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Tritium Waste Control Project

Progress Report: April-June 1976

John C. Bixel and Carl J. Kershner

December 10, 1976

MASTER

MOUND LABORATORY
Miamisburg, Ohio
operated by

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NOTICE

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1

Table of Contents

Summary

Tritiated Liquid Waste Decontamination (Molecular Excitation)

The $LiNbO_3$ crystal to be used in the laser isotope separation experiments was success-fully tested at Stanford University. Assembly of the H_2O/HT flow system was initiated.

A preliminary economic study of water detritiation by laser isotope separation (LIS) indicates possible advantages for LIS over the catalytic exchange process. The electric power requirements are a factor of 5 lower resulting in a 50% reduction in operating costs relative to catalytic exchange. Capital costs for the two methods appear to be comparable.

Additional attempts were made to determine the ir spectrum of HTO around the v_1 band. However, carbon dioxide impurity obscured the HTO absorption around 2265 cm^{-1} making it impossible to obtain a high quality spectrum for use in the LIS experiments. The source of the CO_2 appears to be organics, primarily methane, in the H_2-T_2 gas mixture used to load the cell. Efforts are underway to clean the H_2-T_2 gas.

Electrolysis of High Level Tritiated Water

An experiment was carried out using the General Electric UCT-1 regenerative cell to electrolyze water containing approximately 0.3 grams of tritium. The experiment was partially successful in that about 21 ml of water was electrolyzed. However, the solid polymer electrolyte (SPE) ruptured during electrolysis and components of the cell were damaged beyond repair. A new SPE cell with capability of 10 times the through-put of the UCT-1 has been ordered.

Tritium Monitor Development and Calibration

The calibration system design was modified to allow procurement and fabrication of the major components during FY-1976.

Shipping Container Development for Tritiated Liquid Waste

The bourdon tube pressure gage has been replaced with a pressure transducer especially designed to provide double containment of the enclosed material. A calorimeter has been completed for tritium assay of the shipping container contents.

Catalytic Exchange Detritiation Studies

The Englehard hydrophobic, catalyst for HT/H_2O exchange is being tested. A preliminary experiment to establish the height of one equilibrium plate was completed. Studies are also in progress to determine the mechanical stability and active lifetime of the catalyst.

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.

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 concen-
tration 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 decon-
taminate 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 prin-
ciple, 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, suffici-
ent energy input is needed for processing
the total feed quantity many times to main-
tain the total cascade flow required for
the desired separation. Thus, selective
photoexcitation is a very attractive pro-
cess for an application where one is con-
cerned with the isotopic separation of
trace quantities from a voluminous
quantity of feed such as in the case of
water detritiation or heavy water enrich-
ment.

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 kin-
etics indicates that for low-level wastes,
the effect of the tritium β decay on re-
generation of HTO places a more stringent
limitation on the tritium level allowable
in the hydrogen stream than does the reac-
tion, OH + HT → HTO + H.

A qualitative analysis of the isotopic
selectivity of the two-photon dissociation
process was made. The selectivity or
ratio of HTO and 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. One possi-
bility is pumping a combination band with
a Nd:YAG laser at 1.06 μm.

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 os-
cillator-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 mono-
chromator (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. 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 Systems The LiNbO$_3$ crystal was successfully tested at Stanford University. Construction of the H$_2$O/H$_2$ flow system has been initiated. Further progress on the water detritiation experiments has been impeded by startup problems with the Nd:YAG laser.

A preliminary economic study of detritiation by laser isotope separation (LIS) as applied to the AGNS nuclear fuel reprocessing plant waste stream indicates possible advantages for LIS over catalytic exchange. The electric power requirements are a factor of five lower for LIS relative to catalytic exchange. At $.03/KWh the power reduction converts to a yearly savings of $1M in the operating costs, i.e., a 50% reduction in total operating costs relative to catalytic exchange. The capital costs for LIS and catalytic exchange appear to be comparable (~$5M).

HTO Infrared Spectrum CO$_2$ impurity was found to be present in the oxidized H$_2$-T$_2$ samples. Absorption by the CO$_2$ in the region of interest (4.35 microns) is very strong and prevented observation of the HTO spectrum. The source of the CO$_2$ appears to be methane in the H$_2$-T$_2$ mixture. Efforts were initiated to remove the methane prior to oxidizing the H$_2$-T$_2$.

DISCUSSION

Laser Separation System Various startup problems have been encountered with the Nd:YAG laser. At present the power supply is being repaired and retrofitted by the manufacturer, General Photonics. The alterations should increase the energy output to 50-60 mJ/pulse.

