BNL 21700

DAS

# DEPARTMENT of APPLIED SCIENCE

## TRITIUM STORAGE DEVELOPMENT

Progress Report #7
January-March 1976

Prepared for

NUCLEAR FUEL CYCLE AND PRODUCTION DIVISION

UNITED STATES ENERGY RESEARCH AND DEVELOPMENT ADMINISTRATION
WASHINGTON, D.C. 20545



PROCESS TECHNOLOGY DIVISION, DEPARTMENT OF APPLIED SCIENCE

BROOKHAVEN NATIONAL LABORATORY
UPTON, NEW YORK 11973

INFORMAL REPORT

BNL AUI

# DISCLAIMER

# TRITIUM STORAGE DEVELOPMENT

Progress Report #7
January-March 1976

PROCESS TECHNOLOGY DIVISION

M. Steinberg, Head
P. Colombo, Project Leader

Contributors:

P. Colombo
R. Neilson, Jr.
W. Becker
E. Divis





Brookhaven National Laboratory
Associated Universities, Inc.
under Contract No. E(30-1)-16 with the
UNITED STATES ENERGY RESEARCH AND DEVELOPMENT ADMINISTRATION

## Contents

## SUMMARY

Polymer impregnation has been shown to greatly improve the leach rate of tritiated concrete specimens on a laboratory scale. This technique is proposed for the disposal of high level tritiated aqueous waste. Work has been directed towards the development of a soak impregnation technique for large-scale samples. Four cylindrical specimens of polymer impregnated tritiated concrete (PITC) with approximate dimensions of 27 cm diameter x 28 cm long containing ten curies of tritium each were produced using this technique. These specimens were buried without containers in individual lysimeters at the Savannah River Plant (SRP) and are being monitored to determine the rate of tritium release in the burial environment. To date, no tritium release has been noted in water or air samples taken from these lysimeters. A duplicate PITC sample also containing ten curies of tritium was placed in static leaching in distilled water. After thirty-two days of leaching, the average fraction tritium release rate was $1.82 \times 10^{-5}$ per day.

A technique using an injector to distribute aqueous tritiated waste in dry cement prior to impregnation is under development. This injector method is more compatible with the glove box operations in use with high level tritiated aqueous waste than end-over-end drum tumbling. Initial PITC specimens have been produced using this technique.

## 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 milliliters of tritiated water with a specific activity of 5,000 Ci/ℓ was added to this water to provide a total of ten curies for each specimen. This 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 while the carboy was being 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 contains the formulational data for the four PITC specimens sent to SRP for lysimeter testing. Each specimen contains 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

## 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.

with a density of 106.6±0.2 lb/ft$^3$ with a polymer loading of 16.5±0.3%.

B. Lysimeter Testing at SRP

The four PITC specimens shipped to SRP were buried in individual lysimeters after removal from their shipping containers as shown in Figure 1. 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 specimen is 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 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 is collected weekly with volume and tritium concentration data compiled.

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 24 hours. Figure 2 shows the lysimeter with the top cover in place. Air is 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.

