206/3-8-77

D. 771

MLM-2399

MLM-2399

MASTER

Tritium Waste Control Project

Progress Report: July-September, 1976

Harold F. Anderson and Carl J. Kershner

February 21, 1977

EB

Monsanto

MOUND LABORATORY
Miamisburg, Ohio
operated by
MONSANTO RESEARCH CORPORATION
a subsidiary of Monsanto Company
for the
UNITED STATES ENERGY RESEARCH
AND DEVELOPMENT ADMINISTRATION
U. S. Government Contract No. EY-76-C-04-0053

MLM-2399
Distribution Category:
UC-70

Tritium Waste Control Project Progress Report: July-September, 1976

Harold F. Anderson and Carl J. Kershner

Issued: February 21, 1977

PRINTED IN THE UNITED STATES OF AMERICA
Available from
National Technical Information Service
U. S. Department of Commerce
5205 Port Royal Road
Springfield, Virginia 22161
Price: Printed Copy $4.00; Microfiche $2.25

MONSANTO RESEARCH CORPORATION
A Subsidiary of Monsanto Company

MOUND LABORATORY
Miamisburg, Ohio 45342
operated for

UNITED STATES ENERGY RESEARCH
AND DEVELOPMENT ADMINISTRATION

U. S. Government Contract No. EY-76-C-04-0053

Tritium Waste Control Development Project

H. F. Anderson, Component Development Manager
C. J. Kershner, Monsanto Fellow

A December, 1970, Commission communiqué asked that contractors seek to limit their tritium and other radioactive effluents to levels that are "as low as practicable." Subsequent communiqués 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 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 six years, implementation of this philosophy through facility modifications and additions and changes in operating procedures has resulted in a 50-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.

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, because of 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 from new ERS and GADS systems at Los Alamos and Sandia Livermore, 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 categorie.

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 and handling problems. At the present time, the major development effort is in these areas.

Summary

TRITIATED LIQUID WASTE DECONTAMINATION (MOLECULAR EXCITATION)

Modifications to increase the power output of the Nd:YAG laser were completed. The higher power enabled the optical parametric oscillator (OPO) to be successfully operated for the first time.

The gas recirculation system for the laser isotope separation experiments was assembled and helium leak tested.

TRITIUM FIXATION PACKAGE

The pressure increase with time of the gas over samples of fixed and unfixed tritiated water and octane is being monitored. The gas produced from the tritiated water without fixation was analyzed. A G-value was calculated for the tritiated octane and compares favorably with the G-value for gamma-irradiated pure octane. The authors believe this is the first such data reported for tritiated organics with and without fixation.

Tritiated Liquid Waste Decontamination (Molecular Excitation)

W. R. Wadt and
R. E. Ellis

BACKGROUND

Operations involving tritium produce significant quantities of aqueous waste that 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 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-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.

PRIOR WORK

Laser Separation System 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, $OH + HT \rightarrow HTO + H$.

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., nuclear fuel reprocessing plant waste. 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 about a factor of 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 4.45 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 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).

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. When HDO was used as a surrogate, very satisfactory spectra were obtained from a Digilab FTS-14 Spectrophotometer.

A Barnes Engineering Company spectrometer cell was 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 were operationally tested. Initial experiments with HTO were unsuccessful because the samples were contaminated with CO_2.

ACCOMPLISHMENTS

Laser Separation System Modifications of the Nd:YAG power supply to upgrade the energy output were completed by General Photonics. The other malfunctions of the power supply were located and corrected. The Nd:YAG laser was used to drive the $LiNbO_3$ optical parametric oscillator (OPO) successfully for the first time. The uv flashlamp system was assembled and tested. Finally, a 4 x 10 ft optical table was procured and installed beside the fume hood containing the flow system. The laser excitation system is being assembled on the optical table.

DISCUSSION

Laser Separation System Initial testing of the Nd:YAG laser from General Photonics revealed that the energy output did not meet specifications (30 mJ/pulse). In order to rectify this problem the following changes were made: 1) the concave back mirror in the oscillator cavity, which had a 1-m radius of curvature, was replaced with a 5-m mirror; 2) the aperture controlling the TEM_{00} output in the oscillator was increased in accord with the mirror change; 3) the capacitance on the amplifier flashlamp circuits was increased from 50 μF to 80 μF. Other minor modifications were made on the high voltage d.c. power supply to improve performance.

During the initial tests of the Nd:YAG laser, a problem arose involving power degradation after a few minutes of operation at 10 Hz. The problem was clearly thermal in nature and was located in the simmer circuits for the flashlamps. The simmer circuits were overheating and then failing, shutting down a flashlamp in the amplifier and reducing the power output. A better heat sink and cooling system is being devised to solve the problem.