As to the optical parametric oscillator (OPO), it was learned that some of the LiNbO$_3$ crystals fabricated by Crystal Technology for Exxon Research and Engineering, had failed to oscillate. Therefore, Dr. Wadt took our LiNbO$_3$ crystal to Stanford, where Prof. R. L. Byer, our laser consultant, and Dr. R. L. Herbst tested the crystal. The LiNbO$_3$ crystal did oscillate, although the threshold (27 MW/cm^2) was three times higher than that for an LiNbO$_3$ crystal grown at Stanford. Prof. Byer has kindly loaned to us the low threshold Stanford crystal in order to facilitate the startup of the OPO at Mound.

Construction of the H$_2$O/H$_2$ flow system for the water detritiation experiments has been initiated. The system will be helium leak checked and the pressure, flow, moisture and tritium monitors will be tested shortly under typical operating conditions.

Preliminary Economics for LIS In a previous report,[1] a preliminary economics study of catalytic exchange was presented for detritiation of the low-level aqueous waste (LLAW) expected from the Allied-Gulf Nuclear Services (AGNS) nuclear fuel reprocessing plant under construction at Barnwell, S.C. The treatment of the AGNS plant waste was chosen, since it represented the most stringent and costly application for catalytic exchange in the nuclear fuel cycle. Since laser isotope separation (LIS) is considered to be most applicable to detritiation of LLAW, it is appropriate to perform a comparable economic study for LIS. The results are reported below.

As in the catalytic exchange study,[1] we assume the AGNS plant produces 500 liters/hr of LLAW containing 0.2 Ci/liter of tritium. This corresponds to 750,000 Ci/yr (assuming 330 days/yr on stream operation) or 75 g/yr of tritium. The EPA[2] has estimated the whole body dose arising from the release of this amount of tritium to be 3,700 man-rem/yr. Using the tentative assignment of $1,000/total-body man-rem by the NRC,[3] a cost of $3,700,000/yr is obtained for the biological damage due to the release of tritium. This figure may be used in analyzing the detritiation system from a cost-benefit point-of-view. For catalytic exchange the capital costs were estimated to be $5,153,000 and the yearly operating costs to be $1,180,000 (assuming 1¢/KWh; using 3¢/KWh gives $2,008,000). Therefore, detritiation of the AGNS plant waste by catalytic exchange appears economical.

As with catalytic exchange, the LIS system is designed to strip the LLAW to a level below the newly proposed EPA drinking water standard of 20 nCi/liter.[4]

A small side stream contains the extracted tritium, concentrated by four or more orders of magnitude. Thus, the tritium may be readily recycled from this concentration level.
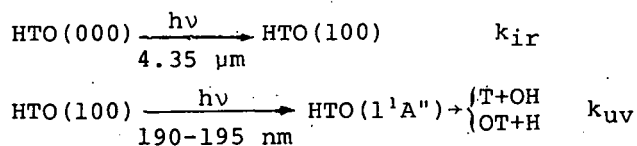
The LIS scheme envisioned in this study consists of five basic steps.

1) Isotopically selective photodissociation of HTO in the vapor phase.

2) Scavenging of the photoproducts with CO; the tritium is captured as formaldehyde.

3) Condensation of the water and phase separation of the CO; the formaldehyde is dissolved in the water.

4) Evaporation of the water and precipitation of the formaldehyde as paraformaldehyde.

5) Processing of the tritiated paraformaldehyde to form tritiated water or hydrogen gas.

We will consider each step separately. Moreover, we will concentrate on the electric power requirements since they represent 62% of the total operating costs (assuming 3¢/KWh) for catalytic exchange. The average power required for operation of the catalytic exchange detritiation system is estimated to be 5.56 MW.[1]

In previous reports[1,5-9] we proposed to selectively photodissociate HTO by means of a two-step process, namely, selective excitation of the OT stretch with an ir laser followed by selective photodissociation with a uv laser or a filtered uv flashlamp. However, crude calculations quickly indicated that this process would not be scaleable to large volume waste treatment.[1] The problem was that nearly all the uv photons were wasted in photodissociating H_2O. However, we proposed to overcome this problem by pumping more vibrational energy into the HTO molecules. For the sake of comparison we will consider both the original scheme and two other processes involving higher vibrational excitation.

