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Tritium Waste Control Project:
October 1976 - March 1977

Harold F. Anderson and Carl J. Kershner

October 6, 1977

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Miamisburg, Ohio
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Foreword

The format of this report has been changed to reflect changes in funding. In this document section one, "Catalytic Detritiation Studies," and Section three, "Fixation of Aqueous Tritiated Waste in Polymer Impregnated Concrete," are funded by 189CAL0219A. The remaining sections are work related to Tritium Waste Control but not directly funded by AL0219A.

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Pressure increase and gas composition were measured over (1) tritiated water (1000 Ci/liter) with and without cement-plaster fixation and (2) tritiated n-octane (1000 Ci/liter) with and without vermiculite or absorbal fixation. The back reaction that limits pressure buildup over water was inhibited by the fixative. The pressure buildup over waste vacuum pump oils was much less than the "worst case" predicted.

MANAGEMENT OF HIGH SPECIFIC ACTIVITY TRITIATED LIQUID WASTES 17

Ninety-six drums of solidified high-activity liquid waste were inspected approximately one year after assembly. Of these, four had internal pressures of 10 psig in the polyethylene primary container. This gas was found to contain mainly hydrogen and nitrogen in addition to the argon originally present.

A study of tritium release from typical waste packages is continuing. To date, a maximum release of 1 Ci occurred from a package containing 90,000 Ci. The average daily fractional release from six packages is 2×10^{-8}.

Pressure tests were performed on both the components of the waste package and on the assembled package. The primary container can withstand a minimum of 30 psig internal pressure and 40 psig when contained in the secondary steel drum.

Catalytic Exchange Detritiation Studies

M. L. Rogers and T. K. Mills

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 ERDA 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 exchange detritiation stripping process as it might apply to a 5 metric ton/day nuclear fuel reprocessing plant.

Accomplishments

Operation of the experimental system, as well as experiments performed by the AECL (Atomic Energy of Canada Limited) at Chalk River, encouraged the design and construction of a pilot-scale Combined Electrolysis Catalytic Exchange (CECE) system.

This system is a combination of two parts, the catalytic exchange section and the electrolysis section. The catalyst used is a hydrophobic precious metal type developed and manufactured at Chalk River by AECL.

CATALYTIC EXCHANGE

The catalytic exchange section (Figure 1) of the process centers around two catalyst-packed columns that are arranged in series to operate as if they were the upper and lower sections of a single column. Each column is 7.5 m long and has an inside diameter of 2.5 cm, which results in a superficial cross sectional area of 5 cm^2 and a gross column volume of 3800 cm^3. The packing in each column consists of 4300 g of catalyst spheres 0.6 cm in diameter. Liquid redistribution rings are placed at 45-cm intervals throughout the length of each column to limit channeling in the packed sections.

In operation, the liquid to be detritiated is supplied at approximately 5 cm^3/min. It is combined with the liquid stream exiting the upper column and introduced at the top of the lower column. The 10 cm^3/min liquid stream from the bottom of the lower column is routed to the electrolysis section of the process where it is used as feed. Currently, the liquid stream entering at the top of the upper column is made up of distilled water, supplied from outside the process. Ultimately, however, this stream is expected to be a reflux stream, provided by a recombiner or fuel cell which would in turn be fed by the hydrogen product from the upper column.

The hydrogen stream from the electrolysis section is fed to the bottom of the lower column and then is routed to the bottom of the upper column. Upon exiting the upper column, it is currently vented to the atmosphere through a stack. As stated previously, however, it is anticipated that this stream will later be fed to either a fuel cell or a recombiner to provide reflux to the process and a detritiated liquid product.

Control of the catalytic exchange section of the process consists of five loops, serviced by a single microprocessor. In each loop the control element is a metering valve driven by a stepping motor. For the gas stream passing through the columns, the sensing element is a turbine meter located downstream from the columns. The two liquid feeds to the process are sensed by hot-wire anemometers, and the levels maintained in the bottom of each column are monitored by capacitive level sensors. Although not used in the control of the process, tritium concentrations are monitored at various points by liquid scintillation counters for liquid streams and ion chambers for gas streams.

ELECTROLYSIS

The principal items of equipment in the electrolysis section (Figure 2) are four General Electric electrolysis stacks. Each stack consists of eight cells, each of which has an active area of 46.45 cm^2. Current density is 1.076 A/cm for the maximum rated current of 50 A. Rated stack voltage is 16.8 V d.c. Operating at these conditions, each stack electrolyzes 2.45 cm^3/min of water to produce approximately 3000 cm^3/min of hydrogen and 1500 cm^3/min of oxygen. The maximum pressure is 100 psig and the upper temperature limit is 66°C. Proper stack operation requires that feed water resistivity be maintained at greater than 500,000 ohm-cm, and that a water circulation rate of approximately 400 cm^3/min per eight-cell stack be maintained.

Feed to the electrolysis section is supplied from a feed tank, which also provides recirculation capacity. From the feed tank, the water is pumped through a deionizer and then to the cells. From the cells, the hydrogen stream passes through a cooler and a phase separator and is returned to the catalytic exchange section. The oxygen stream, after being routed through a cooler and a phase separator, is currently sent to the air detritiation system for purification and disposal. It is anticipated, however, that this stream will ultimately be fed to a recombiner or a fuel cell supplying reflux to the catalytic exchange columns. The water removed from both the oxygen and hydrogen streams in the phase separators is mixed with the fresh feed upstream from the deionizer and recirculated through the system.

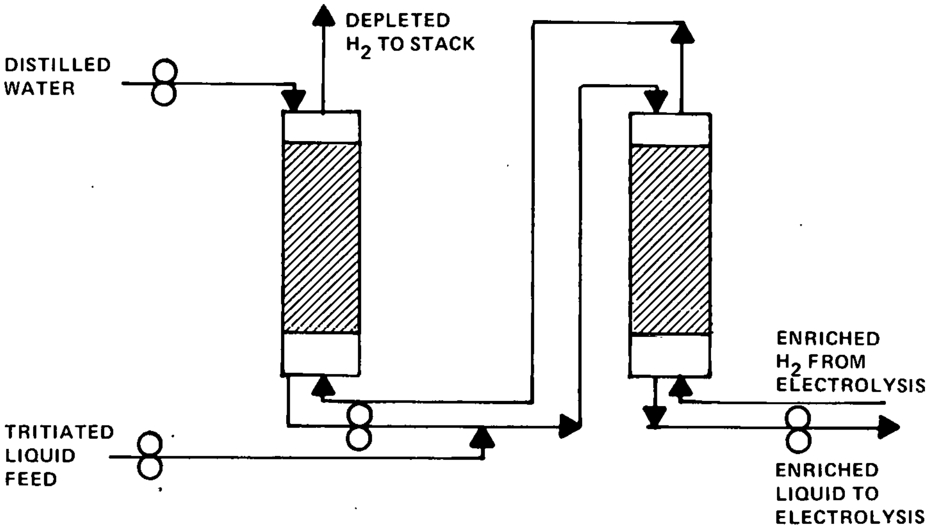


FIGURE 1 - Catalytic exchange section—simplified schematic.

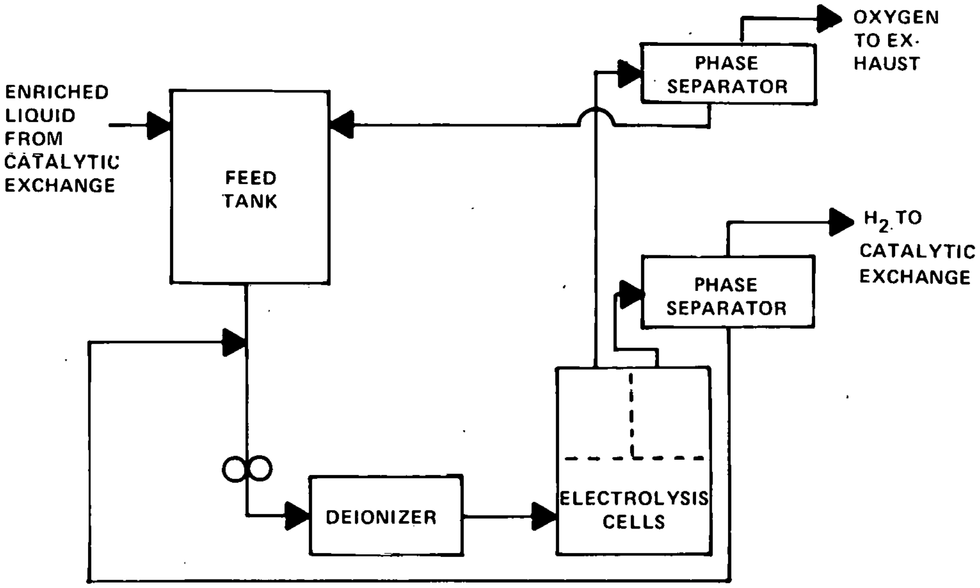


FIGURE 2 - Electrolysis section—simplified schematic.