The Nd:YAG laser was completely realigned with the new 5-m mirror in place. The maximum energy output was just under 30 mJ/pulse. Since we expected at least 50 mJ/pulse, the energy output was disappointing. The problem appears to be the high voltage d.c. power supply which is producing only 820 V instead of the design value of 950 V. As a result, the energy delivered to the flashlamps is only 74% of the design value.

Because of the lower energy output from the Nd:YAG laser, a 2:1 beam reducing telescope was required in order to achieve the power threshold for operating the OPO. Moreover, the OPO was operated in a double pass configuration in order to lower the threshold; i.e., a high reflecting mirror for 1.06 μm was placed behind the OPO to reflect the 1.06-μm radiation back through the OPO. With the help of Prof. R. L. Byer the OPO was operated successfully. Power output measurements from the OPO have not yet been made. The OPO was tuned out to 4 μm, but we have not yet tuned out to 4.35 μm.

The uv flashlamp from Xenon Corporation was assembled and tested. The system appears to work according to specifications; however, we have been unable to check the energy output in the 190-200 mm region for lack of uv detection equipment. The latter deficiency will be rectified shortly and the energy output will be measured.

Construction of the H_2O/H_2 flow system was completed. Initial helium-leak tests proved unsatisfactory. The problem was the nickel gaskets which developed leaks when fittings elsewhere in the system were being tightened. Replacement of the nickel gaskets with softer copper ones has solved the problem. Helium-leak testing of the entire system is nearly completed.

A 4 x 10 ft. optical table was procured from Newport Research Corporation and installed next to the fume hood containing the flow system. The laser system was removed from the fume hood and assembled on the optical table. The new arrangement will greatly facilitate the laser detritiation experiments.

FUTURE PLANS

There are six major objectives for the next quarter: 1) testing of the H_2O/H_2 flow system and reaction cell; 2) testing of the tunable ir laser; 3) alignment of the tunable ir laser, uv flashlamp, and reaction cell; 4) tuning the ir laser to the maximum absorption band in HTO; 5) initiation of feasibility experiments on water detritiation by two-photon ISP; and 6) recording the ir spectrum of HTO using the tunable ir laser.

Tritium Fixation Package

W. E. Tadlock and
G. C. Abell

BACKGROUND

In view of the concern that tritiated waste products could possibly generate explosive gaseous species, a program was initiated to 1) determine the radiolysis-produced pressure buildup of gas over tritiated waste products with and without fixation, and 2) determine the quantity and type of radiolysis products generated as a function of time, tritium content, and nature of fixation agent.

Although a vast amount of research has been done on the radiation effects produced in various materials using gamma radiation, it is not always known whether this type of radiation creates the same radiolysis products as tritium. A comparison of the two types of radiation will be made where appropriate.

The object of this endeavor is to obtain a "worst case" result, and since gamma ray studies have shown that impurities often tend to reduce the effects of radiolysis, relatively pure materials have been used instead of actual waste products. Also, in order to obtain accelerated results, activities approximately 10 times those of the average activity of Mound Laboratory waste products were used. This study is part of a project concerned with the development of a suitable shipping container for recoverable tritiated waste.

PRIOR WORK

Work during this quarter is the first to be reported for this program.

ACCOMPLISHMENTS

The pressure buildup was monitored in the gas over tritiated water and octane (activity = 1 Ci/ml) contained with (w) and without (w/o) fixation. The fixation agent used for water was a cement-plaster mix. Lines D (w/o fixation) and E, Figure 1, illustrate the effect of cement-

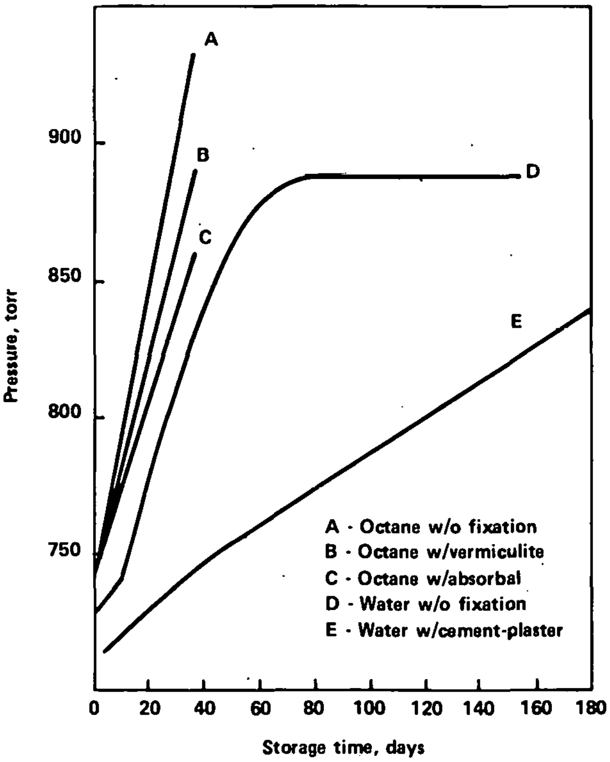

FIGURE 1 - Radiolysis-produced pressure buildup of gas over tritiated waste products with and without fixation.

plaster on the pressure buildup. Line D was terminated when the overgas was sampled for mass spectrometer analysis. The results are listed in Table 1.

