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Tritium Waste Control:
October-March 1979

June 7, 1979

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Monsanto

MOUND FACILITY
Miamisburg, Ohio 45342

operated by
MONSANTO RESEARCH CORPORATION
a subsidiary of Monsanto Company

for the
U. S. DEPARTMENT OF ENERGY

Contract No. DE-AC04-76-DP00053

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Foreword

The work described in the first and second sections is funded by WPAS AL 4.6.2.1 JM. The first section, "Catalytic Exchange Detritiation Studies," corresponds to Work Breakdown Structure (WBS) 4.6.2.1.1 and the second section, "Electrolysis of Tritiated Water," corresponds to WBS 4.6.2.1.3. The remaining sections are work related to Tritium Waste Control but not directly funded through AL 4.6.2.1 JM.

Previous documents in this series are:

MLM-2451
MLM-2484
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MLM-2567

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Summaries

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CATALYTIC EXCHANGE DETRITIATION STUDIES. 5

The Combined Electrolysis Catalytic Exchange (CECE) system was operated to determine the effect of purging the catalyst. Work has begun on the addition of liquid reflux and enriched product storage capabilities to the CECE.

ELECTROLYSIS OF TRITIATED WATER. 8

Several attempts were made to repair the General Electric solid polymer electrolyte cell using the three spare SPE membranes purchased with the cell. Voltage was much too high in all tests, but on GE's recommendation new internal hardware and ten new membranes were purchased. After several additional attemps the cell was successfully reassembled and tests at a level of 1 Ci/ml were initiated. The cell continues to operate satisfactorily after 98 days of exposure to the 1 Ci/ml water.

EFFECT OF TRITIUM β-RADIATION ON Pt-C-TEFLON CATALYSTS 10

A 110 cm^3 sample of the hydrophobic exchange catalyst used in the Combined Electrolysis Catalytic Exchange (CECE) system was exposed to tritiated water at a concentration of 320,000 Ci/kg for 124 days at Mound Facility. The catalyst was then decontaminated and sent to Chalk River Nuclear Laboratories where the activity of the catalyst was measured and compared to its original value. The catalyst retained approximately 80% of its original activity even after this very large dose of β radiation.

GAS GENERATION MEASUREMENTS ON TRITIATED WASTE MATERIALS 11

Gas generation rates due to radiolysis of tritium waste materials were determined for polymer and non-polymer impregnation concrete and fixated and non-fixated tritiated waste vacuum pump oil. In addition, the pressure change of hydrogen cover gas over tritiated water on cement-plaster was determined.

FIXATION OF AQUEOUS TRITIATED WASTE IN POLYMER IMPREGNATED CONCRETE. 13

Tests continued on samples of cement and cement-plaster mixtures which were injected with 386 Ci of tritiated water, cured, and then impregnated with catalyzed styrene monomer. After polymerization, the samples were put into uncontaminated water and the tritium concentration was monitored. No significant differences were noted after 90 weeks of monitoring. One cement block from each of five groups was removed from the polyethylene bottle and returned to the test. The exchange of the tritium between the cement and the leach water increased markedly. Another cement block from each of the five groups was removed from the polyethylene bottle for a strength test made by measuring the compression yield point against a blank sample (no tritium). The yield point on all tritiated cement blocks was lower, probably as a result of radiolytic damage. Full scale (cold) waste drum No. 6 was polymerized with excellent results.

During the last 60-week period the fractional permeation rate of the two oil drums has increased slightly faster than the rates of the water drums. The fractional permeation rate of the octane drums appears to be about the same as the waste water and oil drums when observed over an equivalent storage time.

In Figure 1, the corrected coefficients are shown, along with the values predicted from Butler's bench scale data [1]. The predicted values are obtained from:

$$(K_y a)_p = K_y a^\circ \left(G\right)^{0.3} \left(\frac{L}{0.2}\right)^{0.1} \left(P\right)^{-0.4} \left[4.041 \times 10^5 \exp\left(\frac{-3848.9}{T}\right)\right]$$

where:

$(K_y a)_p$ = predicted coefficient, $m^3(STP)/m^3s$

G = superficial gas velocity, m/s

L = superficial liquid flow, g/cm^2

P = pressure, atm

T = temperature, K

$K_y a^\circ$ = catalyst activity, $m^3(STP)/m^3s$, measured at conditions of G = 1 m/s, L = 0.2 g/cm^2s, P = 1 atm, and T = 298 K

The corrected experimental transfer coefficients, shown in Figure 1, are in better agreement with Butler's data than has been shown previously. These observed values range from 32% under, to 47% over the values predicted, with most observations within 15% of the predicted value. From Figure 1, it is impossible to distinguish any effect attributable to the purging of the beds with hot gas. However, from Table 1 it may be seen that the observed coefficients, as well as their agreement with the predicted coefficients, decreased with time prior to the gas purge, and increased with time following the purge. This suggests the presence of some time-related phenomenon reversed by the gas purge.

Future plans

The CECE will be used to obtain additional transfer data. System modifications will include a liquid reflux capability as well as a hydride storage system for the enriched hydrogen product. Particular emphasis will be placed on ease of operation and reliability of the integrated CECE system.

Table 1 - CATALYST ACTIVITY DATA

Experiment	T K	P atm	G m/s	L g/cm^2s	L/G	$(K_y a)_o$	$(K_y a)_c$	$(K_y a)_c/(K_y a)_p$
1	305	1.7	0.1650	0.0152	0.75	0.374	0.493	1.34
2	300	1.7	0.1622	0.0156	0.76	0.353	0.384	1.04
3A	300	1.7	0.1577	0.0102	0.52	0.302	0.318	0.91
3B	300	1.7	0.1597	0.0200	1.01	0.294	0.311	0.82
4	298	1.6	0.1685	0.0200	1.02	0.254	0.257	0.68
6	301	1.6	0.1688	0.0203	1.03	0.29	0.334	0.88
7A	299	1.7	0.1566	0.0152	0.80	0.35	0.353	0.96
7B	299	1.7	0.1578	0.0102	0.51	0.51	0.515	1.47

Catalytic exchange detritiation studies

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

Background

All radioisotopic contaminants except tritium can be removed from the effluent stream of a light water reactor by routine chemical and physical methods. Tritium removal requires the development of isotopic separation processes.

The objectives of this study:

- Determine technical and economic factors involved in removal of tritium by means of the HT/H_2O exchange process.
- Determine suitability of hydrophobic exchange catalysts in water detritiation systems.
- Through pilot-scale testing, establish design criteria for detritiation systems suited to DOE site operations and the U. S. power reactor industry.

A bench-scale experimental system was built and operated to demonstrate the detritiation of water via catalytic exchange. In addition, an economic evaluation was made of the HT/HTO catalytic detritiation stripping process as it might apply to a 5 metric ton per day nuclear fuel reprocessing plant.

A pilot-scale 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 electolysis cell built by General Electric Company. This system was operated in a series of experiments which reduced the effluent tritium concentration to below Radiation Control Guidelines (RCG).

Following some initial modification aimed at enhanced reliability, the system was operated for approximately 400 hr over a 4-mo period. The catalyst beds were then purged alternately with hot N_2 and O_2 for 300 hr and 50 hr, respectively, for the purpose of drying the catalyst and removing any carbon monoxide which may have accumulated in the beds. After purging, the system was operated for approximately 200 hr during a 2-mo period.

Accomplishments

After the catalyst beds were purged, a series of experiments was conducted to determine effect of the purge on catalyst activity. The parameters of the earlier series of experiments were duplicated (except experiment order) to provide a direct basis for comparison. Table 1 gives the results of both series of experiments. In this tabulation, observed values of transfer coefficient $K_y a$ are shown, along with values for each experiment corrected to standard conditions of temperature (298 K), pressure (1.65 atm), and superficial gas velocity (0.1659 m/s) using the relationship:

$$(K_y a)_c = (K_y a)_o \left(\frac{G}{0.1659}\right)^{0.3} \left(\frac{P}{1.65}\right)^{-0.4} \left[4.041 \times 10^5 \exp\left(\frac{-3848.9}{T}\right)\right]$$

where:

$(K_y a)_c$ = corrected coefficient, $m^3(STP)/m^3s$

$(K_y a)_o$ = observed coefficient, $m^3(STP)/m^3s$

G = superficial gas velocity, m/s

P = system pressure, atm

T = system temperature, K

Electrolysis of tritiated water

R. E. Ellis

Background

At Mound Facility tritiated water is produced as a byproduct of various activities that involve 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. To do this, however, the hydrogen must first be separated from the oxygen by decomposition of the water molecule. Electrolysis, one of the more straight-forward water decomposition methods, is used in the combined Electrolysis Catalytic Exchange (CECE) system under development at Mound. The purpose of this system is to decontaminate low level tritiated water, but the system's vital solid polymer electrolyte (SPE) cells are exposed to high tritium concentrations.

A testing program was started to establish an expected lifetime for the SPE membrane. Previous work in this area includes a single experiment with a regenerative-type cell [2] and, more recently, a series of three experiments [3] using a cell purchased especially for this purpose.

Accomplishments

The General Electric solid polymer electrolyte cell used for tests on electrolysis of high-level tritiated water is all-metal with exception of the SPE membrane-electrode. Upon membrane failure the cell was disassembled, the damaged membrane discarded, and one of the spare membranes installed. Reassembly of the cell in the glovebox proved very difficult, however. Two of the three spare membranes purchased with the cell were damaged during attempts to reassemble the cell. The third attempt was successful in sealing the cell gas and water-tight.

Electrical tests were then made on the assembled cell using nontritiated water. Voltage was above 4 V with less than 10 A current. Normal voltage is about 2 V at 40 A. Since these parameters are unacceptable for cell operation, GE personnel were contacted in an effort to elucidate the problem. According to GE, high electrical resistance between the membrane and collector screen, or collector screen and terminal plates, was most likely responsible for the higher than normal voltage. Therefore, two new sets of collector screens and five new SPE membrane assemblies were purchased and the cell was reassembled using the new parts. The performance was not improved.

The only remaining cell hardware which could have an effect on the operating parameters was the platinum-coated terminal plates. The cell was again disassembled and these plates were cleaned using a fine abrasive. Upon reassembly and testing, the performance was improved, but slowly deteriorated during operation over a period of 3 hr. This behavior indicated oxidation of the titanium terminal plates was again causing high resistance between the collector screens and the terminal plates. GE recommended use of pure tantalum terminal plates to alleviate this problem.

One set of tantalum plates and five new SPE membranes were purchased from GE.

