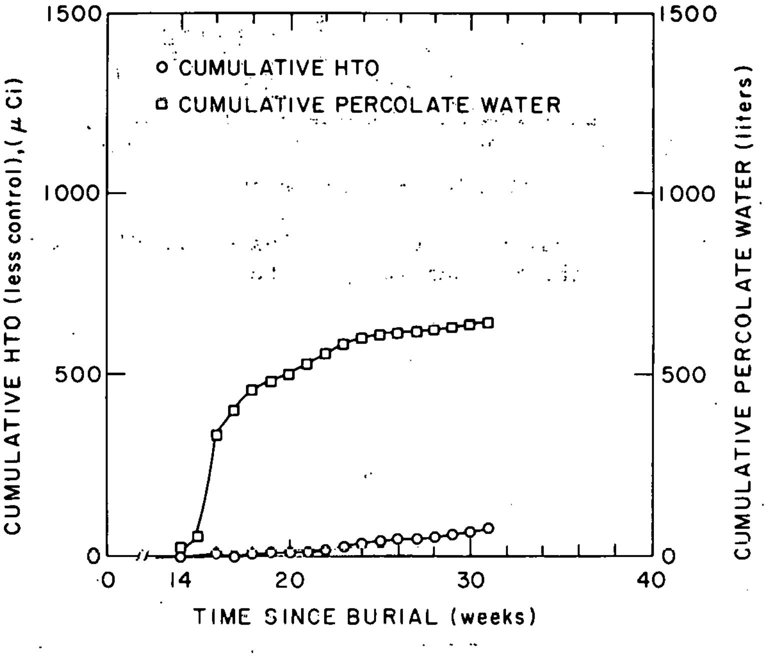


Figure 9. Cumulative tritium (as HTO) and cumulative percolate water collected versus time for the NW sample lysimeter.

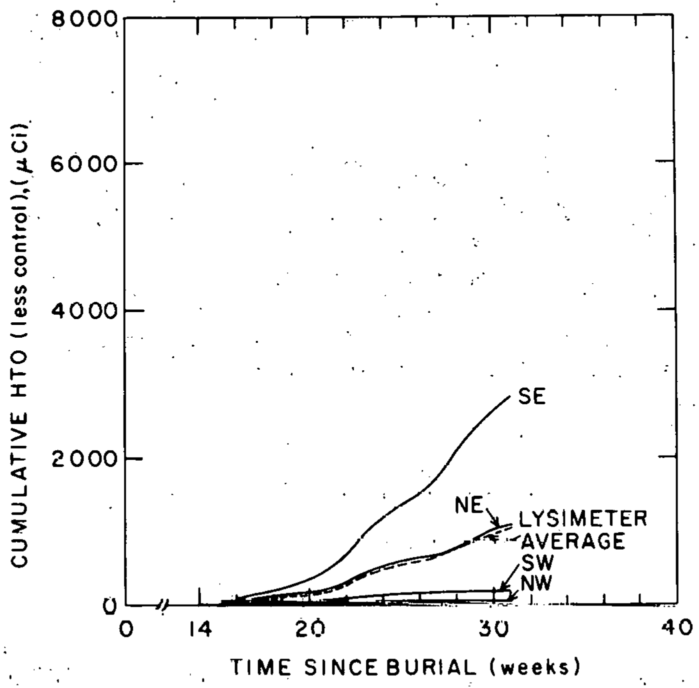


Figure 10. Cumulative tritium release (as HTO) from the SRP sample lysimeters.

2.83 mCi was obtained from the SE lysimeter after thirty-one weeks while the corresponding release was 0.0786 mCi from the NW lysimeter. The cumulative percolate water removed from the lysimeters varied from 646 to 732 liters with an average of 692 liters. As such, the differences in the tritium release determined for the sample lysimeters are attributed to variability in the leach rates of the buried specimens. An average cumulative tritium release as a function of burial time was calculated from the sample lysimeter data and is shown in Figure 10.

