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Tritium Waste Control Project Progress Report: October-December , 1975

John C. Bixel and Carl J. Kershner

July 30, 1976

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Assembly and testing of the cell to be used for the measurement of the HTO ir spectrum was completed. As a result of findings from trial loadings using HD as a surrogate for HT in the oxidation system, it is believed that larger quantities of HTO will be required to obtain the desired ir spectrum. This appears to be a result of a significant adsorption of the water on the inner surface of the spectrometer cell.

Catalytic Exchange Detritiation Studies Leak checking and cold operational testing of the experimental apparatus were completed. Modifications were made to improve the operability and reliability of the system as originally designed by Engelhard Minerals and Chemicals Corp. A computer program was prepared for the calculation of twelve hydrogen isotopic compounds in thermodynamic equilibrium. This program based on the free energy minimization technique produced data on the equilibrium concentrations of tritium compounds from reactants with various T/D/H/O ratios (e.g., T/H = $\sim 10^{-8}$ to $\sim 10^{-2}$) at temperatures ranging from 300 to 800°K.

Development of Shipping Containers for Tritiated Liquid Waste The bourdon tube pressure gage on the prototype shipping container has been replaced with a 316 stainless steel pressure transducer to decrease the mechanical vulnerability of the package. Procedures have been established for usage and safety testing the primary container and a safety analysis review for the complete assembly in the AL-M1 outer shipping container has been initiated.

TRITIUM WASTE CONTROL DEVELOPMENT PROJECT

C. J. Kershner, Science Fellow
J. C. Bixel, Project Leader

A December 1970 Commission communique asked that contractors seek to limit their tritium and other radioactive effluents to levels that are "as low as practicable." Subsequent communiques suggest control of radiological release to less than 10% of the Radioactivity Concentration Guide (RCG) for uncontrolled areas and also suggest moving the point of concentration measurement from plant boundary limits to within the effluent stacks.

Beginning in 1970, an intensive tritium emission control effort was put into effect at Mound Laboratory. This effort has as its goal an ultimate objective of approaching zero emissions and an engineering goal quantified in terms of maintaining stack emission levels at or below 10% of the present RCG values (40 $\mu Ci/m^3$ for HT and 0.2 $\mu Ci/m^3$ for HTO). To accomplish these goals facility design and operating philosophies were revised to those of containment and recycle as opposed to the past practice of high dilution and release. Over the past five years, implementation of this philosophy through facility modifications and additions and changes in operating procedures has resulted in a 30-fold reduction in the gaseous tritium effluents released from the laboratory. However, reduction of tritium effluent levels to 10% of RCG values at the point of emission and nearly complete recycle pose problems that are beyond ready solution with state-of-the-art tritium control technology.

To meet this advanced technology need, the Tritium Effluent Control Project was initiated in January 1972. The experimental direction of this project was predicated on the results of an initial source and facility evaluation which revealed that as much as 80% of the total annual release to the atmosphere could be attributed to "background" diffusion from gloveboxes and other containments to the room ventilation systems which are directly stacked. Treatment of the voluminous quantity of high humidity room air was deemed to be both economically and technically impractical. Therefore, emphasis has been placed on (1) confining the tritium at the source through the use of glovebox atmosphere detritiation and recovery systems and (2) applying room air treatment only for emergency conditions in the event of accidental releases. Initial bench scale research was directed mainly toward gaseous effluent detritiation and recovery. The major portion of the gaseous effluent treatment work is now in the pilot scale development stage. A test laboratory, embodying many of the results of the past research phase of the work, has been designed, and its construction is completed.[1]

As the program has matured, the scope of the development effort has expanded to include liquid tritium wastes as well as gaseous. Over the past several years it has become increasingly evident that the currently acceptable practices for disposing of tritiated liquid waste will not be adequate for the future, due to the expected increases in the quantities to be handled and the growing public concern with radioisotopic releases to the environment. Moreover, in the 1980's a large market will develop for tritium in the CTR program which will make it a valuable fuel resource to be recovered and recycled.

At present, the primary sources of tritiated liquid wastes are the ERDA contractors. Because of the increased emphasis on effluent control, glovebox detritiation (GADS) and other effluent removal systems (ERS) have been and are being installed, resulting in increased production of tritiated liquid waste (primarily high level; >1000 Ci/l). Although modest increases are expected in high level wastes when Los Alamos and Sandia Livermore go on-stream with their new ERS and GADS, the intermediate level liquid wastes (between 1000-0.01 Ci/l) from fuel reprocessing plant operations are expected to dominate by 1985. Moreover, in the period from 1985 to the year 2000 the quantities of tritium being produced from the reprocessing of fission reactor fuels are expected to more than triple. Added to this will be a yet unknown quantity of tritiated liquid wastes generated by fusion experiments and reactors which could significantly contribute to the quantities to be dealt with in the latter part of this century.

The Tritium Waste Control Development Project at Mound Laboratory has been directed toward the development of detritiation and recovery processes that can be directly applied to the tritiated liquid waste recovery problem. We contend that of all the possible approaches to the disposal of tritiated liquid wastes, recovery offers the greatest advantages for the high level and intermediate level tritiated water categories.

In summary, although the initial thrust of the work under this program was oriented toward development of gaseous effluent treatment systems, its natural evolution has been toward the liquid waste recovery problem. At the present time, the major development effort is in this area.

TRITIATED LIQUID WASTE DECONTAMINATION (MOLECULAR EXCITATION)

W. R. Wadt and R. E. Ellis

BACKGROUND

Operations involving tritium produce significant quantities of aqueous waste, which must be disposed of in a safe manner. Much of the waste contains a low concentration of tritium. At present, these low-level wastes are processed and buried at relatively high expense. An alternate procedure would be to discharge the waste after dilution to "safe" levels. However, both methods eventually allow some or all of the tritium to enter the environment. A preferable procedure would be to decontaminate the wastes by extracting the small amounts of tritium. The economic feasibility of detritiating large volumes of low-level (10^{-3}-10 μCi/ml) water is highly dependent on the separation factor of the elementary isotopic separation process employed. The separation factor for most H/T isotopic systems is quite small - ranging from slightly greater than 1 to approximately 10 for the case of water electrolysis. However, one process, 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-level aqueous wastes, 2) control of the tritium level in the primary coolant of light water reactors, and 3) removal of deuterium from water.