The first photodissociation scheme may be written as

$$HTO(000) \xrightarrow[4.35\ \mu m]{h\nu} HTO(100) \qquad k_{ir}$$

$$HTO(100) \xrightarrow[190-195\ nm]{h\nu} HTO(1^1A'') \rightarrow \begin{cases} T+OH \\ OT+H \end{cases} \quad k_{uv}$$

where $HTO(n_1,n_2,n_3)$ denotes n_1, n_2 and n_3 quanta of vibrational energy in the OT stretch, bending mode and OH stretch, respectively. The ir photons might be supplied with an $LiNbO_3$ optical parametric oscillator (OPO) pumped by an Nd:YAG laser[10] and the uv photons with an ArF (193.3 nm) laser.[11]

Since the tritiated photoproducts are removed from the water stream by the scavenger (CO) with an efficiency necessary to achieve the desired 20 nCi/liter level (vide infra) each HTO molecule needs to be photodissociated only once. To calculate the laser power required to photodissociate all the HTO molecules in the waste stream, we consider the three-level model shown in Figure 1. The kinetics for the two-step photodissociation process is given by the following equations

$$\frac{d[HTO]}{dt} = -k_{ir}[h\nu_{ir}][HTO] + \{k_{ir}[h\nu_{ir}] + k_{ir}^{spon} + k_{vr}[M]\}[HTO*] + \{k_{uv}^{spon} + k_{er}[M]\}[HTO**] \qquad (1)$$

$$\frac{d[HTO*]}{dt} = k_{ir}[h\nu_{ir}][HTO] - \{k_{ir}[h\nu_{ir}] + k_{ir}^{spon} + k_{vr}[M] + k_{uv}[h\nu_{uv}]\}[HTO*] + k_{uv}[h\nu_{uv}][HTO**] \qquad (2)$$

$$\frac{d[HTO**]}{dt} = k_{uv}[h\nu_{uv}][HTO*] - \{k_{uv}[h\nu_{uv}] + k_{uv}^{spon} + k_{er}[M] + k_D\}[HTO**] \qquad (3)$$

where k_{ir} and k_{uv} are the rates for both absorption and stimulated emission, k_{ir}^{spon} and k_{uv}^{spon} are the rates for spontaneous emission, k_{vr} and k_{er} are the rates for vibrational and electronic relaxation induced by collisions with M (M = H_2O, CO) and k_D is the rate of photodissociation. For two-step photodissociation to be efficient it is clear that the following conditions must be met:

(i) $k_{ir}[h\nu_{ir}] \gg k_{ir}^{spon}$, $k_{vr}[M]$;

(ii) $k_{uv}[h\nu_{uv}] \gg k_{uv}^{spon}$, $k_{er}[M]$, $k_{vr}[M]$,

and (iii) $k_D \gg k_{uv}[h\nu_{uv}]$.

Using the theoretical value of 0.042 Debye for the $H_2O(000) \rightarrow (100)$ transition moment,[12] one calculates $k_{ir}^{spon} = 6.7$ sec^{-1}, which is extremely slow. On the other hand, vibrational relaxation is expected to be very rapid for HTO because of dimer formation with H_2O. The attractive interaction between HTO and H_2O overcomes the large energy mismatch in the vibrational manifold, analogous to situation in HX – CO_2 systems.[13] The lifetime of the
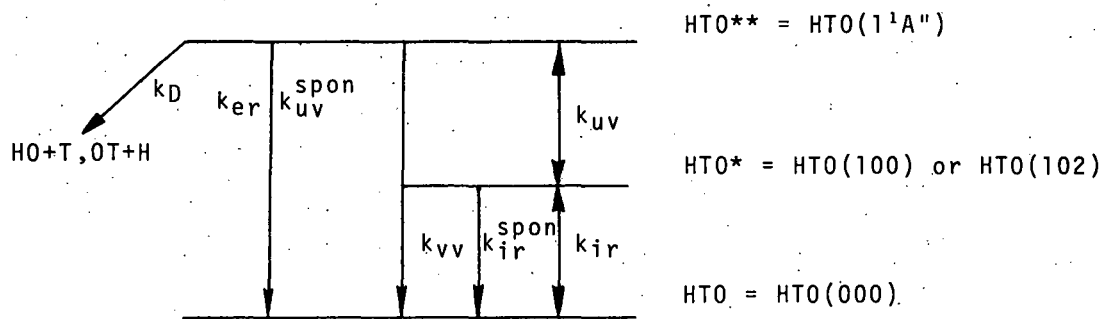
FIGURE 1 - Three-level diagram for two-step photodissociation of
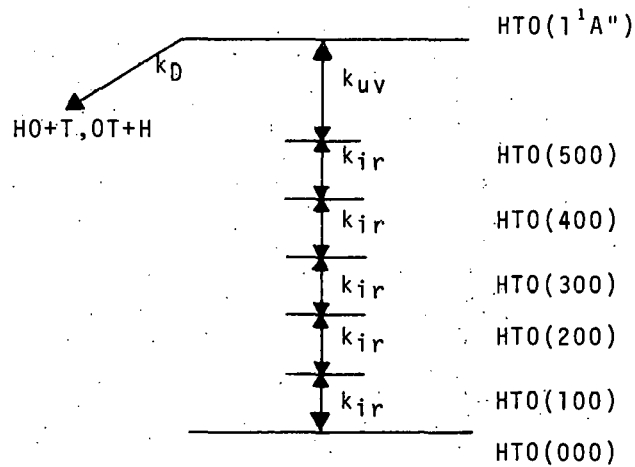HTO: Schemes 1 and 2.

