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Tritium Waste Control:

January-March 1978

May 30, 1978

MASTER

MOUND FACILITY
Miamisburg, Ohio

operated by
MONSANTO RESEARCH CORPORATION
a subsidiary of Monsanto Company

for the
U. S. DEPARTMENT OF ENERGY

Contract No. EY-76-C-04-0053

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Foreword

The work in the first, third, fourth and fifth sections is funded by 189C ALO219A. The remaining sections are work related to Tritium Waste Control but not directly funded by ALO219A.

Previous documents in this series are:

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MLM-2399	MLM-2502

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CATALYTIC EXCHANGE DETRITIATION STUDIES 5

The combined electrolysis-catalytic-exchange pilot system was modified to improve the reliability of the unit for continuous operation. An experimental run for 60 consecutive hours using a single catalytic exchange column was made to estimate values of HTU and HETP for the pilot system. The calculated values were in agreement with existing data from a bench-scale system.

CRYOGENIC DISTILLATION. 8

Further experiments were performed with the cryogenic hydrogen isotope distillation system, this time using H_2-HT mixtures. A mixture containing ~250 Ci/m^3 of HT in H_2 was stripped to less than 0.1 Ci/m^3, while a product of 1100 Ci/m^3 was recovered.

ELECTROLYSIS OF TRITIATED WATER 10

Two experiments were successful in separating gaseous hydrogen containing tritium from tritiated water. Initial tritium concentrations of the water were approximately 1 and 10 Ci/cm^3. The solid polymer electrolyte (SPE) developed a leak during a third experiment with 150 Ci/cm^3 water. Replacement parts have been obtained and the cell is presently being repaired.

DETERMINATION OF RADIOLYTIC DAMAGE TO H_2-H_2O EXCHANGE CATALYST 13

Radiolytic damage tests of a hydrophobic exchange catalyst being used in the development of a process to recover tritium from tritiated waste water are reported.

Upon exposure to water containing 10% T_2O the catalyst appeared to sustain moderate damage in 150 days and severe damage at 210 days. Catalyst pellets used in tests designed to simulate the H_2-H_2O exchange process are being decontaminated in preparation for sending them to Chalk River Nuclear Laboratories for catalyst activity tests.

FIXATION OF AQUEOUS TRITIATED WASTE IN POLYMER - IMPREGNATED CONCRETE 18

Triplicate samples of cement, cement-plaster (1:1 ratio by weight), and cement-plaster (1:1 ratio by volume) were injected with 386 Ci of tritium, cured for five days, and then impregnated with catalyzed styrene monomer. After polymerization, the samples were put into a test program to measure the tritium release. No differences were noted from the data on these groups until the polyethylene bottle was removed. In one sample, 144 Ci of tritium of the original amount had moved from the concrete. This is 70 times greater than the 2 Ci released from similar samples still in polyethylene bottles.

MANAGEMENT OF HIGH SPECIFIC ACTIVITY TRITIATED LIQUID WASTES 24

The tritium release study of actual burial packages is continuing. Two additional drums have just been added to the study. These contain octane waste, and now all types of liquid waste packaged are represented in the test. The average daily fractional release from six packages containing oil or water waste is 4×10^{-7}.

Catalytic exchange detritiation studies

M. C. Embury, T. K. Mills and M. L. Rogers

Background

In the operation of a light water reactor, all radioisotopic contaminants except tritium can be removed from the effluent stream by ordinary chemical and physical methods. Tritium removal in this case requires special considerations. Isotopic separation processes, therefore, need to be developed for removing tritium from contaminated water streams.

The objectives of this study are to:

1. Determine technical and economic factors of HT/H_2O exchange as a process for treating tritium contaminated water;

2. Determine suitability of hydrophobic exchange catalysts for use in water detritiation systems; and

3. Through pilot-scale testing, establish design criteria for detritiation systems capable of meeting the tritium control needs of DOE site operations and the U. S. power reactor industry.

Limited operation of the Englehard experimental system indicated that the principles involved in the catalytic-exchange process are valid. Use of the system has been discontinued, however, because the experimental error incurred was too large for further operation to be of value.

A preliminary economic evaluation was made of the HT/HTO catalytic detritiation stripping process as it might apply to a five metric ton/day nuclear fuel reprocessing plant.

A pilot Combined Electrolysis Catalytic Exchange (CECE) system was designed and built using a hydrophobic precious metal catalyst developed by AECL at Chalk River and a solid polymer electrolyte electrolysis cell built by General Electric Company.

This system was used in an experiment to prove that the process does indeed strip tritium from gaseous hydrogen and concentrate it in water. However, several deficiencies were found in the system and modfications were undertaken to correct them.

The system was operated intermittently over a two-month period without major equipment failure. Equilibrium conditions were reached in the stripping section midway through the test schedule.

Accomplishments

The basic CECE system described in previous reports [1,2] was modified to upgrade the reliability of the process equipment and to provide fail-safe measures against damage to the system during continuous operations. Changes to process equipment include the installation of low-flow capacity, positive-displacement pumps on the liquid lines servicing the two exchange columns. Inline filters were installed in the liquid lines from the bottom of each column to remove any particulate matter from the exchange catalyst. Flow alarms and switches were installed on the electrolysis system to prevent damage to the cells in the event of low flow or no flow to these units. With the addition of the flow switches to the electrolysis system, the elec-

trolysis cells have automatic protection against excess temperature and pressure, overvoltage, and inadequate water flow. The venting system in the electrolysis section was also modified to prevent excess pressure buildups causing an overflow of liquid water into the air detritiation system.

This modified CECE system was run to determine the Height of a Transfer Unit. The HTU is defined by the equation

$$H_{og} = \frac{\tilde{G}}{K_{\tilde{y}} a}$$

where: H_{og} = HTU based on the overall gas phase mass transfer coefficient (cm)

$\tilde{G}$ = molar flow rate of hydrogen (g-moles/cm^2-sec)

$K_{\tilde{y}}$ = overall mass transfer coefficient based on gas phase composition (g-moles/cm^2-sec)

a = interfacial area per unit volume of packed bed (cm^2/cm^3)

The heighth of a separating device is related to HTU by

$$z = H_{og} \frac{y_0 - y_1}{(y-y^*)_{lm}}$$

where: z = height of packed bed (cm).

y_0 = mole fraction of HT in the gas phase at the enriched end of the bed.

y_1 = mole fraction of HT in the gas phase at the lean end of the bed.

y^* = mole fraction of HT in the gas phase in equilibrium with the liquid phase mole fraction of HTO,X.

$(y-y^*)_{lm}$ = logarithmic mean-concentration-difference driving force.

The relationships between the above concentrations and the equilibrium and operating lines can be seen in Figure 1. Since the equilibrium relationship for the hydrogen-water exchange reaction is known, a graph similar to Figure 1 may be constructed for any set of operating conditions by measuring the gas and liquid flow rates and the concentrations in each stream at one end of the column. An experimental value of HTU can then be determined by measuring either the gas or liquid concentration at the other end of the column.

For these experiments a special flow configuration with only one exchange column was used. The flow diagram for the experimental system is shown in Figure 2. The use of this system, which contained no intermediate feed and no reflux, allowed the simple calculation of HTU presented above. In addition, one column operation simplified the task of controlling the process and reduced the number of possibilities for equipment failure.

Tritiated water at approximately 15 mCi/liter was used as a feed solution to the electrolysis section. The hydrogen produced by water electrolysis formed the inlet gas stream to the column. The entering liquid at the top of the column was distilled water at 0.008 μCi/liter. By maintaining constant concentration of tritium in the inlet streams, the column was expected to equilibrate within a few hours [3]. Water samples from the outlet liquid stream and electrolysis section were collected every 4 hr. The outlet gas stream was diverted through a catalytic recombiner to obtain a liquid sample for scintillation counting. The liquid flow rate was manually controlled using a metering pump and rotameter, whereas the gas flow was

maintained by controlling the current to the electrolysis cells. The experimental system was operated in this manner for 60 consecutive hours.

Column operations did not stabilize to a final steady-state condition because of changes in the liquid flow rate and a significant increase in the tritium concentration in the electrolysis section. However, midway through the run, the system leveled out for 12 hr, and the data from the end of this period were used to calculate a value of HTU. For a liquid flow rate of 4.5 cm^3/min and a gas flow rate of 7400 Std cm^3/min at 32°C and 1.7 atm, a value of 68 cm (2.2 ft) was calculated for H_{og}. The resulting value of $K\tilde{y}a$ was approximately 65% of that obtained from the bench-scale data by Butler.[3]

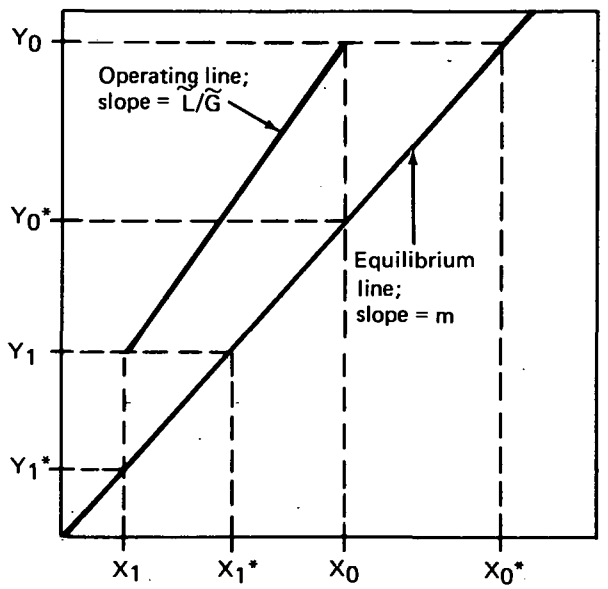

FIGURE 1 - Graph of contacting dilute solutions.

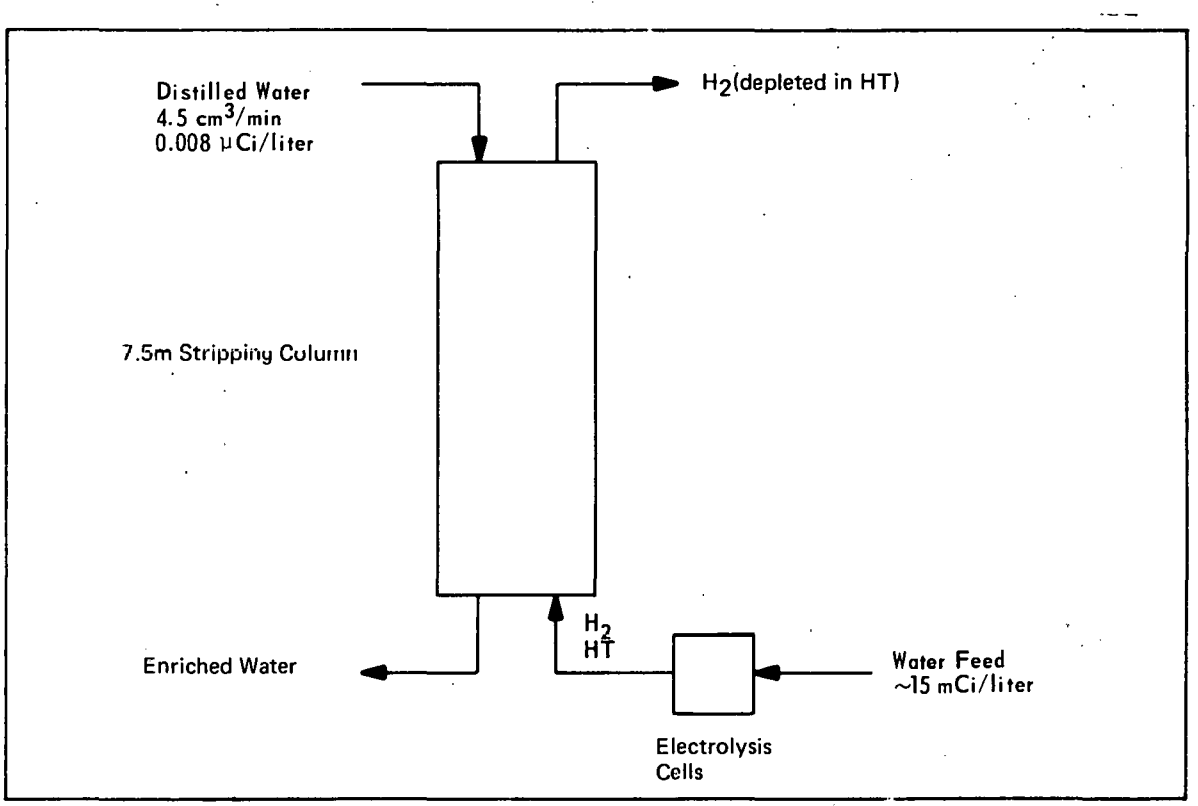

FIGURE 2 - Combined electrolysis catalytic exchange system for HTU determination.