After thirty-one weeks in burial, the average cumulative tritium release from the lysimeter specimens was 1.052 mCi corresponding to an average total fraction release into the percolate water of 1.05×10^{-4}. As shown in Figure 11, the rate of tritium release increased during the initial weeks of percolate water collection until it reached an approximately linear value of 1.16×10^{-6} day^{-1} after the twentieth week (140 days). The projected tritium release versus time for PITC lysimeter specimens (without containers) in burial at SRL is shown in Figure 12 assuming no decay and corrected for tritium decay ($t_{\frac{1}{2}}$ = 12.26 years). This projection is based on the average release rate of 1.16×10^{-6} day obtained from lysimeter testing after the twentieth week, but is expressed as a (cumulative fraction release per unit time) x (V/S) equal to 5.26×10^{-6} cm/day. The inclusion of the factor (V/S) which is the ratio of the specimen volume to its geometric surface area allows an expression of the tritium release which is independent of surface area effects and as such can be projected to other sample sizes and geometrics. The value of (V/S) for the lysimeter specimens is 4.545 cm. The release projection in Figure 12 assumes a constant tritium release of 5.26×10^{-6} cm/day from the first day of burial which results in a complete tritium release from the PITC in 2,370 years. The maximum fraction of the initial tritium content present in the environment is 2.76×10^{-3} after 17.7 years in burial when decay is considered.

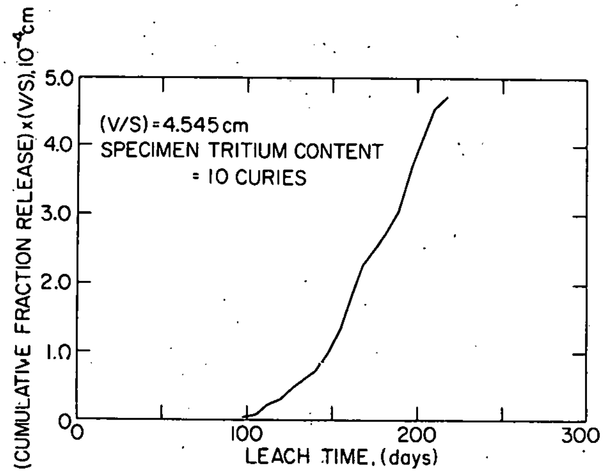


Figure 11. Average (cumulative fraction tritium release) x (V/S) versus time for SRL lysimeter test specimens (without containers) in burial.

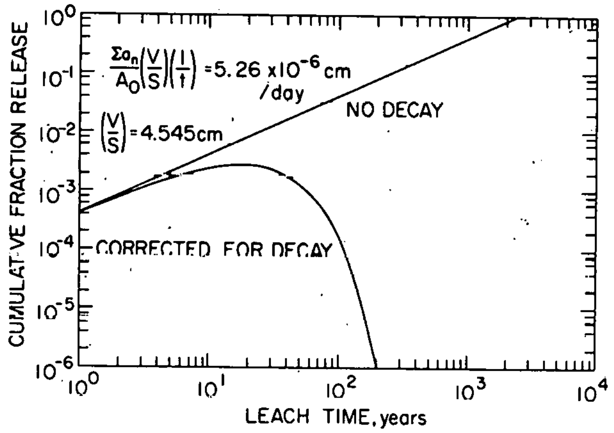


Figure 12. Projected tritium release versus time for SRL lysimeter test specimens (without containers) in burial.

II. STATIC LEACH TESTING OF THE SRL LYSIMETER DUPLICATE SPECIMEN

A PITC specimen (without container) of the same dimensions and formulation as those in lysimeter testing at SRP is in static leaching to determine the rate of tritium release in distilled water. The data from this specimen, which also contains ten curies of tritium, will be correlated with that obtained from the lysimeter test specimens. This specimen had a density of 95.4 lb/ft^3 prior to impregnation and 107.7 lb/ft^3 afterwards with 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 composite and a minimization of polymer on the composite's upper surface. The specimen was immersed 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 daily for analysis during the first thirty-two days of leaching, weekly for the next sixteen weeks, and on approximately monthly intervals thereafter. The results of the first 295 days of leaching are shown in Figure 13. The tritium release is expressed in terms of (fraction tritium release) x (V/S) where V is the specimen volume and S is its geometric surface area. For this specimen, (V/S) equals 4.545 cm. Multiplying the fraction tritium release by the factor (V/S) makes the release independent of surface area effects and allows correlation of data with that for other specimen sizes and geometries.

The tritium release as a function of leach time shown in Figure 13 is linear with a rate of 8.61×10^{-5} cm/day. This corresponds to a cumulative tritium fraction release of 5.59×10^{-3} after 295 days of leaching. The projected tritium release for this specimen as a function of leach time is shown in Figure 14 assuming a constant release rate of 8.61×10^{-5} cm/day both with and without tritium decay. By this projection, tritium release from the specimen will be complete after 145 years. The maximum fraction of the initially contained tritium present in the environment is 4.49×10^{-2} after 17.7 years.

