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J. L. Maienschein
F. Magnotta
I. P. Herman
F. T. Aldridge
P. Hsiao

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TRITIUM REMOVAL FROM CONTAMINATED WATER

VIA INFRARED LASER MULTIPLE-PHOTON DISSOCIATION

J. L. Maienschein, F. Magnotta, I. P. Herman, F. T. Aldridge, and P. Hsiao
University of California, Lawrence Livermore National Laboratory
P. O. Box 808, Livermore, California 94550
(415) 423-1816

ABSTRACT

Isotope separation by means of infrared-laser multiple-photon dissociation offers an efficient way to recover tritium from contaminated light or heavy water found in fission and fusion reactors. For tritium recovery from heavy water, chemical exchange of tritium into deuterated chloroform is followed by selective laser dissociation of tritiated chloroform and removal of the tritiated photoproduct, TCl. The single-step separation factor is at least 2700 and is probably greater than 5000. Here we present a description of the tritium recovery process, along with recent accomplishments in photochemical studies and engineering analysis of a recovery system.

INTRODUCTION

The removal of tritium from contaminated water is important in fission and fusion reactors. Present levels of tritium contamination in heavy-water fission reactors can result in high release rates of tritium to the environment and high occupational dose rates. The use of water (light or heavy) as a coolant in fusion reactors will pose a hazard at least as severe, since large quantities of tritium will be present and will permeate into the coolant.

Infrared laser multiple-photon dissociation (IRMPD) offers a novel and efficient method to recover tritium from contaminated water. By utilizing the shift in infrared absorption for halomethanes containing different hydrogen isotopes, single-step isotope enrichment factors of tritium with respect to hydrogen or deuterium can be 1000 or more.[1-3] In contrast, conventional hydrogen isotope separation processes such as Sulzer or CECE (combined electrolysis catalytic exchange) have equivalent separation factors of 2 to 10.[4] The very high separation factors attainable with IRMPD promise a significant reduction in process size and cost.

Our current efforts studying photochemistry and process design are focused on tritium removal from heavy water, since the need exists now for detritiation of the reactor moderator at the Savannah River Plant (SRP) and the Canadian CANDU heavy water reactors. However, tritium removal from light water is also feasible and should be further studied for possible application in fusion reactors. Here we describe the IRMPD process for tritium removal from water, and present our recent accomplishments and our program goals.

INFRARED MULTIPLE-PHOTON DISSOCIATION

In IRMPD, irradiation of a molecule with pulsed infrared radiation at a strongly absorbed wavelength can result in the absorption of over 30 photons and subsequent dissociation of the molecule. By irradiating tritiated molecules at a wavelength at which deuterated or protonated molecules are transparent for T/D and T/H separation respectively, primarily tritiated molecules are dissociated. Then, simple chemical separation of the dissociation products allows recovery of highly enriched tritium. The halomethanes have large vibrational absorption spectral shifts with different hydrogen isotopes. We have found that trichloromethane (chloroform) is best suited for T/D separation. Studies at LLNL and in Japan have shown that trifluoromethane (fluoroform) may be suitable for T/H separation.[1,3]

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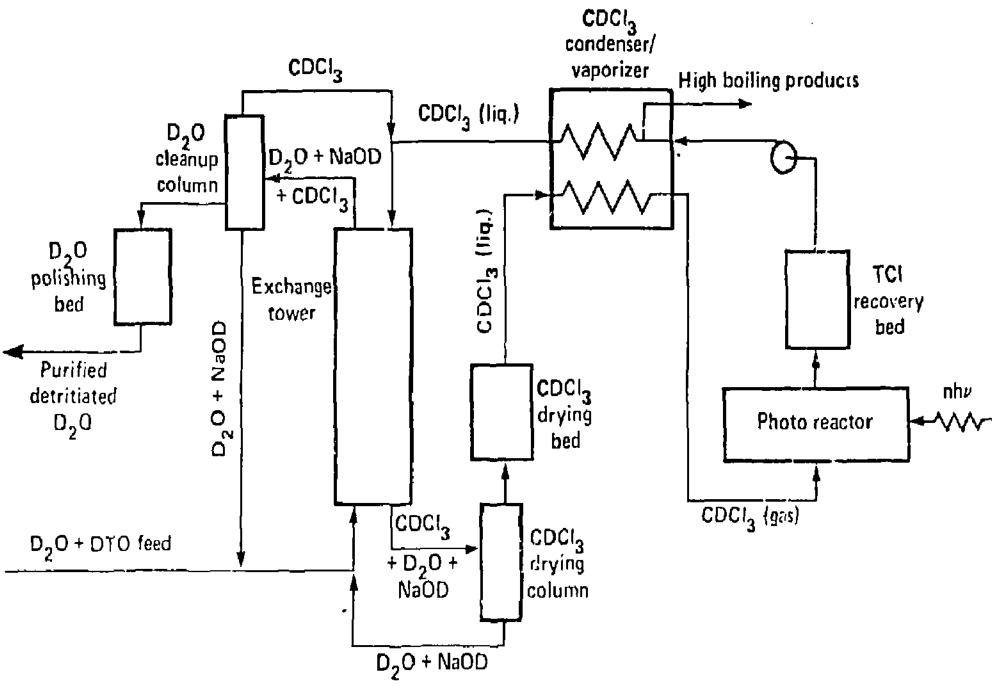