The formulas used above to calculate H_{og} are valid only for chemical systems with linear equilibrium and operating lines and negligible heat effects due to absorption or chemical reaction. In such instances, the Height Equivalent to a Theoretical Plate (H.E.T.P.) may be obtained from H_{og} by the following equation

$$\text{H.E.T.P.} = H_{og}\left[\frac{\ln\ (m\tilde{G}/\tilde{L})}{(m\tilde{G}/\tilde{L}) - 1}\right]$$

where: H.E.T.P. = height equivalent to a theoretical plate (cm)

$\tilde{G}$ = molar flow rate of hydrogen (g-moles/cm^2-sec).

$\tilde{L}$ = molar flow rate of liquid water (g-moles/cm^2-sec).

m = slope of the equilibrium line ($y^*=mx$).

Using this conversion an H.E.T.P. of 38 cm (4.5 ft) was obtained.

Future plans

The experimental system will be operated to obtain data at different flow conditions for comparison with existing bench-scale values of H_{og} and $K\tilde{y}a$. Future tests are scheduled for automatic control via microprocessor. The complete CECE system will be operated to determine the overall separation capability of the two columns in series following the one-column experiments.

Cryogenic distillation

W. R. Wilkes

Background

The most economical method of enriching hydrogen isotopes of high concentrations, e.g., more than a few percent of deuterium or tritium, is by cryogenic distillation. The reason for this is that the vapor pressure ratios of the isotopes are large, of the order of 1.5 to 3, and the isotopes are much more dense in the liquid state than in the gaseous state required for another common separation method, gaseous thermal diffusion. Thus, large amounts of space and high electrical power inputs, as are required for thermal diffusion, can be avoided in a distillation system.

A cryogenic distillation column was built and operated a few years ago to study hydrogen isotope distillation. This column was constructed in a laboratory which is unsuitable for tritium work, so a new column was constructed in the Tritium Effluent Control Laboratory.

Preliminary measurements of stage height and maximum vapor velocity were performed using a 10 cm long x 6 mm diameter packed column containing a mixture of H_2, HD, and D_2. Further stage height measurements were made with H_2-HD mixtures in a 50-cm long column. These results generally confirmed those of the earlier experiments, although stage heights were somewhat larger, being on the order of 1.8 to 2.6 cm.

Accomplishments

Further study of the experiments of the previous quarter revealed some minor errors in the way that stage heights were determined. The net effect of these errors is not great, however, so the results remain largely unchanged.

First, the Fenske-Underwood equation was used in its standard form, appropriate

for infinite reflux

$$N+1 = \ln(X_{H_2 top} X_{HD\ bottom}/X_{HD\ top} X_{H_2 bottom})/\ln \alpha$$

where α is the relative volatility, X is the concentration of a component, and N is the number of stages, exclusive of the boiler or condenser. It is usually assumed that the boiler acts as a separate stage, whereas the condenser does not. In the present apparatus, one product leaves the condenser as a vapor and the other leaves the boiler as a liquid, hence the boiler and condenser each constitute one stage. Thus, N+1 in the above equation should be replaced by N+2. This has the effect of making N smaller (or the H.E.T.P. larger) for a given set of product concentrations. The error is larger for short columns, hence the corrected values for the short column are brought closer to the corrected values for the long column. In the case of a separation of H_2 and HD at 1500 torr in the 50-cm column, with an enrichment factor of 2.7×10^5, the HETP estimated from the Fenske-Underwood equation is raised from 1.76 to 1.83 cm.

A second error, which had been known beforehand, is the use of vapor pressure ratios instead of true volatility ratios for α. The computer program does not yet have a provision for determining α by means other than vapor pressure ratios. In fact, volatility ratios for most hydrogen isotopic combinations have never been measured and may not be measurable without an unreasonable amount of effort. Fortunately, these errors are usually small in moderately concentrated mixtures. In weak mixtures, such as HD dissolved in H_2, however, the effect can be substantial. The true volatility ratio for H_2/HD in an H_2-rich mixture is about 0.95 times the vapor pressure ratio in the limit of pure H_2. The effect of this correction is to <u>increase</u> the number of stages required for a given separation. At the HD-rich end of the column, however, the relative volatility for H_2/HD is about 5% <u>larger</u> than the ideal vapor pressure ratio, creating a correction in the opposite direction. In the previous experiments, the major portion of the distillation occurred in mixtures which were rich in H_2, hence a small (5%) decrease in calculated stage height might be expected if true volatility ratios had been used in the calculations.

Finally, it had been observed in experiments on the 50-cm column that there appeared to be a high degree of separation near the top of the column and near the bottom, but not near the middle. The column was repacked to prevent this, but in later runs, the problem recurred. Discussions with Dr. W. M. Rutherford revealed that it is characteristic in a separation system for the first evidence of separation to occur at the ends of the system and then to spread toward the middle of the system. Thus, it is probable in the cases where samples of the two intermediate taps were measured, that insufficient time had been permitted for the column to come to a true steady state. Had this been done, larger separation factors would have been measured, with corresponding decreases in HETP.

As was planned earlier, a new thermometer was installed at the column midpoint. Its resistance-temperature characteristic, like that of the previous one, was substantially different from the ones used earlier. Rather than attempt to duplicate the earlier R-T characteristic, a new calibration curve will be prepared for the existing thermometer.

After the runs with H_2-HD mixtures, a few runs were performed with HD-D_2 mixtures and then an H_2-HT mixture was tried. For the H_2-HT experiments, all concentration measurements were made with a tritium monitor, as the HT concentration is far below the sensitivity of the chromatograph. A mixture of 1 Ci in roughly four liters of H_2 was prepared and allowed to remain overnight so that virtually all the tritium would be in the form of HT. The mixture concentration was roughly 190 ppm HT (about 240 Ci/m^3) so that the T_2 concentration should be $<10^{-8}$. This mixture was put into the still, and shortly afterward, with a boiler power of 1 W and top and bottom flows of 20 std. cm^3/min each (reflux ratio = 72), the concentration in the bottom stream reached 1100 Ci/m^3. The tritium concentration monitor was then valved into the top product (low level HT) stream. Within 20 min., the tritium level on the monitor had fallen to 0.3 Ci/m^3 and after another hour, it reached an indicated level of zero. As the resolution of the monitor is only 0.1 Ci/m^3, it is only possible to be certain the level was less than 0.1 Ci/m^3.

These concentrations correspond to a separation factor of 11,000 and about 12.2 stages if N is determined from the Fenske-Underwood equation with a relative volatility of 1.92 [4]. By using the computer simulation, N is determined to be 14 stages. As the computer program uses vapor pressure ratios rather than relative volatilities, this value of N is too small. Using $\alpha = 1.92$ instead of the value 2.26 which is in the program would increase N to 18 stages for an HETP of 2.8 cm.

This rather large discrepancy between the 12.2 stages calculated from the simple equation and the 18 determined by simulating the column arises from a poor choice of experimental conditions and the fact that the Fenske-Underwood equation calculates only the minimum number of stages. In order to optimize the column performance, the bottom flow should have been very much smaller than the overhead flow (say 10^{-3} to 10^{-4} times the latter) rather than equal to it. Because this was not done, mass balance requirements permitted only a small degree of enrichment of HT in the lower end of the column. This was evident in the results of the computer simulation where it could be seen that almost no separation occurred between the feed and the boiler.

Future plans

The HT tests will be run again with much lower bottom flow rates so that greater enrichments can be obtained. If possible, a second, more sensitive tritium concentration monitor will be installed in the overhead product line. This will increase the range of concentrations that can be measured and shorten the time required to measure the product concentrations.

Electrolysis of tritiated water

R. E. Ellis

Background

At Mound Facility tritiated water is produced by various activities involving handling of tritium. The tritium content of such water is often high enough to be economically used as feed for existing gaseous hydrogen isotope separation processes. The hydrogen must first be separated from the oxygen by decomposition of

the water molecule. Electrolysis is one of the more straightforward methods for doing this.

Previous work in this area includes a single successful experiment using a solid polymer electrolyte (SPE) cell [5]. Subsequently, a new, higher capacity SPE cell was purchased from General Electric Company and an experimental system was built around it to further test the process [6].

Accomplishments

A schematic drawing for the tritiated water electrolysis system was presented in a previous report [6] and is included in this report (Figure 3) for reference. The basic configuration of the system was not changed when the system was installed in the glovebox. Operation of the system was first checked using nontritiated water, then tritiated water of various tritium concentrations was used in three experiments.

In normal operation, water is transferred via argon pressure from a storage vessel connected to the water inlet port of the system. The water is allowed to fill the oxygen-water reservoir and the oxygen side of the cell. Capacity of the oxygen-water side of the system is approximately 70 cm^3, but a normal charge is limited to 60 cm^3 to prevent overflow into the ERS (Effluent Recovery System) line. After the water is in the oxygen-water reservoir, the pump is turned on and the valves are opened to permit circulation of the water through the oxygen side of the cell. The flow rate must be at least 50 cm^3/min (as indicated by the flow meter) to provide sufficient cooling for proper cell operation.

The valves are then set to allow the hydrogen to flow into the storage tank and the oxygen to flow to the ERS line. The cell is then turned on and current and voltage settings on the power supply are adjusted. Differential cell pressure is kept low (never more than 100 psi) with the hydrogen pressure slightly higher than the oxygen during electrolysis. This is desirable because a check valve located in the hydrogen line between the system and storage tank will limit backflow of hydrogen in the event of SPE rupture. Operating with a positive differential on the hydrogen side also prevents oxygen contamination of the hydrogen in the storage tank.

Electrolysis is continued until either the hydrogen side fills with water [the reason for this is discussed in a previous report [5] or the oxygen side empties. Both conditions are sensed by the ultrasonic level detectors with a margin of several minutes. When either of these conditions exists, the cell power must be turned off and water transferred (via argon pressure) from the hydrogen to the oxygen side. The gas must first be evacuated from the hydrogen reservoir to avoid mixing hydrogen and oxygen. After the water is transferred, the hydrogen reservoir must again be evacuated to avoid contaminating the gas in the hydrogen storage tank. The water circulation pump must also be turned off during the transfer to avoid blowing water into the ERS line. Completion of the water transfer is indicated by a sudden rise in the oxygen side pressure and a momentary "dry" indication on the oxygen reservoir level sensor.