PRIOR WORK

Laser Separation System A plausible scheme to detritiate low-level aqueous wastes by molecular photoexcitation has been formulated. The process, which is carried out 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, while 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. By recycling the hydrogen stream the tritium may be significantly enriched 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, $OH + HT \rightarrow HTO + H$.

The rate of HTO regeneration via the exchange reaction, $T + H_2O \rightarrow HTO + H$, was determined theoretically. Ab initio calculations on the potential surface for the hydrogen atom-water exchange reaction have been performed. Calculations have shown that the energy barrier can be expected to be 20-25 kcal/mole, so that the exchange reaction $T + H_2O \rightarrow HTO + H$ is at least 10^9 times slower than the exchange reaction $T + H_2 \rightarrow HT + H$.

A qualitative analysis of the isotopic selectivity of the two-photon dissociation process was made. The selectivity or ratio of HTO to H_2O molecules that are photodissociated was found to be on the order of 25. Although this selectivity is

sufficient for bench scale proof-of-principle experiments, it is inadequate for application to large scale detritiation projects, e.g., nuclear fuel reprocessing plant waste. The selectivity is such that most of the laser energy is wasted in photodissociation of H_2O. This obstacle may be overcome by pumping more vibrational energy into the HTO molecules.

A tunable ir laser developed by Prof. R. L. Byer and coworkers at Stanford University was determined to be the most appropriate for our purposes. The laser consists of an $LiNbO_3$ optical parametric oscillator (OPO) pumped by a Q-switched Nd:YAG oscillator-amplifier-isolator chain. The laser is tunable from 1.4 to 4.45 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 ordered from General Photonics Corporation.

The $LiNbO_3$ crystal for the OPO and associated optical components were also procured. Finally, a long-path two-photon absorption cell (Wilks Scientific Corporation) and an appropriate xenon flashlamp (Xenon Corporation) were ordered.

HTO Infrared Spectrum The exact wavelengths and absorption intensities of the HTO molecule in the infrared region around 4.35 μm are necessary for determining parameters for the experiments in water decontamination via molecular excitation. Using HDO as a surrogate very satisfactory spectra were obtained from a Digilab FTS-14 Spectrophotometer.

A Barnes Engineering Company spectrometer cell has been modified for use in determining the HTO spectrum in the 4.35 μm region. The system to load this cell was assembled and the active components operationally tested.

ACCOMPLISHMENTS

Laser Separation System Delays in the deliveries of the Nd:YAG laser, the flashlamp system and the two-photon absorption cell have impeded progress on the proof-of-principle experiments for water detritiation by molecular excitation. A 0.6 meter high resolution monochromator has been ordered from J-Y Optical Systems.

Further calculations were performed on the hydrogen atom-water and hydrogen atom-hydrogen fluoride exchange reactions. The configuration interaction calculations on the $H + H'F \rightarrow HF + H'$ reaction point toward a nonlinear saddle point geometry and an energy barrier on the order of 30-35 kcal/mole. This result may have important implications for vibrational deactivation of HF, and hence, for the HF chemical laser.

HTO Infrared Spectrum The cell to be used for measurement of the HTO ir spectrum was helium leak tested to 4.5×10^{-8} std cc/sec. Two unsuccessful cell loadings using HD were made with the hydrogen (tritium) oxidation system previously described.[2] Neither run produced HDO spectra of sufficient intensity. It is suspected that much more water is required to satisfy the adsorption and absorption demands of the cell surfaces and NaCl windows before the required vapor density can be achieved. Experiments are being carried out to determine what quantity of adsorbed water is present on the windows at the vapor pressures of interest.

DISCUSSION

Laser Separation System The deliveries of the Nd:YAG laser, the flashlamp system and the two-photon absorption cell have been delayed such that the equipment will not arrive until next quarter. In the meantime, a 0.6 m high-resolution monochromator has been ordered from J-Y Optical Systems. The monochromator will be used to tune the ir laser and record the ir spectrum and laser induced fluorescence of the H_2O/H_2 system.

The results of GVB (3/PP) calculations on the $H + H_2O$ exchange reaction were reported in the previous quarterly.[2] The optimum geometry for H_3O was determined to possess C_{3v} symmetry with ∠HOH = 106.6° and R(OH) = 1.87 a_o. The calculated energy of H_3O at the optimum geometry was 31.9 kcal/mole higher than that of the separated products, $H_2O + H$. The fact that the optimum geometry for H_3O is similar to that for H_2O [∠HOH = 104.45° and R(OH) = 1.8111a_o] led us to construct a two-dimensional grid in which the bond angles were fixed at 104.45° and one bond length fixed at 1.8111 a_o. The resulting surface should describe the optimal reaction pathway quite well. For reasons discussed in detail previously,[2,3] the two-dimensional potential surface possesses a well corresponding to H_3O, i.e., there is an energy barrier to dissociation of H_3O into $H_2O + H$ (cf. Figure 7 of reference 2). The optimum geometry for H_3O in this well is calculated to have the remaining two OH bond lengths equal to 1.9a_o and the energy at this geometry is 33.0 kcal/mole. Consequently, the geometry restrictions imposed on the H_3O system to

obtain the two-dimensional surface leads to errors on the order of only 1 kcal/mole or 3%.

The next step in the calculations is to make a more quantitative determination of the energies at key geometries, namely, the separated products, the saddle point and the well. At present, we plan to perform a configuration interaction calculation consisting of all single, double and triple excitations from the dominant configuration with the restriction that only single excitations are allowed out of the space spanned by the orbitals in the GVB (3/PP) wavefunctions. This type of configuration interaction (CI) calculation is denoted as POL(3) CI. These calculations are in progress.

HTO Infrared Spectrum The spectrometer cell to be used in the HTO spectra measurements was helium leak tested to 4.5×10^{-8} std cc/sec. This is a sufficiently small leak rate to preclude a significant tritium release during the experiment.

Accordingly, a sufficient amount of 4:1 H_2:D_2 mixture to produce ~20 torr vapor pressure was oxidized and condensed in the cell. The helium carrier gas was pumped off, the cell valves closed and the cell removed from the system and placed in a secondary container for transport to the spectrophotometer.