---

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

## FIGURE 1

## SRP Test Lysimeter

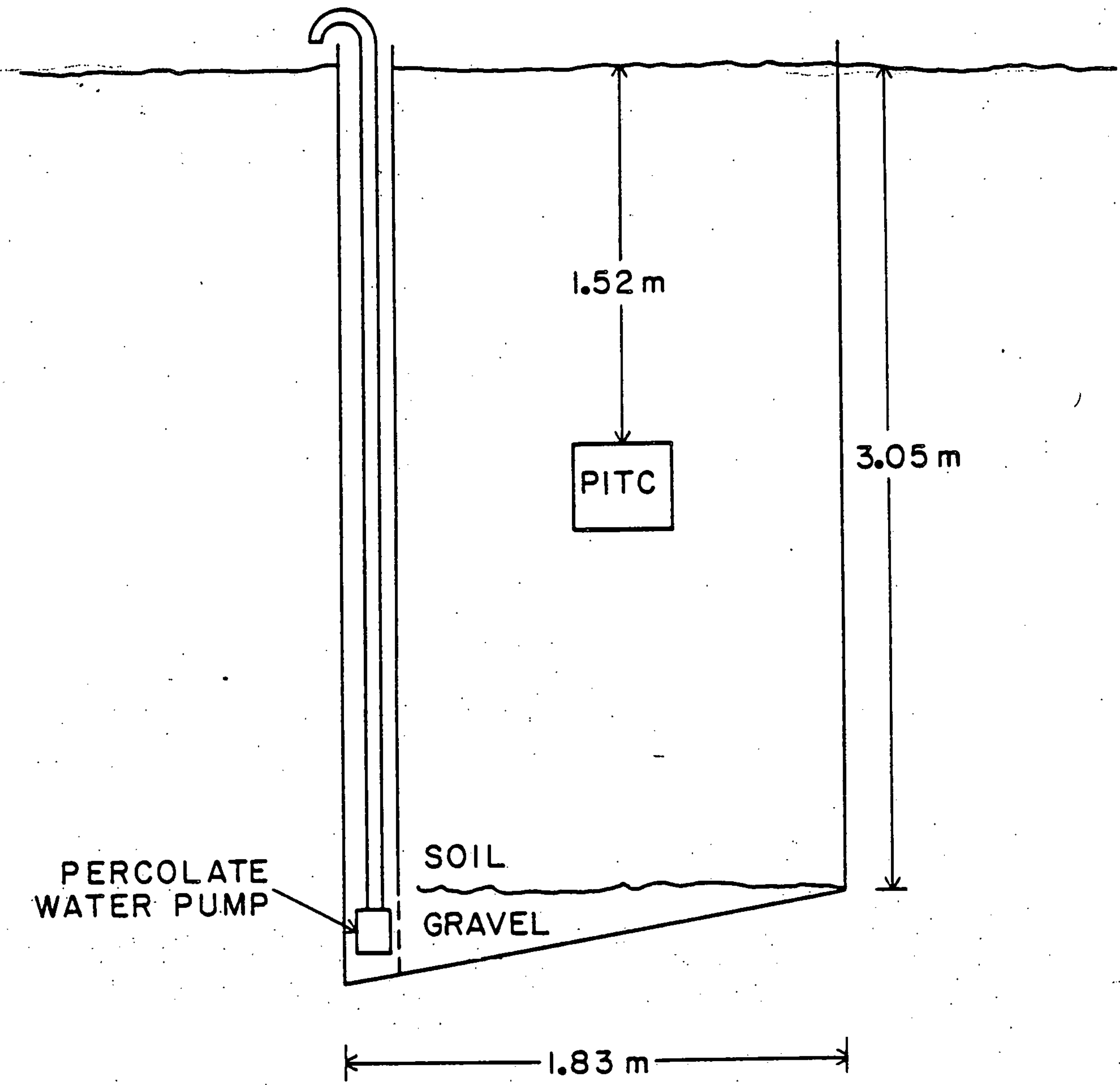
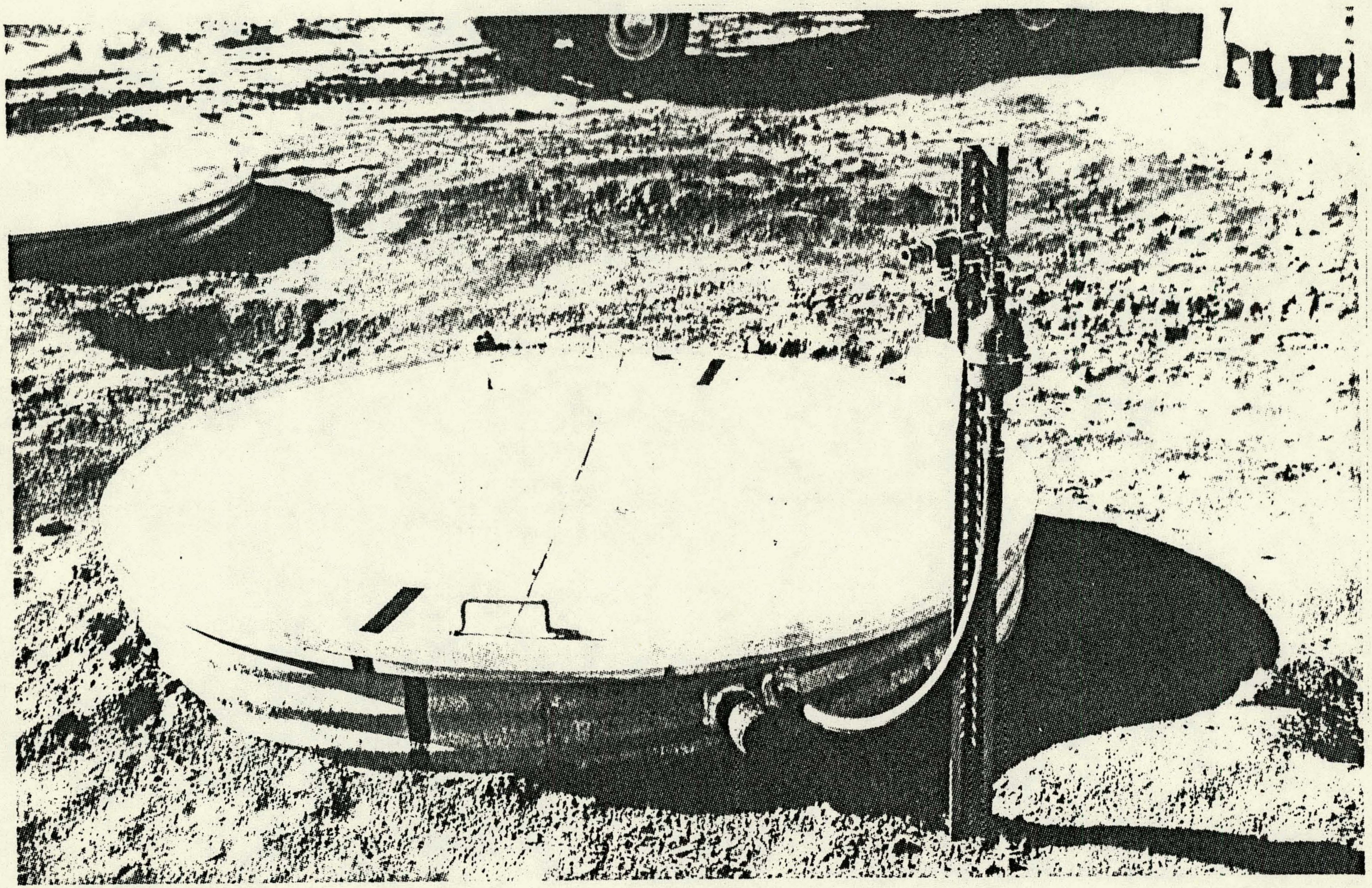