When the transfer is completed and the circulating pump is turned on, cell power

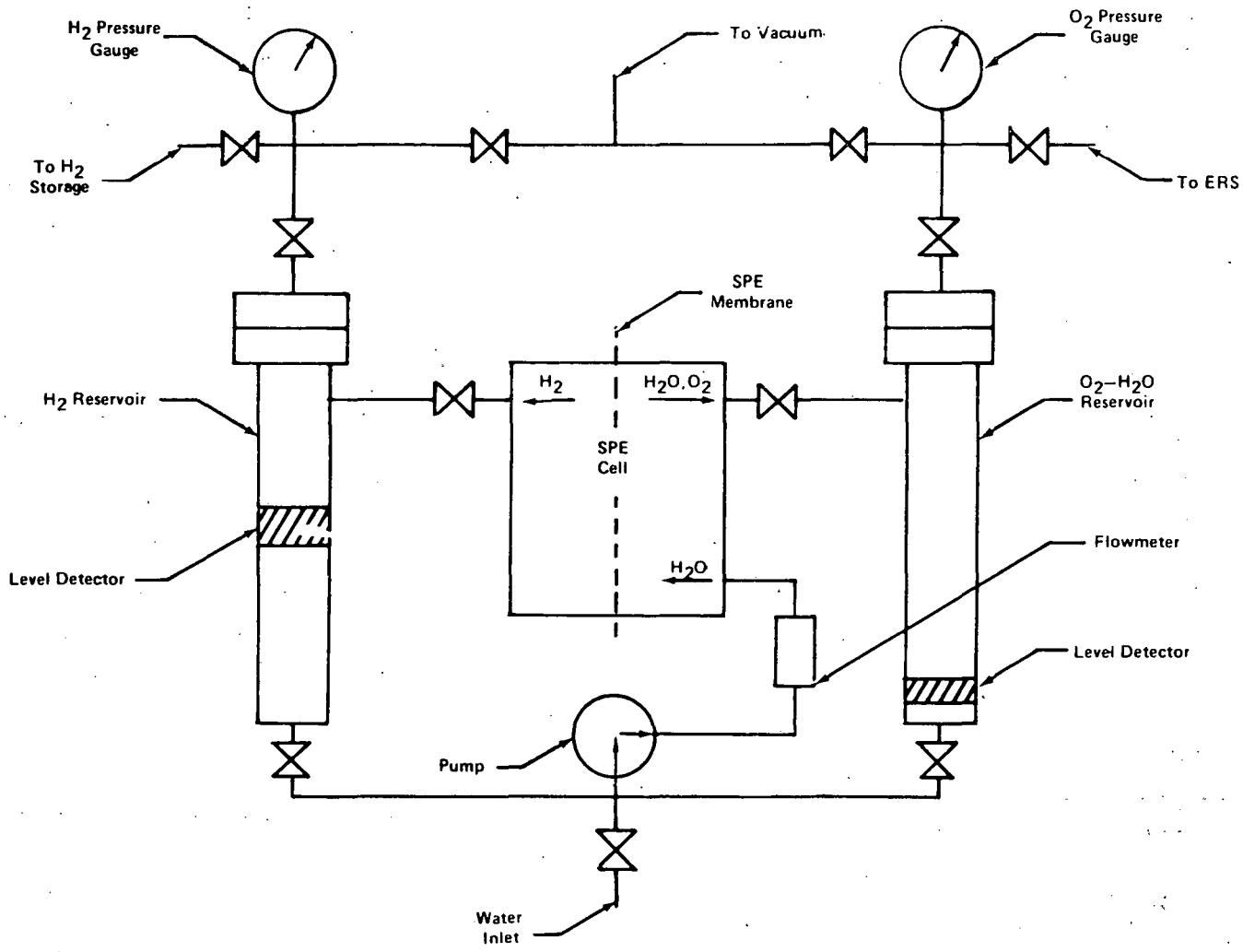

FIGURE 3 - Electrolysis system schematic.

is again applied and electrolysis resumes. This cycle is repeated until the total electrolysis time per cycle is down to 5-10 min. In this time range, depending on the hydrogen storage tank pressure, it becomes uneconomical to run the process since as much hydrogen is lost in the water transfer process as is produced during electrolysis. This problem could be minimized by increasing the storage tank volume and the volume of water on the oxygen side.

After the initial charge of tritiated water is electrolyzed to the point described above, another charge of nontritiated water is added to the system and electrolyzed. This flushes out the residual tritium from the system and lowers the contact time of the concentrated tritiated water with the cell membrane and other system components.

Two experiments were completed in which tritiated water was electrolyzed and the resulting hydrogen gas was collected. In the first of these, EL-1, 60 cm^3 of water containing 0.006 g of tritium (determined by calorimetry) and 60 cm^3 of nontritiated water were electrolyzed according to the above procedure. The electrolysis current was 40 A and total electrolysis time was 338 min. The gas mixture was analyzed by mass spectrometry. This analysis showed no tritium, but 0.03 mole % deuterium. Any small amount (such as naturally occurring) deuterium in the system would almost certainly show up as HD; therefore it is assumed the deuterium is really HT. Since the final hydrogen pressure, volume of the storage tank, and concentration of tritium are known, the total amount of tritium recovered from the operation can be estimated. (The gas is assumed to obey the ideal gas law.) The equation for such a calculation is shown below:

$Wt.T_2$ = H_2 pressure (in atm.) x tank volume x mole fraction HT x at. wt. T x gas temperature (in °K)/273 ÷ vol/mole (for ideal gas at STP)

For EL-1 the final hydrogen pressure was 3.53 atm and tank volume was 40 liters ± 10%. The estimate can then be made.

$$\frac{3.53(40)(298/273)(0.0003)(3)}{22.4} = 0.0062 \text{ g of tritium}$$

Considering the precision of the measurements involved (volume of the tank, ±10%, mass spectrometry analysis, ±60%) it is likely this estimate represents most of the tritium.

In the second experiment, EL-2, 60 cm^3 of water containing 0.06g of tritium and 60 cm^3 of nontritiated water were electrolyzed. The experimental procedure used was identical to that used in the EL-1 experiment. The estimated total electrolysis time was much longer, 498 min. This indicates some quantity of water was left in the system from EL-1. The electrolysis times for these experiments are only a rough estimate since they are read to the nearest minute from a wall clock during each electrolysis cycle.

The mass spectrometry analysis of the hydrogen gas in the storage tank at the end of the experiment showed 0.1% HT. The amount of tritium can be calculated as in EL-1.

$$\frac{3.73(40)(298/273)(0.001)(3)}{22.4} = 0.022 \text{ g tritium}$$

This accounts for only ~37% of the tritium charged into the system. In all the experiments some hydrogen is lost due to evacuation of the hydrogen reservoir

during the water transfer cycle. However, this loss would not account for 0.04 g of tritium. Also during the last few cycles of the system, a slight voltage increase (from 2.9 to 3.1 V) was noted. Such increases sometimes indicate degradation of the solid polymer electrolyte membrane.

EL-3 was conducted in a manner similar to EL-1 and 2, but the initial 60 cm^3 of water contained 0.9 g of tritium. This water was electrolyzed for a total of 205 min, then 30 cm^3 of nontritiated water was added to dilute the remaining material and the system was allowed to set overnight.

The system was run for 113 min of electrolysis before another 30 cm^3 of nontritiated water was added. After another 55 min of electrolysis, the system was allowed to set dormant for approximately six days.

Upon restarting, it was noted that the voltage necessary to maintain 40 A had risen to approximately 3.6 volts. Also water immediately began to fill the ERS line from the cell. Although several attempts were made to alleviate this problem, none were successful. Since increasing voltage is a sign of deterioration of the SPE, a differential pressure test was done by pressurizing the hydrogen side to 10 psi with argon. Within 30 sec the pressure on the oxygen and hydrogen sides of the cell had equilibrated indicating a leak across the SPE.

Following this discovery, the remaining water was transferred out of the system and the cell was dried by evacuating it with a vacuum pump for approximately 36 hr. Upon disassembly, only traces of the SPE around the seal areas could be found. The electrodes and active portion of the SPE were apparently embedded in the hydrogen current collector screen. Since no facilities were available in the glovebox to clean the screen, General Electric Company, manufacturer of the cell, was contacted. Two sets of new screens were sent, but these have not yet been installed in the cell.

It seems likely that radiation damage was the cause of the SPE failure. The damage did not become apparent until water at the 150 Ci/cm^3 level was placed in the cell. Radiation damage is normally accumulative, e.g., a flux integrated over some period of time produces a given effect. Since the tritium concentration in the cell was variable, no meaningful estimate of the dose-to-failure can be made. However, it can be stated that the radiation dose to the SPE from EL-1 and EL-2 was relatively small compared to EL-3.

Future Plans

The new collector screens and a new SPE will be installed and the cell will be leak tested. After completion of the electrolysis of the EL-3 water, additional experiments will be done at lower tritium levels to confirm SPE failure on contact with tritium.

Determination of radiolytic damage to H_2-H_2O exchange catalyst

W. E. Tadlock

Background

One of the objectives connected with the development of technology to concentrate tritium in waste water is to determine radiolytic damage to the hydrophobic exchange catalyst. This determination is

a cooperative effort between Mound Facility (DOE) and Chalk River Nuclear Laboratories (AECL).

Two tests have been performed to determine radiolytic damage. The first test determined the time period that the catalyst can withstand exposure to 10% tritiated water and still retain some degree of catalytic behavior. This time period was then used in the second test to subject the catalyst to a hydrogen-10% tritiated water environment. Finally the catalyst is to be sent to Chalk River Laboratories to determine whether it is still functional.

Accomplishments

Radiolytic damage tests have been performed to determine the extent of deterioration of the catalyst as a function of time when exposed to 10% tritiated water. Catalyst spheres were submerged in 10% tritiated water which was contained in a stainless steel container. A reusable seal incorporating a knife-edge flange with a copper gasket served to allow periodic removal of one sphere at a time. After removal from the reactor, the spheres were vacuum dried and then photographed through a glovebox window. The photographs are shown in Figures 4 through 10 and are identified by the exposure time in days. As can be seen in the photographs, some degradation occurs at about 124 days, becoming more prominent at 150 days. Severe deterioration occurs from 210 days on. The photographs are limited in illustrating the actual condition of the catalyst because of the inadequate lighting conditions and other restraints resulting from taking the photographs through the glovebox window.

A second test was started at a later date in which an approximate 110 cm^3 volume was filled with a catalyst similar to that used in the pilot Combined Electrolysis Catalytic Exchange System. The catalyst was contained between two stainless steel screens so that a space existed at each end of a hermetically sealed reactor. The reactor contained 10% tritiated distilled water in a hydrogen atmosphere. Twice daily the reactor was turned end for end to allow the tritiated water to flow down through the catalyst. These laboratory conditions were chosen to duplicate, as nearly as possible, the conditions that the catalyst would endure during a tritium recovery process. After 124 days, the catalyst was removed from the reactor and decontamination initiated. This was accomplished by soaking the catalyst in approximately 110 cm^3 of distilled water contained in the reactor. Table 1 gives the soak time and the activity of the water from each rinse. The tritium concentration of the first three rinses was evaluated by calorimetry, and that of the remaining rinses was determined by a scintillation counting method.

Future plans

After the tritium contamination of the catalyst has been reduced to an acceptable value, it will be shipped to Chalk River Nuclear Laboratories for evaluation of catalytic behavior.

Table 1 - DECONTAMINATION OF CATALYST

Rinse No.	Soak Time (days)	Tritium Concentration of Rinse Water (mCi/cm^3)
1	1	486,000
2	1	2,400
3	1	300
4	3	94
5	1	4
6	2	193
7	5	73
8	6	32
9	7	224
9b[a]	7	22
10	7	59

[a]Second sample of nine.

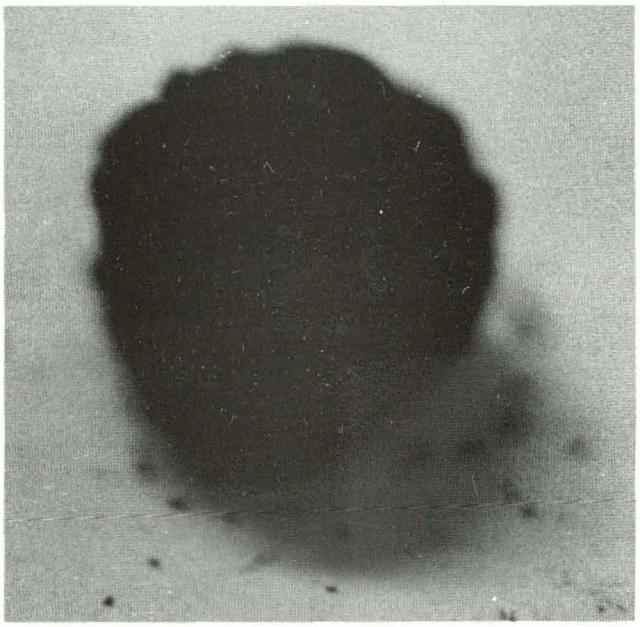

FIGURE 4 - Radiolytic damage after 90-day exposure.