The resulting spectrum showed no discernable absorption lines in the region around 2700-2750 cm^{-1}. As reported earlier[4] a similar experiment produced several strong absorption lines in the 2720-2725 cm^{-1} region corresponding to ν_1 for HDO.[5] Therefore, a second loading was made leaving the helium in the cell along with the cryogenically trapped water. This was done to make sure that the water was not being pumped out of the cell along with the helium. The spectrum from this loading was similar to the first with only a very slight absorption in the range of interest.

Due to the above findings the differences in loading procedures between the previous successful spectra measurements and the two present ones were examined. The major difference was that in the previous loadings liquid H_2O-D_2O mixtures were allowed to evaporate to the equilibrium vapor pressure at a controlled temperature in order to fill the cell. In the two present experiments only enough gas to fill the cell volume to 20 torr with water vapor was introduced into the system. Therefore, in the previous experiments an excess quantity of water vapor was present. There is a possibility, then, that some quantity of the water vapor was adsorbed on the NaCl windows. This water would, of course, be in the beam path and contribute to the ir absorption intensity. The significance of this effect is that the amount of vapor necessary to achieve the desired absorption intensity would be larger than previously calculated.

FUTURE PLANS

There are eight major objectives for the next quarter: 1) completion of the CI calculations on the H + H_2O and H + HF exchange reactions; 2) construction and testing of the H_2O/H_2 flow system and reaction cell; 3) assembly and testing of the tunable ir laser; 4) alignment of the tunable ir laser, uv flashlamp and reaction cell; 5) tuning the ir laser to the maximum absorption band in HTO; 6) initiation of feasibility experiments on water detritiation by two-photon ISP; 7) a test run of the cell loading system to obtain the ir spectrum of HDO; and 8) recording the ir spectrum of HTO.

CATALYTIC EXCHANGE DETRITIATION STUDIES

J. C. Bixel, B. W. Hartzell and W. K. Park

BACKGROUND

With the exception of tritium, all the radioisotopes produced in the operation of a light water reactor are amenable to some form of chemical or physical separation process for removal from the effluent water streams. The detritiation of these aqueous wastes, however, requires development of isotopic separation processes.

Over 100 ideas have been considered for effecting the isotopic separation of tritium from water. Alternative methods have been discussed in a review by Ribnikar and Pupezin.[6] A number of technical and economic feasibility studies have been carried out on possible detritiation schemes - mostly based on experience and data from heavy water (D_2O) separation processes.[7-10]

Many of the basic separation methods used for heavy water production processes are technically feasible for detritiating water. Detritiation, however, requires larger stripping and recovery factors than does heavy water production. To be capable of obtaining the needed high recovery, a feasible detritiation process will require a high isotopic separation factor.

The hydrogen-water chemical exchange has the required high isotopic separation factor and is uniquely suited to a water feed. In addition, the technical feasibility of hydrogen isotopic enrichment through the exchange between hydrogen and water is not questioned. The process has been employed to produce heavy water on a large scale.[11] The HT/H_2O catalytic exchange process was selected on the basis of high isotopic separation factor and technical feasibility to be the most likely process for development and demonstration of waste water detritiation.

The objectives of this study are:

- Determination of technical and economic factors of HT/H_2O exchange as a possible detritiation process for treating tritium contaminated water from power reactor and fuel reprocessing plant operations,
- Determine suitability of hydrophobic exchange catalysts for use in water detritiation systems, and
- Through pilot scale testing, establish design criteria for detritiation systems capable of meeting the tritium control needs of the U.S. power reactor industry and ERDA site operations.

PRIOR WORK

Fabrication and installation of the experimental system were completed, and analytical instruments were integrated into the apparatus. The system was leak checked and operational checks were performed. All electrical hook-ups were traced and verified. The system was loaded with water and helium and operated for three days. Several problems with the basic operation of the system were identified, and corrective actions were initiated.

A preliminary economic evaluation was made of the HT/H_2O catalytic exchange detritiation stripping process as it might apply to a 5 metric ton/day nuclear fuel reprocessing plant.

ACCOMPLISHMENTS

Leak checking and cold operational testing of the experimental apparatus were completed. Modifications were completed to improve the operability and reliability of the required system as designed by Engelhard Minerals and Chemicals Corp.

A computer program based on the free energy minimization technique was used to calculate equilibrium concentrations of tritium compounds from reactants with various T/D/H/O ratios.

DISCUSSION

Equilibrium Calculation of Concentrations of Hydrogen Isotopic Compounds in Multicomponent Ideal Gas Mixture In chemical exchange reaction systems involving tritium (T), deuterium (D) and protium (H), it is necessary to find the distribution of molecular species that is expected at thermodynamic equilibrium. For a lean gas mixture where tritium and deuterium amounts are very small in relation to protium, the limiting equilibrium may be assumed and a simple hand calculation can be carried out to obtain approximate concentrations of a few species. However, as the input concentrations of tritium and/or deuterium increase, the system takes a complex form and the concentrations of various molecular species (in thermodynamic equilibrium at a specified temperature and density) must be rigorously calculated either by solving a set of algebraic equations consisting of conservation of mass equations and equilibrium constants, or by using the numerical method based on the minimization of free energy. In following sections, we will outline the method used in this report for the numerical minimization of free energy.

At equilibrium the concentrations of molecular species depend on the temperature, density (or pressure) and elemental composition of the whole system. Composition is also a function of the molecular formulae and the standard free energies of formation of the species.