Figure 1. Process flow for tritium recovery from heavy water by infrared laser multiple-photo dissociation of chloroform.

Tritiated chloroform selectively absorbs infrared radiation near 12μm due to $\nu_4 \leftarrow 0$ where $CDCl_3$ is transparent. Our measurements demonstrate that at 12.08μm the T/D selectivity in absorption is $>10^4$ at low fluences and is >400 at the fluences required for near-unity $CTCl_3$ dissociation probability ($\sim$20 J/cm^2). This highly selective absorption means efficient utilization of infrared photons.

We have recently shown that the products of 10.9μm IRMPD of $CDCl_3$ are DCl and $:CCl_2$.[5] Therefore, 12μm photolysis of the $CTCl_3/CDCl_3$ gas mixture will yield TCl as the tritium-bearing product and chlorinated hydrocarbons. Experiments to date, conducted with a CO_2 laser optically pumping an NH_3 laser, have shown that the single-frequency IRMPD probability peaks near 825 cm^{-1}, with a saturation fluence of $\sim$20 J/cm^2. The $CTCl_3$ dissociation probability begins to decrease as the total chloroform pressure increases beyond 2 torr when using 1.1 μs pulses of 12μm radiation.[2] Since the allowable gas density (and pressure) is inversely related to the pulse duration, operating pressures as high as 50 torr are feasible using 50 ns irradiation pulses.

By measuring depletion in 100 ppm mixtures of $CTCl_3/CDCl_3$, we have found that the single-step T/D enrichment factor (defined as the ratio of the T/D fraction in the product to that in the reactant) is >> 2700. No evidence for any $CDCl_3$ depletion or $TCl/CDCl_3$ scrambling has been observed.

Carbon dioxide laser IRMPD of T/H mixtures near the 9μm CTF_3 peak ($\nu_2 \leftarrow 0$) yields TF. The single step enrichment factor is greater than 500, as shown in studies in Japan.[3] We have shown that the T/D enrichment factor in 9μm photolysis of CTF_3/CDF_3 is only $\sim$19, and is therefore not useful for T/D recovery.

PROCESS FOR TRITIUM REMOVAL FROM WATER

To remove tritium from contaminated water, the tritium must be transferred from the water to a working molecule (chloroform or fluoroform). The tritiated molecules are then photolyzed, and the photoproducts collected. A process to accomplish this is shown in Fig. 1 and described in this section. Our development of the process and its individual components are discussed in the next section. We will refer to T/D rate of ~150 Hz. Photons from a 9μm CO_2 laser will be converted to the required 12 μm wavelength by a process such as Raman scattering in NH_3. The goal of near-term research is the final selection of desired laser parameters and subsequent design of a sufficiently powerful and efficient laser at the appropriate frequency, pulse length, and repetition rate.

Another area of study is the identification and collection of non-tritiated photoproducts such as C_2Cl_4, C_xCl_y and $C_xD_yCl_z$. For IR photolysis of pure $CDCl_3$, there is some evidence for the formation of heavy C_xCl_y compounds or polymers. This must be studied further for the quite different mixtures of interest, in which only a small fraction of the molecules (5 ppm $CTCl_3$) are excited in a bath of cold molecules ($CDCl_3$).

Photoproduct Removal

Removal of the tritiated photoproduct, TCl (TF), will be accomplished by sorption on a solid. This has the advantage of isolating the tritium as an easily handled solid. In addition, gas or liquid streams of high tritium concentration are eliminated which would otherwise require expensive containment provisions. For TCl recovery, solids such as type-X zeolite, alumina, activated carbon, and silica gel are promising candidates for adsorption (for TF recovery, sodium fluoride is a likely absorbent). By passing the $CDCl_3$ (CHF_3) gas through a packed bed of suitable solid, the TCl (TF) can be easily removed. The solid containing tritium can be regenerated later to recover the tritium.