FIGURE 2

Lysimeter with Top Cover in Place
for Air Sampling



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 shipped to SRP in a nylon sling, wrapped in a polyethylene bag, and placed into a 30 gallon drum. 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.

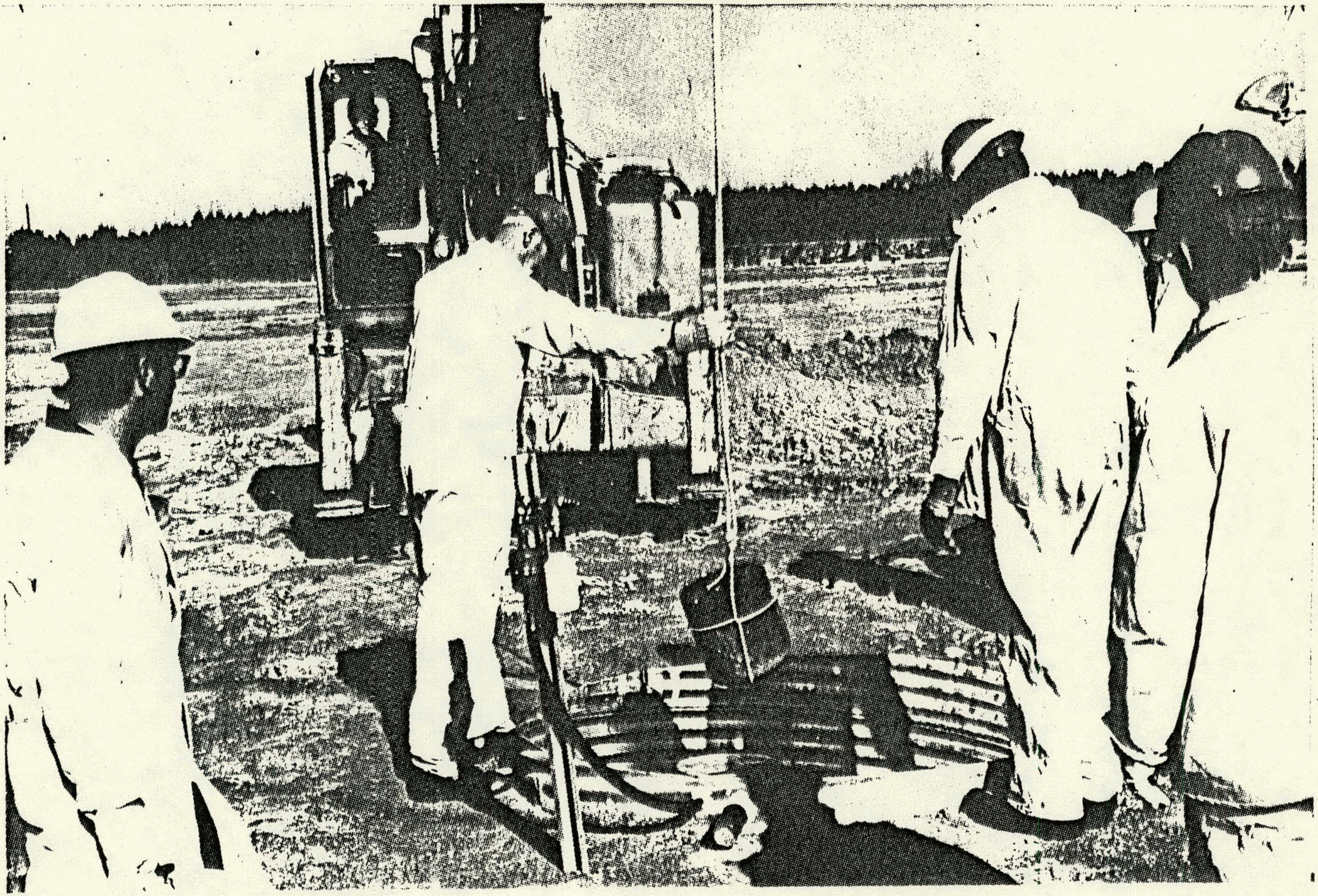
The ten curie PITC specimens were buried in their individual test lysimeters on February 24, 1976. To date there has been no tritium release above background noted in either water or air samples from any of the lysimeters.