Future Plans

The pilot CECE system will be functioned to obtain operating experience, determine scale-up parameters, and improve system dependability.

Independent tests are also in progress to determine the effect of high specific activity tritiated water on the catalyst and the electrolysis membrane.

Tritiated Liquid Waste Decontamination (Molecular Excitation)

C. J. Kershner, R. E. Ellis, and
F. W. Bobrowicz

Background

The decontamination or volume reduction of tritiated water wastes require isotopically selective separation processes which are generally more involved and costly than the physical and chemical processes applicable to other types of radioactive wastes. Although the isotope effects associated with the hydrogen isotopes are among the largest possible, a multistage process is required to achieve any significant enrichment or volume reduction. Moreover, in all "classical" separation processes energy must be supplied to the entire mixture to induce the required physical or chemical changes, whereas in principle only the entropy of unmixing is required. For example, approximately 500,000 times as much energy is required to produce heavy water by distillation than would be required if the process involved merely the unmixing of the HDO from natural water. For low-level liquid wastes containing tritium, e.g., 0.2 Ci per liter water, the energy required to remove the tritium by a classical separation process, such as water distillation, is approximately 100 million times that required if the energy to unmix would be applied only to the HTO molecules in the mixture.

Of the 100 or more separation processes considered for hydrogen isotopes, only one, selective photoexcitation, has the potential for orders-of-magnitude higher separation factors and, in principle, requires much less separative work because the separation energy is applied to the minor constituent rather than to the entire feed mixture. In conventional multistaged separation processes, sufficient energy input is needed for processing the total feed quantity many times to maintain the total cascade flow required for the desired separation. Thus, selective photoexcitation is a very attractive process for an application where one is concerned with the isotopic separation of trace quantities from a voluminous quantity of feed such as in the case of water detritiation or heavy water enrichment.

The goal of this study is to determine the feasibility of decontamination by selective molecular excitation. If the process proves successful, further applications will be considered, such as (1) extension to the treatment of high-specific-activity aqueous wastes, (2) control of the tritium level in the primary coolant of light-water reactors, and (3) removal of deuterium from water.

A plausible scheme to detritiate low-level aqueous wastes by molecular photoexcitation has been formulated. The process, which is conducted in the gas phase, consists of isotopically selective photodissociation (ISP) of HTO in the presence of H_2 which scavenges the photoproducts. The ISP is achieved by a two-photon process employing an infrared (ir) laser and an ultraviolet (uv) flashlamp. The ir laser selectively excites the OT stretching vibration in HTO at 4.35 μm, whereas the uv flashlamp is filtered to photodissociate only the vibrationally excited HTO molecules. The photoproducts, T and OH, both react rapidly with H_2 to produce HT and H_2O, respectively. Recycling the hydrogen stream may significantly enrich the tritium relative to the water stream. An analysis of the kinetics indicates that for low-level wastes, the effect of the tritium β decay on regeneration of HTO places a more stringent limitation on the tritium level allowable in the hydrogen stream than does the reaction, OH + HT → HTO + H.

Although this scheme is a convenient and appropriate system for proof-of-principle experiments, further analysis has shown that it is not applicable to large-scale detritiation projects, e.g., waste from nuclear fuel reprocessing plants. First, qualitative calculations indicated that the isotopic selectivity of the process was not sufficient. The photodissociation rate for HTO exceeds that for H_2O only by a factor of about 25. In light of the low tritium levels being considered, 1 ppm or less, most of the laser energy is wasted in photodissociation of H_2O. Second, H_2 has two serious drawbacks as a scavenger: (1) tritium enrichment requires recycling of the hydrogen, and (2) the HTO may also photodissociate into OT and H with OT reacting with H_2 to regenerate HTO.

The problem of isotopic selectivity may be overcome by pumping more vibrational energy into the HTO molecules. The best approach towards this end is multiple vibrational excitation by a very high power laser at 4.35 μm. The drawbacks of using H_2 for a scavenger may also be circumvented by using CO. These modifications were used in a preliminary economic study of detritiating the waste stream from the AGNS nuclear fuel reprocessing plant. The results indicate possible advantages for laser isotope separation (LIS) over catalytic exchange, presently the most promising approach.

A tunable ir laser developed by Prof. R. L. Byer and coworkers at Stanford University was the most appropriate for our purposes. The laser consists of a $LiNbO_3$ optical parametric oscillator (OPO) pumped by a Q-switched Nd:YAG oscillator-amplifier-isolator chain. The laser is tunable from 1.4 to 4.40 μm with relatively high powers (∿1 mJ/pulse). Prof. Byer was retained as a consultant on the procurement of a comparable laser system. A Q-switched Nd:YAG oscillator-amplifier-isolator chain was procured from General Photonics Corporation. The other major components that have been procured include a $LiNbO_3$ crystal (Crystal Technology) for the OPO, a multipass two-photon absorption cell (Wilks Scientific Corporation), a xenon flashlamp system (Xenon Corporation), and an 0.6-m monochromator (J-Y Optical Systems).

Accomplishments

The entire scavenger and irradiation cell apparatus including the monitoring and control instrumentation was completed for the two-photon ISP system. The uv source, xenon flashlamp, was adapted to the photolysis cell and is ready for use in "control" experiments. A problem with OPO operation has been traced to prelasing due to a degradation in isolator rejection, and a modification to the laser power supply is being made to correct an output deficiency which appears to be the cause.

Construction and assembly of the entire H_2O/H_2 flow and reaction cell system were completed. The entire system was leak checked and all pressure, flow, and moisture transducers were made operable. Calibration of the flow meters was initiated so that calibration curves can be provided for the different gas mixtures to be used in the photolysis experiments. A quadrupole mass spectrometer, Extranuclear Laboratories, Inc., was installed, and a sampling port was connected to the photolysis cell system. This analytical instrument coupled with an ion chamber radiation monitor will provide the isotopic analysis required for the separation experiments. The spectral emission characteristics of the uv flashlamp from Xenon Corporation were determined using a Jobin Yvon HRS2 monochromator with a 2440 g/mm grating, a RCA 4837 photomultiplier, and a Molectron LP-20 gated integrating photometer.

Initially, the procured xenon flashlamp assembly did not transmit any radiation in the desired 185-195 nm region. However, this problem was quickly traced to the supplied focusing lens, and when it was replaced by a suprasil lens, radiation in the desired 185-195 nm range was obtained with little or no transmission at undesirable shorter wavelengths. From the spectral distributions obtained, it was estimated that about 1% of the total energy lies in the 185-195 nm range. It was also estimated that only about 5% of the total 10 J output of the flashlamp can be directly utilized. From these data it is deduced that about 0.4 mJ/cm^2 per pulse or about 4×10^{14} $photons/cm^2$ per pulse at 190 nm will be available.

Since it is felt that there is no need to filter out the longer wavelength radiation produced by the flashlamp, preparations are now under way to use this source in "control" experiments on H_2O: HDO mixtures (no laser excitation).

Reliable and consistent operation of the OPO has been hampered by what appears to be prelasing caused by a degraded rejection ratio for the Faraday rotator isolator. The problem has been traced to a lower than design voltage output for the high-voltage d.c. power supply. The rejection ratio of the isolator has been found to be only 20:1 which is nearly two orders of magnitude lower than design specifications. Thus a parasitic oscillator can be formed in the amplifier section of the laser that bleeds off most of the amplifier power in a long ($\geq$100 μs) pulse prior to the "Q" switch trigger. Thus, although total power output remains the same, power density is degraded below the threshold for optical parametric pumping.