The remaining photoproducts will consist primarily of C_xCl_y compounds such as C_2Cl_4 (C_2F_4). These may be removed by condensation or distillation of the $CDCl_3$ (CHF_3) stream. It should be acceptable to allow these photoproducts to build up so that they can be removed by treatment of a small side-stream. This will result in a small unit size for the non-tritiated-photoproduct removal system.

Identification of the best sorbent for TCl (TF) recovery is the major task in development of this unit. We are beginning a program to screen promising sorbents with the goal of identifying the best sorbents for TCl recovery. The removal of the C_xCl_y products is under study, and should not be complicated.

Overall Process Considerations

In integrating the units into a complete process, several interactions arise which must be considered.

The gas pressure in the photoreactor should be low (<6 kPa) for optimal photochemistry; however, the cost of compression of the gas to near atmospheric pressure for the rest of the cycle favors higher reactor pressure. With the additional complication that a more expensive laser of shorter pulse length allows higher reactor gas pressures and lower compression costs, the tradeoffs become complex. Other tradeoffs exist in selection of overall gas flow rate when laser power and fraction of tritium removed are considered. The question of suitable construction materials must also be addressed.

CLEANUP SYSTEM FOR SAVANNAH RIVER PLANT

We have produced a preliminary design of a tritium cleanup system for a typical SRP or power heavy-water reactor. Although it includes many uncertainties, the design serves to illustrate the magnitude of equipment and costs involved with the IRMPD process. Table 1 summarizes the design and shows system specifications, flow rates, and approximate unit sizes. As we see from the table, the cleanup system is of modest size and is characterized by small individual units, low flow rates, and acceptably low power consumption. Because of the small scale of the process, the estimated capital cost is also low.

Although specific requirements will be different, the scale of the system illustrated here indicates that such a system should be practical for T/H separation in fusion reactors at a reasonable cost.

ADVANTAGES OF IRMPD

In comparison with more conventional detritiation processes such as Sulzer (gas-phase DTO/D_2 exchange followed by cryogenic distillation) or CECE (liquid phase DTO/D_2 exchange plus electrolysis), separation using deuterated chloroform, but the comments apply equally to T/H separation using fluoroform.

The transfer of tritium from water to chloroform can be accomplished by simple hydrogen exchange in the presence of a base catalyst such as sodium deuteroxide (NaOD). The base-catalyzed chloroform/water exchange is rapid (although the base-catalyzed fluoroform/water exchange is slow, the addition of dimethyl sulfoxide (DMSO) accelerates the rate to an acceptable level). The effluent water, reduced in tritium, is treated to remove $CDCl_3$ and NaOD (and DMSO) before return to the fission or fusion reactor. The deuterated chloroform (partially tritiated) is dried and then fed as gas to the photoreactor. There it is subjected to laser pulses which dissociate the tritiated molecules. The gas leaving the photoreacter contains photoproducts (halocarbons and TCl) diluted in a large excess of unreacted $CDCl_3$. The tritiated product, TCl, is recovered by adsorption onto a solid getter such as a zeolite or sodium fluoride, and the other photoproducts are removed by condensation or distillation. The bulk of the working molecule, which did not contain tritium and was not photolyzed, is then recycled back to the tritium exchange unit.

PROCESS DEVELOPMENT

Our efforts in process development have been focused primarily on the selection of suitable techniques for each unit operation and on identification of the major unknown parameters which strongly affect unit and overall process design. Some of our findings are discussed below.

Tritium Exchange Unit

In the tritium exchange unit for T/D (T/H) separation, tritium-contaminated water is contacted in a countercurrent flow with the gaseous or liquid $CDCl_3$ (gaseous CHF_3) working molecule in the presence of NaOD catalyst (NaOH and DMSO). A simple packed tower will provide sufficient contacting.

The exchange unit must contain means to purify the water and working molecule streams after contacting. Distillation is satisfactory for removal of most of the dissolved impurities such as NaOD and $CDCl_3$ (NaOH, CHF_3, DMSO) from the treated water. Final purification with activated-carbon beds will be needed to remove residual $CDCl_3$ (CHF_3). Distillation followed by a molecular-sieve drying bed will adequately remove impurities such as D_2O and NaOD (H_2O, NaOH, DMSO) from the $CDCl_3$ (CHF_3) stream.