C. Leach Testing

A PITC specimen of the same dimensions and formulation as those in lysimeter testing at SRP is being statically leached 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 13.0%. The lower polymer loading in this specimen as compared

FIGURE 3

PITC Specimen Being Lowered into Lysimeter



to the lysimeter test specimens results from the higher initial density of the composite and a minimization of the polymer on the composites 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 by liquid scintillation counting. The results of the first thirty-two days of leaching are shown in Figure 4. The tritium release is expressed in terms of (fraction tritium release)·(V/S) where V is the specimen volume and S is its geometric surface area. For this sample, (V/S) equals 4.545 cm so that the cumulative fraction tritium release rate after thirty-two days is $1.82 \times 10^{-5}$ per day.

II. Preparation of PITC by the Injector Technique

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. Such a technique using an injector to distribute the aqueous tritiated waste in dry cement is in development.

A schematic diagram of the injector technique is shown in Figure 5. 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

FIGURE 4

STATIC LEACHING OF THE SRL LYSIMETER TESTING DUPLICATE SPECIMEN IN DISTILLED WATER. (SPECIMEN CONTAINS TEN (10) CURIES OF TRITIUM.)

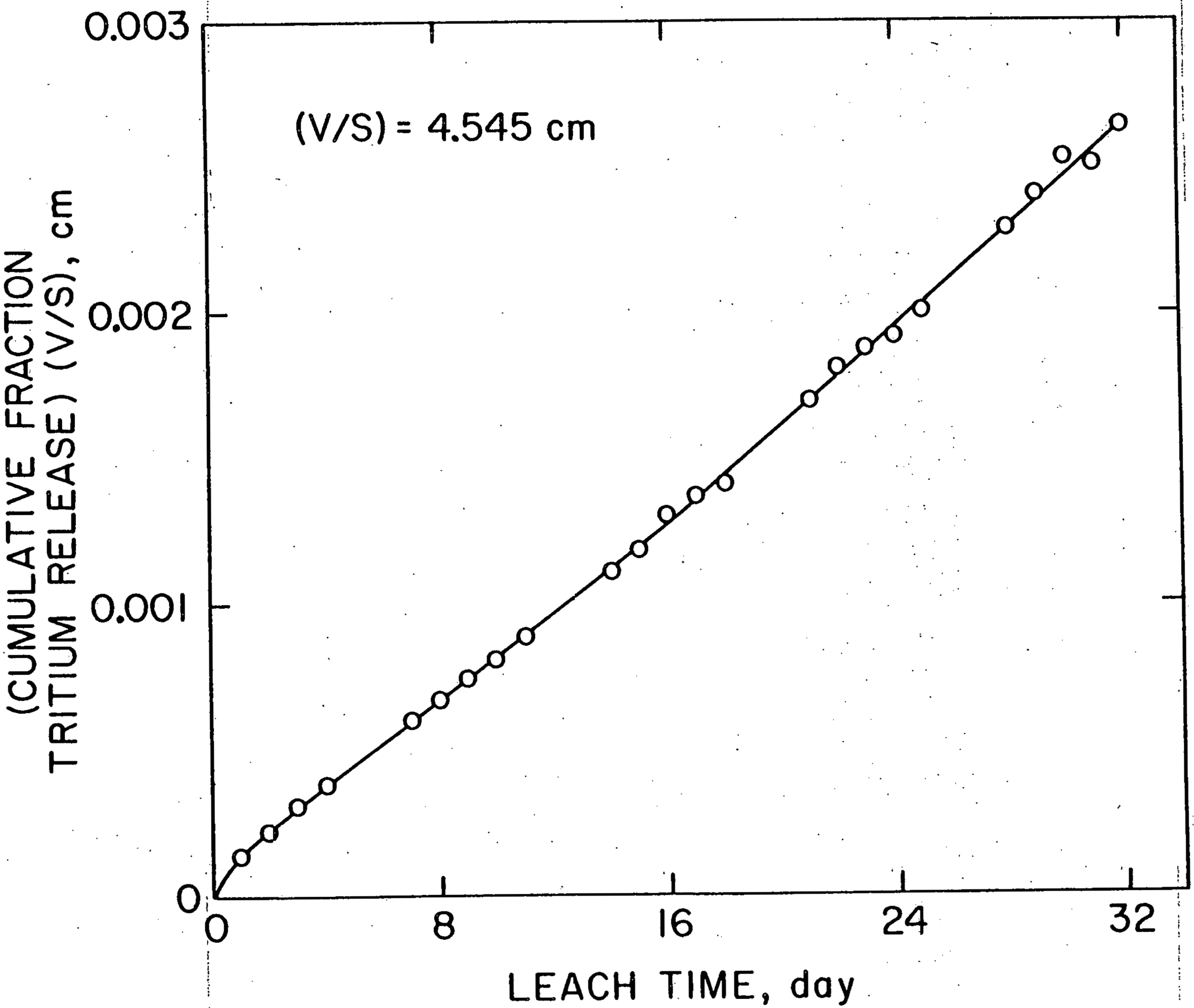
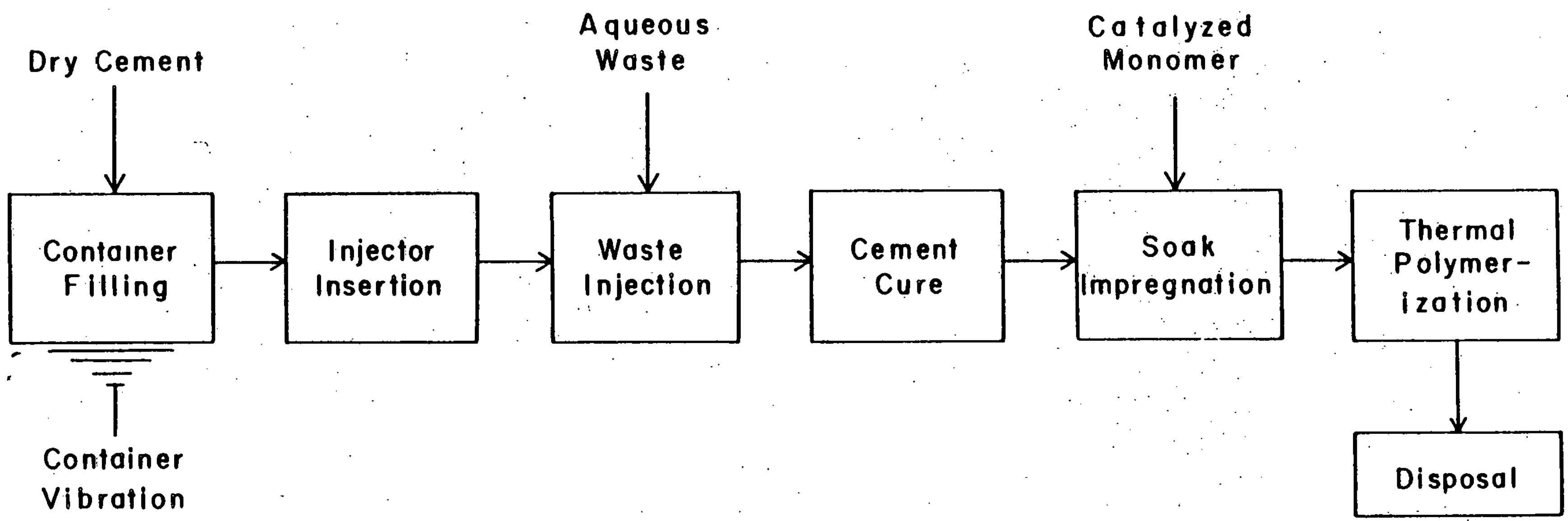