Static leaching in distilled water is a more severe test of the rate of tritium release from PITC than is expected in burial. An estimate of this increased severity can be derived by comparing the ratio of the tritium

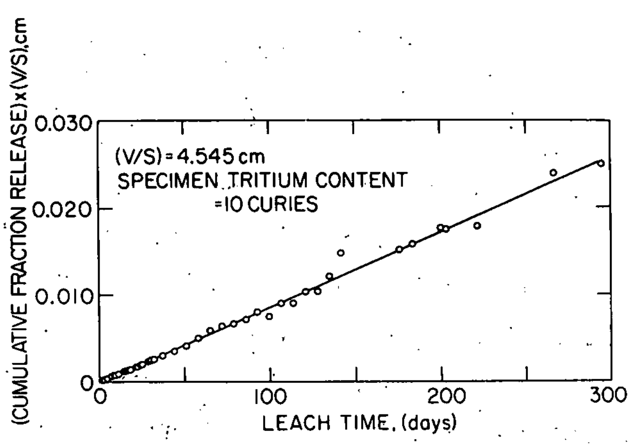


Figure 13. (Cumulative fraction tritium release) x (V/S) versus time for static leaching of the SRL lysimeter testing duplicate specimen (without container) in distilled water.

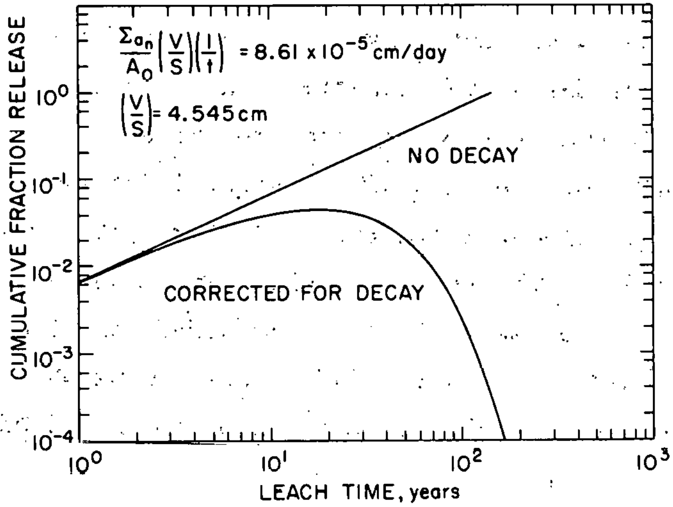


Figure 14. Projected tritium release versus time for static leaching of the SRL lysimeter testing duplicate specimen (without container) in distilled water.

release rate in static leaching with that for lysimeter testing:

$$\frac{8.61\text{x}10^{-5}\ \text{cm/day}}{5.26\text{x}10^{-6}\ \text{cm/day}} = 16.4$$

The average leach rate for lysimeter testing was derived from data for four specimens where the differences in tritium release between specimens were fairly large. Also, the rate for static leaching was based solely on one specimen, which, if the inter-specimen variation in lysimeter testing is an example, may not be truly representative of PITC specimens. As such, this indication of the increase severity for static leaching may have limited significance.

III. PREPARATION OF POLYMER IMPREGNATED TRITIATED CONCRETE BY THE INJECTOR METHOD

While the end-over-end drum tumbling method has been pursued to date and developed to a workable form, it is desirable to produce PITC by a technique which is more directly compatible with the glove box operations in use with high level tritiated aqueous waste. Development of such a technique using an injector to distribute the aqueous tritiated waste in dry cement is continuing.

A schematic diagram of the injector technique is shown in Figure 15. In this process, the cement casting container is filled with dry cement and compacted by vibration. The injector, which is simply a hollow tube containing several orifices along its length through which the aqueous waste is dispersed, is inserted into the dry cement. Tritiated aqueous waste is then introduced into the cement through the injector. Aqueous waste is added to the cement until the waste reaches the external surfaces of the cement as evidenced by dampness. The injector is withdrawn and the cement casting is allowed to cure. After the casting has cured, catalyzed styrene monomer is introduced into the casting container and allowed to soak through the composite. After the casting has been completely permeated by the monomer, the monomer is thermally polymerized. Subsequent to the waste injection, this process is the same as the previously developed end-over-end drum tumbling method.

As shown in Figure 16, this process does not produce a homogeneous composite. Rather the aqueous waste content is higher near the centerline of the composite coincident with the injector and decreases as the surface is approached. The polymer loading, however, is highest near the surface of the composite and decreases as the centerline is approached, although polymer is present throughout the composite. This effectively encapsulates the waste. An apparatus for producing PITC by this technique is shown in Figure 17.