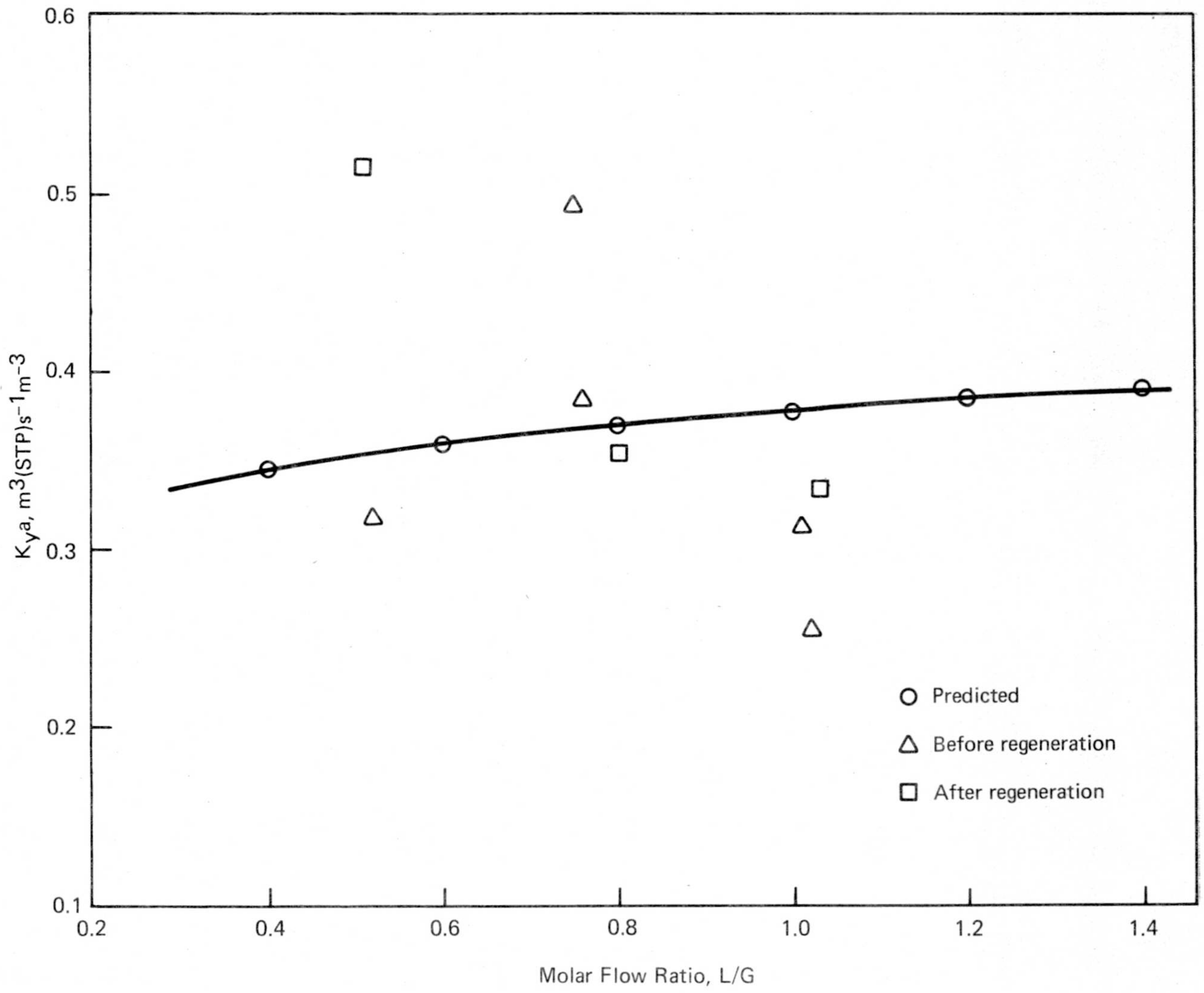


FIGURE 1 - Observed catalyst activity vs. molar flow ratio.
Data corrected to 25°C, 1.65 atm; gas velocity = 0.1659 m/s.

The SPE membranes are a new type developed for use in one of GE's fuel cells and are more resistant to damage from peroxide attack than the original electrolysis membranes. Since peroxide formation is likely in high-level tritiated water, longer life is expected from these membranes.

The cell was reassembled using the new screens, tantalum terminal plates, and a peroxide inhibitor membrane. Electrical tests were carried out using nontritiated, deionized water. Satisfactory (40 A at 3.4 V) operation was achieved for the first time since the cell membrane failure. While 3.4 V is about 1 V higher than normal, the voltage did not appear to be rising during several hours of operation at 40 A. Since the new membrane was designed for use in fuel cells, an overvoltage of approximately 1 V may be required for electrolysis operation.

Tritiated water for use in testing the cell was made by circulating tritium gas over hot CuO to make approximately 1/6 mole T_2O. When mixed with 97 ml of deionized H_2O this made tritiated water with a tritium concentration of 98.9 Ci/ml. Part of this material was used to produce water containing approximately 1 Ci/ml for the initial membrane radiolysis tests.

These tests will determine the maximum dose the membrane can withstand and still remain intact and operational. As indicated, the first tests are being done at a 1 Ci/ml level. The cell system used in these experiments has been illustrated in a previous report [3]. The test consists of introducing the tritiated water and operating the system for 15-20 min, once a week, for the duration of the test. Although the cell is being operated for only a short period each week, the membrane is constantly exposed to the tritiated water and any damage done by beta radiation will take place whether electrolysis is being carried out or not.

At the time this report was written the cell had been under test for 98 days without failure at the 1 Ci/ml level. Voltage necessary to produce 40 A has remained at approximately 3.4 V with exception of a curious "initiation period" at the beginning of the weekly operational tests. The effect is to limit the current (at approximately 3.5 V) to less than 40 A for a period of 2-5 min after the cell is turned on. The cause of this behavior is not known, but it has been noted that the length of the initiation period is shortened by circulating the water through the cell for several minutes before turning on the electrolysis power. This implies that a build-up of impurities, perhaps gas bubbles, on the membrane is responsible. Regardless, the operating current of 40 A has always been reached within 5 min and operating voltage remains at 3.4 V.

Future plans

Barring failure of the SPE, the 1 Ci/ml test will be continued until at least 6 mo exposure to this level has been attained. At that time a decision will be made as to how the testing will proceed.

Effect of tritium β-radiation on Pt-C-Teflon catalyst

J. P. Butler and F. W. Molson, Physical Chemistry Branch, CRNL, and W. E. Tadlock, Mound Facility

Background

To supplement previous γ-radiation damage studies at Chalk River Nuclear Laboratories (CRNL), a catalyst sample was exposed to tritiated water containing 10 mol % T_2O at Mound Facility. The catalyst, 0.25% Pt-C-Teflon on ceramic spheres, was mixed with an equal quantity of hydrophilic spheres (6.1 mm diameter) to give a total volume of 110 cm^3. The volume of water used was 30 cm^3 and the tritium concentration is equivalent to 3.2×10^5 Ci/kg or 1.2×10^{16} Bq/kg. The catalyst sample was contained between two stainless steel screens so that space existed at each end of the sealed reactor. The cover gas was 0.1 MPa of hydrogen. Twice daily the reactor was turned end for end to allow tritiated water to flow down through the catalyst bed. These conditions were chosen to simulate as closely as possible the conditions in a trickle bed reactor in a tritium recovery plant.

After 124 days the tritiated water was removed and the catalyst was decontaminated by soaking repeatedly in 110 cm^3 aliquots of distilled water. After nine rinses the tritium concentration in the rinse water was reduced from 320 Ci/cm^3 (1.2×10^{13} Bq/cm^3) to 22 mCi/cm^3 (8.0×10^8 Bq/cm^3). This is equivalent to a decontamination factor of about 1.5×10^4. The catalyst was vacuum dried at room temperature and then shipped to CRNL for evaluation of catalyst activity. The polyethylene shipping bag contained an appreciable amount of loose Pt-C-Teflon powder. However, the Teflon layer was sufficiently well bonded that, under flow conditions in a trickle bed reactor, further losses of Pt-C-Teflon were insignificant. The catalyst and the hydrophobic ceramic spheres were loaded into a column as received from Mound Facility.

Accomplishments

The catalyst activity was measured as a function of hydrogen flow rate at 25°C and 0.11 MPa, with a liquid flow of 2 $kg \cdot s^{-1} \cdot m^{-2}$. The volume transfer rate $k_y a$, for deuterium-hydrogen exchange on the second day was 0.78 $m^3 (STP) \cdot s^{-1} \cdot m^{-3}$ at a hydrogen flow of 1.0 $m \cdot s^{-1}$ (STP). Over 5 days of continuous operation the activity decreased slightly, as is normal for this type of catalyst. The observed activity is to be compared with the average initial activity of this catalyst of $k_y a = 0.95 \pm 0.05$ measured over 2 yr ago. The irradiated catalyst has retained 81% ± 7% of its original activity. Assuming that the radiation damage is proportional to the total energy absorbed and independent of dose rate, this very high irradiation dose would be equivalent to the irradiation received by a catalyst in 110 yr of column operation at a tritium concentration of 1000 Ci/kg. The assumption is reasonable for polymers, especially for irradiations done in the absence of air [4]. This study has shown that the catalyst activity is unaffected by tritium β-particle radiation for 10 times longer than previously reported [5].

Radiation damage to the catalyst can now be completely discounted as a serious problem in tritium recovery processes.

The tritium remaining on the catalyst received from Mound Facility appears to be strongly bonded since tritium is only slowly exchanged into water. As a result of the high radiation dose, the tritium has probably been incorporated as a hydrocarbon into the carbon-Teflon matrix. Repeated washings of the catalyst and inert ceramic spheres with boiling water and boiling aqua regia indicate that the total amount of tritium remaining on the catalyst charge is about 0.3 Ci (1.1×10^{10} Bq), with about 90% of the tritium on the catalyst pieces and 10% on the non-catalytic ceramic spheres. This amount of tritium is equivalent to 0.003% of the total tritium, 9,600 Ci (3.6×10^{14} Bq), used in the radiation study.

Gas generation measurements on tritiated waste materials

W. E. Tadlock and G. C. Abell

Background

As part of an ongoing evaluation of tritium waste packages at Mound Facility, gas generation is measured on samples of polymer and non-polymer concrete and fixated and non-fixated waste vacuum pump oil. In addition, the pressure buildup of hydrogen cover gas over tritiated cement-plaster samples is studied for a possible hydrogen back-reaction.

The preparation of polymer and non-polymer tritiated samples have been previously reported [6]. Two 20-g samples each of fixated (on 8 g of vermiculite) and non-fixated titiated waste vacuum pump oil (activity = 109 mCi/cm^3) were placed in stainless steel containers. Each container was equipped with a 0-30 psia (0-210 kPa) pressure transducer and a reusable seal incorporating a knife-edge flange and copper gasket. Argon containing small amounts of gaseous impurities was used as the cover gas for the above-mentioned samples.

The samples of tritiated water on cement-plaster fixative were prepared by slowly dripping 10 g of tritiated water (activity: 1 Ci/cm^3 = 0.1 mg T_2/cm^3) onto 23 g cement-plaster mix (41% No. 1 Portland cement) which had previously been placed in a stainless steel container. After hermetically sealing and evacuating these two sample containers, a hydrogen cover gas at the predetermined pressure was provided.

Accomplishments

The rate of gas generation of polymer and non-polymer tritiated concrete is illustrated in Figure 2. This data has been normalized to STP conditions with the use of the equation:

$$\text{cm}^3\text{(STP)/Ci} = \frac{P_1 - P_0}{760} \frac{V}{Ci} \frac{273}{298}$$

where P_1 = Final Pressure (Torr)

P_o = Initial Pressure (Torr)

V = Void Volume

Ci = Activity of Material in Curies

The polymer-impregnated concrete is at a disadvantage compared to regular concrete in suppressing the generation of gas, but the difference is small. Since the main goal of polymer impregnation is to inhibit the exchange of fixated HTO with the ambient water vapor [7], this small difference is of minor importance.

The effect of fixation on tritiated waste vacuum pump oil is shown in Figure 3.