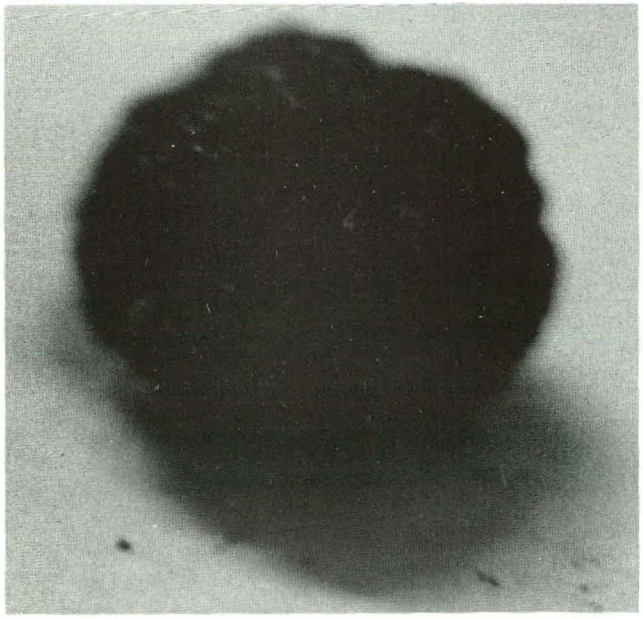

FIGURE 5 - Radiolytic damage after 124-day exposure.

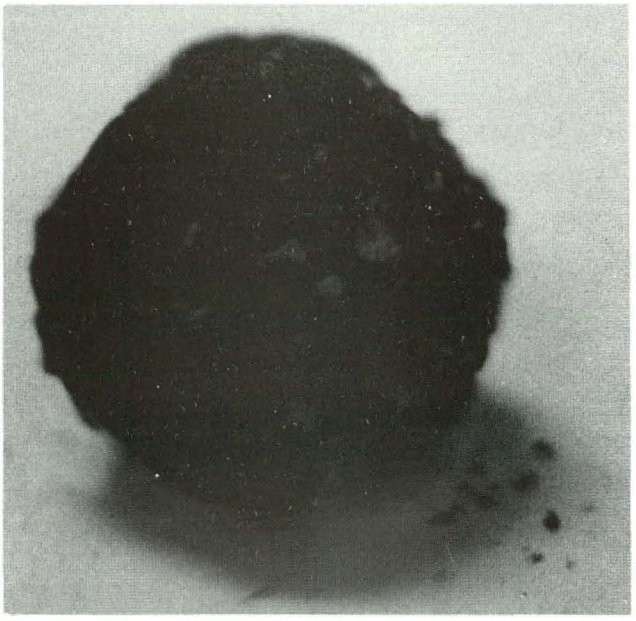

FIGURE 6 - Radiolytic damage after 150-day exposure.

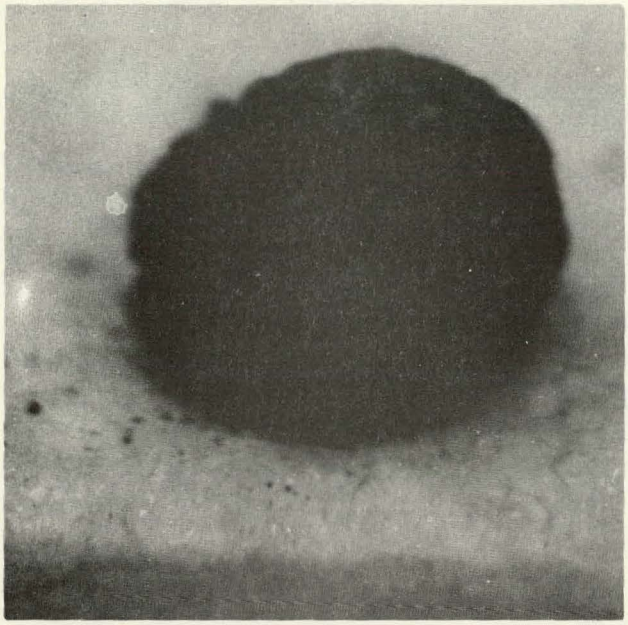

FIGURE 7 - Radiolytic damage after 180-day exposure.

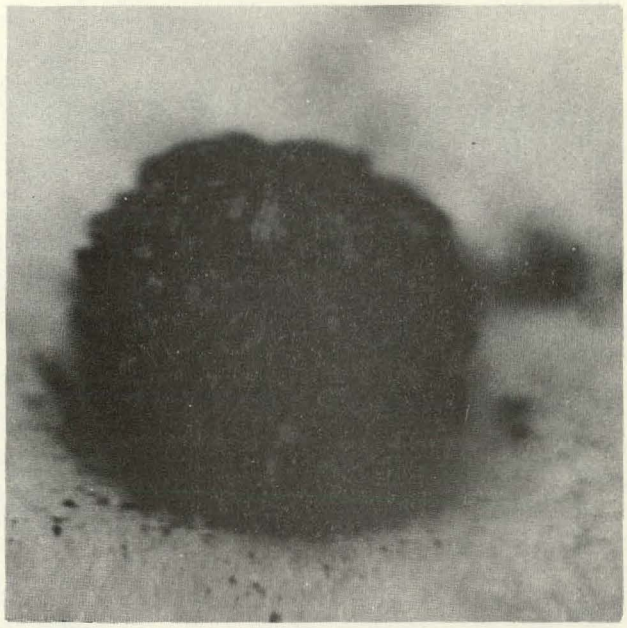

FIGURE 8 - Radiolytic damage after 210-day exposure.

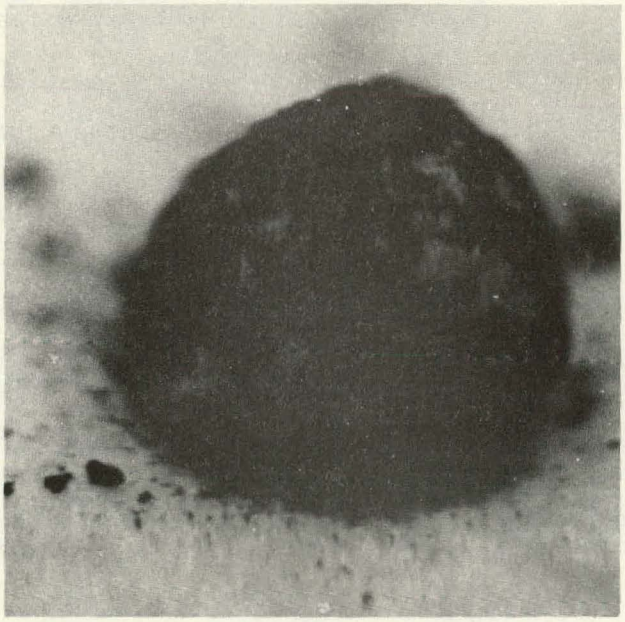

FIGURE 9 - Radiolytic damage after 241-day exposure.

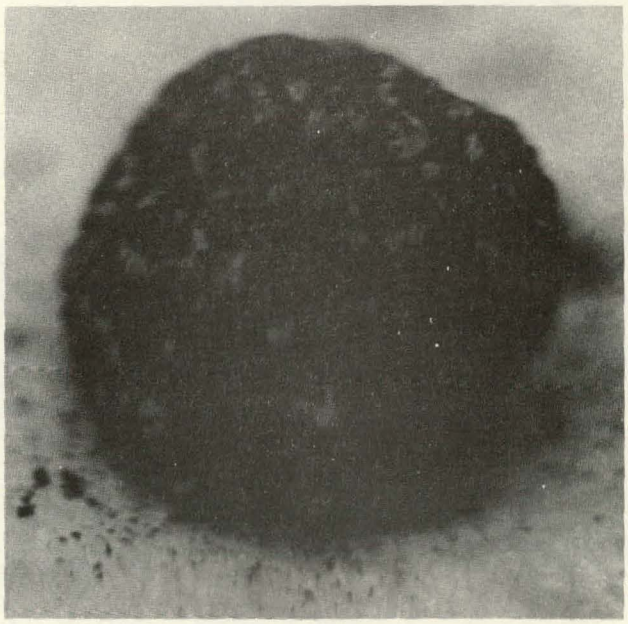

FIGURE 10 - Radiolytic damage after 270-day exposure.

Fixation of aqueous tritiated waste in polymer impregnated concrete

J. J. Dauby, R. E. Wieneke and
G. E. Gibbs

Introduction

Mound Facility, in cooperation with Brookhaven National Laboratory (BNL), has undertaken a program to test and develop the BNL method [7] for fixation of aqueous tritiated waste and adapt it to current procedures and facilities for packaging tritiated water waste. Concrete has been used at Mound since 1972 as a fixing agent for aqueous wastes containing 0.1 to 0.2 g of tritium per liter. In the BNL polymer impregnation technique, the cured concrete is impregnated with styrene monomer. The monomer fills the pores; then polymerization of the monomer binds and immobilizes the radioactive waste in the concrete. This decreases the tritium release from the concrete and reduces contamination hazards at the burial site. Because the styrene permeates the concrete the waste is, in effect, "microencapsulated". This will significantly reduce the tritium release rate in the event the containment is breached. Thus incorporation of the BNL procedure can improve the present waste package and allow us to establish a lower tritium release rate for a waste burial container.

As a method for transferring the BNL technology to Mound, "cold" samples were prepared using the techniques and parameters suggested by BNL. The details of this work have been given in previous reports in this series. Our work confirmed the work done at BNL.

A test program was instituted to measure and compare the release of tritium from tritiated concrete with and without styrene impregnation. All samples were prepared in 16-oz polyethylene bottles with a 2.625 in. (6.67 cm) diameter and filled to a height of 2.28 in. (5.79 cm).

Approximately 62.5 ml of tritiated water containing 386 Ci was injected into each of the 16 samples containing 250 g of dry mix. This is six times the concentration of tritium that is in a normal tritiated waste package. Hot samples consisted of triplicate mixtures of cement-plaster mixtures in a 1:1 volume ratio, and 10 samples of cement III. Details of the preparation of these "hot" samples may be found in a previous report [8].

The samples were put into a test program to measure the release rate of the tritium from the samples. The test method (shown in Figure 11) consists of submerging each sample, still contained in the polyethylene bottle, in 1600 cm^3 of water which is sampled periodically to measure the tritium released from the sample.

Attempts have been made to prepare full-scale, cold prototype burial packages. Early tests without adequate temperature monitoring revealed unexpected damage to the polyethylene drum liner. It was later learned that the BNL work was done using linear high-density polyethylene (LHPE), whereas the drum liners in use at Mound are linear low-density polyethylene (LPE). As expected, tests have shown that LHPE is more resistant to attack by styrene monomer than is LPE. Options for investigation include: 1) reducing the bulk temperature while styrene monomer is in contact with the drum liner, 2) reducing

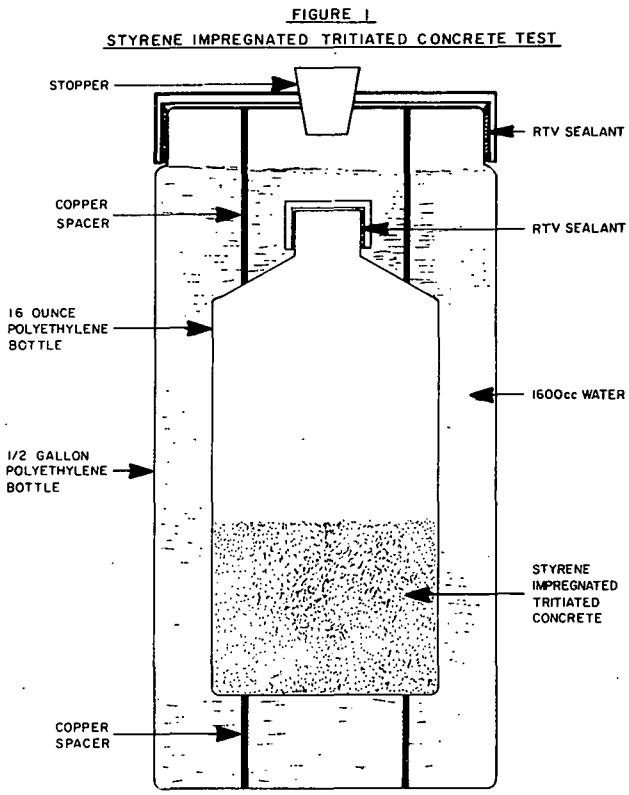

FIGURE 11 - Styrene impregnated tritiated concrete test.

the contact time of the drum liner and the monomer, and 3) using drums of cross-linked high-density polyethelene (CLPE).