A separate and controllable high voltage d.c. power supply was installed on the isolator, and timing and rejection tuning were initiated.

Future Plans

The major objectives to be accomplished in the next reporting period are:

1) The achievement of consistent OPO operation; 2) Measurement of OPO tuning capabilities; 3) Determination of "control" parameters such as exchange rates without irradiation and with uv irradiation only; and 4) The initiation of two-photon ISP using HDO.

Fixation of Aqueous Tritiated Waste in Polymer Impregnated Concrete

E. E. Johns and J. J. Dauby

Introduction

Mound Laboratory, in cooperation with Brookhaven National Laboratory (BNL), has undertaken a program to test and develop the BNL method for fixation of aqueous tritiated waste and adapt it to our current procedures and facilities for packaging tritiated water waste. Concrete has been used at Mound Laboratory as a fixing agent for high specific activity tritiated waste water since 1972. In the BNL polymer impregnation technique, the cured concrete is impregnated with styrene monomer. The monomer fills the pores; polymerization of the monomer binds and immobilizes the radioactive waste in the concrete. This significantly decreases the tritium release from the concrete and reduces contamination hazards at the burial site. 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.

Previously, numerous small samples were prepared at Mound with 250 g of Type III cement and 62 g of H_2O injected into the center of the cement. Varying amounts of styrene monomer containing 0.5 wt % of catalyst were added and placed into an oven at 40°C as in the BNL method. These samples did not polymerize after three days so further work was discontinued. Arrangements were made for one week of first-hand training at BNL on its latest polymer impregnation techniques for tritiated waste water fixation in cement. A refined procedure was then developed which could be used to duplicate the Brookhaven results.

Accomplishments

Small-scale tests are being conducted to optimize parameters for polymerization of styrene and the manufacture of styrene impregnated concrete as applied to the typical burial package generated at Mound Laboratory. The scale model samples consist of 250 g of type III Portland cement with 63 g (25 wt %) of water added to the center of the cement by an injector. The sample is contained in a 16-oz polyethylene bottle. A schematic diagram is shown in Figure 3. The polyethylene bottle is loaded with the dry cement which is then compacted by vibration. The injector, a hollow glass tube with a small orifice in the tip, is inserted into the dry cement. Water is then slowly introduced through the injector at a rate of 2 ml/min. When all the water has been added, the injector is withdrawn and the cement casting is allowed to cure at room temperature for five days. After curing, catalyzed styrene monomer is added to the container and allowed to permeate through the composite. Following permeation, the sample is held at 55°C for 24 hr for polymerization to occur with a peak temperature of 70°C recorded.

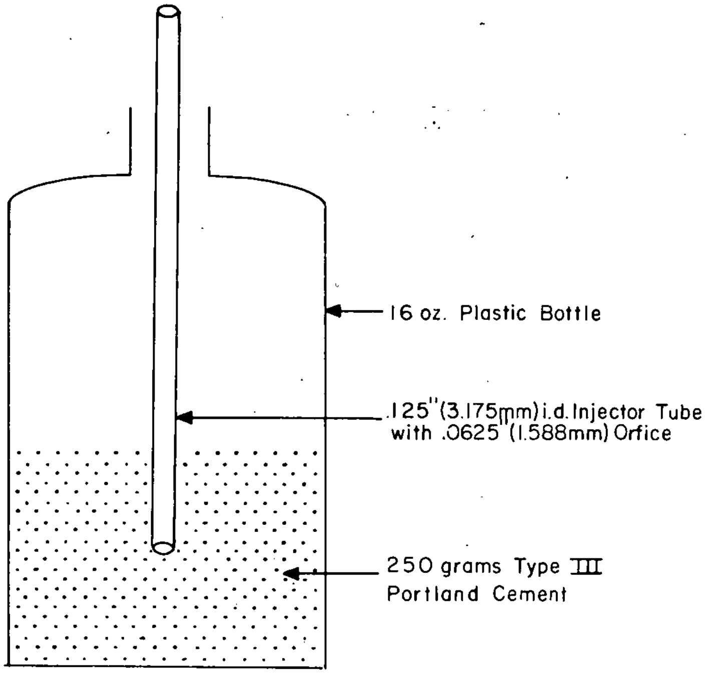


FIGURE 3 - Container filled with dry cement. Waste injector inserted.

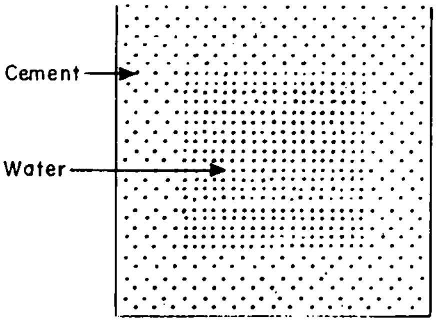


FIGURE 4 - Aqueous waste diffuses through the cement. The waste content in the cement decreases as the casting surfaces are approached.

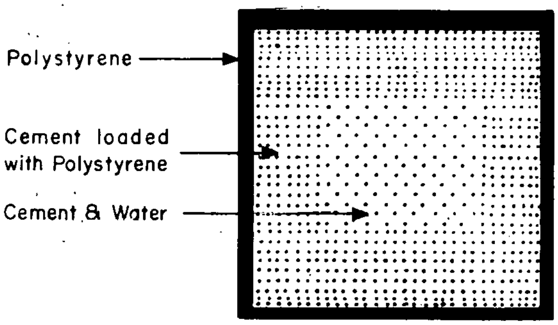


FIGURE 5 - After impregnation, the composite polymer loading is highest at the casting surfaces, effectively encapsulating the waste. Polymer is present throughout the composite.

As shown in Figure 4 this process does not produce a homogeneous composite. The aqueous waste content is higher near the center of the composite coincident with the injector and decreases as it approaches the surface. The polymer loading, however, is inverse to this effect with a thin layer of monomer completely encasing the cement casting. The styrene soaks into the entire concrete block with a greater concentration near the outside. This effectively encapsulates the waste. See Figure 5.

The results of the samples prepared to date have established an optimum weight percent of catalyst in the monomer at 0.5% and an oven curing temperature of 55°C. The optimum weight ratio in a typical package remains under study but samples to date favor a ratio of 0.20 monomer to concrete.

Future Plans

The optimum weight ratio for monomer in the concrete block will be determined. Mixtures of varying proportions of Type III cement and plaster will be investigated and will be compared to the Type III cement as the fixing agent. The best fixing agent will be used to solidify high specific activity (∿1000 Ci/liter) tritiated water. The resulting blocks will be impregnated with styrene, which will then be polymerized, and the samples will be entered into a test program to determine tritium release.

Radiation Chemistry Studies of Tritium Fixation Packages

G. C. Abell and W. E. Tadlock

Background

Development of suitable containers for the disposal or storage of tritiated waste materials, especially oils and water, must be based on an adequate understanding of radiation chemical effects by the tritium beta decay. Thus it is known [1] that gamma radiolysis of hydrocarbon oils generates appreciable quantities of hydrogen gas. The same is true for water; however, in this case a back-reaction limits the pressure buildup [2]. Against this background, two questions about the suitability of a given containment package must be addressed: (1) what is the likelihood that an explosive material will develop? and (2) what are the chances for container rupture due to pressure buildup?

A study was designed to deal with these two questions for the particular tritiated waste packages developed at Mound Laboratory [3]. Generally speaking, for these containment packages the waste liquid is mixed with a fixation agent (water with cement-plaster; oil with either vermiculite or absorbal) and sealed (for details see Reference 3). In this study pressure increase and gas composition were measured over the following samples: (1) tritiated water (1000 Ci/liter) with and without fixation and (2) tritiated n-octane (1000 Ci/liter) with and without fixation. The activities in the octane samples are about 10 times those of typical Mound Laboratory waste products, giving accelerated results. The activity of the tritiated water is typical of Mound waste water. Since radiation chemistry studies show that impurities reduce the production of gases [4] relatively pure starting materials were used to obtain "worst case" results. Studies also show that irradiation effects on saturated hydrocarbons are nearly independent of chain length[1], and so the results for n-octane should be a good "worst case" representation for a variety of waste oils.