FIGURE 5

CONCEPTUAL FIXATION OF AQUEOUS WASTE IN POLYMER IMPREGNATED CONCRETE BY THE INJECTION TECHNIQUE



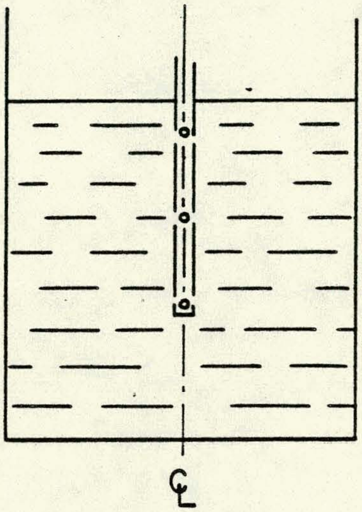
into the cement through the injector. Aqueous waste is added to the cement until the waste reaches the external surfaces of the cement as evidenced by dampness. The injector is withdrawn and the cement casting is allowed to cure. After the casting has cured, catalyzed styrene monomer is introduced into 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 6, 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 surfaces 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 7.

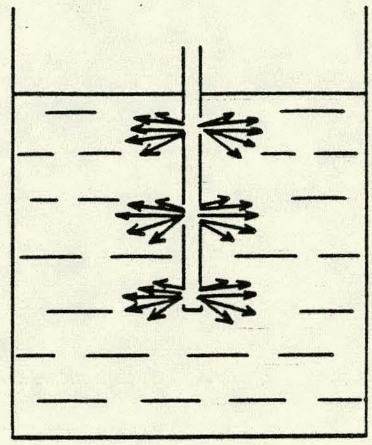
Initial experiments used a battery jar with a diameter of 11.5 inches to which dry cement was added under vibration to a height of ten inches. A 1.2 cm I.D. glass tube with one end fused down to a 1/16 inch diameter opening and four 1/16 inch diameter openings located equidistant about the circumference of the tube, one inch above the end opening was used as the injector. The injector was placed along the centerline of the battery jar with its end opening five inches above the bottom of the battery jar.

FIGURE 6

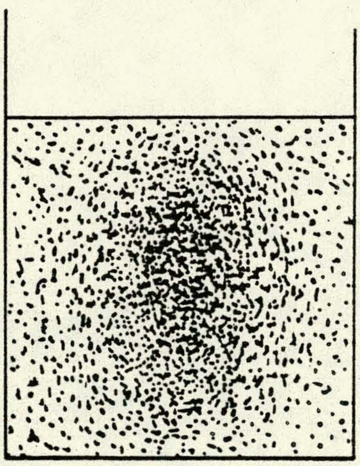
## FIXATION OF AQUEOUS WASTE IN POLYMER IMPREGNATED CONCRETE BY THE INJECTOR TECHNIQUE