Accomplishments

The permeation data in Table 2 are given for the first 33 weeks of each of the first four groups. No significant difference can be noted from the data on these groups of cement III, 1:1 by weight of cement and plaster or the 1:1 by volume of cement and plaster (see Figures 12 through 15). The fifth group did not have styrene added, therefore it was not heated as the other groups. After 25 weeks there is no significant difference from the other four groups (see Figure 16). However, no significant difference is expected since the polyethylene bottle is much thicker than the layer of polystyrene.

Samples 59 and 72 were prepared with cement III and styrene with 5% and ½% catalyst, respectively, as in Groups 1 and 4. They were not put into the test program until 25 and 21 weeks after their preparation and then with the polyethylene bottle removed. The amount of tritium that has leached into the water bath is over 50 times greater than the diffusion of tritium through the polyethylene bottles. The data are shown in Figures 12 and 15 in Groups 1 and 4. The greatly increased tritium release from these samples is attributed to the removal of the polyethylene bottle. Without the polyethylene there is only a thin layer of polystyrene between the concrete and the water.

The effect of the catalyst concentration is shown in samples 59 and 72. The release from sample 72 is an order of magnitude less than from sample 59. This is due to a lower rate of polymerization which yields a lower bulk temperature and results in the polystyrene containing less bubbles.

The sample data for the last ten weeks have shown essentially no increase in the amount of tritium diffusing through the polyethylene bottle from the concrete blocks. An equilibrium has been established or is being approached.

Sample 59 which had the polyethylene bottle removed is approaching tritium equilibrium with the leach water. In this sample 144 Ci of tritium (37% of original amount) has moved from the concrete into the leach water, which is 70 times greater than the 2 Ci released from similar samples still in polyethylene bottles.

In further attempts to develop a workable procedure for preparing full-scale cold

Table 2 - PERMEATION TESTS

Group	Sample No.	Curies	Preparation Date	Type	Water/Dry Mix Ratio	Styrene (%)	Catalyst (%)	Polymerization Temperature (°C)	Total Permeation (Ci)	Group Fractional Release
1	55	0	5-10-77	Cement III	0.250	20	5	40		
1	56	0	5-10-77	Cement III	0.250	20	5	40	None	
1	57	386.6	5-10-77	Cement III	0.250	20	5	40	2.15	
1	58	386.5	5-10-77	Cement III	0.250	20	5	40	1.68	$5x10^{-3}$/33 wk
1	59	386.3	5-10-77	Cement III	0.250	20	5	40	153	
2	61	0	5-12-77	1:1 by weight	0.250	23	1/2	55	None	
2	62	386.1	5-13-77	1:1 by weight	0.250	23	1/2	55	1.69	
2	63	385.9	5-13-77	1:1 by weight	0.250	23	1/2	55	1.73	$4.6x10^{-3}$/33 wk
2	64	386.6	5-13-77	1:1 by weight	0.250	23	1/2	55	1.68	
3	65	0	5-12-77	1:1 by volume	0.305	20	1/2	55	None	
3	66	386.6	5-13-77	1:1 by volume	0.305	20	1/2	55	1.00	
3	67	386.9	5-13-77	1:1 by volume	0.305	20	1/2	55	1.89	$5.0x10^{-3}$/33 wk
3	68	386.6	5-13-77	1:1 by volume	0.305	20	1/2	55	3.18	
4	60	0	5-12-77	Cement III	0.250	20	1/2	55	None	
4	69	386.5	6-03-77	Cement III	0.250	20	1/2	55	1.79	
4	70	386.6	6-03-77	Cement III	0.250	20	1/2	55	1.52	$3.5x10^{-3}$/33 wk
4	71	386.3	6-03-77	Cement III	0.250	20	1/2	55	0.70	
4	72	386.5	6-03-77	Cement III	0.250	20	1/2	55	38.2	
5	73	386.6	7-22-77	Cement III	0.250	None	None	None	0.84	
5	74	387.0	7-22-77	Cement III	0.250	None	None	None	0.89	$2.6x10^{-3}$/25 wk
5	75	193.4	7-22-77	Cement III	0.250	None	None	None	0.58	

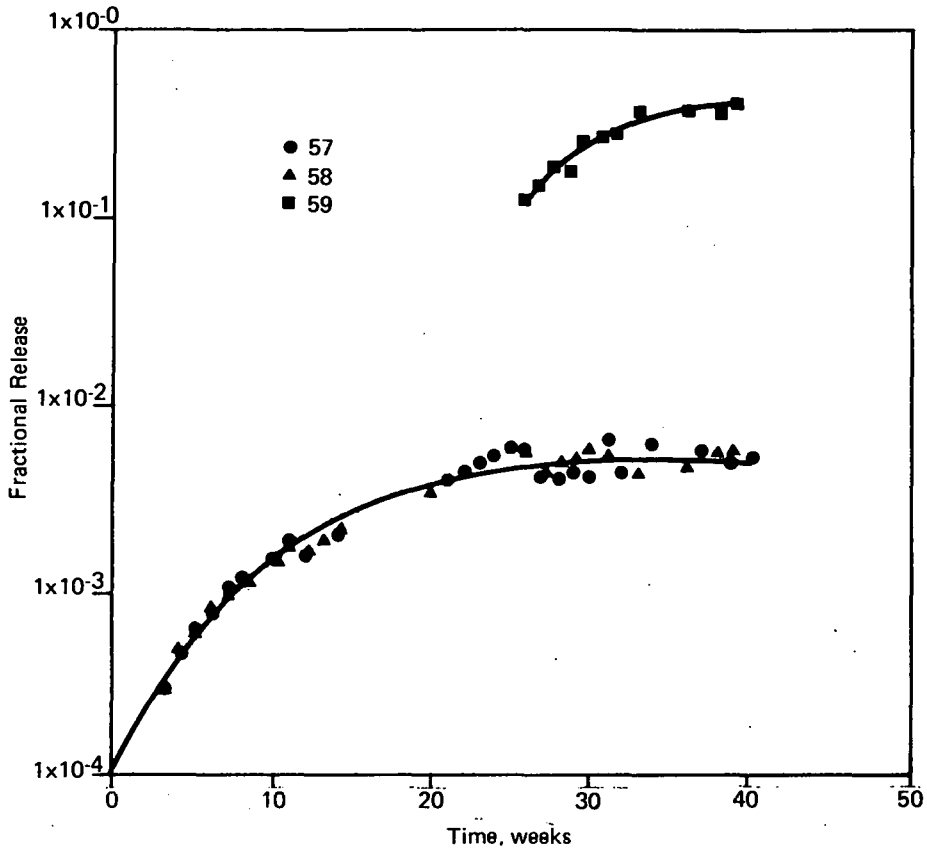

FIGURE 12 - Fractional release from Cement III samples, Group 1.

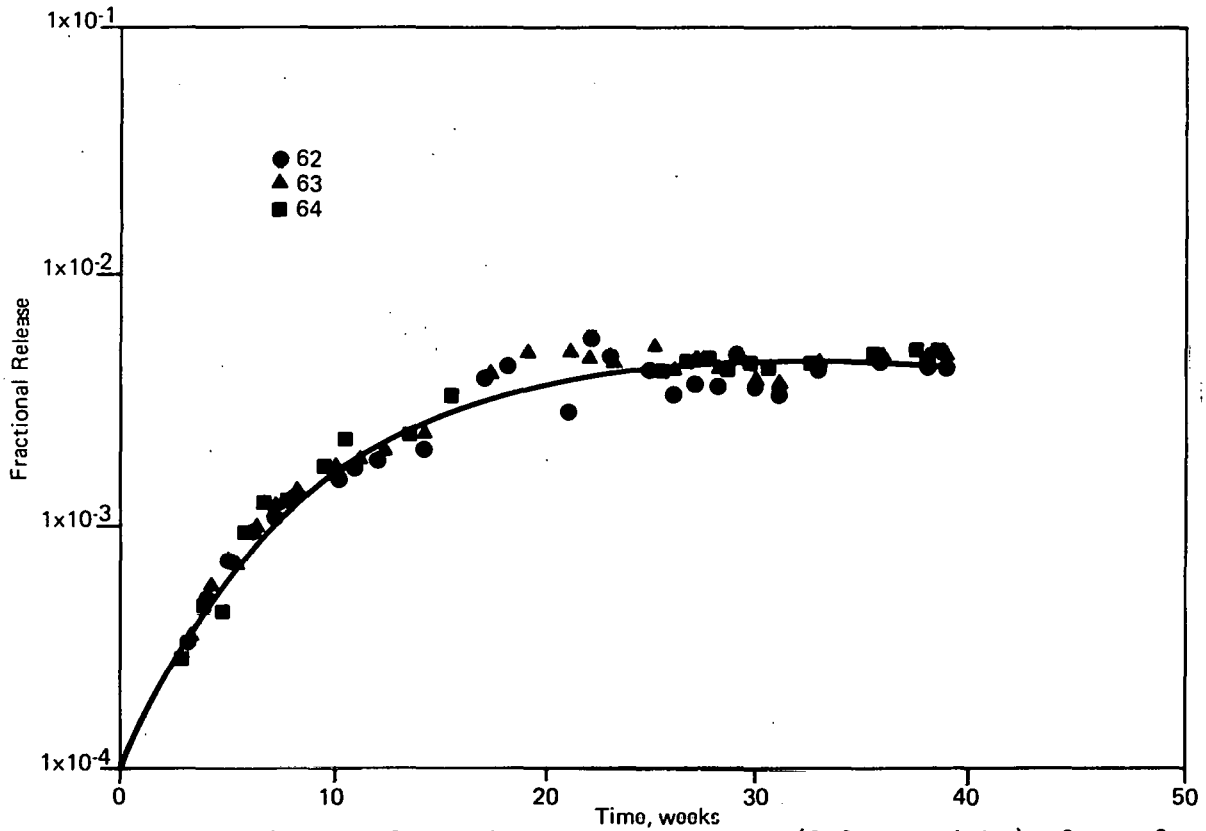

FIGURE 13 - Fractional release from cement/plaster (1:1 by weight), Group 2.