Elemental Compositions As listed in Table 1, two sets of six representative elemental compositions have been used for the computation of equilibrium concentrations of

Table 1

ELEMENTARY COMPOSITIONS AND REPRESENTATIVE
MOLE PERCENT OF INPUT COMPONENTS

	Mole				Mole % (1/100)			
	T	D	H	O	HTO	HDO	H_2O	H_2
COMPOSITION A								
1	9.7×10^{-3}	8.7×10^{-6}	2.0	2.9×10^{-2}	9.7×10^{-8}	8.7×10^{-6}	2.9×10^{-2}	9.7×10^{-1}
2	9.7×10^{-7}	8.7×10^{-6}	2.0	2.9×10^{-2}	9.7×10^{-7}	8.7×10^{-6}	2.9×10^{-2}	9.7×10^{-1}
3	9.7×10^{-6}	8.7×10^{-6}	2.0	2.9×10^{-2}	9.7×10^{-6}	8.7×10^{-6}	2.9×10^{-2}	9.7×10^{-1}
4	9.7×10^{-5}	8.7×10^{-6}	2.0	2.9×10^{-2}	9.7×10^{-5}	8.7×10^{-6}	2.9×10^{-2}	9.7×10^{-1}
5	9.7×10^{-4}	8.7×10^{-6}	2.0	3.0×10^{-2}	9.7×10^{-4}	8.7×10^{-6}	2.9×10^{-2}	9.7×10^{-1}
6	9.6×10^{-3}	8.65×10^{-6}	1.98	3.8×10^{-2}	9.6×10^{-3}	8.65×10^{-6}	2.88×10^{-2}	9.6×10^{-1}
COMPOSITION B								
1	1.5×10^{-7}	1.5×10^{-4}	2.0	0.5	1.5×10^{-7}	1.5×10^{-4}	0.5	0.5
2	1.5×10^{-6}	1.5×10^{-4}	2.0	0.5	1.5×10^{-6}	1.5×10^{-4}	0.5	0.5
3	1.5×10^{-5}	1.5×10^{-4}	2.0	0.5	1.5×10^{-5}	1.5×10^{-4}	0.5	0.5
4	1.5×10^{-4}	1.5×10^{-4}	2.0	0.5	1.5×10^{-4}	1.5×10^{-4}	0.5	0.5
5	1.5×10^{-3}	1.5×10^{-4}	2.0	0.5	1.5×10^{-3}	1.5×10^{-4}	0.5	0.5
6	1.48×10^{-2}	1.48×10^{-4}	1.98	0.5	1.48×10^{-2}	1.48×10^{-4}	0.49	0.49

hydrogen-isotopic compounds. Composition A represents input mixtures of low (D+O)/H elemental proportion for a wide range of T quantity.

Composition B represents input mixtures of high (D+O)/H elemental proportion for a wide range of T quantity. Sets of mixtures can be prepared by adding varying amounts of HTO to the mixture of one mole of H_2 and one mole of H_2O which includes 150 ppm deuterium.

Standard Free Energies of Formation The standard Gibbs free energies of formation (P_O = 1 atm) of the following species under ideal gas state were taken from NBS Monograph 20:[12]

H_2, D_2, T_2, HD, HT, DT

The values for H_2O, D_2O, T_2O, HDO, HTO and DTO were obtained from Libby.[13,14] The value for O_2 was taken from JANAF Table.[15]

Reference Internal Energies Since standard internal energies at absolute zero temperature have been used as the reference energies for the standard free energies, these reference energies were calculated for the computation of free energy functions (see Table 2).

The reference internal energies (E8) for molecular species were calculated from the dissociation energies (D)[16] of proper constituents, e.g.,

$$E8\ (HT) = 1/2\ D(H_2) + 1/2\ D(T_2O) - D(HT) \qquad (1)$$

or calculated from zero point energies[17] by taking isotopic effects. For this calculation gaseous H_2, D_2, T_2 and O_2 were used as the standard compounds. The choice of standard compounds does not affect the final results on the concentration.

Table 2

REFERENCE INTERNAL ENERGIES

E_o^8	kcal/mole
H_2	0
D_2	0
T_2	0
HD	0.083
HT	0.187
DT	0.024
H_2O	-57.104
D_2O	-58.880
T_2O	-59.636
HDO	-57.932
HTO	-58.297
DTO	-59.232
O_2	0

Derivation of Equations for Equilibrium Concentration Mass conservation equation can be written as follows:

$$\sum_{i=1}^{n} \nu_{ij} C_i = \alpha_j \qquad (2)$$

where C_i are number of atoms (or molecules) of ith species at some temperature T and mass density ρ. For example, for a mass conservation of tritium in a mixture containing 9.7×10^{-5} % of HTO,

$$2T_2 + HT + DT + 2T_2O + HTO + DTO = 9.7 \times 10^{-7} \qquad (3)$$

The coefficients ν_{ij} correspond to the above numbers 2, 1, 1, etc. The original fractions of elements, α_j (j = 1, ..., r) are such that

$$\sum_{j=1}^{r} \alpha_j = 1 \qquad (4)$$

To convert from C_i to number density per cm^3, we can use:

$$N_i\ (cm^{-3}) = 2.687 \times 10^{19}\ \frac{\rho}{\rho_o} C_i \qquad (5)$$

where ρ_o corresponds to mass density in standard state, at T_o = 273.16°K and P_o = 1 atm.

For an ideal gas, the equation of state can be written as:

$$\frac{P_i}{P_o} = C_i\left(\frac{\rho}{\rho_o}\right)\frac{T}{T_o} \tag{6}$$

$$P = \sum_{i=1}^{n} P_i \tag{7}$$

Using the equation of state, the Helmholtz free energy can be written as a function of density.

$$\frac{A_i}{RT} = \frac{A_i^\circ}{RT} + \ln \frac{C_i RT}{\rho_o T_o} \tag{8}$$

where A_i° is the Helmholtz free energy of ith species at standard state (P_o = 1 atm). Therefore, for the mixture of n species, the total Helmholtz free energy is

$$\frac{A}{RT} = \sum_{i=1}^{n} C_i\left(\frac{A_i}{RT}\right) \tag{9}$$

Therefore

$$\frac{A}{RT} = \sum_{i=1}^{n} C_i\left[\frac{A_i^\circ}{RT} + \ln C_i + \ln\left(\frac{\rho T}{\rho_o T_o}\right)\right] \tag{10}$$

or substituting a thermodynamic equation $(A^\circ/RT)_i = (F^\circ/RT)_i - 1$ into the above equation the equation is rearranged as a function of Gibbs standard free energy.

$$A = RT\sum_{i=1}^{n} C_i\left[\left(\frac{F^\circ - E_o^\circ}{RT}\right)_i - 1 + \left(\frac{E_o^\circ}{RT}\right)_i + \ln C_i + \ln\left(\frac{\rho T}{\rho_o T_o}\right)\right] \tag{11}$$