Previously pressure buildup in the various samples was monitored, and the overgas from the water without fixation was sampled via mass spectroscopy. Pressure monitoring for that particular sample was then reinitiated after it had been evacuated and backfilled with argon. Curve A shown in Figure 7 is based on data taken after the restart.

Accomplishments

Figure 6 shows the pressure increase for three samples of octane with an initial overpressure of argon. The rate of total gas production, normalized to 4 Ci of tritium, for each sample is: 6.3 cm^3 stp/yr for octane; 4.9 cm^3 stp/yr for octane with vermiculite; and 3.6 cm^3 stp/yr for octane with Absorbal. The pressure measurements were terminated after 150-200 days, and the units were sampled for gas analysis. The units were then cooled to about -95°C, evacuated, and backfilled with argon. This procedure served three purposes: (1) to prevent overpressurizing the 0-30 psia pressure transducer, (2) to facilitate sampling of the overgas (an internal pressure not greatly exceeding 1 atm for mass spectrometry "grab" samples is preferred by Mound analytical personnel), and (3) to minimize back reactions consistent with the desire for worst case results.

Table 1 gives the mass spectrographic analysis of the overgas and shows that H_2 gas is the predominant gaseous radiolytic product (about 90%). This agrees with gamma ray results [5].

Table 1 - MASS SPECTROMETRIC ANALYSIS OF OVERGAS FROM OCTANE STORAGE UNITS

Constituent	Mass	Without Fixation (mole %)	Over Vermiculite (mole %)	Over Absorbal (mole %)
H_2	2	48.7	47.45	48.15
CH_4	16,17	1.39	1.4	1.07
C_2H_2	26	0.12	0.0	0.0
N_2:C_2H_4:CO	28	0.0	4.7	3.46
CO:C_xH_x	29	0.0	1.85	0.88
CO	30	0.54	0.5	0.43
Ar	36-40	44.26	43.7	44.79
CO_2	44	0.0	0.3	0.28
C_3H_8	44	4.94	0.1	0.59

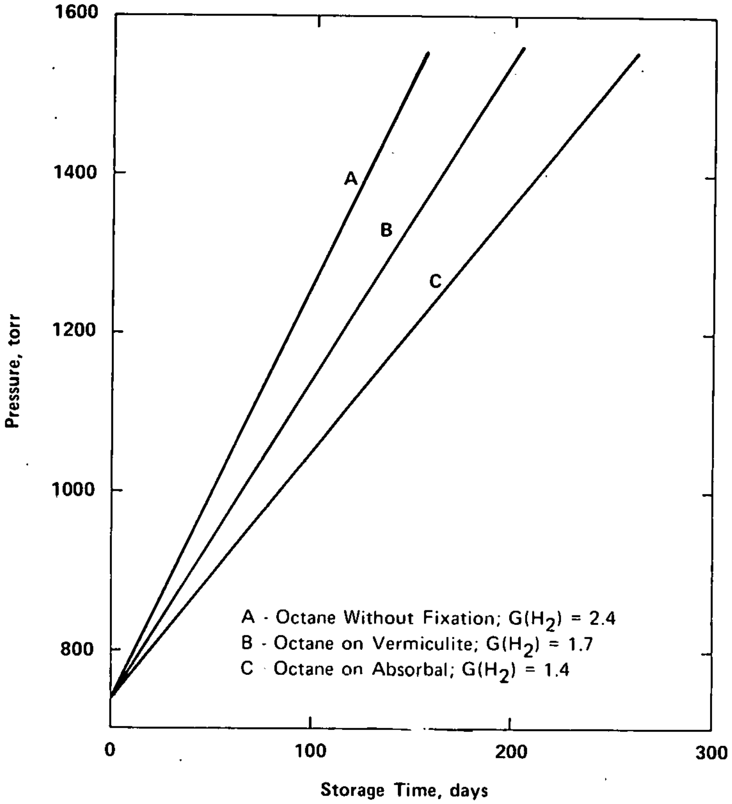


FIGURE 6 - Pressure buildup over tritiated octane with and without fixation.

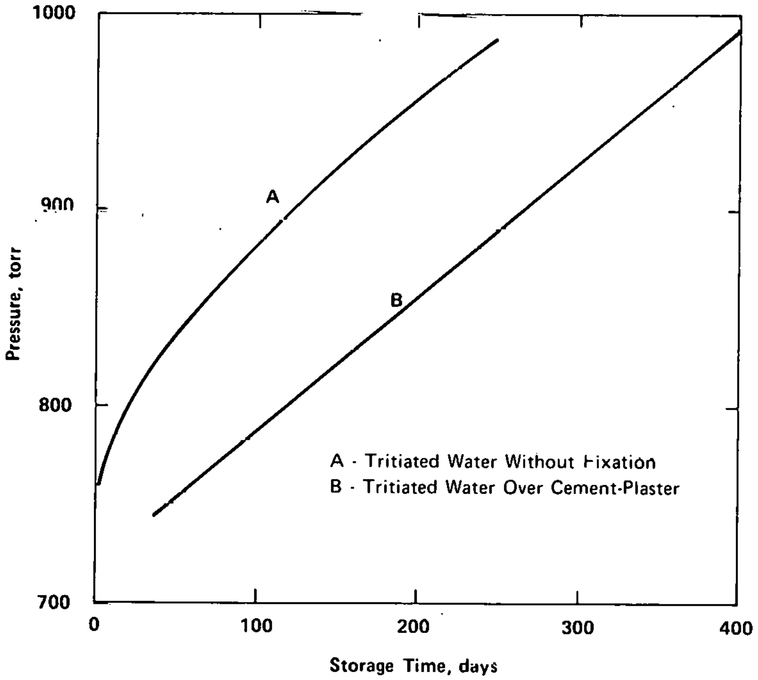


FIGURE 7 - Pressure buildup over tritiated water with and without fixation.

Figure 7 shows the pressure increase of tritiated water with and without cement-plaster fixative. The most interesting aspect of this figure is that the fixative apparently inhibits the back-reaction. Monitoring the extent of this effect will be continued.

Tests units containing waste vacuum pump oils with and without vermiculite have also been placed in storage. These units will give direct information concerning typical Mound waste oil (activity ≃100 Ci/liter). In order to standardize the composition of the overgas and thus reduce the complexity associated with the analysis of the radiolysis products, the waste oil units were evacuated and backfilled with argon.

The total pressure buildup of the waste vacuum pump oils after 160 days of storage was 4 torr for the oil without fixation and a -3 torr for the waste oil with vermiculite. This is much less than the worst case prediction (about 50 torr). It may be that the chemical composition of this waste oil has shifted significantly from saturated to unsaturated hydrocarbons, for which radiolytic gas production is considerably lower [5].

The measured G-value for the production of hydrogen, $G(H_2)$, is shown for each sample. Gamma radiolysis of pure n-octane [1] gives a G-value of 5.1 for the production of hydrogen, compared with our value of 2.4 (Figure 6). This indicates that even our relatively pure n-octane contains sufficient impurities to scavenge about 50% of the H_2 precursors (about half the H_2 precursors are purported to be unscavengeable [1]). The fixation agents are seen to reduce the rate of gas production. This is probably caused by one or more of the following effects: (1) additional scavenging, (2) sufficient dispersion to enable partial deposition of beta energy in the fixative, and (3) entrapment or adsorption of H_2 gas.

Future Plans

Monitoring of pressure buildup over water with cement-plaster fixative will be continued. If the pressure continues to rise steadily with no indication of a back-reaction, then the assumption about a low limiting value for the pressure buildup over tritiated waste water packages will have to be reexamined.

In addition, we have restarted and will resume monitoring the various octane samples up to the 30 psia level. Analysis of the overgas will then be performed and that will complete this phase of the octane work.

Acknowledgement

The authors would like to acknowledge H. Steinmeyer for synthesizing the tritiated water and M. Prisc who provided the tritiated octane.