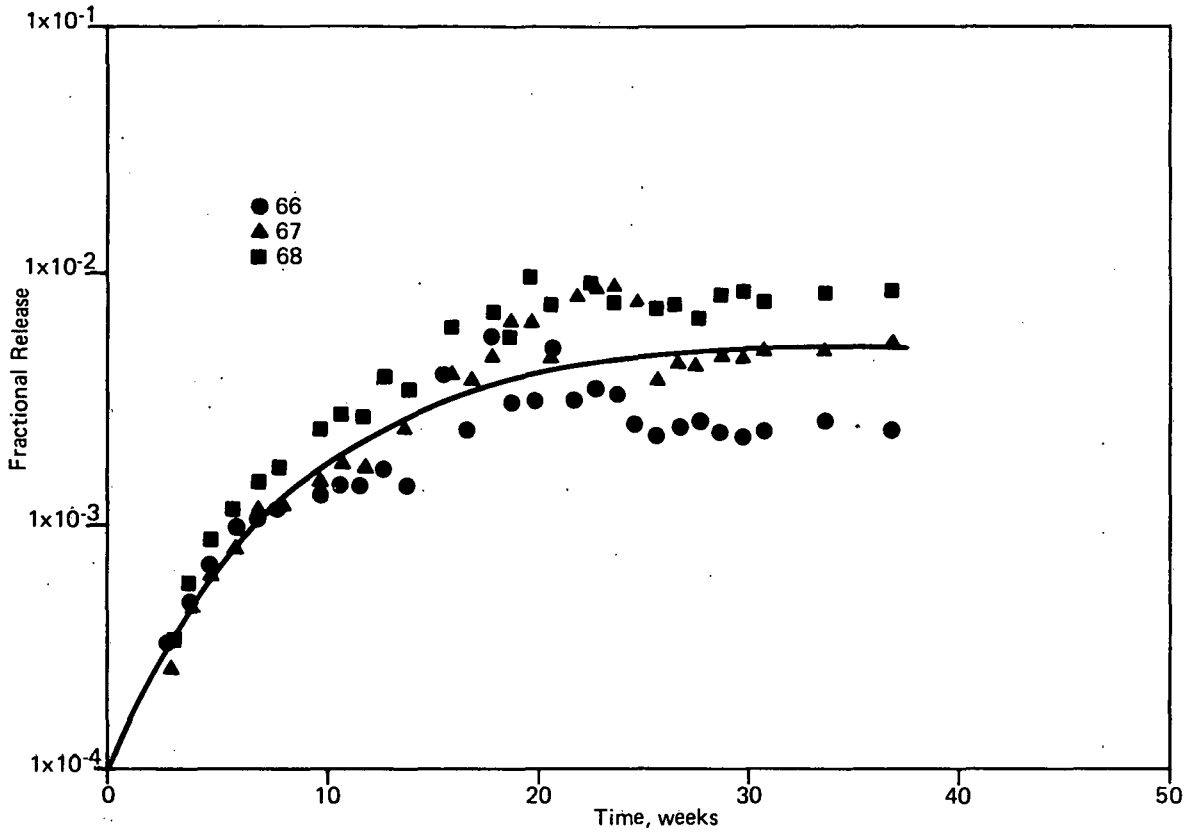

FIGURE 14 - Fractional release from cement/plaster (1:1 by volume), Group 3.

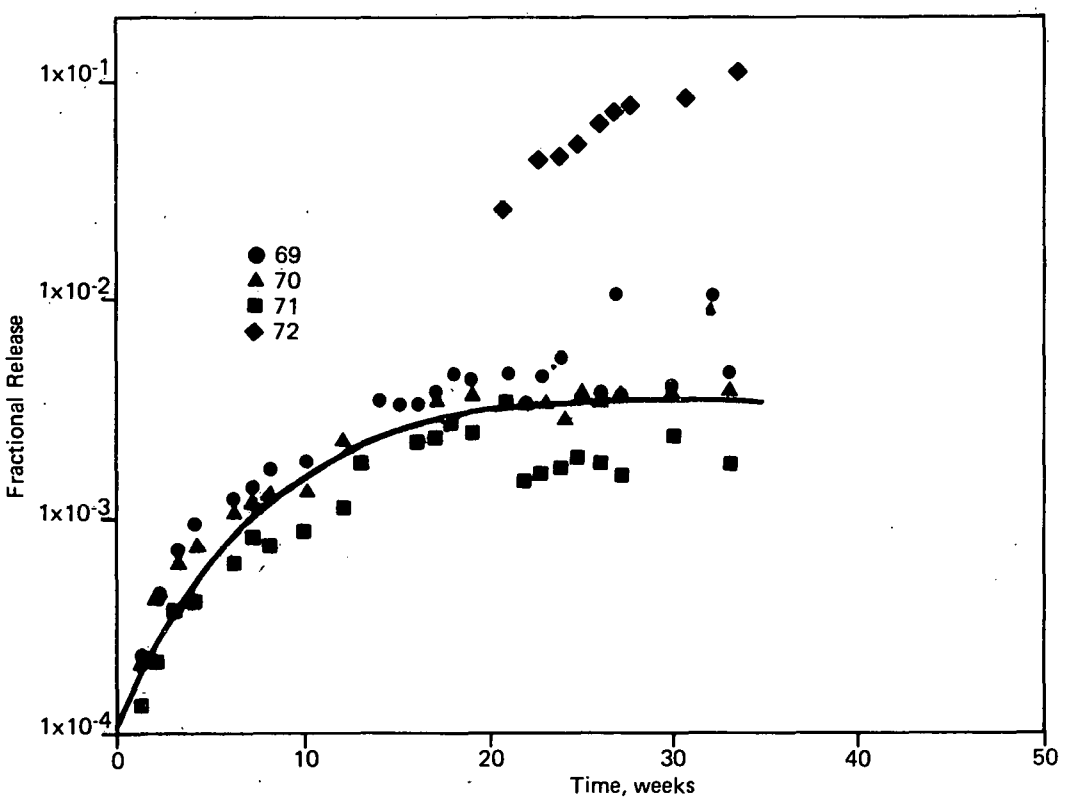

FIGURE 15 - Fractional release from cement III, Group 4.

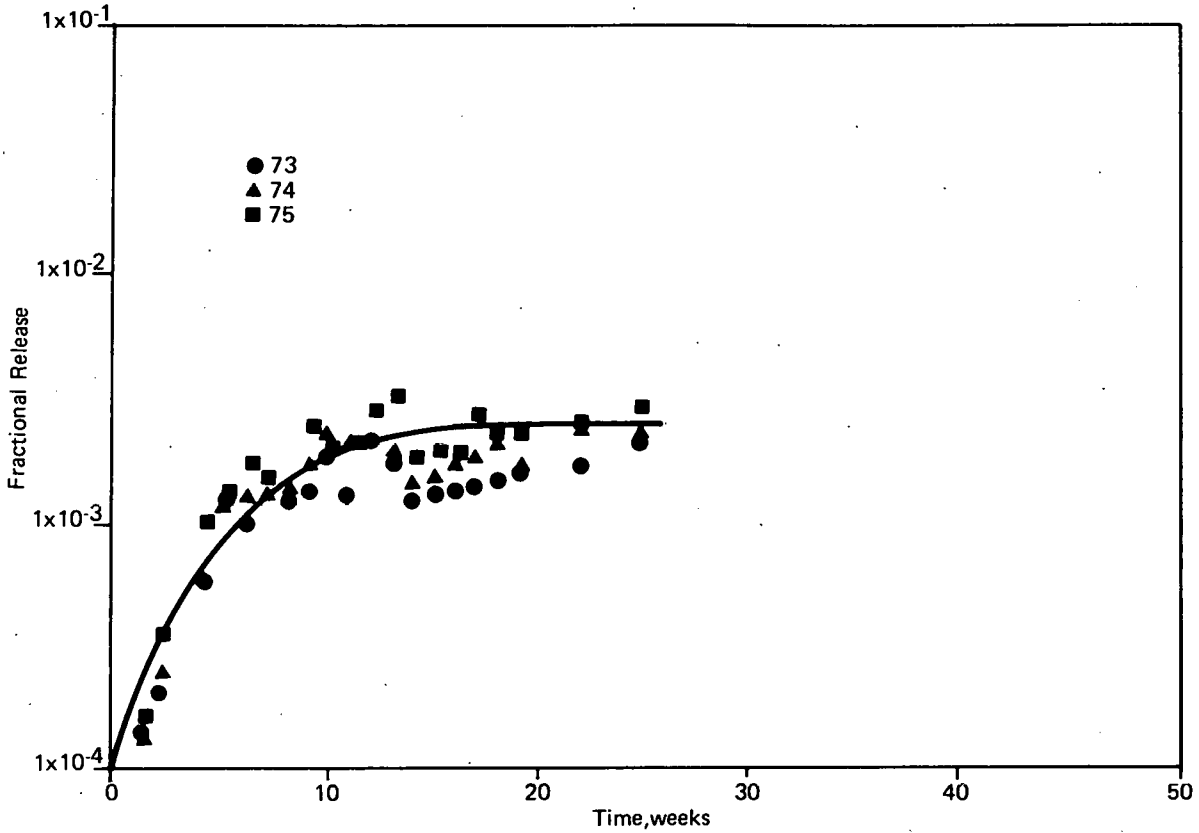

FIGURE 16 - Fractional release from cement III, Group 5.

prototype burial packages two additional packages were prepared. The first (#3) was prepared in a manner similar to packages #1 and #2 with the exception of: 1) a reduction in the bulk temperature at time of styrene addition from 65°C to 45°C, 2) an increase in the catalyst concentration from 1/2% to 2%, and 3) the removal of the heaters and insulation at the onset of polymerization. It was hoped that these changes would reduce temperature dependent styrene damage to the polyethylene liner.

It was evident, after a vigorous polymerization reaction, that the catalyst concentration was increased much more than necessary. The center temperature of the cement block reached 104°C, which is to be avoided since it might evaporate some of the waste water entrained in the cement. It has also been found that the water evolution can cause porosity in the polystyrene. The main part of the polymerization occurred quickly (4 to 6 hr) but the temperatures attained were higher than desired. No damage to the polyethylene liner was visible.

When full-scale (cold) burial package #4 was prepared the injection tube was removed completely and the hole was filled with cement, at the suggestion of P. Colombo of BNL. The heat generated during the curing process was also monitored, with the temperature reaching a 100°C plateau throughout the package (within 5 hr of water injection) and this temperature profile was maintained for 2-1/2 hr before cooling began. This temperature is the result of the heat of hydration of the cement.

Future plans

Material tests are planned to compare the behavior of low-density polyethylene, high-density linear polyethylene, and high-density cross-linked polyethylene damage when they are exposed to styrene at various temperatures.

The four groups of cement and cement-plaster samples impregnated with styrene polymer will be checked periodically to measure the tritium released. Samples of cement III without styrene polymer will also continue in the test program.

Full-scale test package #4 will have styrene added and polymerized in a manner similar to #3 but only 1/2% catalyst will be used in an attempt to reduce the maximum temperatures.

Management of high specific activity tritiated liquid wastes

G. E. Gibbs and J. J. Dauby

Background

Mound generates high-activity tritiated liquid waste from a variety of tritium handling operations and from stack effluent control systems [9-11]. There are two general categories of liquid waste which can be described as water (~1000 Ci/liter) and vacuum pump oil (~50 Ci/liter). Since 1972 these materials have been packaged for disposal in an improved container and the work has been done in a glovebox facility. Handling is accomplished with virtually no release to the environment and no significant operator exposure. The facility, package, and operating experience have been described in detail in the literature [12]. Twenty-five liters of waste oil is sorbed on vermiculite in the polyethylene drum whereas twenty-seven liters of liquid water waste is sorbed on a cement-plaster mixture in the polyethylene drum. The packaging procedure thereafter is the same, that is sealing in a 30-gal drum and finally in a 55-gal drum.

A tritium release rate study of actual burial packages was initiated in May 1975 and is continuing. The study consists of the individual immersion of representative actual burial packages in a known volume of water contained in a secondary drum. By periodic sampling of the surrounding water and analysis for the presence of tritium, a permeation rate can be calculated. Figure 17 is a schematic of a typical burial package under test within the permeation apparatus.

Accomplishments

The drum release rate study has been continued. Figures 18-23 are the resultant permeation rates (total permeation as a function of time in test) to date for the

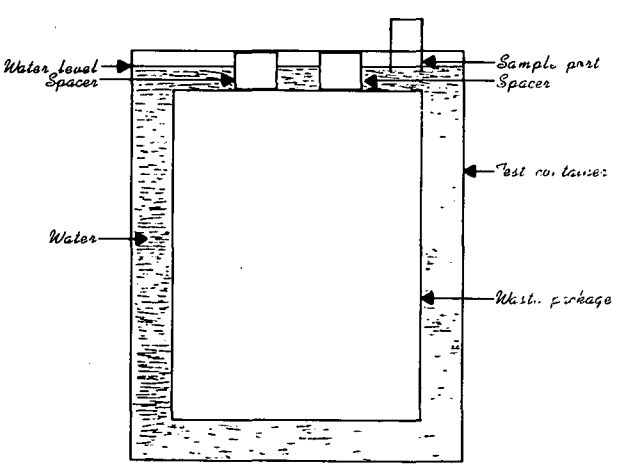

FIGURE 17 - Schematic of test package.

study. Two additional drums, 113 and 114, have recently been added to the drum release study. These drums contain solidified octane waste and they are packaged similarly to the standard oil and water waste drums. The difference is that the 83-gal drum is included as part of the burial package and is immersed in water contained inside a 146-gal drum. The drum release study now includes the three types of liquid waste generated from this area.