Measurement of the exchange rate and equilibrium constant must be made before exchange unit design can be finalized; the reactions are:

$$DTO + CDCl_3 \rightleftharpoons D_2O + CTCl_3 \qquad (1)$$

$$HTO + CHF_3 \rightleftharpoons H_2O + CTF_3 \ . \qquad (2)$$

We are currently making these measurements for $CDCl_3$ exchange. The equilibrium constant for Reaction (1) is 0.5 ± 0.02 and is nearly independent of temperature. The rate constant, first-order in NaOD and DTO concentration, is 0.14 ± 0.04 l/mole·s at 25°C and increases sharply with increasing temperature. Symons et al. have made related measurements for CHF_3 exchange.[6,7]

Special care must be taken during design of the water purification steps, since the removal of dissolved $CDCl_3$ (CHF_3) must be essentially complete. Any residual halocarbons in the water will be subject to radiolysis in the fission or fusion reactor, with release of corrosive chloride (fluoride) ions. The SRP requirement is that the chloride ion concentration be no more than 100 ppb (conservatively, $CDCl_3$ concentration must be no more than 33 ppb). Sorbent beds of granular activated carbon should provide sufficient $CDCl_3$ (CHF_3) removal,[8,9] but this must be demonstrated under process conditions.

Photoreactor and Laser

In the photoreactor, the working molecules are exposed to infrared radiation to dissociate the tritiated species. The photoreactor is a multi-pass infrared cell through which the $CDCl_3$ (CHF_3) flows transverse to the laser beam at a pressure of $\sim$6 kPa. The 12μm laser will provide $\sim$4.5 kW of power in 50 ns pulses containing 30 J of energy, with a repetition

TABLE 1. Preliminary design of tritium removal system using IRMPD for typical heavy water reactor

System requirements	
Heavy water volume	630 m^3
Tritium level in D_2O	20 Ci/l
Desired tritium level	3 Ci/l
Time to reach desired level	3 y
System Specifications	
D_2O flow rate	30 cm^3/s
$CDCl_3$ flow rate	270 cm^3/s
Tritium recovery rate	1-2 g/d
Product T/D ratio	0.024
Electric power for laser	200 kW
Compressor power	~30 kW
Exchange tower	
diameter	40 cm
height	6 m
D_2O cleanup column	
diameter	15 cm
height	3 m
$CDCl_3$ drying column	
diameter	15 cm
height	3 m
D_2O polishing beds (4 req.)	
diameter	30 cm
height	1.5 m
$CDCl_3$ drying beds (4 req.)	
diameter	30 cm
height	1.5 m
Photoreactor	
diameter	~10 cm
length	5-10 m
TCl recovery beds (2 req.)	
diameter	30 cm
height	1.5 m
$CDCl_3$ condenser surface area	9 m^2
Estimated capital cost	
Non-laser components	1-5 M\$
Laser	~5 M\$

the major difference is the high separation factor in IRMPD. For IRMPD the separation factor is >>2700 while for conventional processes the separation factors are less than 10. This gives rise to several advantages.

With the high separation factor, it is not necessary to recirculate process streams in order to produce a concentrated tritium stream as is required with conventional processes. Thus process streams and associated equipment are smaller and less costly. The energy consumption is also much lower without process stream recirculation; for D/H separation, IRMPD energy requirements are about one-twentieth those for the CECE process.[10]

Containment of streams containing high concentrations of tritium is expensive and inconvenient. In conventional processes, recirculating streams that are necessary to produce high tritium concentrations must have special containment precautions, since the tritium is concentrated far above initial levels. With the IRMPD process, the only unit containing concentrated tritium is the sorbent bed that recovers TCl/DCl (TF/DF), and the tritium is isolated there in a solid form. In all gas and liquid process streams the tritium concentration is no higher than in the feed water. The absence of highly concentrated tritium in these streams greatly reduces containment requirements and costs. A secondary benefit of the absence of tritium-concentrated recirculating streams is that tritium holdup in the process is reduced to negligible levels.

PROJECT GOALS

We plan to complete experiments basic to the IRMPD process for DTO/D_2O separation in the near future. These include more precise measurement of the $DTO/CDCl_3$ exchange reaction rate and equilibrium constant, determination of photolysis products and associated yields, and identification and characterization of the best TCl adsorbent. We will also verify the feasibility of cleaning effluent water adequately for use at SRP.

We plan to start design of a lab-scale pilot plant for application at Savannah River, with construction possibly starting in FY85. With data from this, we can begin design of a full-scale plant for Savannah

River. Concurrent with pilot-plant and full-scale design efforts, we will engage in development of lasers to provide the necessary power, wavelength, pulse rate, and *repetition rate*.

CONCLUSIONS

Laser IRMPD offers a novel way to remove tritium from contaminated water, with many advantages as a result of its high separation factor. Incorporation of IRMPD into a process appears to be practical. Our current emphasis is on tritium removal from heavy-water reactors at SRP because the need there is immediate. However, tritium removal from light water using IRMPD is also feasible and *should be considered if water is used in* fusion reactors.

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