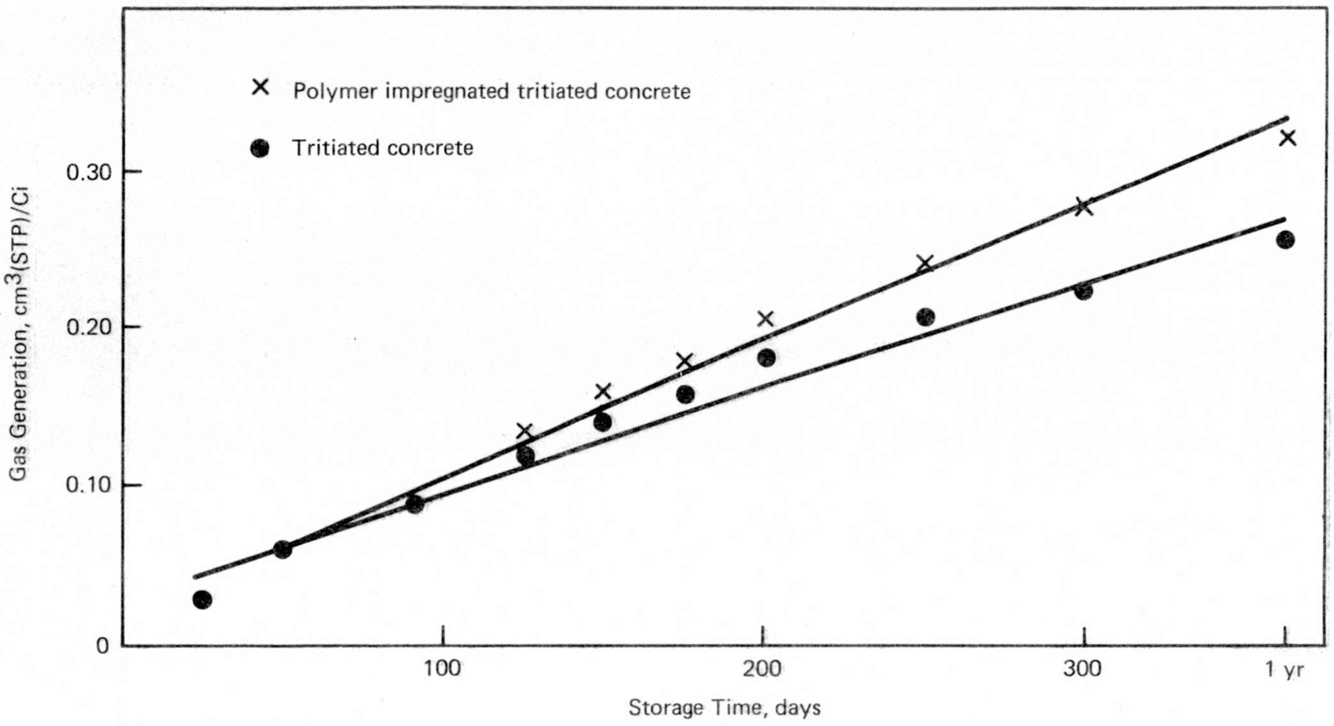


FIGURE 2 - Gas generation by polymer impregnated and nonpolymer concrete.

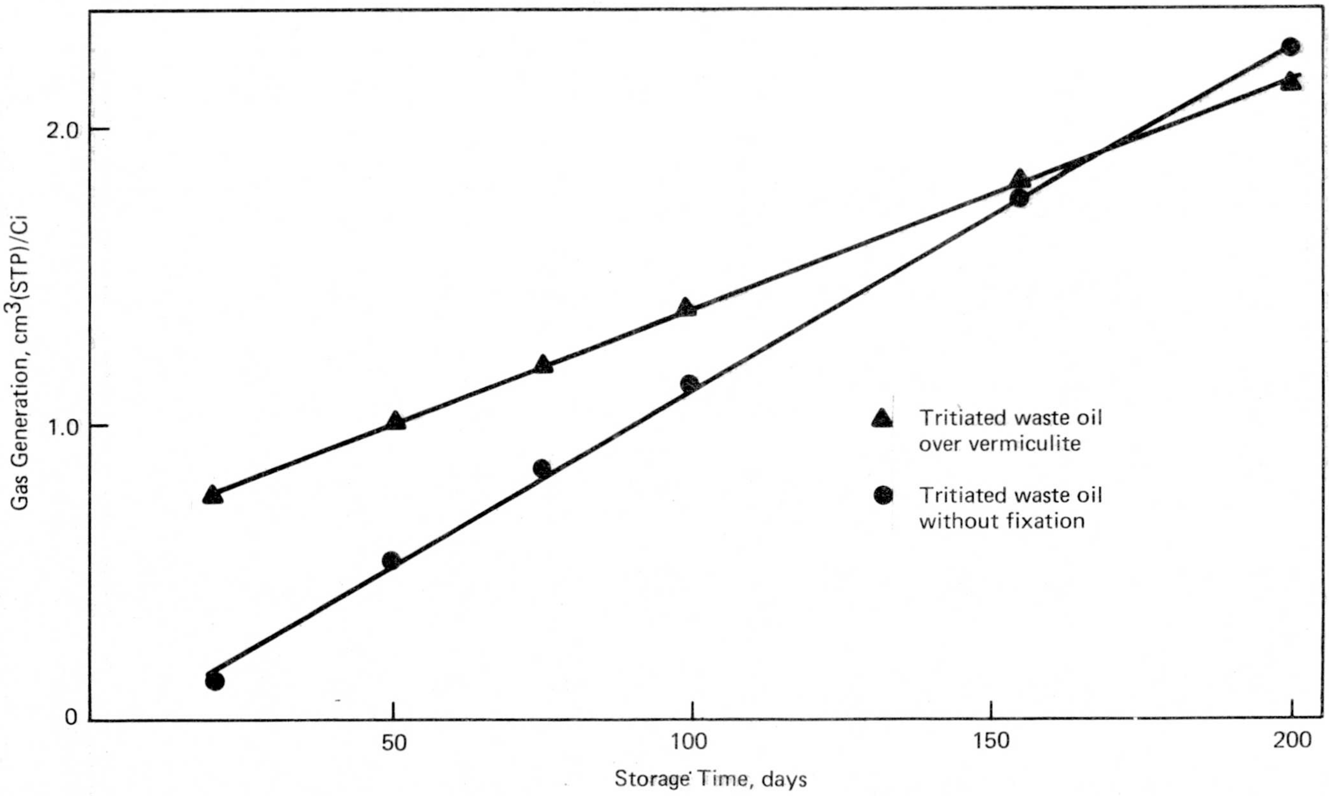


FIGURE 3 - Gas generation by tritiated waste vacuum pump oil.

This oil had been subjected to relatively high levels of tritium over a period of 6-12 mo prior to the present study. A previous measurement [8] on relatively pure tritiated octane on vermiculite, gave a gas generation value of 2.9 cm^3 (STP)/Ci for a period of 200 days. Since impurities tend to reduce gas generation, the waste oil data giving 1.5 cm^3(STP)/Ci for 200 days compares very well.

Figure 4 shows the pressure change over tritiated water on cement-plaster with 30 psia (210 kPa) and 35 psia (244 kPa) initial hydrogen cover gas pressure. The rate of change is about 2.7 psi/yr at 30 psi and 1.8 psi/yr at 35 psi hydrogen pressures. At the present time there is no direct evidence of a hydrogen back-reaction for these packages; however, the decreasing rate of change with increasing hydrogen overpressure does seem to suggest this.

Future plans

These samples will continue to be monitored for pressure increase.

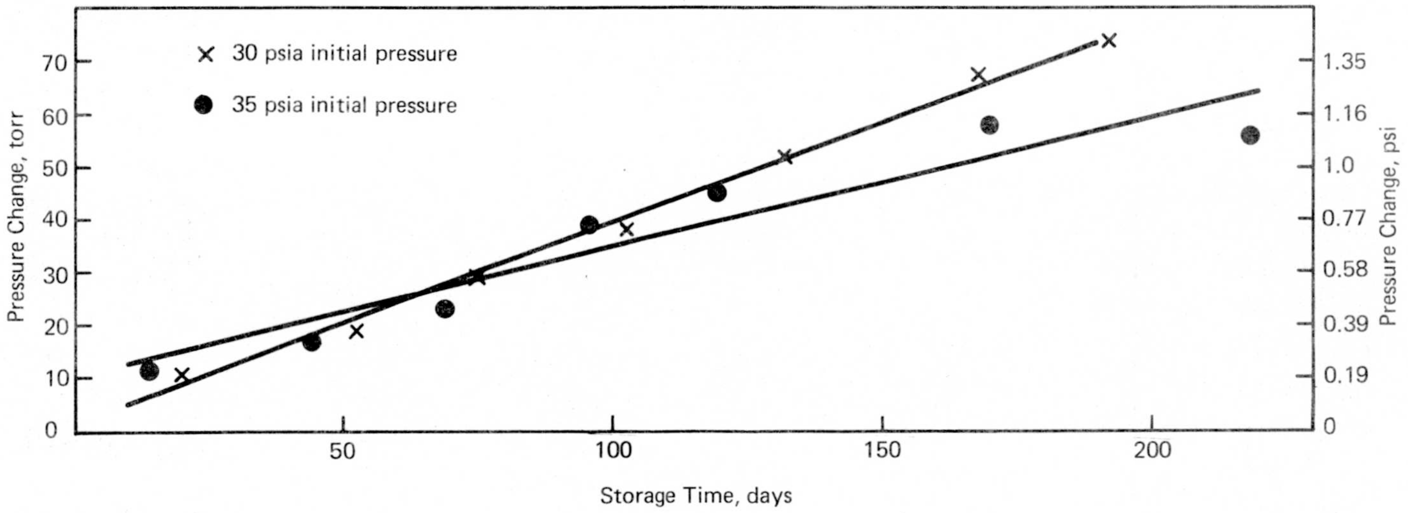


FIGURE 4 - Gas generation by tritiated water on cement-plaster with hydrogen cover gas.

Fixation of aqueous tritiated waste in polymer impregnated concrete

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

Background

Mound Facility, in cooperation with Brookhaven National Laboratory (BNL) undertook a program to test and develop the BNL polymer impregnation method [9] 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 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.

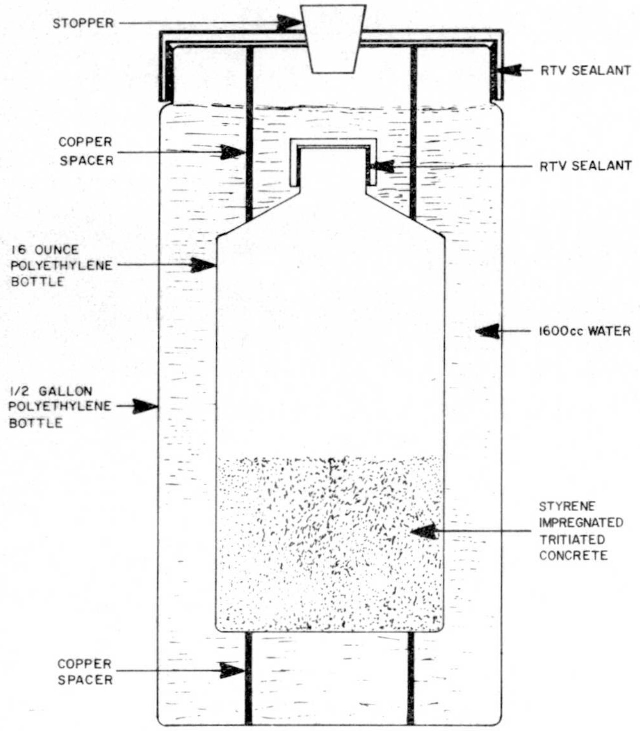


FIGURE 5 - Styrene impregnated tritiated concrete test.

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" (tritium-free) 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 cold 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.

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 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 (high early strength). Details of the preparation of these "hot" samples may be found in a previous report [10].