Figure 24 presents the fractional release (total curies permeation ÷ total curies contained) as a function of the time since the package was prepared. This illustration takes into account the total amount of tritium actually in the package with consideration given to tritium decay since the package was first assembled.

Three of the drums have essentially the same fractional release. Two of these, 217 and 218, contain oil and 205 contains water. The two drums containing octane wastes (113 and 114) were recently added to the test and have not yet reached an equilibrium. These octane wastes were packaged in the 55-gal drum about 6 yr ago and the 83-gal drum was added in 1977.

The drum with the lowest fractional release (318) contains water and was prepared most recently. We attribute the lower release to be due to closer attention to detail in the actual procedure of package preparation.

Future plans

The test will be continued and future data will be reported.

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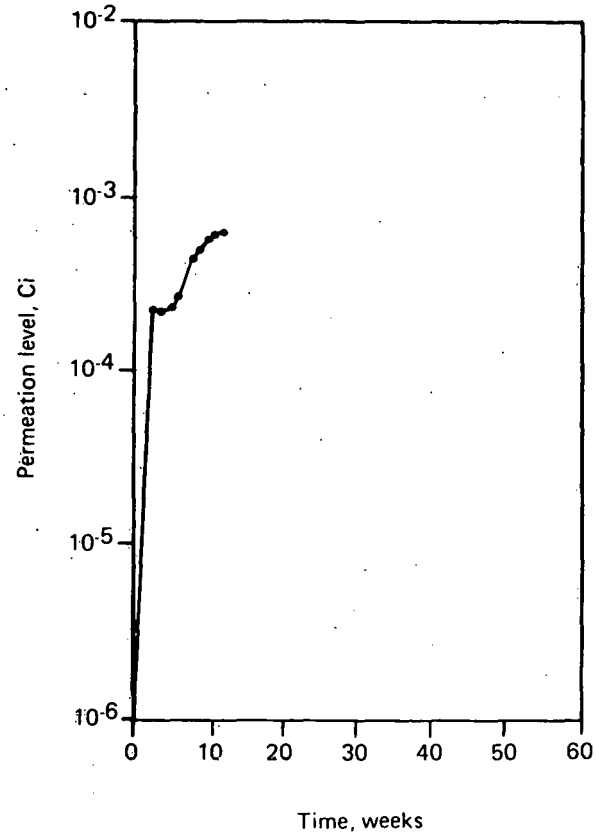

FIGURE 18 - Tritium permeation rate for drum No. 113 (octane).

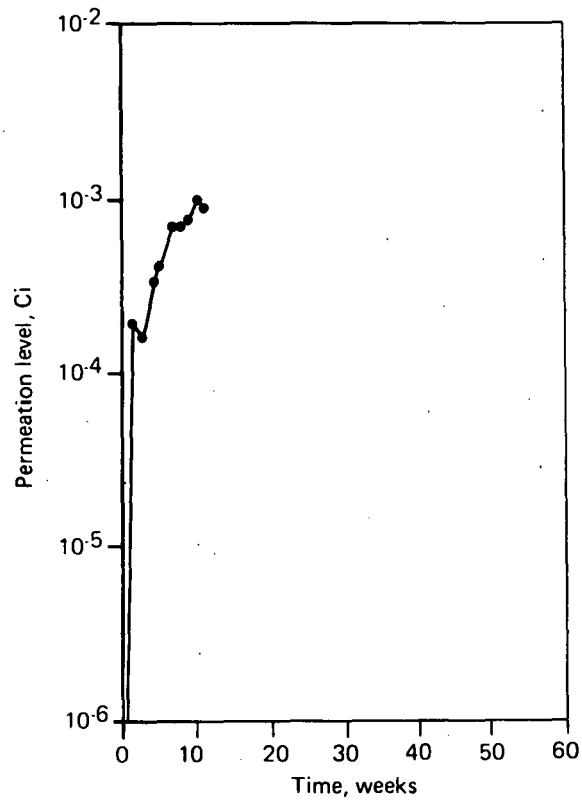

FIGURE 19 - Tritium permeation rate for drum No. 114 (octane).

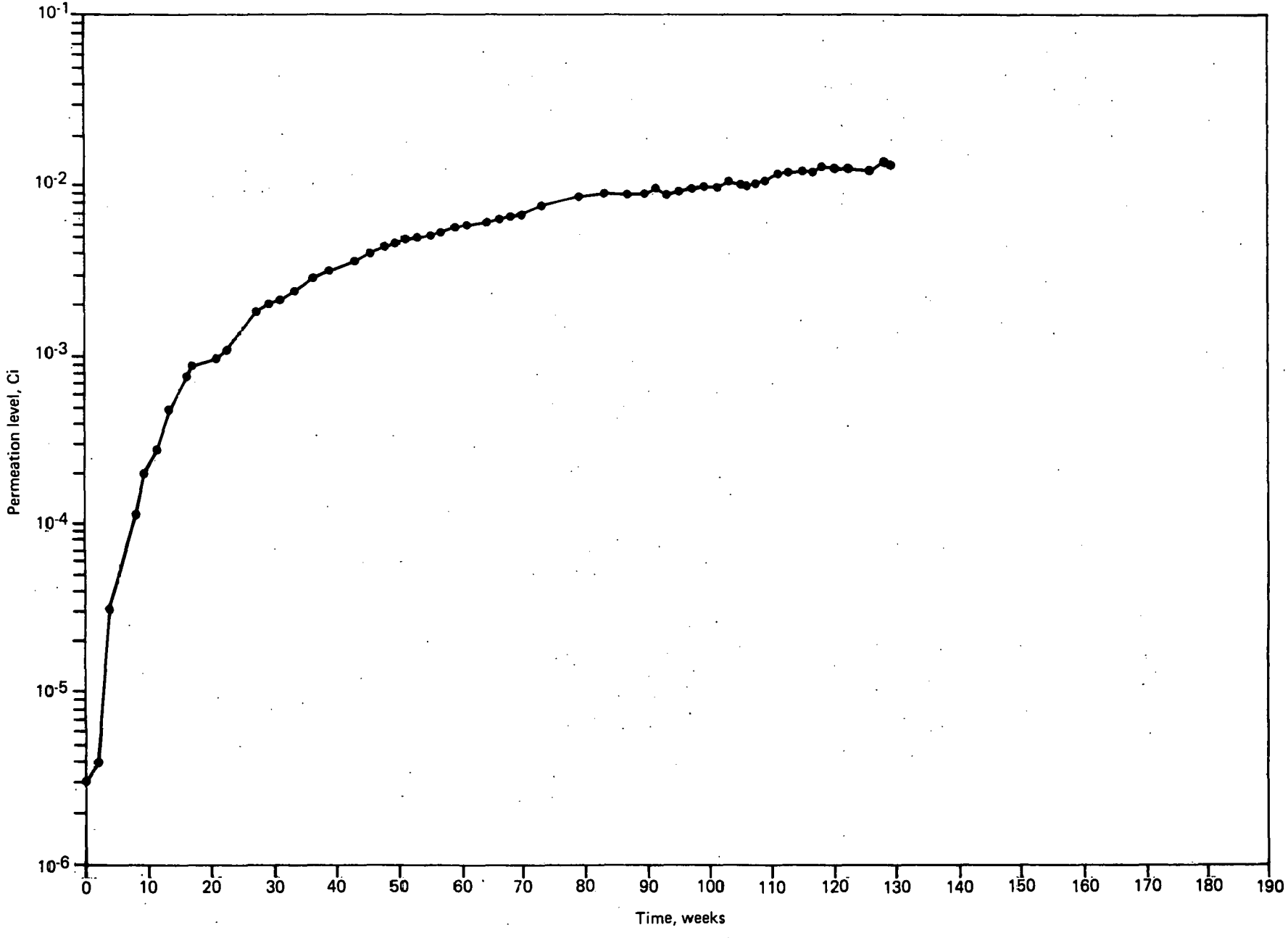

FIGURE 20 - Tritium permeation rate for drum No. 205 (water).

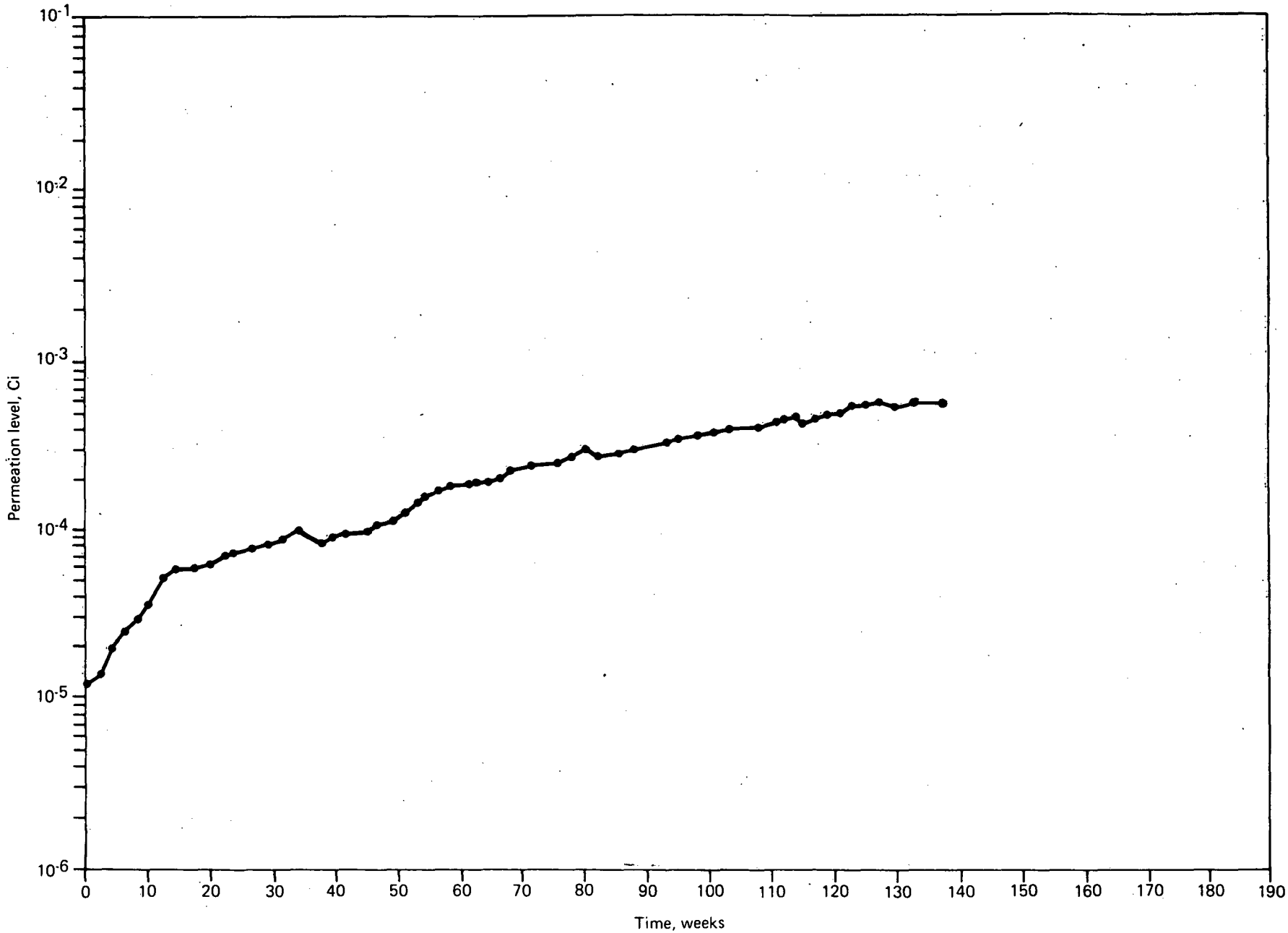

FIGURE 21 - Tritium permeation rate for drum No. 217 (oil).