By the definition of equilibrium, one has to minimize the total free energy with constraints of mass conservation in the system. For this, a function ϕ can be defined such that

$$\phi = A + RT\sum_{j=1}^{r}\lambda_j\left(\alpha_j - \sum_{i=1}^{n}\nu_{ij}C_i\right) \tag{12}$$

where λ_j is the Lagrangian multipliers. By differentiating ϕ with respect to a given concentration, holding temperature, density and all other concentrations constant, and equating the derivative to zero, we obtain extreme values of A satisfying mass balance. Thus,

$$\left(\frac{\partial\phi}{\partial C_k}\right)_{T,\rho,C_{i\neq k}} = \mu_k - RT\sum_{j=1}^{r}\lambda_j\nu_{kj} = 0,\ k = 1, 2, \ldots, n \tag{13}$$

where μ_k is the chemical potential, or

$$\frac{\mu_k}{RT} = \frac{1}{RT}\left(\frac{\partial A}{\partial C_k}\right)_{T,\rho,C_{i\neq k}} = \left(\frac{F^\circ - E_o^\circ}{RT}\right)_k + \left(\frac{E_o^\circ}{RT}\right)_k + \ln\left(\frac{\rho T}{\rho_o T_o}\right) + \ln C_k \tag{14}$$

This equation can be rearranged for $\ln C_k$,

$$\ln C_k = -\left(\frac{F^\circ - E_o^\circ}{RT}\right)_k - \left(\frac{E_o^\circ}{RT}\right)_k - \ln\left(\frac{\rho T}{\rho_o T_o}\right) + \sum_{j=1}^{r}\lambda_j\nu_{kj} \tag{15}$$

The above set of n equations is to be solved with r mass conservation equations to find r λ_j and n C_k (r + n unknowns). Since these nonlinear equations for complex mixtures cannot be solved in an easy way, the following basic equations are derived as the numerically approximate method first used by White, Johnson and Dantzig.[18]

$$C_k = \bar{C}_k\left(1 + \frac{C_k - \bar{C}_k}{\bar{C}_k}\right) \tag{16}$$

where $\bar{C}_k$ is a guessed value close to C_k. Then

$$\ln C_k \simeq \ln \bar{C}_k + \frac{C_k - \bar{C}_k}{\bar{C}_k} \tag{17}$$

Therefore, by using the above relationship n linear equations in C_k and λ's becomes

$$C_k \simeq \bar{C}_k\left[-\left(\frac{F^\circ - E_o^\circ}{RT}\right)_k - \left(\frac{E_o^\circ}{RT}\right)_k - \ln\left(\frac{\rho T}{\rho_o T_o}\right) + \sum_{j=1}^{r}\lambda_j\nu_{kj} - \ln \bar{C}_k + 1\right] \tag{18}$$

which together with r linear mass conservation equations form a linear set in n + r unknowns (n C's and r λ's). With these values known, one can find improved concentrations for the trial guess value for the next step from the above equation. The iteration continues until convergence is met. When this is done, a set of final concentrations is calculated by using the exact equation (15). The calculations were made on the IBM 360 computer at Mound Laboratory as discussed below:

Results of Computer Calculations for Equilibrium Mixtures The variations of the equilibrium concentration of major compounds are shown in several figures. Figures 1A and 1B correspond to Composition A-2 and Composition A-5, respectively (see Table 1). Similarly, Figures 1C and 1D are for Composition B-3 and Composition B-6, respectively.

From these figures it can be seen that concentrations of isotopic hydrogen (HD, HT, etc.) increase as the temperature increases, while water (HDO, HTO, etc.) concentrations decrease as the temperature increases; however, above 600°K, the changes are small.

The amount of oxygen in relation to hydrogen also affects the final distribution of equilibrium composition. In the systems (Composition A) associated with a low water/hydrogen ratio, isotopic hydrogen (HD, HT, etc.) concentrations are larger than their corresponding water (HDO, HTO, etc.) concentrations. Accordingly, the variation of hydrogen concentrations are smaller than water concentrations. On the other hand, in the systems (Composition B) associated with a high water/hydrogen ratio, the isotopic hydrogen concentrations are smaller than their corresponding water concentrations.