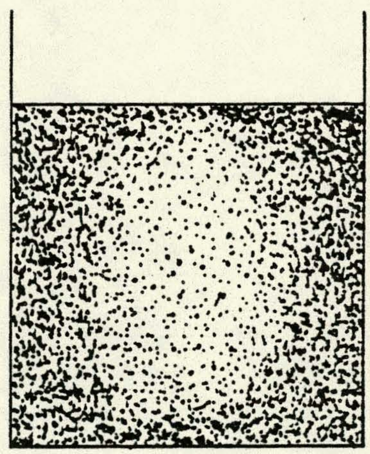

1. CONTAINER FILLED WITH DRY CEMENT; WASTE INJECTOR INSERTED.



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



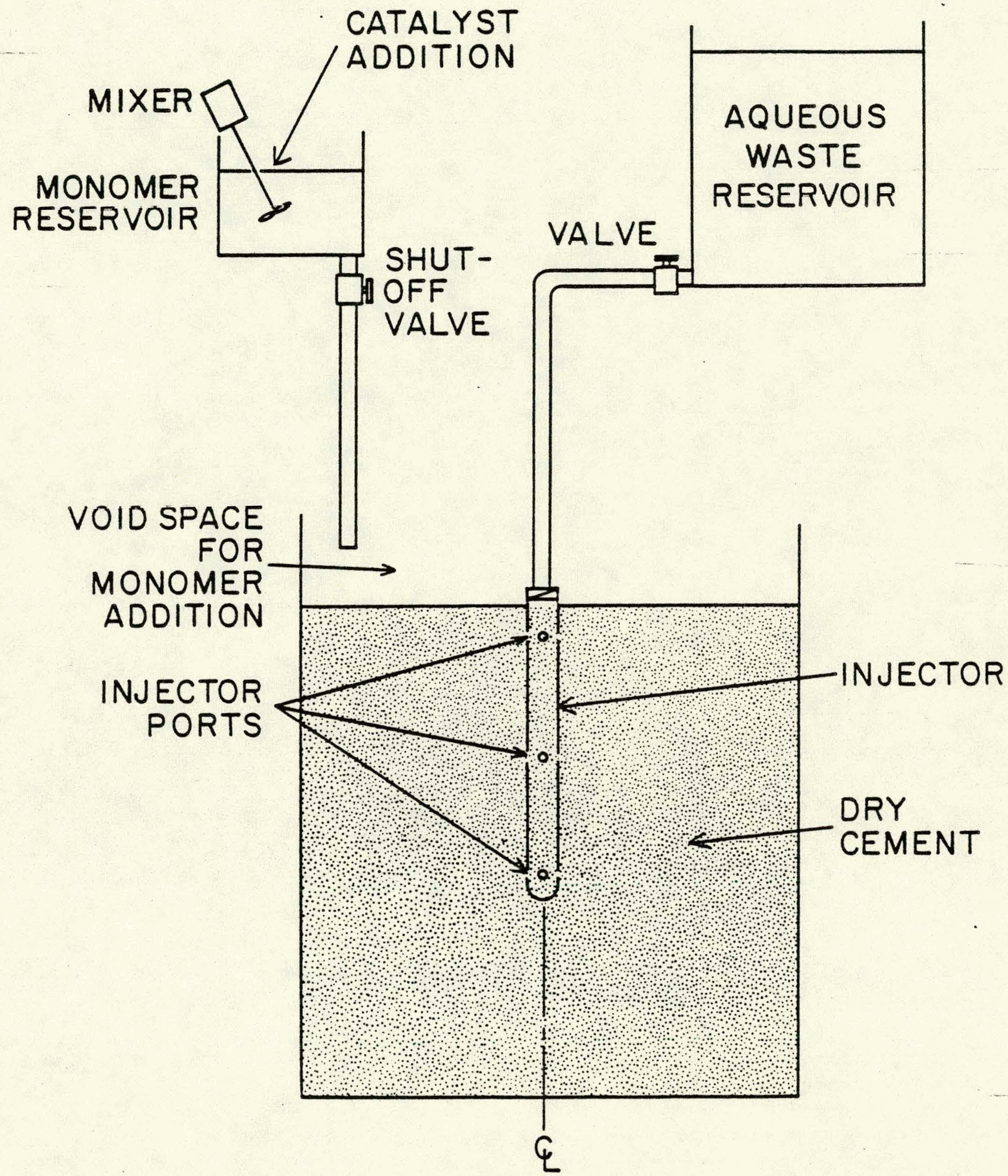
3. AQUEOUS WASTE DIFFUSES THROUGH THE CEMENT. THE WASTE CONTENT IN THE CEMENT DECREASES AS THE CASTING SURFACES ARE APPROACHED.