The samples were put into a test program to measure the relase rate of the tritium. The test method (shown in Figure 5) 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 were 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 used by Mound were linear low-density polyethylene (LPE). As expected, tests showed that LHPE is more resistant to attack by styrene monomer than is LPE. Options for investigation included: 1) reducing the bulk temperature while styrene monomer is in contact with the drum liner, 2) reducing the contact time of the drum liner and the monomer, and 3) using drums of LHPE or cross-linked high-density polyethylene (CLPE).

Accomplishments

The permeation data for the test samples are given in Table 2. No significant differences can be noted in the data on the first four groups which are still in the polyethylene bottles: cement III (Groups 1 and 4), 1:1 by weight of cement and plaster, or the 1:1 by volume of cement and plaster (see Figures 6 through 9). The fifth group did not have styrene added, therefore it was not heated as were the other groups. After 80 to 90 weeks there is no significant difference from the other four groups (see Figure 10). However, no significant difference is expected since the polyethylene bottle is much thicker than the layer of polystyrene and constitutes a considerable barrier to tritium permeation.

In addition to samples 59 and 72, samples 64, 67, 70, and 74 were removed from the polyethylene bottle and then submerged in the same test water and packaged as shown in Figure 5. Now the study has at least one nude cement block in each of the five groups. The exchange of the tritium from the cement to the leach water began to increase markedly, going from a fractional release of 10^{-3} in 65 weeks to 0.6 in only 16 additional weeks. Groups 2, 3, and 4 are the best; while Group 1 (high catalyst and high internal temperature) and Group 5 have a larger leach rate. In fact Group 1 and 5 values are approximately 3 times greater than Groups 2, 3, and 4 (see Table 2). Group 4 (sample 70) is the test block using the BNL method and is 3 times better than Group 5 (sample 74), which does not have the polystyrene protection.

Samples 59 and 72 were prepared with cement III and styrene with 5% and 1/2% 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 50 - 90 times greater than the amount that has passed by diffusion through the polyethylene bottles. The data are shown in Figures 6 and 9 for Groups 1 and 4. The greatly increased tritium release from these samples is attributed to the removal of the polyethylene bottle. Without the polyethylene, a thin layer of polystyrene is the only barrier between the concrete and the water.

The effect of the catalyst concentration is shown in samples 59 and 72. The release from sample 72 using the BNL recommended catalyst concentration is approximately one-half the release from sample 59. This is caused by a lower bulk temperature which results in fewer bubbles in the polystyrene.

Two sets of data, taken from samples 59 and 72, were analyzed by non-linear regression with the BMDP biomedical computer programs package, and curves were fitted to this data using equations of the form:

$$FR = P_1 + P_2 e^{-P_3/t}$$

Variables FR and t are fractional release and time, respectively, and P_1, P_2 and P_3 are constants. The results were excellent.

For 59:

$$FR = 0.5135 - 0.5135e^{-0.1272(t)}$$

Table 2 - PERMEATION TESTS

Group	Sample No.	Curies	Preparation Date	Type	Water/Dry Mix Ratio	Styrene (%)	Catalyst (%)	Polymerization Temperature (°C)	Total Permeation (Ci)	Fractional Release from Test Package	Fractional Release from Nude Block
1	58	386.5	5-10-77	Cement III	0.250	20	5	40	4.68	1.34 x 10^{-2} /93 wk	
1	59	386.3	5-10-77	Cement III	0.250	20	5	40	224.9		0.64/93 wk
2	63	385.9	5-13-77	1:1 by weight	0.250	23	1/2	55	2.96	8.48 x 10^{-3} /93 wk	
2	64	386.6	5-13-77	1:1 by weight	0.250	23	1/2	55	56.22		016/16 wk
3	67	386.9	5-13-77	1:1 by weight	0.305	20	1/2	55	74.23		0.21/16 wk
3	68	386.6	5-13-77	1:1 by weight	0.305	20	1/2	55	5.70	1.63 x 10^{-2} /92 wk	
4	70	386.6	6-03-77	Cement III	0.250	20	1/2	55	68.47		0.20/16 wk
4	71	386.3	6-03-77	Cement III	0.250	20	1/2	55	1.32	3.77 x 10^{-3} /88 wk	
4	72	386.5	6-03-77	Cement III	0.250	20	1/2	55	116.03		0.33/91 wk
5	74	387.0	7-22-77	Cement III	0.250	None	None	None	213.33		0.60/16 wk
5	74	193.4	7-22-77	Cement III	0.250	None	None	None	1.35	7.64 x 10^{-3} /82 wk	

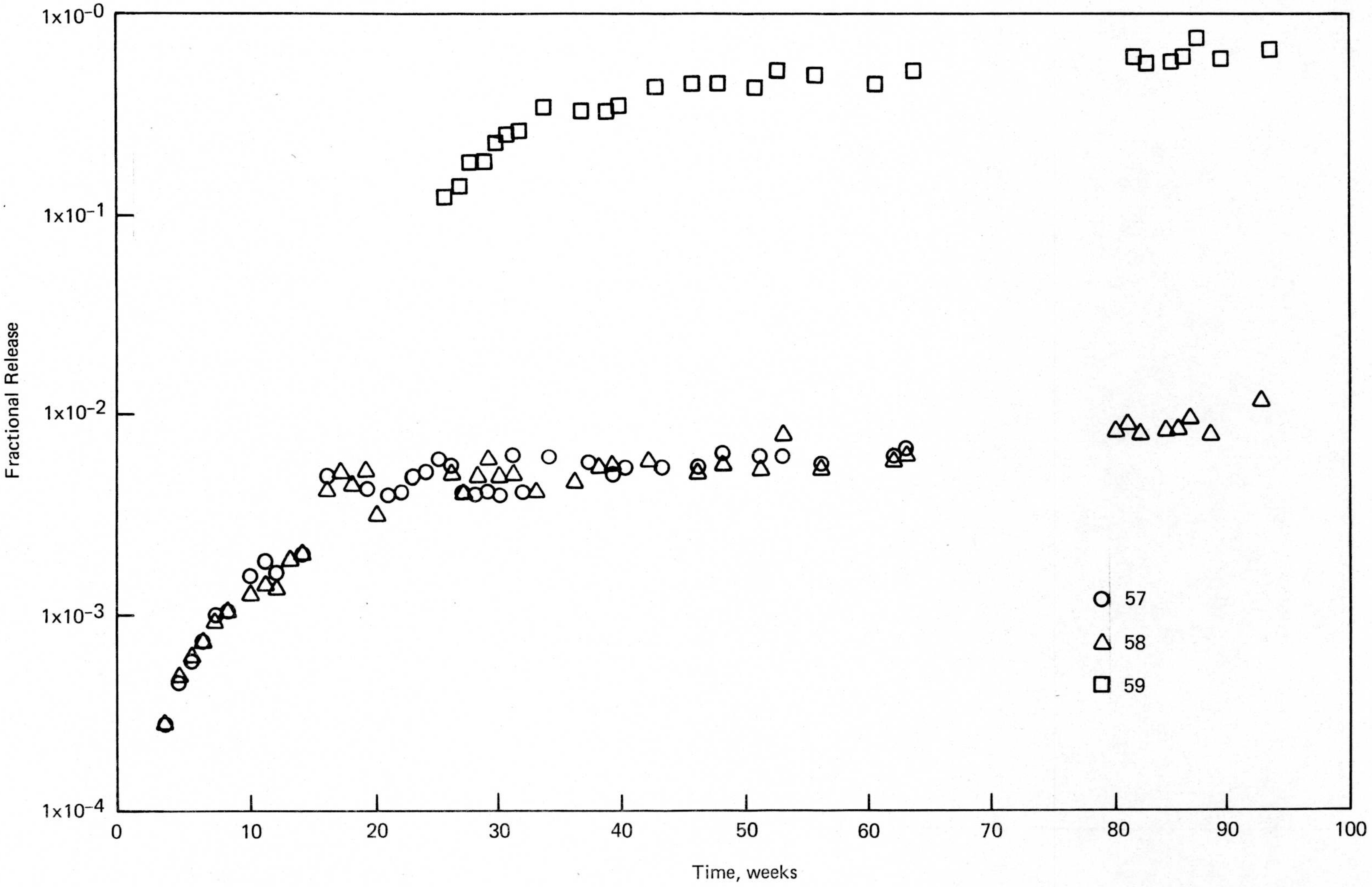


FIGURE 6 - Fractional release from cement III samples, Group 1.

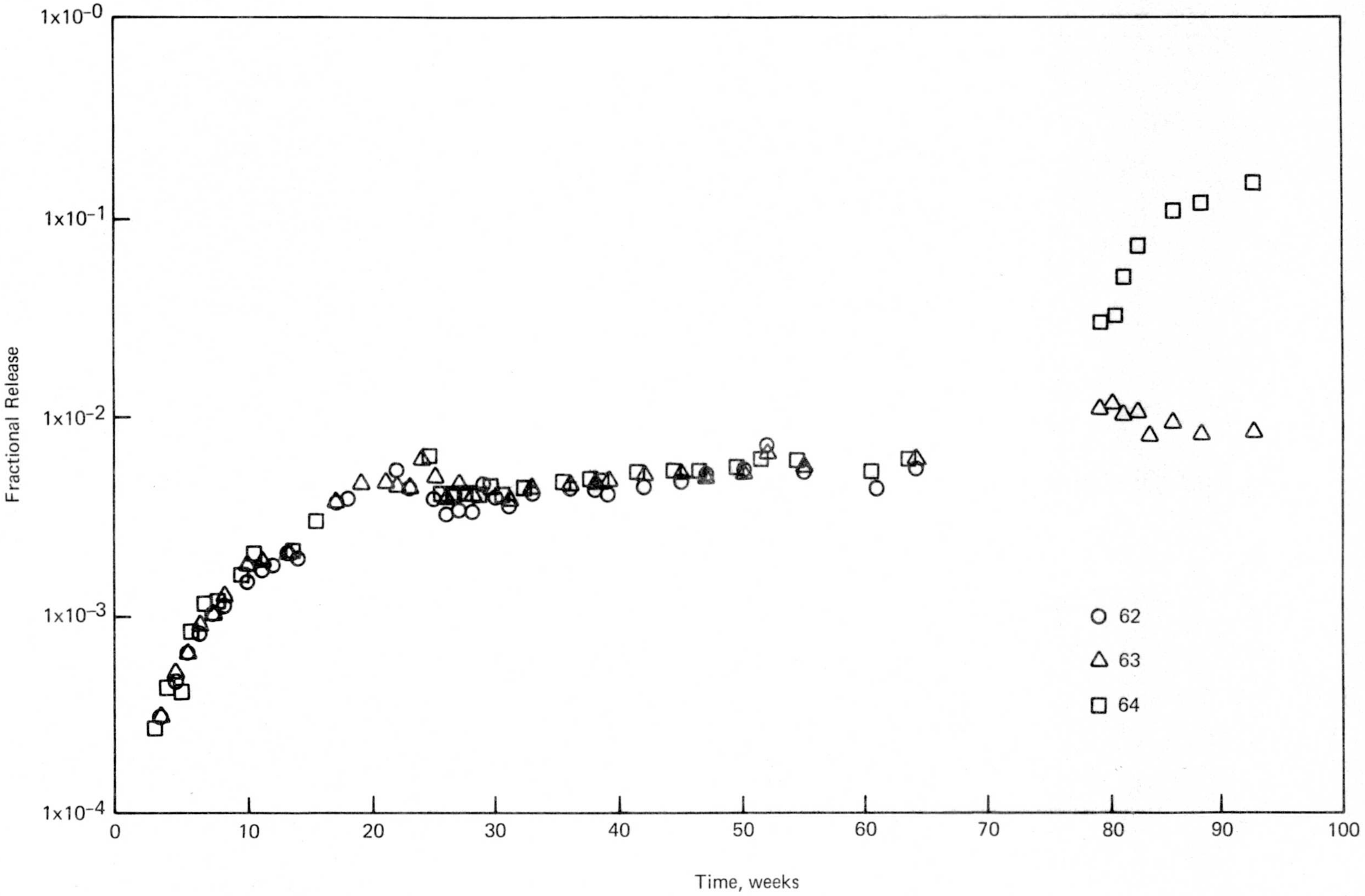


FIGURE 7 - Fractional release from cement-plaster (1:1 by weight), Group 2.