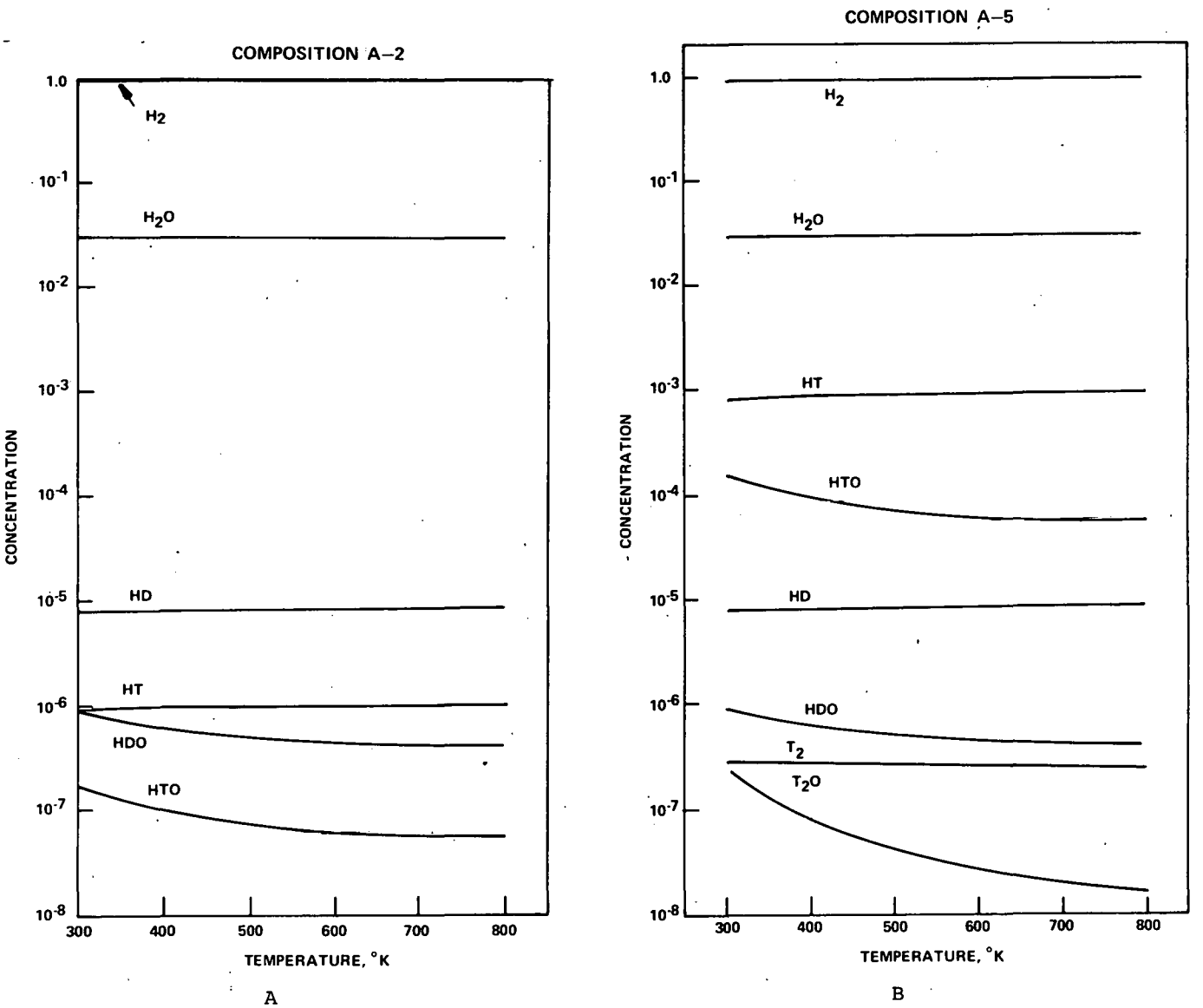
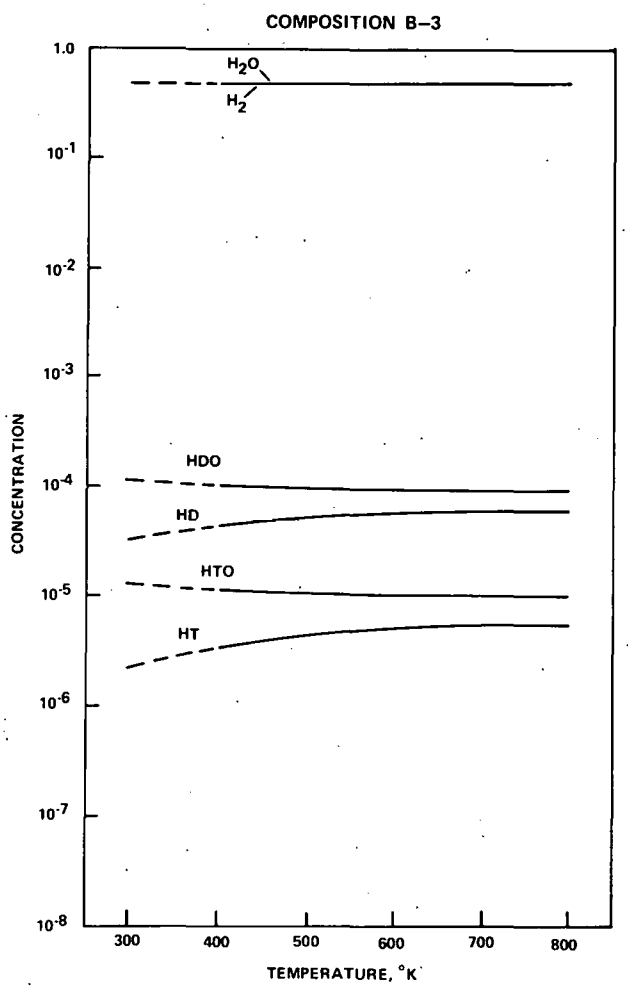


FIGURE 1 - Concentrations of major compounds in equilibrium as a function of temperature and density from the composition shown in figure:

$$N_i(cm^{-1}) = L_o C_i \left(\frac{\rho_2}{\rho_o}\right), \quad L_o = 2.68 \times 10^{19}, \quad \frac{\rho_2}{\rho_o} = 0.1 \sim 10.$$



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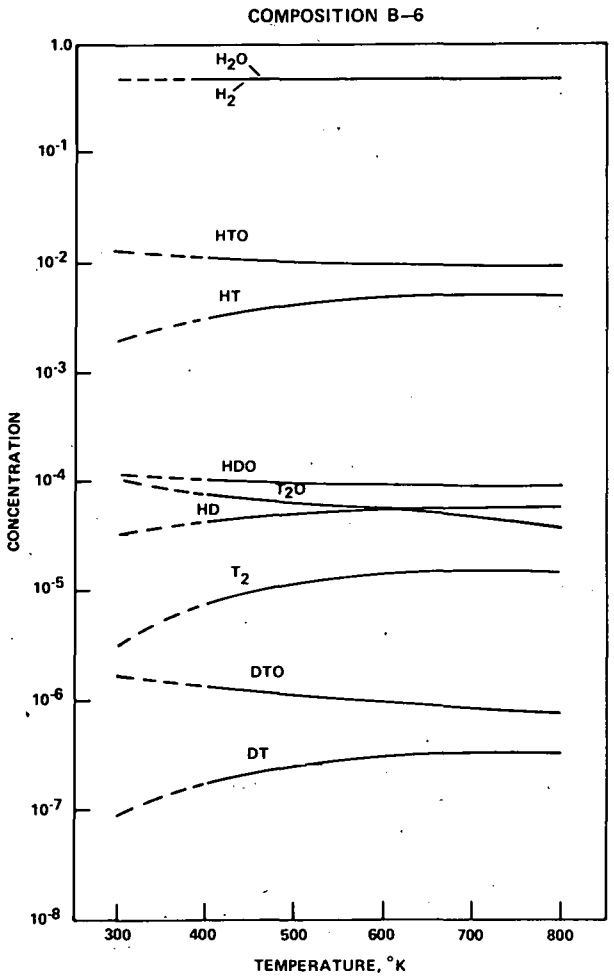

D

FIGURE 1 - (Continued)

The variation of hydrogen concentrations in these cases is relatively larger than water concentrations.