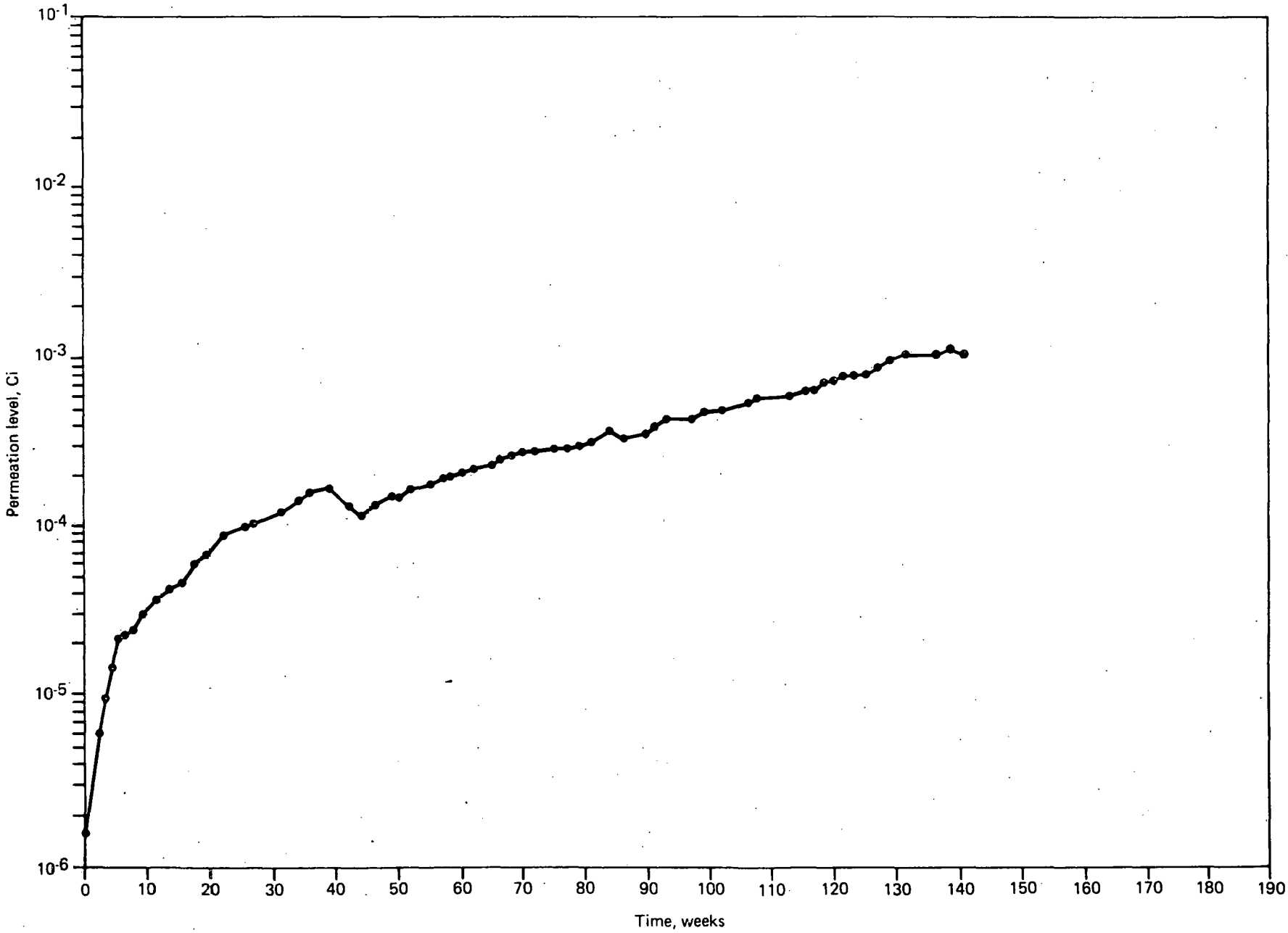

FIGURE 22 - Tritium permeation rate for drum No. 218 (oil).

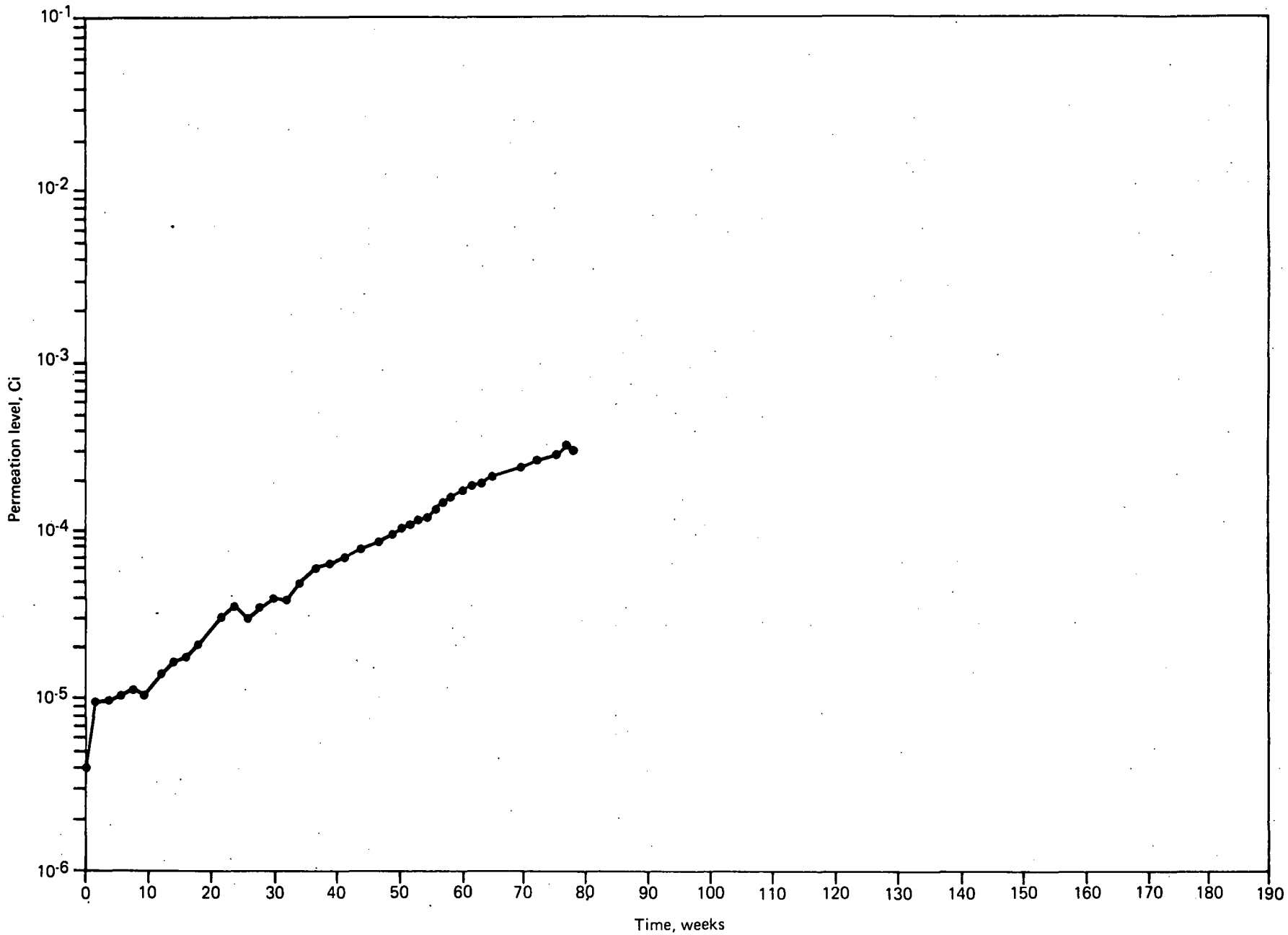

FIGURE 23 - Tritium permeation rate for drum No. 318 (water).

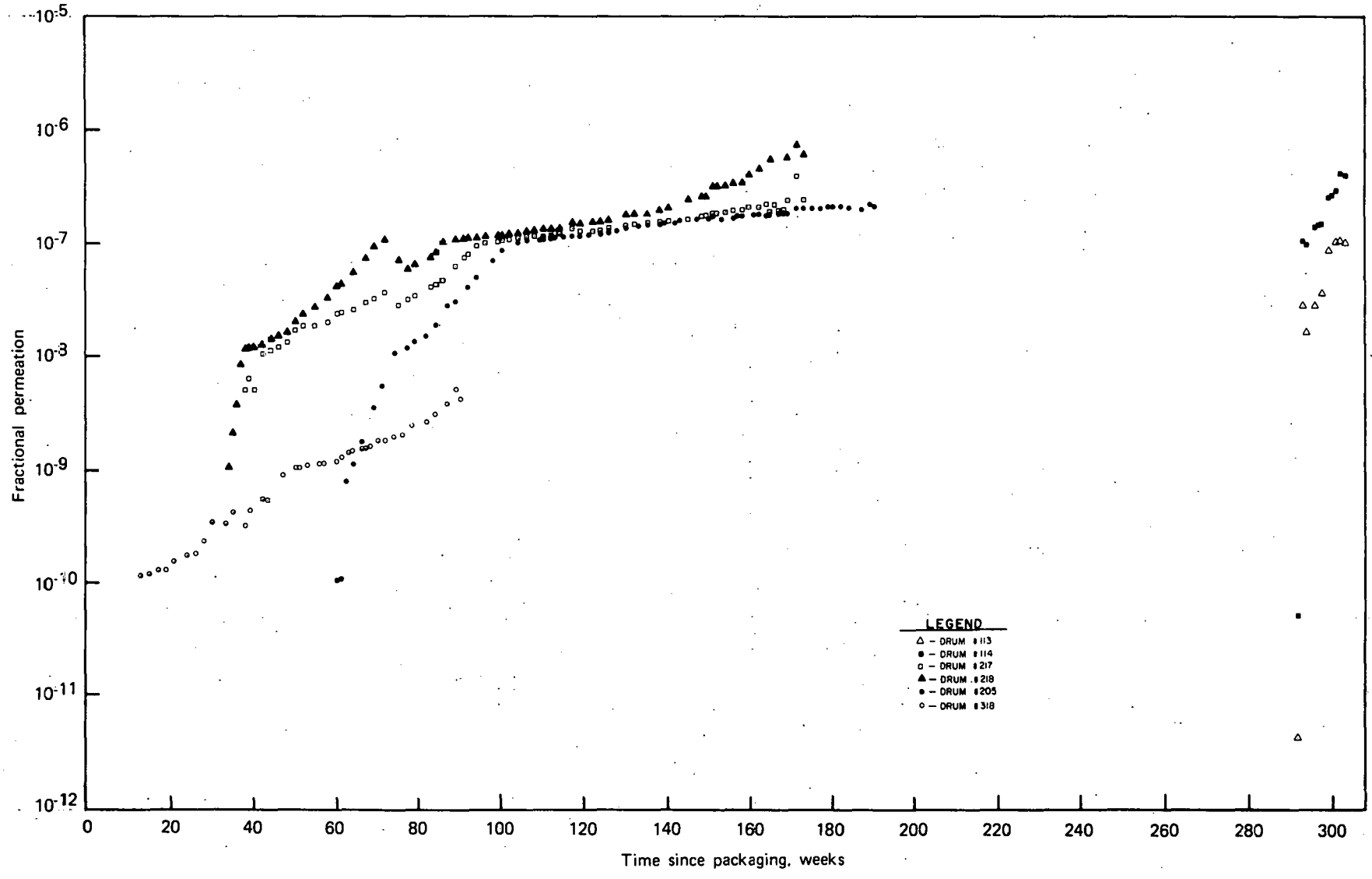

FIGURE 24 - Composite of fractional permeation for six drums.

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