The injector technique was employed to produce a full scale casting, which with present considerations coincides with the 27 gallon size utilized for tritiated waste immobilization at Monsanto Mound Laboratory. In this demonstration, a thirty gallon mild steel drum containing a 27

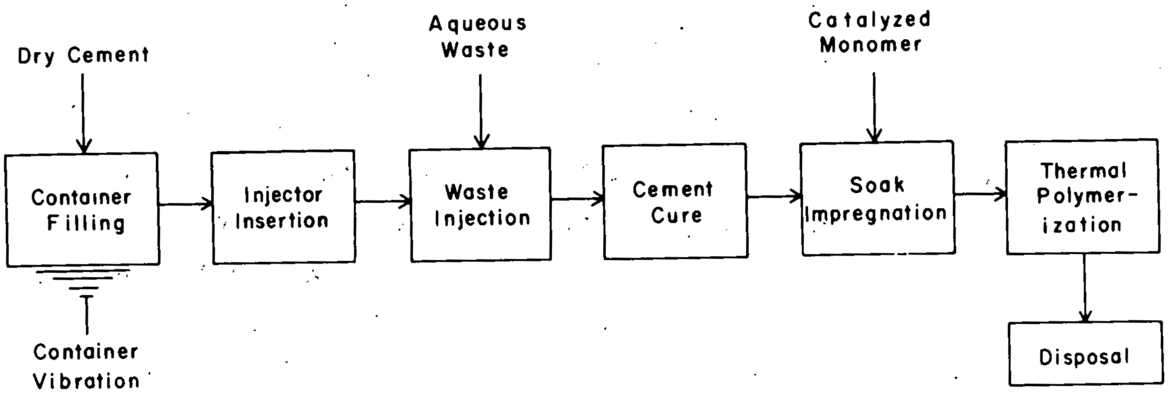
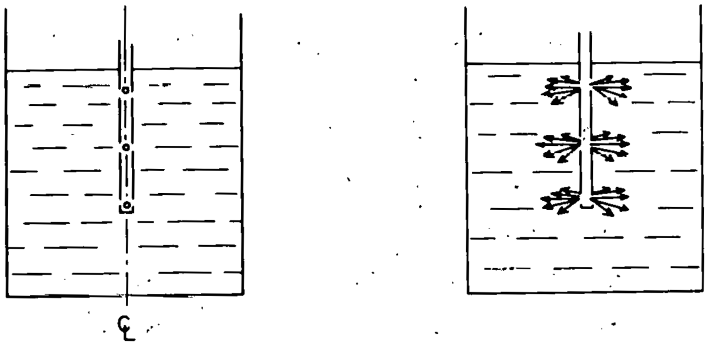
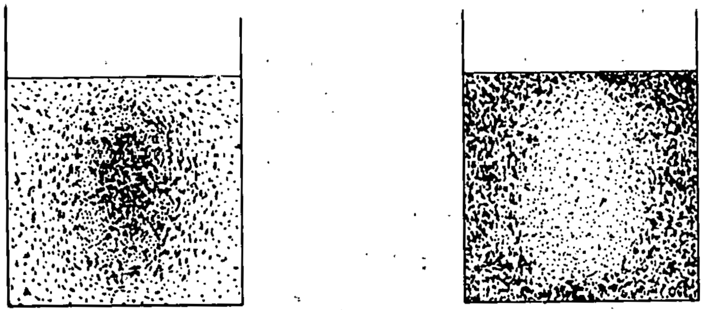


Figure 15. Conceptual fixation of aqueous waste in polymer impregnated concrete by the injection technique.



1. CONTAINER FILLED WITH DRY CEMENT; WASTE INJECTOR INSERTED.

2. INJECTION BEGUN. AQUEOUS WASTE DIFFUSES INTO DRY CEMENT THROUGH INJECTOR PORTS.



3. AQUEOUS WASTE DIFFUSES THROUGH THE CEMENT. THE WASTE CONTENT IN THE CEMENT DECREASES AS THE CASTING SURFACES ARE APPROACHED.

4. AFTER IMPREGNATION, THE POLYMER LOADING OF THE COMPOSITE IS HIGHEST AT THE CASTING SURFACES, EFFECTIVELY ENCAPSULATING THE WASTE. POLYMER IS PRESENT THROUGHOUT THE COMPOSITE.

Figure 16. Fixation of aqueous waste in polymer impregnated concrete by the injector technique.