In order to determine the effect of tritium/protium proportion in the reactant elemental compositions on the variation of the concentration of equilibrium compounds, computations were carried out and the results were plotted. Figure 2A shows such effects of Composition A associated with a low water/hydrogen mixture at 300°K, and Figure 2B shows effects of Composition B associated with a high water/hydrogen mixture at 400°K.

As these figures show, by increasing the tritium level holding deuterium and protium levels constant in the reactant mixtures, one can almost linearly (on the log-log scale) increase the concentrations of major tritium compounds (e.g., HT, HTO). As a result, the presence of other minor tritium compounds such as T_2O, T_2, DT, DTO, etc. also becomes significant, making their enrichment and/or depletion process more complicated. In the systems studied here, the density (or pressure) had a negligible effect on the compound distribution. This may be attributable to a low system temperature and simple compounds involved.

The high level tritium operation is experienced in the multistage enriching/stripping process, where tritium and deuterium are concentrated. Especially, when such an equilibrium process involves chemical reactions, designing of a process scheme may have to be modified for application to complex systems.

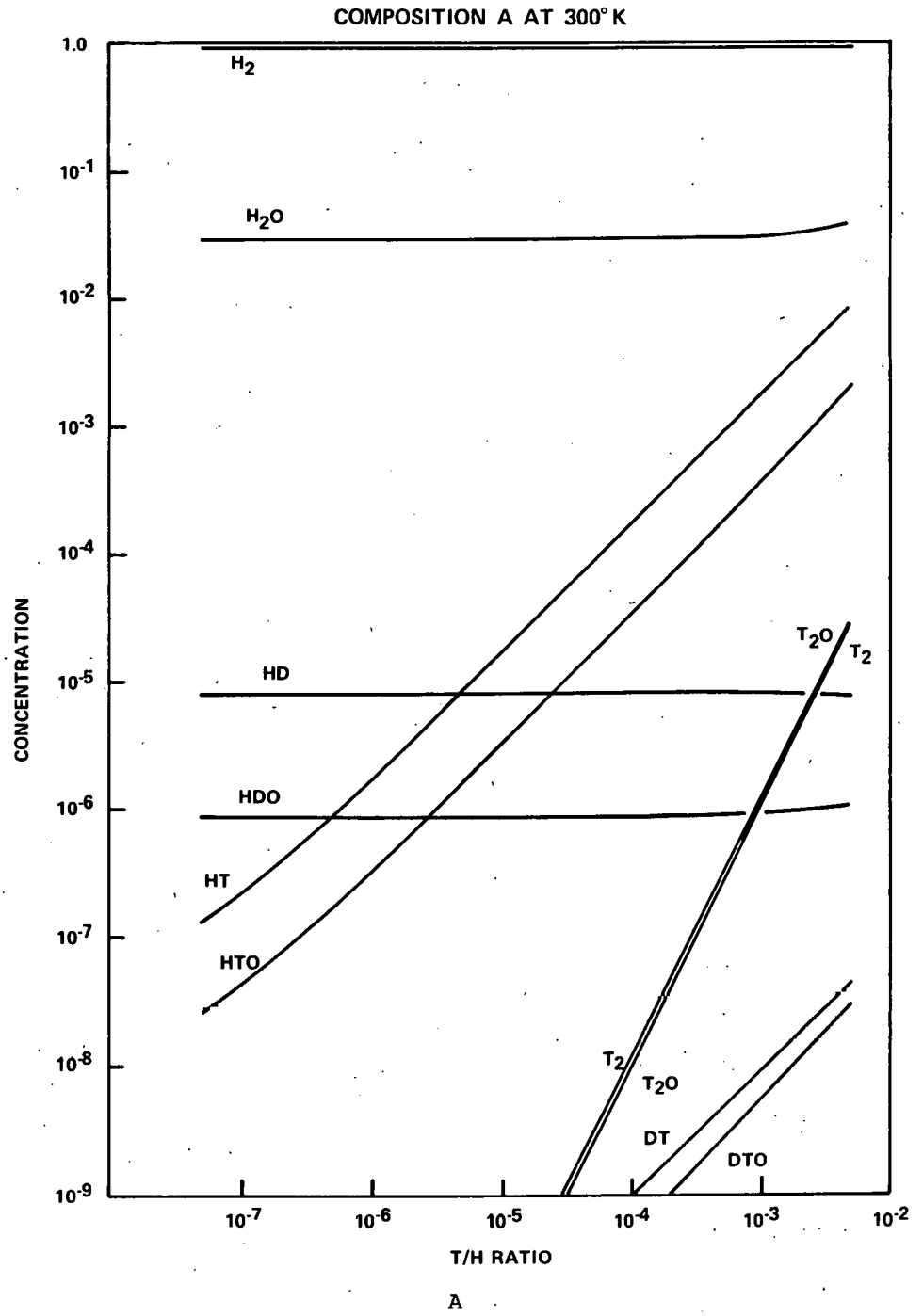

FIGURE 2 - Concentrations of major compounds as a function of tritium/hydrogen ratio from the elemental composition shown on figure.