Management of High Specific Activity Tritiated Liquid Wastes

G. E. Gibbs, J. J. Dauby and C. B. Voth

Background

Mound Laboratory generates high specific activity tritiated liquid waste from a variety of tritium handling operations and from stack effluent control systems [6-8]. 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 [9]. A schematic of the water package is shown in Figure 8. Waste oil is sorbed on vermiculite in the polyethylene drum but the remainder of the package is the same as for water. In both cases 27 liters of liquid is disposed of in each package.

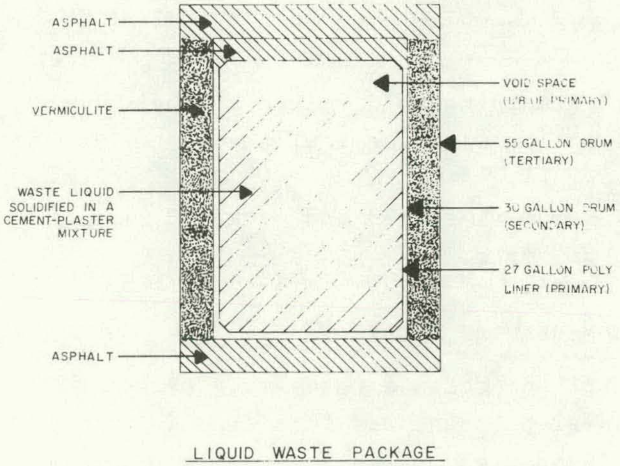


FIGURE 8 - High specific activity tritiated water waste package.

Accomplishments

INSPECTION OF WASTE DRUMS ON INVENTORY

Mound Laboratory's present method of fixing aqueous waste utilizes a mix of three parts plaster and one part cement. Radioactive oil and organics are sorbed on vermiculite.

Prior to the shipment of our high specific activity waste to the Nevada Test Site, 96 drums of solidified liquid waste (water and oil) from our inventory were inspected (primary, secondary, and/or tertiary container) to verify their condition and containment characteristics.

It became necessary to recall drums from our inventory containing solidified liquid waste packaged by the Mound facility to verify the lid seals of both the 30-gal drum and the 55-gal drum. The packages were recalled when it was discovered that one particular chemical operator had not used RTV sealant on some of the secondary (30-gal drum) containers. All 11 secondary containers packaged by him prior to August of 1975 had a seal on the lid. The other nine done by him after this date did not have a seal and were properly resealed for shipment to NTS.

During these inspections it was noted that one of the tertiary (55-gal) containers had a bulged lid; when the lid was removed to check the secondary seal, pressure was released. After the secondary container was removed, the bung on the primary (27 gal polyethylene) container was punctured to release the pressure.

The pressure measured 10 psig and was released to the Effluent Removal System (ERS). Three other primary containers had pressure (10 psig) which had to be released before the secondary container lid could be reinstalled.

Gas samples were taken from one of the four primary containers and analyzed by mass spectrometry. This container had 44,000 Ci of tritium when packaged 16 months earlier. Analytical results are shown in Table 2.

Table 2 - MASS SPECTROMETRIC ANALYSIS OF GAS TAKEN FROM PRIMARY CONTAINER

Constituent	Amount Present (%)
H_2	7.3
D_2	0.0
T_2	0.0
^3He	0.73
N_2	5.0
O_2	0.59
CO_2	0.05
Ar	86.16

Since the waste is packaged in an argon atmosphere, the major component was argon. Decomposition of the water by the beta radiation accounts for the presence of hydrogen and oxygen.

The containers were properly resealed and returned to inventory to await shipment to the NTS. Nine drums containing liquid waste octane were opened to evaluate the integrity of the waste package. Six of the packages contained exceptionally high internal tritium concentrations. An older method of packaging this type of waste that is no longer in use appeared to be the major cause for the high tritium concentrations. The old method of packaging octane waste was to sorb 250 cm^3 of octane on vermiculite in one-quart polyethylene bottles. Four such bottles in a 5-gal can with a press fit lid were sealed with RTV sealant. Then up to three of the 5-gal cans were placed in a 50-gal steel liner surrounded with vermiculite and the lid was sealed with RTV. The 50-gal liner was placed in a 17H 55-gal drum.

Tritium was well contained in drums containing contaminated octane packaged according to present procedures. These procedures are as follows:

1. After filtering and calorimetry, octane (200 cm^3) is poured into a 32-oz. plastic bottle containing vermiculite. (Visual inspection to ensure no free liquid exists).

2. Bottles are sealed in argon atmosphere glovebox and passed out of the drybox.

3. Up to 10 bottles are placed in an asphalt-coated 30-gal drum which is 1/2 full of tar (bottles are imbedded in the liquid asphalt).

4. Remaining void volume in the drum is filled with vermiculite.

5. Drum is sealed and packaged in a 55-gal drum.

DRUM RELEASE STUDY

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 drums in a known volume of water. By periodic sampling of the surrounding water and analysis for the presence of tritium, a permeation rate can be calculated. Figure 9 is a schematic of a typical burial package under test within the permeation apparatus. Figures 10-13 are the resultant permeation data for solidified water, and Figures 14 and 15 are the resultant permeation data for oil test drums.

As indicated by the figures, there is a rapid increase in permeation rate at the start of each test. This increase is attributed to the initial equilibration of tritium between the burial package and the water in the 83-gal drum. Drums numbered 105 and 133 (solidified water) resulted in a greater than normal amount of tritium permeation. It was found that drum 133 leaked and water ran into it. This happened during the first week of testing. The increase for drum 105 is attributed to the greater initial quantity of tritium and the greater time interval between packaging and testing. The sudden rise around week 44 is unexplained. The permeation test on these two drums was terminated because they are not representative in tritium quantities of present burial packages. They were packaged to establish design parameters for the high specific activity waste solidification facility and are comparable to present packages. These drums were inspected prior to shipment and all seals were found satisfactory. Drums numbered 205 and 318 (also solidified water) remain in the test and future results will be reported. Drums numbered 217 and 218, (fixed oil) have identical package characteristics, tritium quantities, and packaging dates and virtually identical permeation rates. These drums will also remain in test and future results will be reported.