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 7

INJECTOR TECHNIQUE FOR THE FIXATION
OF AQUEOUS WASTES IN
POLYMER IMPREGNATED CONCRETE



In the first experiment, 4.6 kg of water, providing a water to cement ratio of 0.22, was added at an average rate of 0.044 kg/min under a constant head of 24 inches of water. Injection was completed in one hour and forty-five minutes. The resultant casting had a density prior to impregnation of 94.6 lb/ft$^3$ while the composite density after impregnation was 118 lb/ft$^3$ with a polymer loading of 24.7%. Increasing the water to cement ratio to 0.25 and decreasing the rate of water addition provided a better water distribution and produced a composite with a density before and after impregnation respectively of 95.7 lb/ft$^3$ and 108 lb/ft$^3$ with a polymer loading of 13.2%. Work is continuing to optimize injector design and to determine the water and polymer distributions in the composites. This technique will be scaled up to a thirty gallon casting size.

## 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.

DISTRIBUTION

Mr. George Abell
Monsanto Research Corporation
Mound Laboratory
Miamisburg, Ohio 45352

Dr. Victor Benaroya, Chief
Effluent Treatment Systems Branch
Directorate of Licensing
U. S. Atomic Energy Commission
Washington, D.C. 20545

Dr. C. A. Burchsted
Oak Ridge National Laboratory
P. O. Box X
Oak Ridge, Tennessee 37830

Dr. L. L. Burger
Pacific Northwest Laboratory
Battelle-Northwest
325 Bldg.
Richland, Washington 99352

Dr. W. H. Carr
Barnwell Nuclear Fuels Plant
Allied-Gulf Nuclear Services
P. O. Box 847
Barnwell, South Carolina 29812

Dr. F. E. Coffman
Division of Operational Safety
U. S. Atomic Energy Commission
Washington, D. C. 20545

Dr. J. J. Cohen
Lawrence Livermore Laboratory
University of California, Lawrence
P. O. Box 808
Livermore, California 94550

Dr. John Dempsey
Division of Waste Management
and Transportation
U. S. Atomic Energy Commission
Washington, D. C. 20545

Dr. J. P. Duckworth
Plant Manager
Nuclear Fuel Services
P. O. Box 124
West Valley, New York 41471

Dr. Herschel W. Godbee
Holifield National Laboratory
P. O. Box X
Oak Ridge, Tennessee 37830

Dr. C. J. Kershner
Mound Laboratory
Miamisburg, Ohio 45342

Dr. E. H. Kobisk
Oak Ridge National Laboratory
P. O. Box X
Oak Ridge, Tennessee 37830

Dr. L. T. Lakey
Exxon Nuclear Company
2101 Horn Rapids Road
Richland, Washington 99352

Dr. K. H. Lin
Oak Ridge National Laboratory
P. O. Box X
Oak Ridge, Tennessee 37830

Dr. W. H. McVey, Chief
Fuel Cycle Branch
Division of Reactor Research
and Development
U. S. Atomic Energy Commission
Washington, D. C. 20545

Mr. Emil Mershad
Monsanto Research Corp.
Mound Laboratory
Miamisburg, Ohio 45342

Dr. B. C. Musgrave
Allied Chemical Corporation
550 2nd Street
Idaho Falls, Idaho 83401

DISTRIBUTION (CONTINUED)

Dr. R. I. Newman, Vice President
Barnwell Nuclear Fuels Plant
Allied-Gulf Nuclear Services
P. O. Box 847
Barnwell, South Carolina 29812

Dr. D. A. Orth
Savannah River Plant
Bldg. 773-A, Room 117
Aiken, South Carolina 29801

Dr. H. E. Parker
International Atomic Energy Agency
Karntneering 11, P. O. 590
Vienna, Austria

Dr. D. T. Pence
General Atomic Company
P. O. Box 81608
San Diego, California 92138

Dr. Martin Steindler
Argonne National Laboratory
Bldg. 205
9700 South Cass Avenue
Argonne, Illinois 60439

Dr. N. Thomasson
Environmental Protection Agency
401 M Street, S.W., Room 910
Washington, D. C. 20460

Dr. L. E. Trevorrow
Argonne National Laboratory
9700 South Cass Avenue
Argonne, Illinois 60439

Mr. A. K. Williams
Allied General Nuclear Services
Barnwell, South Carolina 29812

Dr. G. Winsor
Manager Safety and Analytical Ser.
Midwest Fuels Recovery Plant
Morris, Illinois 60450

Brookhaven National Laboratory Distribution

Joseph M. Hendrie
Meyer Steinberg
Peter Colombo
Jacob Pruzansky
Robert Neilson
Walter Becker
B. Manowitz
John Jewett - ERDA
Leonard Belkin - ERDA