Table 1

ANALYSIS OF OVERGAS FROM SAMPLE D

Constituent	Mass	Sample 1 (mole %)	Sample 2 (mole %)
H_2	2	15.81	15.92
HD	3	0.0	0.0
D_2	4	0.0	0.0
DT	4	0.0	0.0
T_2	6	0.0	0.0
He	3	1.27	1.29
He	4	44.89	45.24
H_2O	18	0.04	0.04
	19-24	0.0	0.0
N_2	28	3.46	3.45
O_2	32	0.0	0.0
Ar	40	32.00	31.64
CO_2	44	2.52	2.43

The fixation agents used with octane were vermiculite and Absorbal, and their effects on the pressure buildup are illustrated by lines A (w/o fixation), B (w/vermiculite), and C (w/Absorbal). No analysis of this overgas has been made at this time. A G-value for the production of gas of 3.2 ± 0.1 was calculated from these data and compares favorably with the G-value of 6.8 [1] measured for pure octane using gamma radiation. (The G-value of a reaction is defined as the number of product molecules formed or reactant molecules consumed per 100 eV of energy absorbed by the system.[2])

DISCUSSION

Two samples each of tritiated water (activity = 1 Ci/ml) with and without fixation were stored in small stainless steel containers fitted with a valve and a pressure transducer. The water was prepared by mixing distilled water with a mixture of D_2O and T_2O which had previously been prepared by passing a mixture of deuterium and tritium gas over heated copper oxide. A mixture of cement-plaster of the same ratio as is used on a larger scale for the storage and shipment of tritiated waste water was used for fixation. Boxline atmosphere composed of helium-4, argon, nitrogen, moisture, and possibly oxygen was used as initial overgas. No analysis of this box atmosphere was made.

At storage times of 154 and 160 days, the containers of tritiated water without fixation were attached to a gas sampling station, the water frozen out at -50°C, and the overgas expanded into a previously evacuated sample bulb. This gas was then analyzed by a mass spectrometer. The results are listed as sample 1 and 2 in Table 1. Surprisingly, no oxygen was found. After sampling, the overgas was removed by evacuating, and the containers were backfilled with argon. The overgas in these containers will be sampled at a later date.

Three samples of tritiated octane (activity = 1 Ci/ml) (one without fixation, one fixed on vermiculite and one fixed on Absorbal) were monitored for pressure buildup. Tritiated octane was used as a substitute for vacuum pump oil since relatively pure octane with the desired activity was available, but clean pump oil with the desired activity was not. Most vacuum pump oil is a mixture of aliphatic hydrocarbons, and gamma radiation experiments have shown that the G-value is nearly independent of the length of the carbon chain in aliphatic hydrocarbons. Therefore, the radiolysis products from octane should be nearly the same as for pump oil.

Purified boxline atmosphere was used as the initial overgas in these containers. The boxline atmosphere was argon with a small amount of nitrogen (1.49 mole %) as found by mass spectrometer analysis. Oxygen and moisture were removed via a Dri-train purifier.

FUTURE PLANS

The pressure buildup of the containers holding tritiated water and octane will continue to be monitored. Samples of the overgas will be analyzed at the appropriate time depending upon the pressure buildup. Samples of waste vacuum pump oil will be stored with vermiculite and without fixation to obtain data concerning pressure buildup of this actual low-level waste.

References

1. J. F. Kircher and R. E. Bowman, Effects of Radiation on Materials and Compounds, Reinhold Publishing Corp., N.Y., p. 28 (1964).

2. ibid, p. 27.

Distribution

EXTERNAL

TID-4500, UC-70 (261)

M. B. Biles, DOS/Headquarters
L. L. Burger, Battelle Pacific NW Lab.
J. A. Chacon, DAO
R. B. Craner, SLA
D. Davis, Jr., NMWMD/ALO
J. C. Dempsey, DWMT/Headquarters
R. K. Flitcraft, MRC, Dayton
W. H. McVey, DRRD/Headquarters
W. E. Moddeman, U.D. Research Institute
D. K. Nowlin, SPD/ALO
W. A. Reese, SRO
J. R. Roeder, OSD/ALO
M. J. Steindler, CED/ANL
Monsanto Reports Library, St. Louis

INTERNAL

H. F. Anderson (30)
W. T. Cave
C. W. Huntington
L. V. Jones
C. J. Kershner
J. R. McClain
H. L. Turner
R. E. Vallee

Records Center
Library (15)
Publications (15)