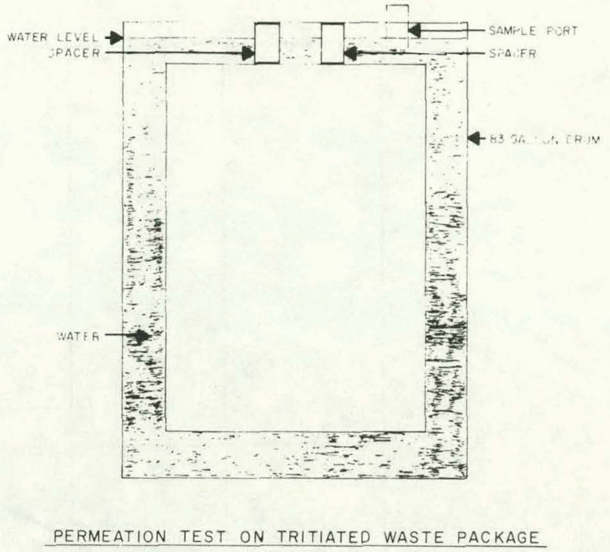
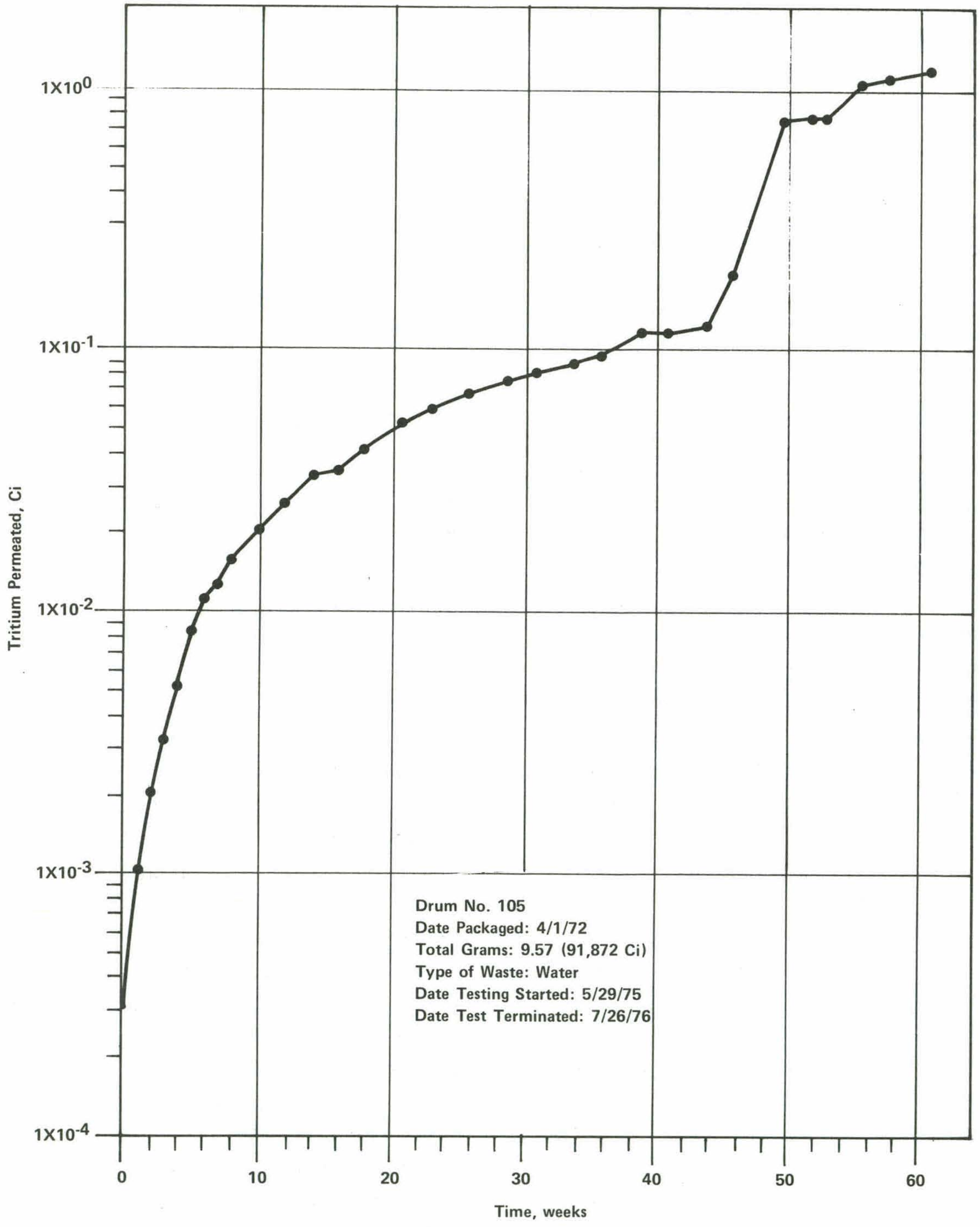


FIGURE 9 - Permeation test on tritiated waste package.

Calculations have been made of the maximum expected increase in internal pressure in the existing burial package due to decay of the tritium to helium-3 for a period of 85 yr. With 7 g of tritium in 35 liters of water producing 52 liters of helium-3 after 85 yr, the maximum pressure in the primary polyethylene drum would be 22 psig (250 kPa) (52 liters in a 35-liter void). Rupture or leakage of the primary containment would result in a pressure of 20 psig (240 kPa) in the secondary (52 liters in a 39-liter void). Rupture or leakage of both primary and secondary would result in a pressure of 8 psig (150 kPa) in the tertiary containment (52 liters in a 104-liter void).



Drum No. 105
Date Packaged: 4/1/72
Total Grams: 9.57 (91,872 Ci)
Type of Waste: Water
Date Testing Started: 5/29/75
Date Test Terminated: 7/26/76

FIGURE 10 - Tritium waste package permeation rate.

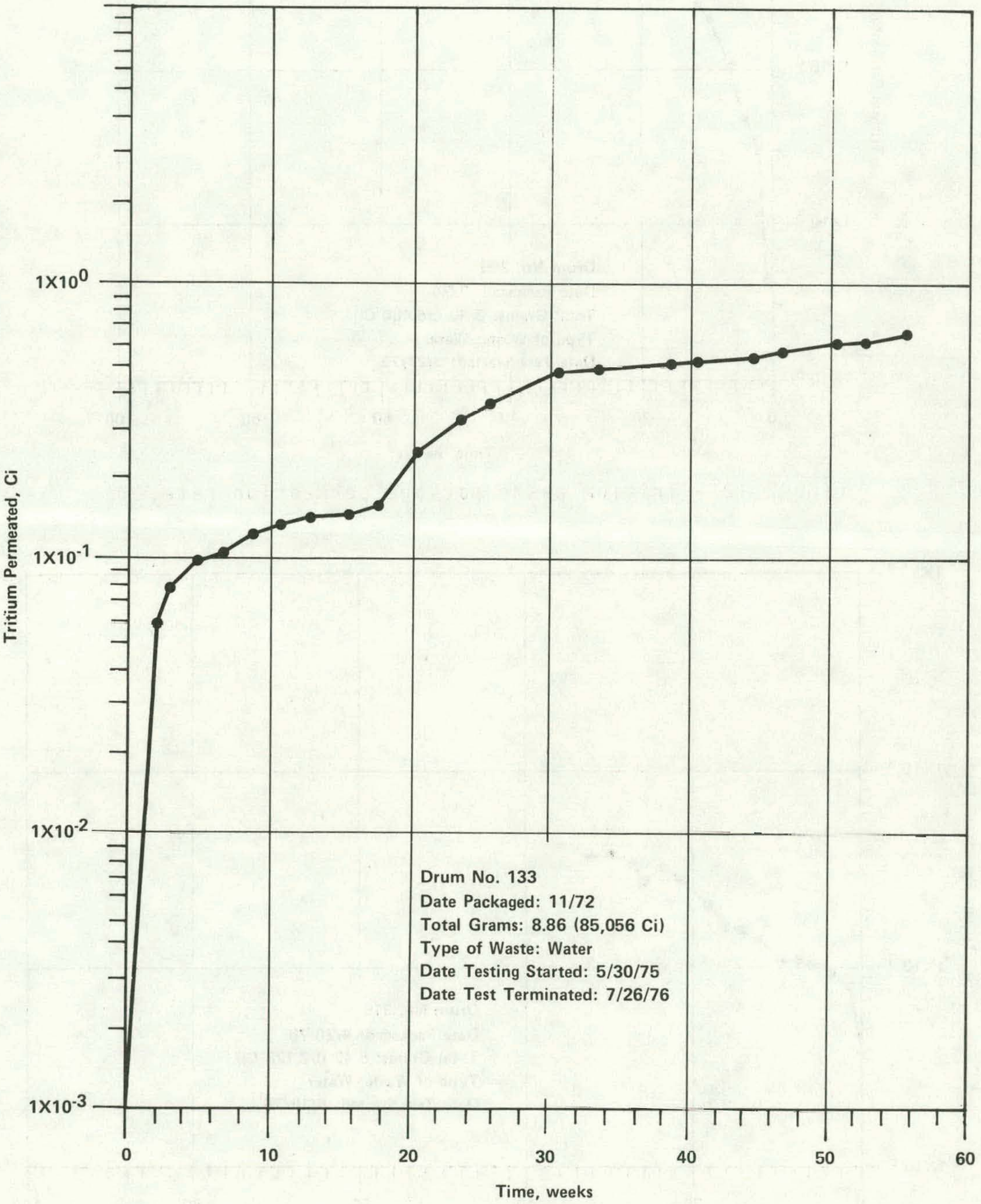


FIGURE 11 - Tritium waste package permeation rate.