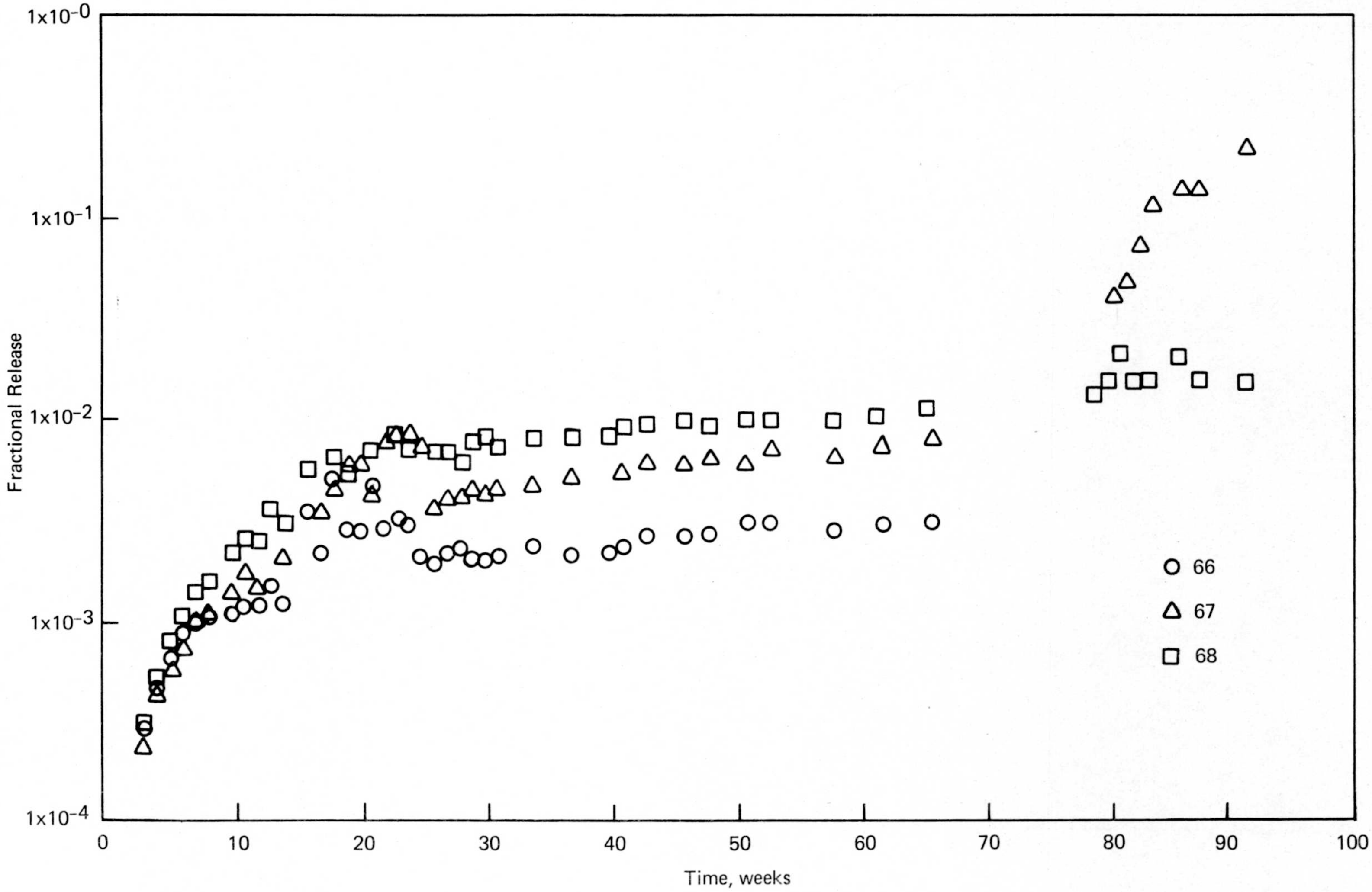


FIGURE 8 - Fractional release from cement-plaster (1:1 by volume), Group 3.

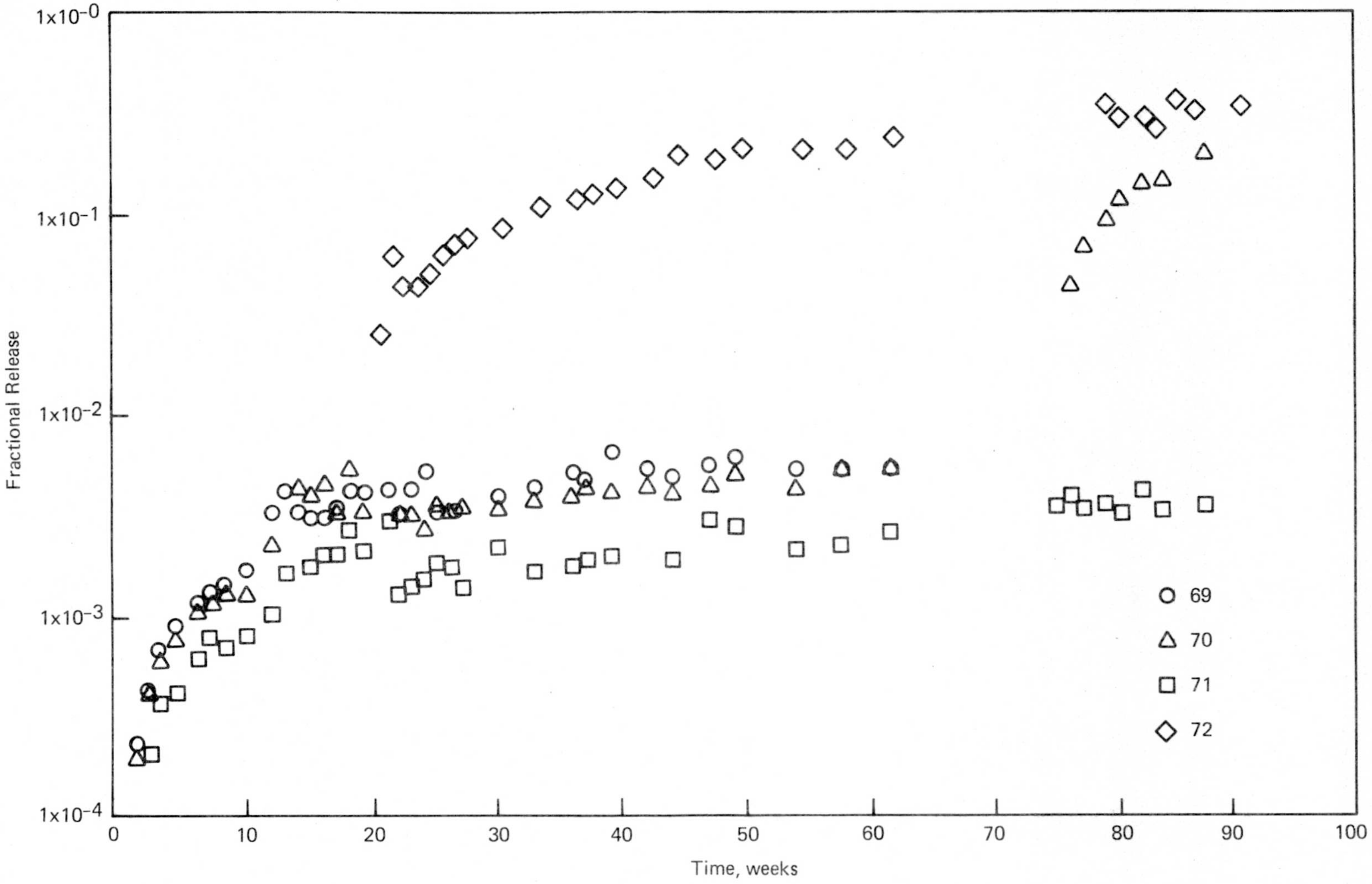


FIGURE 9 - Fractional release from cement III, Group 4.

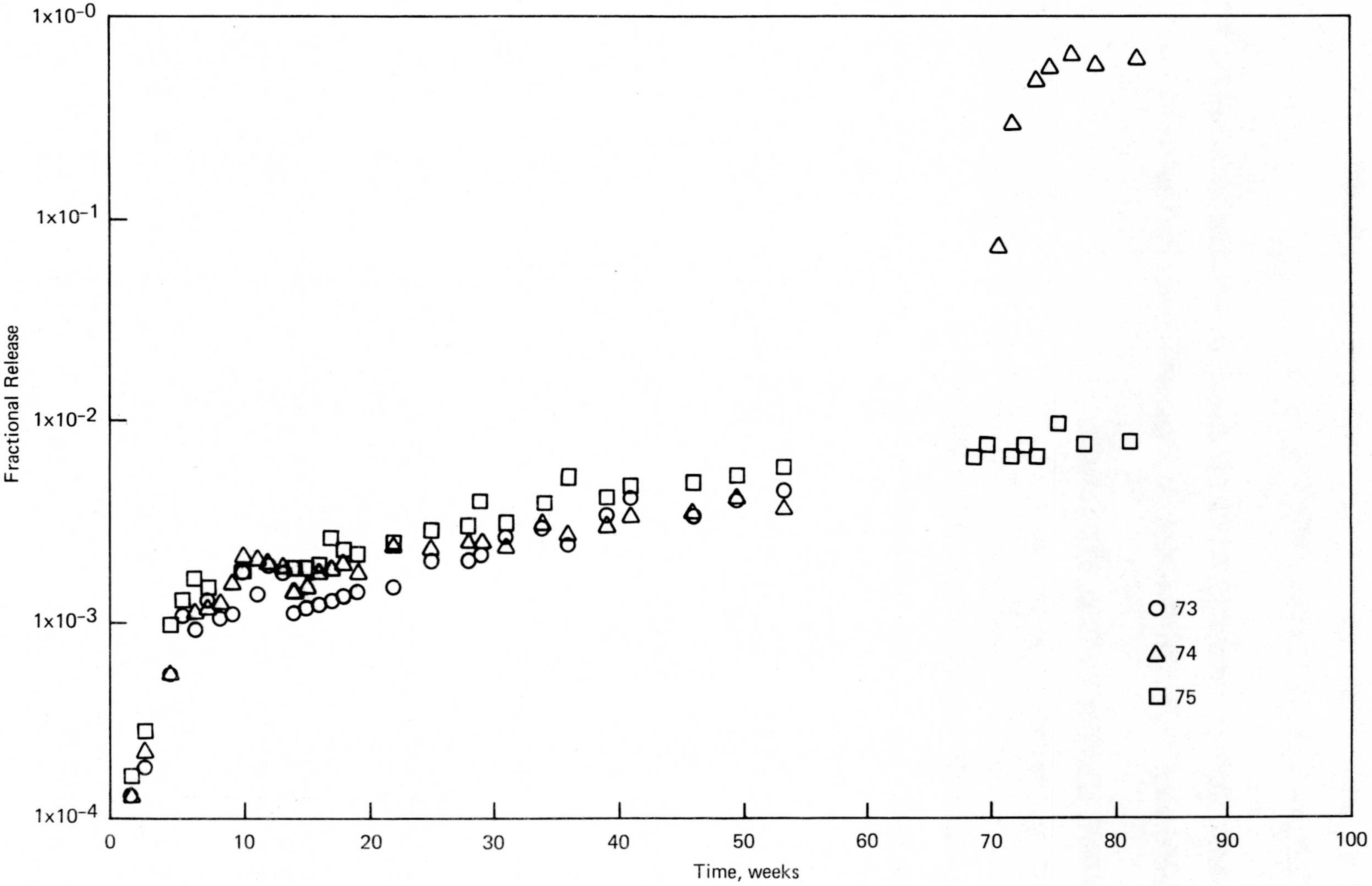


FIGURE 10 - Fractional release from cement III, Group 5.