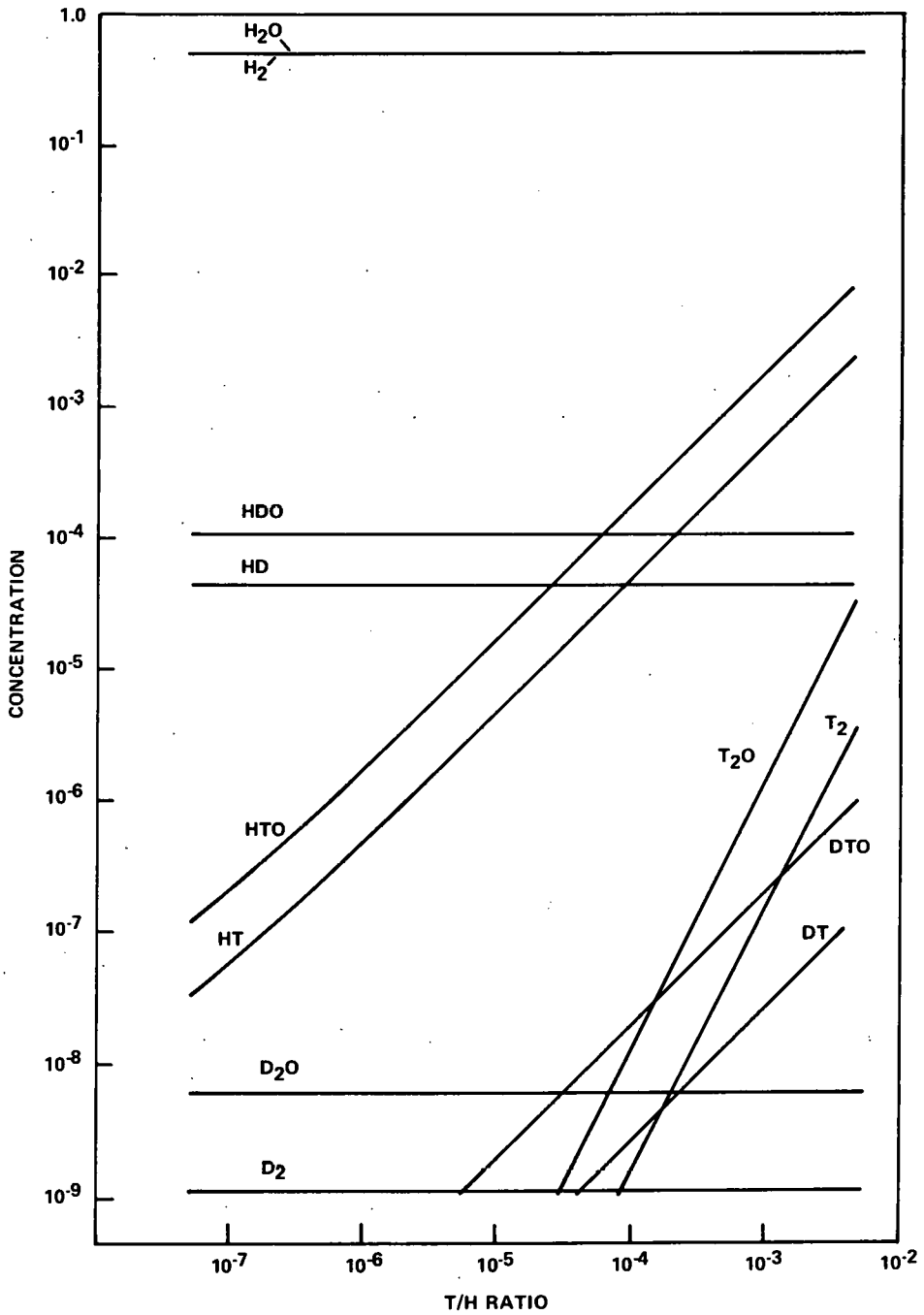

FIGURE 2 - (Continued)

FUTURE PLANS

Catalyst evaluation experiments will be conducted, and kinetic and thermodynamic performance data will be obtained and evaluated. More detailed economic feasibility studies will then be made. If the catalyst evaluation tests are successful, a multistage pilot detritiation system will be evaluated before proceeding to a field demonstration.

DEVELOPMENT OF SHIPPING CONTAINERS FOR TRITIATED LIQUID WASTE

T. B. Rhinehammer

BACKGROUND

The choice of containers and methods of packaging are particularly critical for the shipment of tritiated liquids, whether for disposal by burial or for tritium recovery and recycle. The contents can be easily lost to the atmosphere if the shipping package is involved in a fire or if the primary package is ruptured, allowing the contents to be exposed to the air. Hence, multiple containment and/or fixation of the tritiated liquid waste into an inert form appear to be mandatory needs in achieving absolute containment.

In past years, tritium waste generation has been totally within ERDA organizations but relatively small in quantity with the waste receiving special handling and disposal. Due to the potentially large quantities of liquid wastes from reactors, fuel reprocessing plants and CTR experiments through the 1980's and the associated risk of population exposure when shipping high level HTO wastes, a shipping package must be developed which will withstand the most severe accident conditions. High-level tritiated water will be available for shipment and recovery as a result of the water detritiation-enrichment technology now under study and development at Mound for application to low-level waste for PWR's, HWR's and fuel reprocessing plants. Initially, it is conceived that not only primary containment but secondary and perhaps tertiary containment may be necessary to achieve the required safety. A study, therefore, is necessary to provide the technical information and limits pertinent to container requirements, development, compatibility, construction, use, and safety.

PRIOR WORK

A reusable shipping container, for tritium recovery and recycle rather than burial, was initially chosen for development because of the potential availability of high-level wastes and the economic feasibility of recycle. A container has been built for use with an AL-M1 secondary shipping container, a form of secondary containment already approved by ERDA-ALO and DOT for shipment of plutonium-239 and uranium-235. This free-standing container was fabricated from off-the-shelf components and of 316-type stainless steel, to provide maximum resistance to corrosion and hydrogen embrittlement. It weighs less than 45 pounds and can be accommodated in a calorimeter for the purpose of tritium accountability. With an active volume of 10 liters it can hold up to 2 kg of tritiated water adsorbed on molecular sieves.

The top of the container is fitted with two standard bellows valves which serve as inlet and outlet ports, a pressure gage, a thermowell and a Cajon-sealed port for filling the vessel with the adsorbent. Each valve terminates in a Cajon fitting and also in a filter within the container. An O-ring sealed cap attaches to the top of the container to provide secondary containment and physical protection of the valves and gage.

The container may be used indefinitely because water can be removed by regenerating the adsorbent to a low tritium background and dew-point with heat and vacuum. Use of the container would normally involve connection of an effluent removal or detritiation system to the inlet and outlet valves of the container by means of Cajon fittings.

ACCOMPLISHMENTS

Because of the vulnerability of a bourdon tube pressure gage and lack of secondary containment, the original gage is being replaced with a 316 stainless steel pressure transducer which is now on order. Engineering drawings have been altered to reflect these changes.

Testing procedures have been determined for establishing guidelines on the usage and safety of the container.

FUTURE PLANS

Assuming that additional funding can be made available, a safety analysis review for packaging (SARP) will be started during the next quarter for the primary container assembled in the AL-M1 outer shipping container.

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