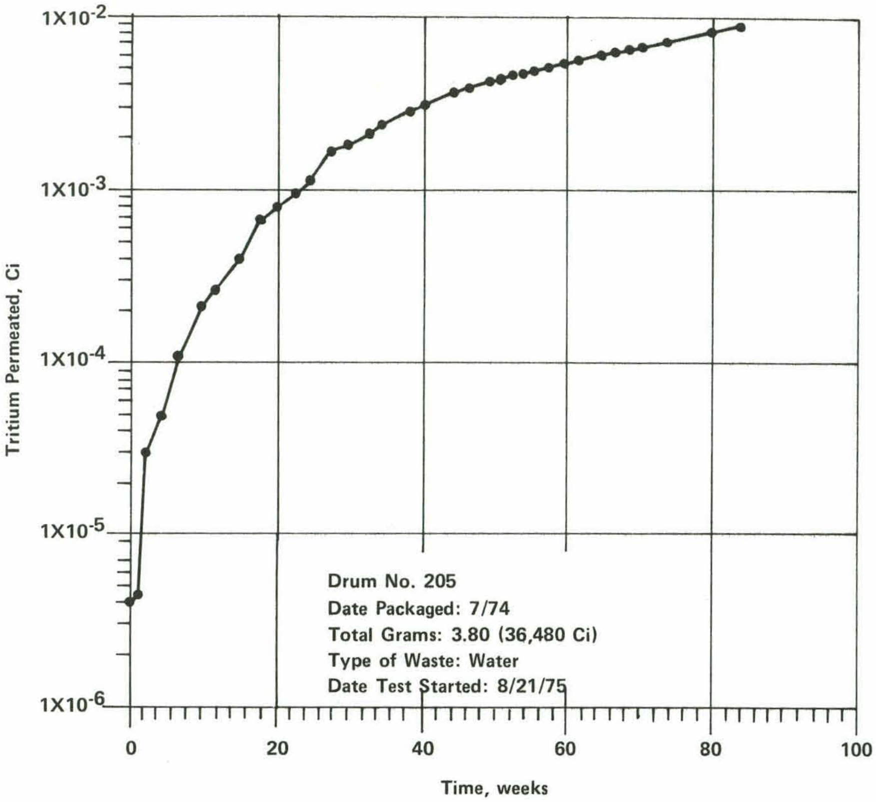


FIGURE 12 - Tritium waste package permeation rate.

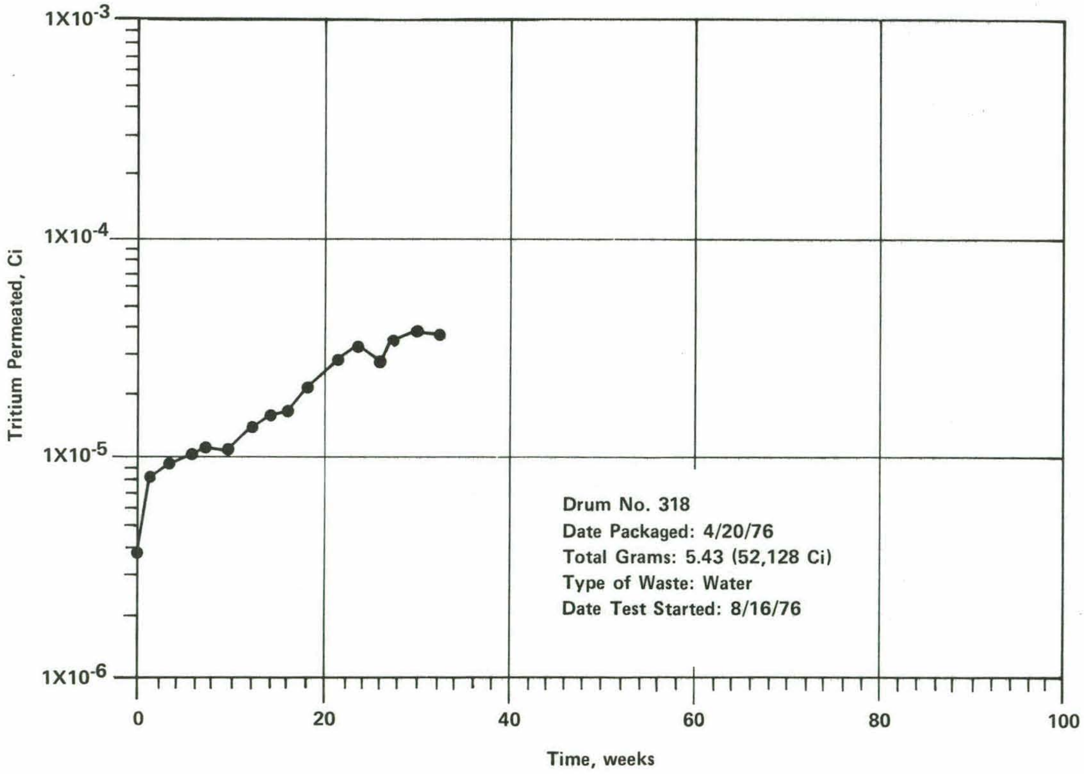


FIGURE 13 - Tritium waste package permeation rate.

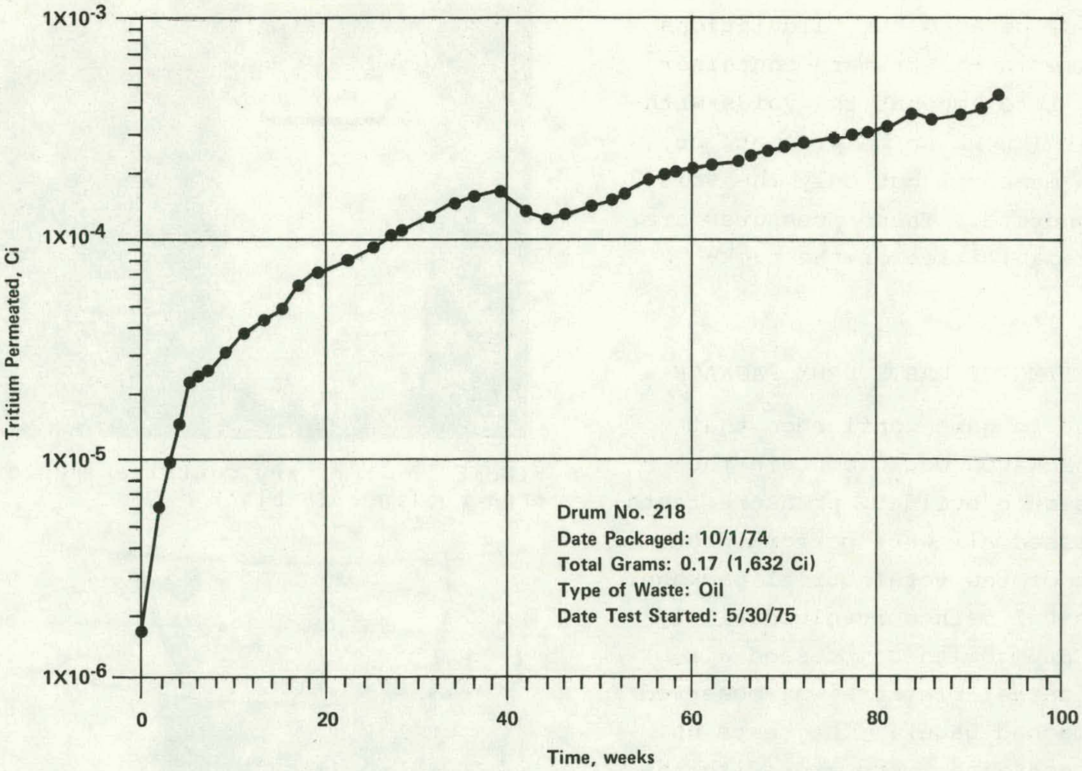


FIGURE 14 - Tritium waste package permeation rate.