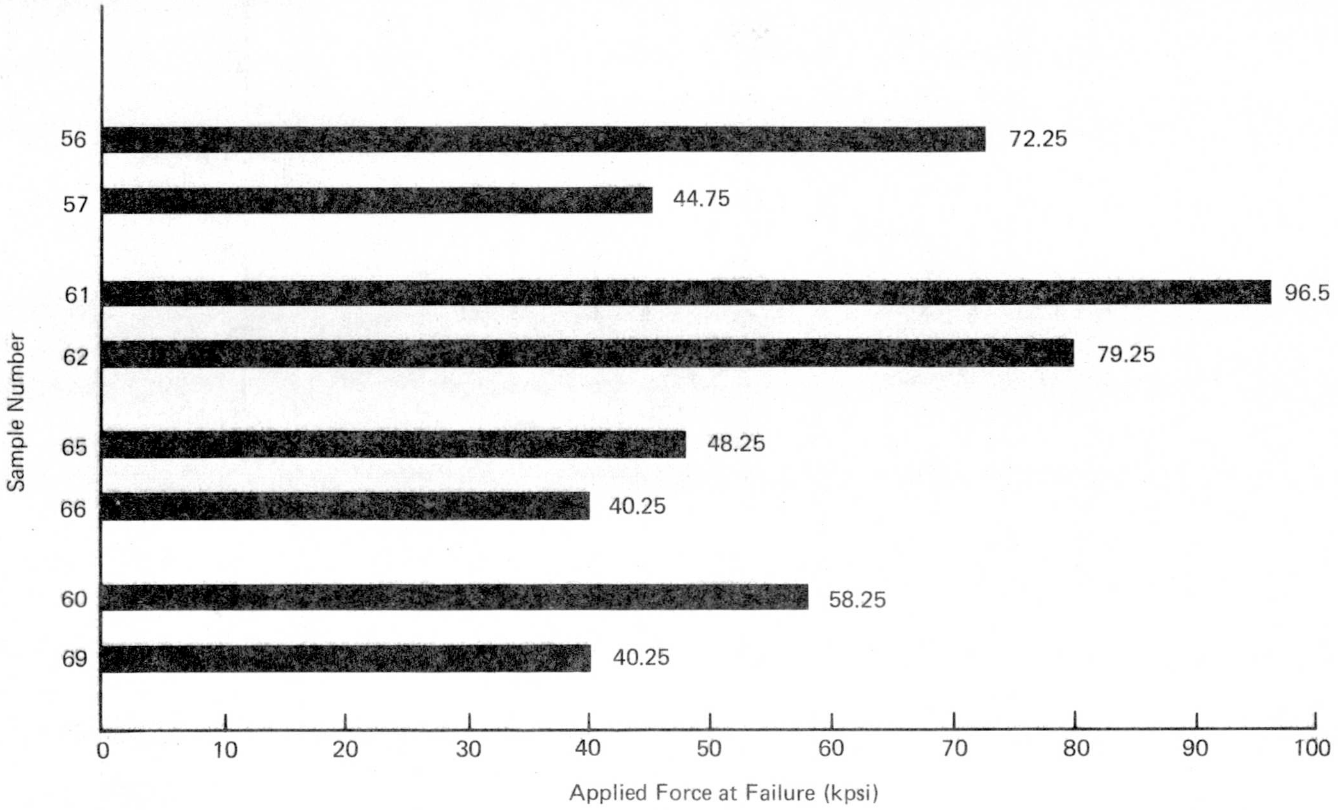


FIGURE 11 - PITC compressive test data.

Where FR is released tritium/total tritium, corrected for decay and t is time in weeks since immersion in the leach water.

For 72:

$$FR = 0.2761 - 0.2761e^{-0.0476(t)}$$

Because of the data variation, a one exponential term equation gives the optimum fit.

The sample data on the five groups for the last 75 weeks show little increase in the amount of tritium diffusing through the polyethylene bottle from the concrete blocks.

The probable cause for the difference in values between samples 66, 67, and 68 of Group 3, and the differences in the other groups is variations in the stock polyethylene bottles.

One tritiated specimen and one non-tritiated control specimen from Groups 1 through 4 were removed from leach testing and stripped of their polyethylene bottle. These samples (tritiated 57, 62, 66, 69; non-tritiated 56, 61, 65, 60) were tested individually to determine their compressive yield strength by placing them in a MTS closed-loop electrohydraulic testing system. The cylindrical samples were placed such that the compressive force was normal to the axis of the sample. A bar graph of the test results is shown in Figure 11. The 1-yr old tritiated samples in each group exhibited a yield point consistently lower than the non-irradiated sample in that group, suggesting that radiolytic damage to the polystyrene does indeed occur. This damage may be in the form of broken polystyrene bonds, or it may be that gas generated by radiolysis weakened the polystyrene bonding.

In further attempts to develop a workable procedure for preparing a full-scale cold prototype burial package, test drums 6 and 7 were prepared. They were prepared in a manner similar to drums 1 through 5, that is, 28 liters of water was injected into 113 kg of Portland type III cement in accordance with the developed procedure. These drums containing cured cement were heated to 45°C, then 24.3 kg of styrene monomer containing 3/4 wt % AIBN (2,2' -[azobis-2-methylpropronitrile]) catalyst was added. The heater setting on drum 6 was increased manually after 3 hr (styrene soak period) to accelerate the polymerization process.

On drum 6 the maximum temperature at the center of the package was 97°C after 7 hr. This is within the 100°C limitation and all other aspects of the polymerization were nominal. The 30-gal steel drum was cut off and the 27-gal low density polyethylene liner was found to be in excellent condition. No discoloration and very slight deformation was noticed where the rib area of the drum had been. There was also good adherence between the polyethylene liner and styrene layer.

Drum 7 used a new heater controller to program the temperature used to start the styrene polymerization. It was found that the polymerization occurred more rapidly than expected. The peak temperature in the center of the package was lower (65° as opposed to 97°C) than in previous runs. The heater problem may be due to controller readout error and is being investigated.

Styrene monomer containing 3/4 % by weight AIBN catalyst was tested for polymerization at ambient temperature. After 2-1/2 weeks the styrene was noticeably more viscous, and after one month had solidified. Based on this, no problems are anticipated in cleaning the lines of styrene monomer in the new packaging facility which is planned as an addition to the SW-149 waste packaging facility.

Future plans

Funding for this project ended 9/30/78. A final report is being written on the progress achieved during the past 3 yr in the area of polymer impregnated tritiated concrete (PITC). Funding was received early in FY 1979 for a general plant project (GPP) to permit the application of the PITC concept to all high-activity aqueous tritiated waste at Mound. A greatly reduced level of development effort will be maintained in the PITC area. Some final polymerization experiments will be performed prior to the preparation of a full-scale, "hot" test package. Development will be continued as required to define equipment and operating parameters for the new Tritiated Waste Fixation Facility. The five groups of samples currently in the test program will be maintained and checked periodically to determine the tritium release rate.

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 [11-13]. There are two general categories of liquid waste: water (1000 Ci/liter) and vacuum pump oil (50 Ci/liter). Since 1972 these materials have been packaged for disposal in an improved container. 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 [14]. Twenty-five liters of waste oil is sorbed on vermiculite in a polyethylene drum, whereas 27 liters of liquid water waste is sorbed on a cement-plaster mixture in the polyethylene drum. The packaging procedure thereafter is the same: containment in a 30-gal drum and finally in a 55-gal drum.

A study of the tritium release rate from actual burial packages was initiated in May 1975 and continues. The study consists of the individual immersion of representative actual burial packages in a known volume of water. The surrounding water is periodically sampled and analyzed for the presence of tritium; a release rate is then calculated from these data. Figure 12 is a schematic of a typical burial package under test.

Two drums containing octane waste (113 and 114), are positioned in the water similarly to the positioning of the oil and water drums; however, the internal package is quite different: 250 ml of contaminated octane waste is sorbed on vermiculite contained inside a 32-oz polyethylene bottle which is then sealed. Three of these bottles are sealed inside a 50-gal steel drum liner. This liner is then sealed inside a 55-gal steel drum, which is in turn sealed inside a 83-gal steel drum. All void volumes within the package are filled with vermiculite and asphalt. These octane wastes were packaged in the 55-gal drum about 6 yr ago and the 83-gal drum was added in 1977.

The 83-gal drum now becomes the waste package primary container and is immersed in water contained inside a 146-gal drum. Here the 146-gal drum becomes the test container, whereas in the case of the water and oil waste drums, the 83-gal drum is the test container.

Accomplishments

Figures 13 to 19 are the resultant permeation rates (total permeation as a function of time in test) to date for the study.

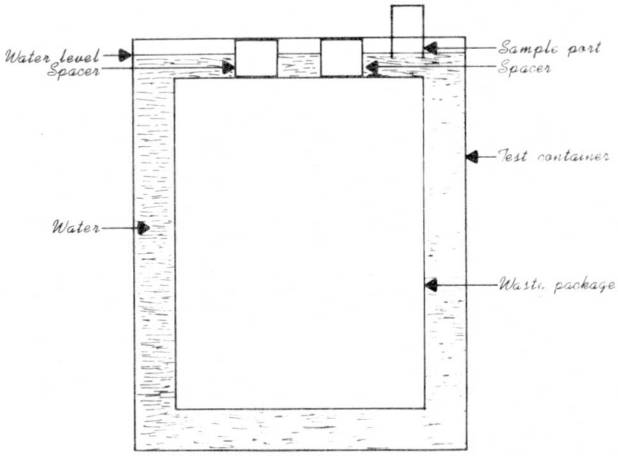


FIGURE 12 - Schematic of test package.