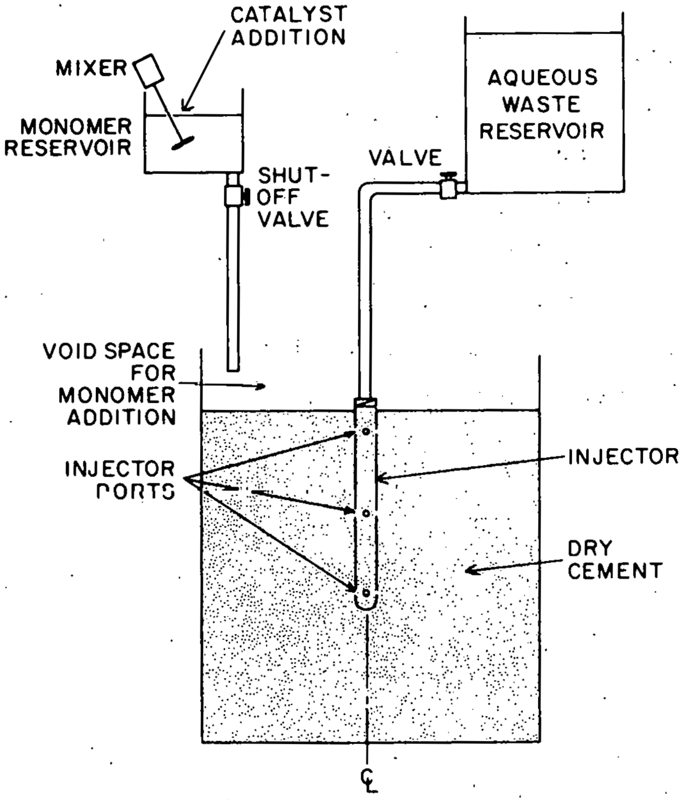


Figure 17. Injector technique for the fixation of aqueous wastes in polymer impregnated concrete.

gallon polyethylene insert was filled to 80% capacity by volume with portland type III cement. The drum was vibrated as the cement was added to aid compaction. This drum filling process was completed in fifteen minutes with the addition of 112.3 kg of dry cement. A glass injector tube with a diameter of 1.2 cm was inserted along the longitudinal axis of the container such that the lower end of the tube was located three inches above the bottom of the container. The injector tube had a 1/16 inch diameter opening at its bottom and four sets of four 1/16 inch diameter openings located equidistant around the circumference of the tube with the lowest set 1/2 inch above the bottom opening and each subsequent set spaced at four inch intervals along the length of the injector. A total of 28.0 kg of water was injected into this casting over a period of two hours. After curing for twenty-four hours in a clamshell heater maintained at 30°C to ensure complete hydration, the casting was impregnated by a soak technique with styrene monomer containing 0.5 wt.% AIBN (2,2' - [azobis-2-methylpropionitrile]) as the polymerization catalyst. The casting was not cooled to ambient temperature prior to the soak impregnation which was allowed to continue overnight. The casting was heated to 50°C for twenty-four hours to polymerize the styrene. The initial casting density of 96.3 lb/ft^3 was increased to 110.9 lb/ft^3 by impregnation with a resultant polymer loading of 15.3%.

The casting was sectioned longitudinally and examined for its physical appearance, integrity, and polymer distribution. The polymer loading was greatest at the external surfaces, however, penetration to the center of the casting was noted. The casting exhibited good integrity and did not crumble or otherwise fall apart during sectioning.

IV. PITC TECHNOLOGY TRANSFER

Mr. Joyce Dauby of Monsanto Mound Laboratory, Dayton, Ohio, spent one week at Brookhaven National Laboratory in September to study the techniques of producing PITC. The areas of discussion and demonstration included the following:

1. Styrene-catalyst behavior
    a. mixing procedures
    b. safety
    c. effect of the catalyst concentration
    d. effect of the polymerization temperature
2. End-over-end drum tumbling method
    a. water/cement ratio
    b. mixing procedure
    c. soak impregnation
    d. polymerization procedure
3. Injector method
    a. water/cement ratio
    b. injector design
    c. injection rates
    d. soak impregnation
    e. polymerization procedure
4. Availability and suppliers of materials for PITC production
5. Review of the Mound facility layout as relevant to the implementation of PITC techniques.

Reference

(1) Colombo, P., et. al., "The Fixation of Aqueous Tritiated Waste in Polymer Impregnated Concrete and in Polyacetylene", BNL-20898, Brookhaven National Laboratory, Upton, New York, October 1975.

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