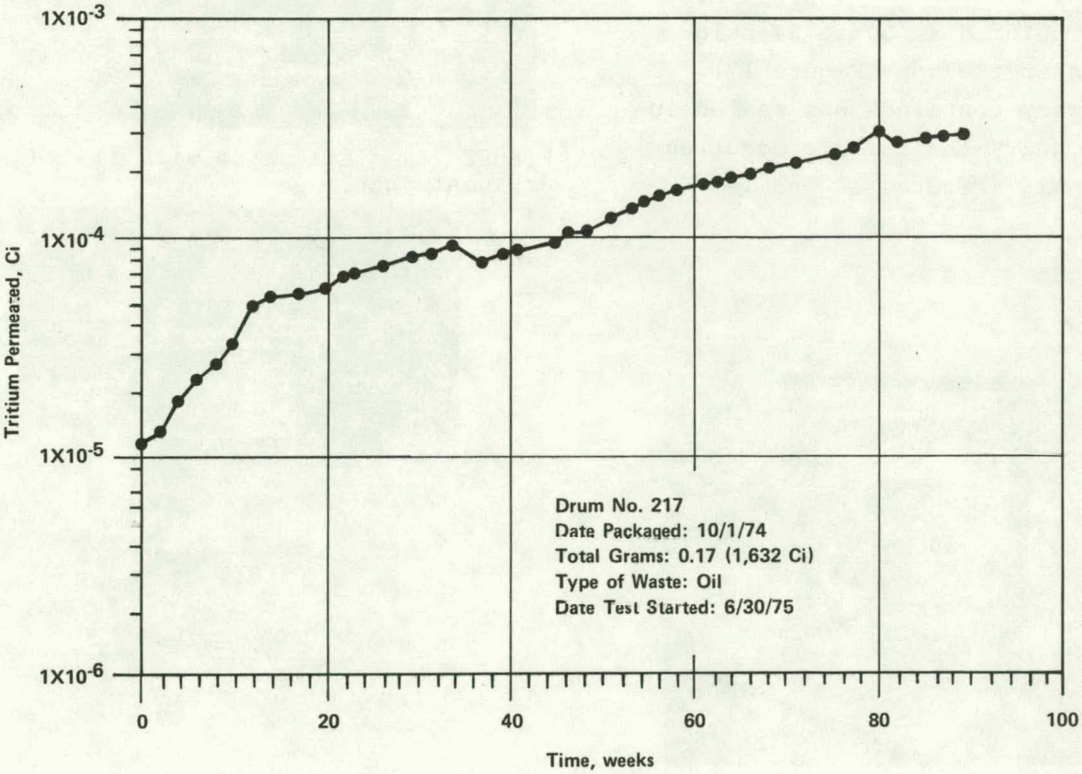


FIGURE 15 - Tritium waste package permeation rate.

These pressures are believed to represent the worst case because the calculations of void volume in the primary container did not take into account the voids within the cement (known to be present, but difficult to measure) but only the void above the concrete. These pressures are within the capabilities of the package.

PRESSURE TESTING OF WASTE DRUM PACKAGE

In an attempt to gain confidence that our burial packages would contain the observed pressure buildup, pressure tests using compressed air were performed on two mock-ups of the total burial package. The experimental method involved slowly filling the drums with compressed air while the internal pressure was observed (using a compound gage). The tests on the primary container were made with the primary inside the secondary but without the lid on the secondary (Figure 16). The primary ruptured at 30 to 34 psig on the side near the top (Figure 17). When the primary container was sealed inside the secondary the failure occurred at 40 to 50 psig (Figures 18 and 19).

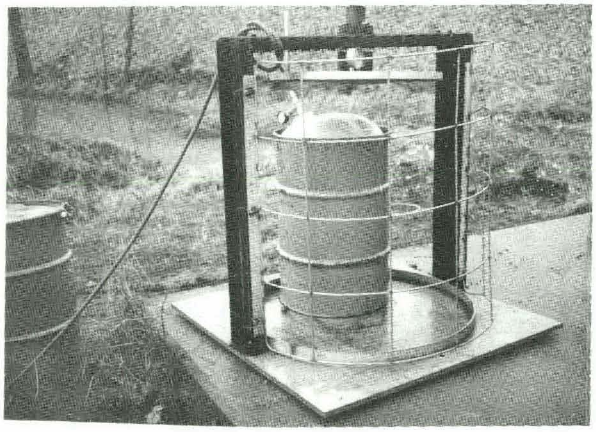


FIGURE 16 - Test setup with primary container being pressurized.

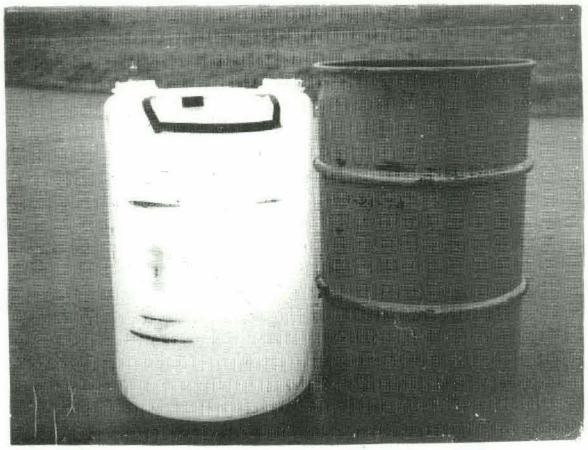


FIGURE 17 - Primary container ruptured in area outlined in black

FIGURE 18 - Test setup with lid on secondary container.

FIGURE 19 - Ends of secondary container bulged before primary failed.

For these tests the inlet pressure line was sealed in the primary container bung and on the secondary drum lid.

When the secondary container was opened, failure of the primary was again near the top and at the bung.

Several tests were made of the complete package. One drum package contained 28 liters of water in a 3-to-1 plaster-cement mix cured for two months. Another contained 28 liters of oil in vermiculite. The primary, secondary, and tertiary containers used in these tests were packaged and sealed as specified in the standard procedure. An inlet pressure line was sealed on the primary container bung and passed through the secondary and tertiary container lids. Appropriate gaging and valving were connected for safety. Weights were added to the package before lowering into the water (see Figure 20). Compressed air was applied until failure, as indicated by a stream of bubbles, was noted. Under pressure, the weakest point on the steel drums is the steel ring above the bolt connection. Failure on these packages was at 30 to 38 psig. Autopsies on the mock packages showed failure on the side near the top of the primary container as shown in Figure 17.

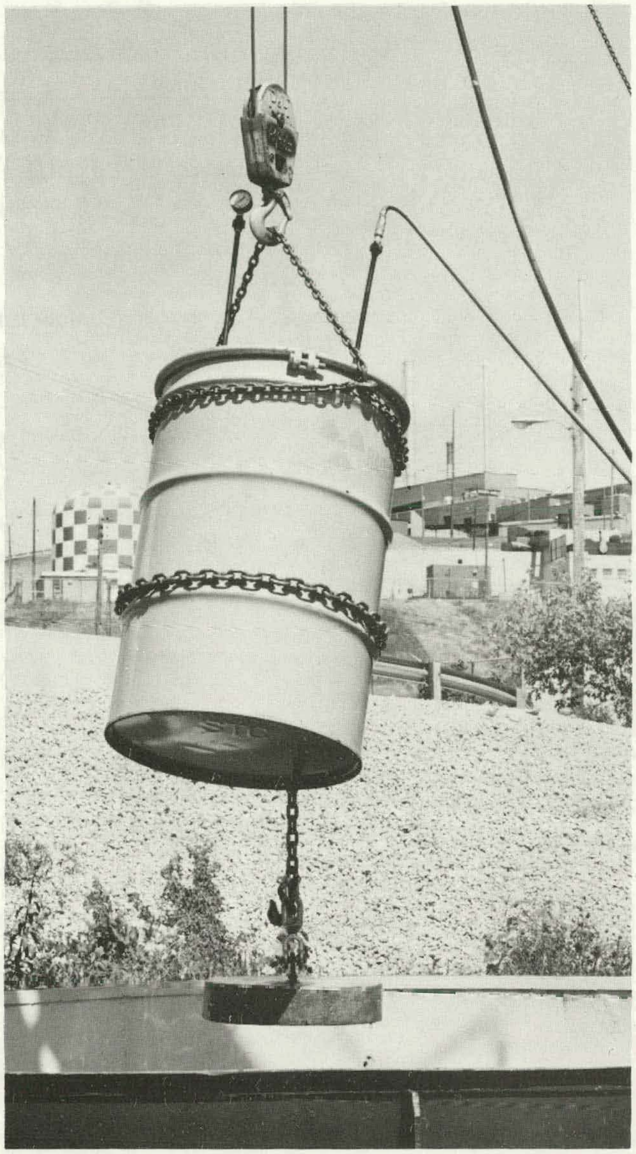


FIGURE 20 - Secondary container with weights added being lowered into water tank for test with compressed air.

Future Plans

Monitoring of tritium release from typical waste packages will be continued.

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