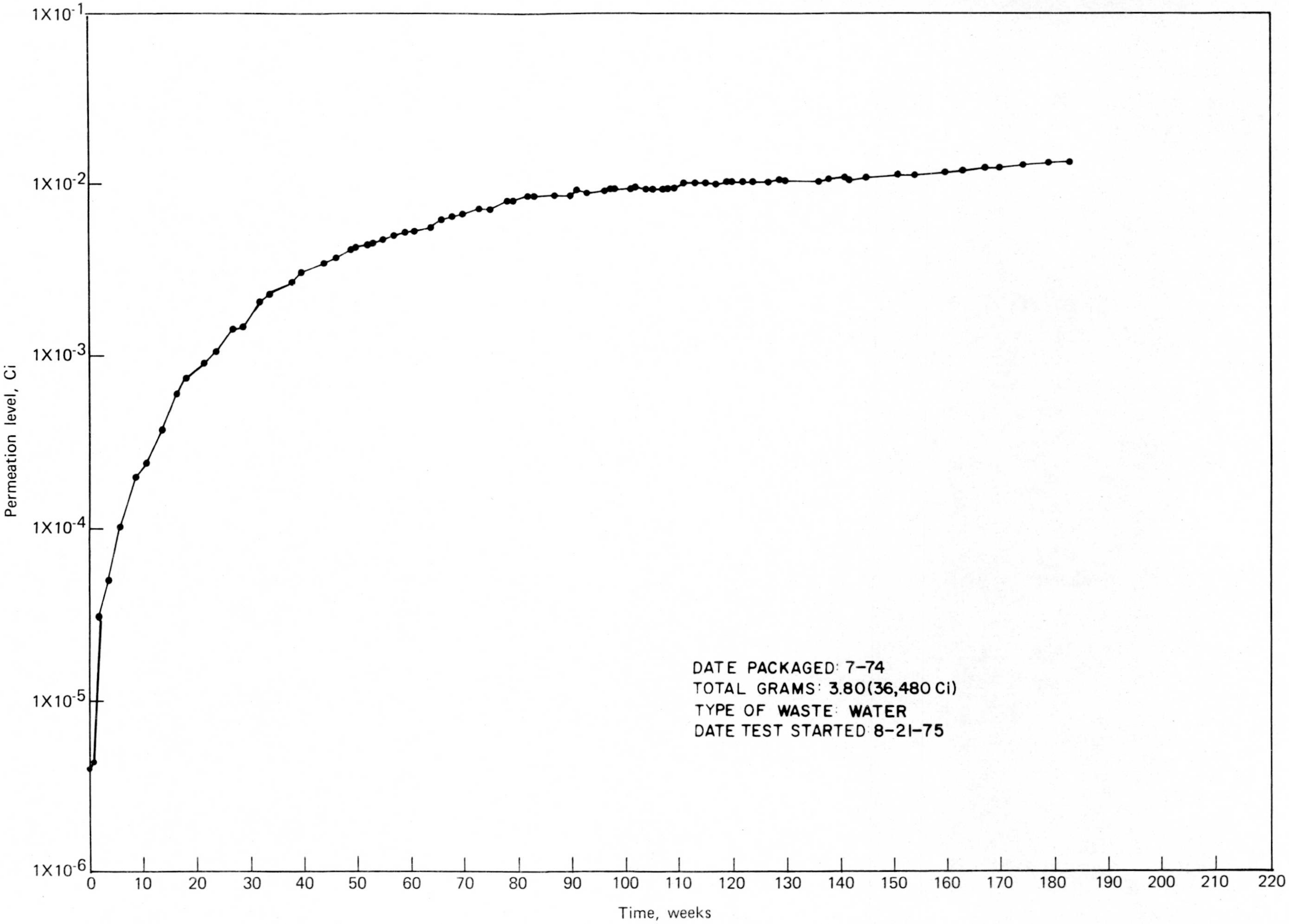


FIGURE 13 - Tritium waste package permeation rate for drum No. 205.

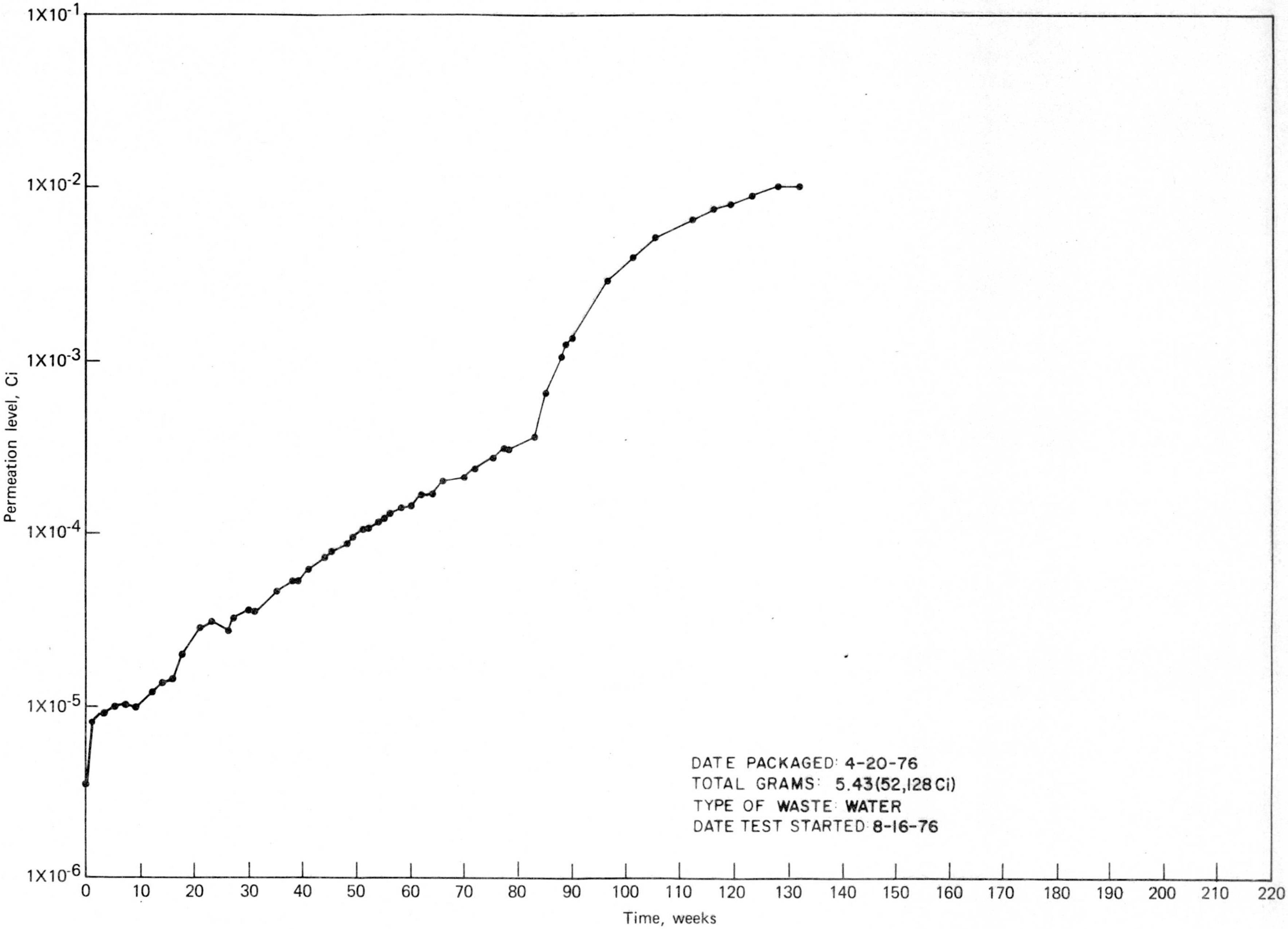


FIGURE 14 - Tritium waste package permeation rate for drum No. 318.

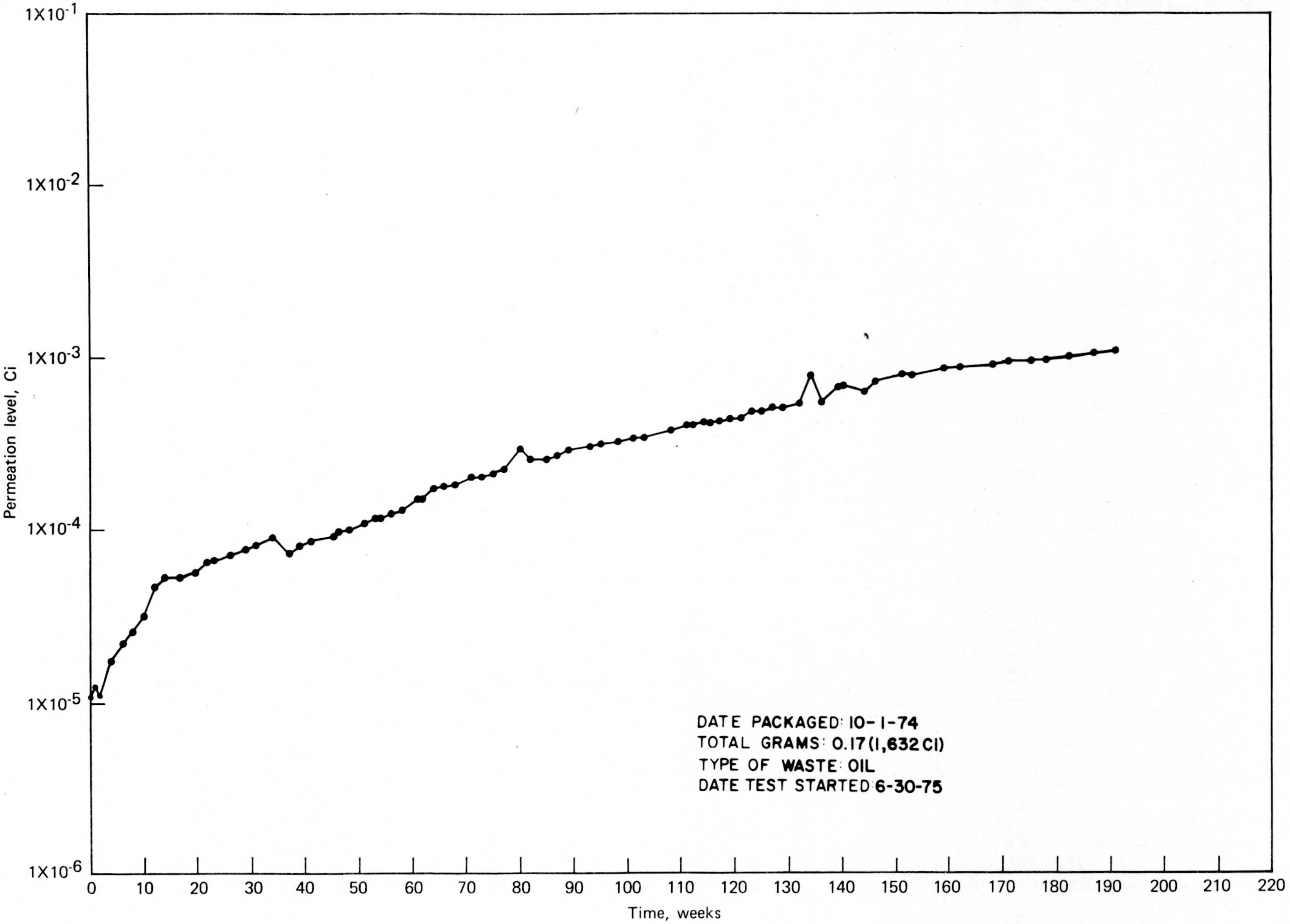
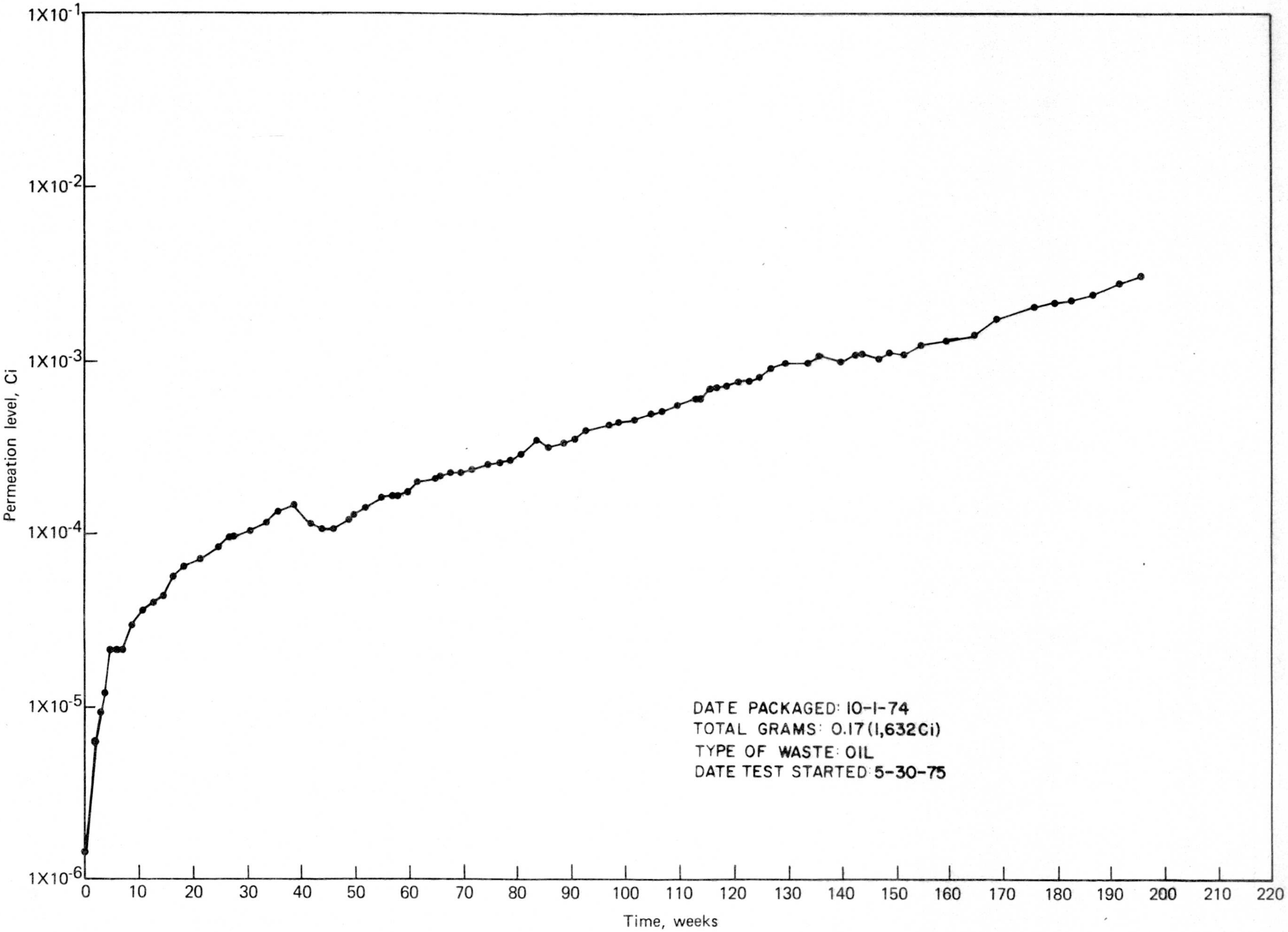


FIGURE 15 - Tritium waste package permeation rate for drum No. 217.



DATE PACKAGED: 10-1-74
TOTAL GRAMS: 0.17 (1,632 Ci)
TYPE OF WASTE: OIL
DATE TEST STARTED: 5-30-75

FIGURE 16 - Tritium waste package permeation rate for drum No. 218.

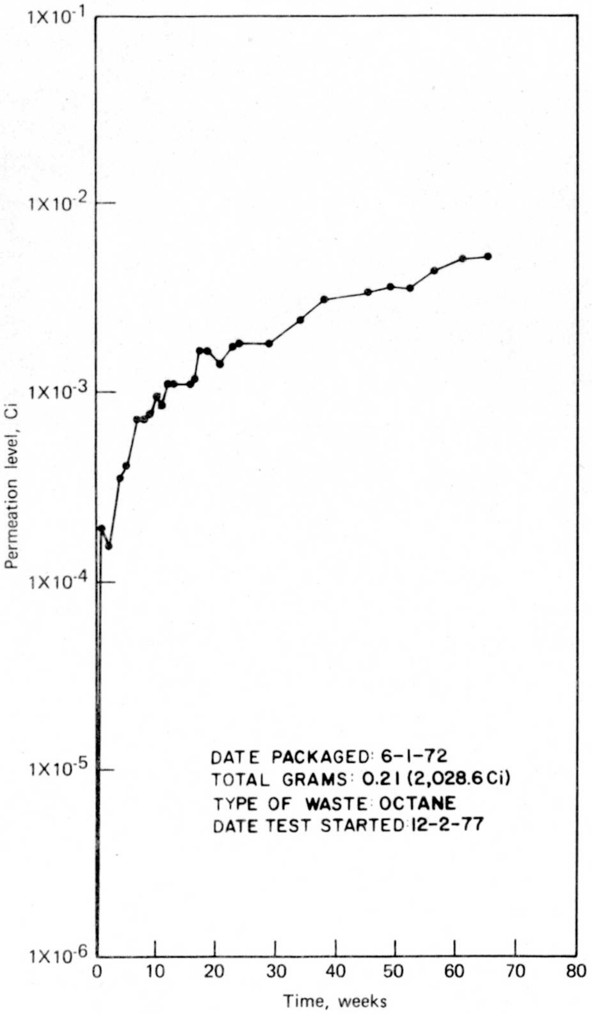


FIGURE 17 - Tritium waste package permeation rate for drum No. 114.

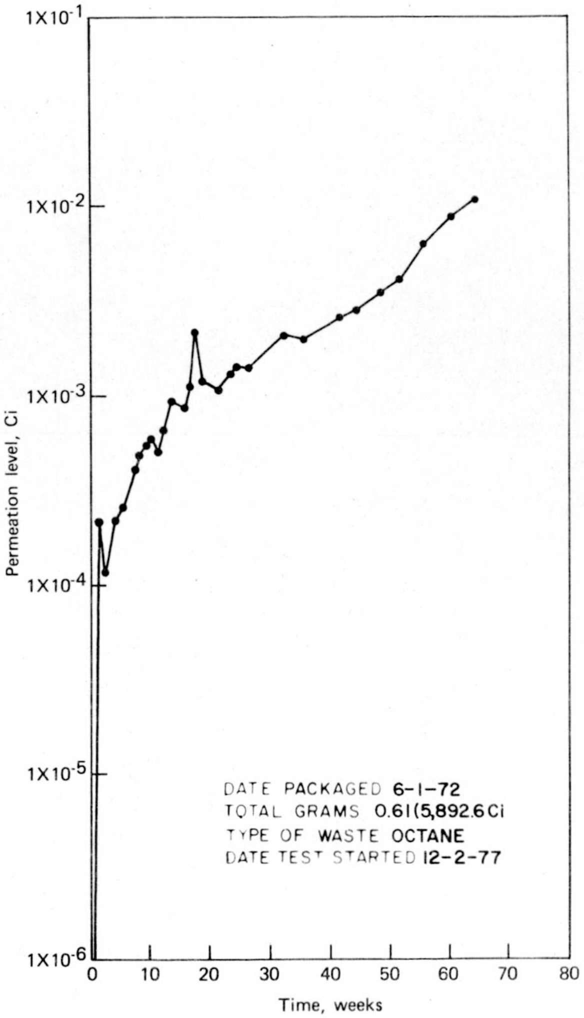


FIGURE 18 - Tritium waste package permeation rate for drum No. 113.

Figure 19 was prepared to compare the fractional release values (total curies permeation ÷ total curies contained) of all packages as a function of the time since the packages were prepared. This illustration takes into account the total curies actually in each package with consideration given to tritium decay since the burial package was first assembled.

The drum study of the release of tritium from actual burial packages has continued. There was a 35-week period (weeks 110-145) when the oil and water drums had essentially the same fractional permeation rates. During the last 60-week period, the fractional permeation rates of the two oil drums have increased slightly faster than the rates of the water drums (Figure 19).

The drum release study now includes all three types of high-activity tritiated liquid waste generated at Mound (see Figures 13 to 19). Note that the maximum fractional release rate on these drums is only 3 x 10^{-6} after 360 weeks since preparation of the burial package.

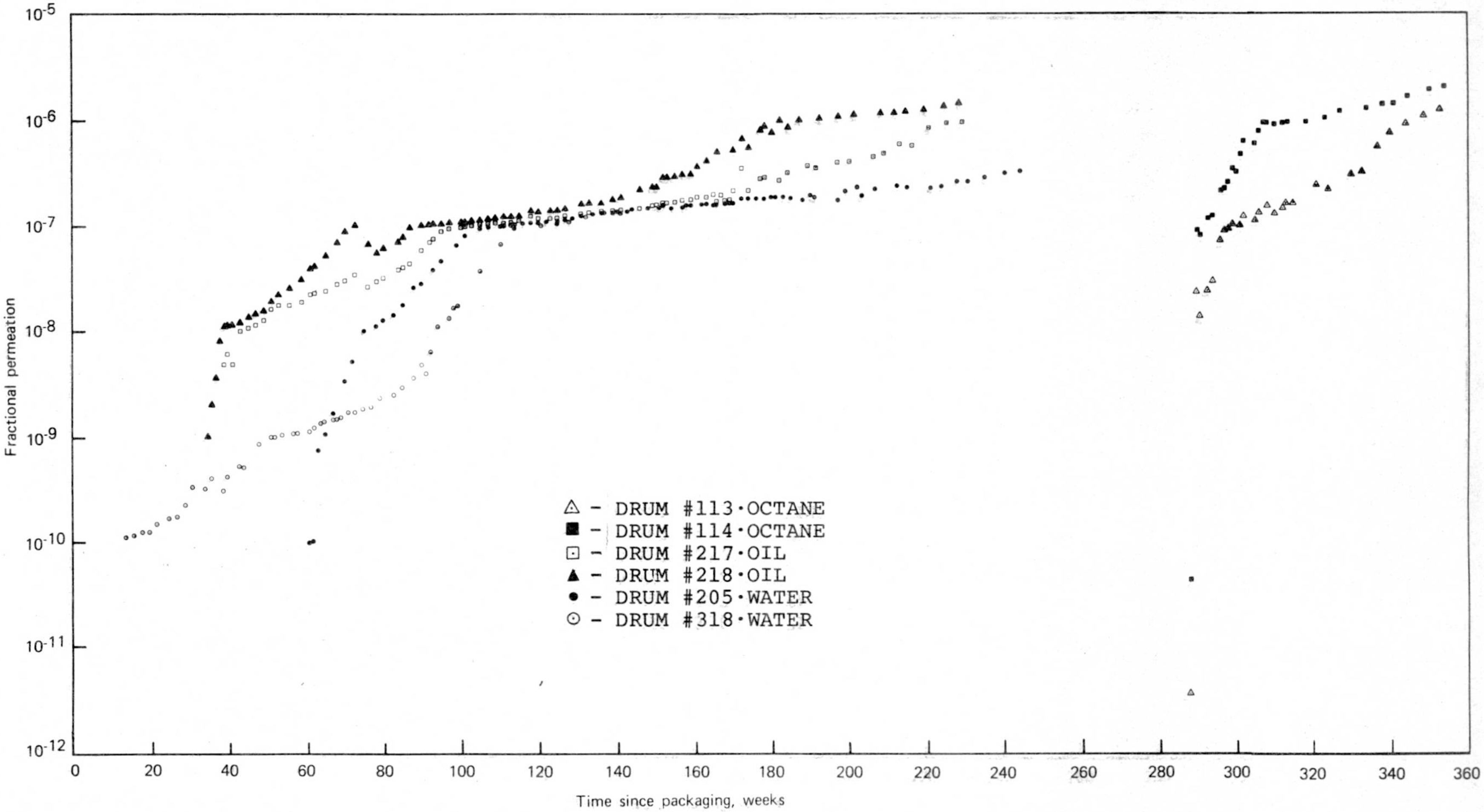


FIGURE 19 - Comparison of fractional releases from all drums.

Future plans

The test will be continued and an attempt will be made to determine the actual tritium and hydrogen release mechanisms.

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