FIGURE 2 - Three-level diagram for two-step photodissociation of
HTO: Scheme 3.

8

vibrationally excited HTO molecules is expected to be on the order of a few collisions. Given the assumed operating conditions of 373°K, P_{H_2O} = 650 torr and P_{CO} = 65 torr, the average time between collisions is 0.2 nsec. Therefore, we have $k_{vr}[M] \lesssim 5 \times 10^9$ sec^{-1} and we require $k_{ir}[h\nu_{ir}] \gg 5 \times 10^9$ sec^{-1}. In addition, $k_{ir} = c\sigma_{4.35 \mu m}^{HTO}$ where $\sigma_{4.35\mu m}^{HTO}$ is the absorption cross section for the HTO(000) $\xrightarrow{4.35 \mu m}$ (100) transition and c is the speed of light. Using the theoretical band intensity[12] the absorption cross section is estimated to be 1×10^{-18}cm^2, so that $k_{ir} = 3 \times 10^{-8}$ cm^3/sec and $[h\nu_{ir}] \gg 1.6 \times 10^{17}$ cm^{-3}. For the sake of argument, we will take $[h\nu_{ir}] = 1.6 \times 10^{18}$ cm^{-3}, so that the required laser power at 4.35 µm is 2.15 GW/cm^2.

Turning to the uv laser, the observed oscillator strength for the transition to the comparable 1^1B_1" state in H_2O is 0.061,[15] so that the transition moment is 1.47 Debye. Using this information, one finds k_{uv}^{spon} = 1.5×10^8 sec^{-1}. From our calculated vibrational relaxation, we have $k_{er}[M] \lesssim k_{vr}[M] \cong 5 \times 10^9$ sec^{-1}. Therefore, we require $k_{uv}[h\nu_{uv}] \gg 5 \times 10^9$ sec^{-1}. At 193.3 nm the absorption cross section for HTO is estimated to be 2×10^{-20} cm^2,[1] so that $[h\nu_{uv}] \gg 7.9 \times 10^{18}$ cm^{-3}. Assuming that $[h\nu_{uv}] = 7.9 \times 10^{19}$ cm^{-3}, the required laser power at 193 nm is 2.43 TW.

As to the rate of photodissociation, k_D, it is known that the quantum yield for photodissociation is near unity for excitation to the 1^1B_1 state in H_2O (1^1A" in HTO).[16] From this we may conclude that $k_D \gg k_{uv}^{spon}$, $k_{er}[M]$ or $k_D \gg 1.5 \times 10^8$ sec^{-1}. Moreover, the 1^1B_1 state in H_2O, and hence the 1^1A" state in HTO, manifests no potential barriers to dissociation; it is strictly repulsive.[1,17] Therefore, we will assume $k_D \gg k_{uv}[h\nu_{uv}]$.

With these assumptions equations (1)-(3) may be simplified.

$$\frac{d[HTO]}{dt} = -k_{ir}[h\nu_{ir}][HTO] + k_{ir}[h\nu_{ir}][HTO^*] \qquad (4)$$

$$\frac{d[HTO^*]}{dt} = k_{ir}[h\nu_{uv}][HTO] - \{k_{ir}[h\nu_{ir}] + k_{uv}[h\nu_{uv}]\}[HTO^*] \qquad (5)$$

$$\frac{d[HTO^{**}]}{dt} = k_{uv}[h\nu_{uv}][HTO^*] - k_D[HTO^{**}] \qquad (6)$$

where we have used the fact $[HTO^{**}] \ll [HTO^*]$, which derives from $k_D \gg k_{uv}[h\nu_{uv}]$. Of course, one should solve the coupled differential equations (1)-(3) or (4)-(6) to determine the laser power needed

to achieve the desired rate of photo-dissociation, R. However, a crude measure of the required laser power may be made by invoking the partially valid steady-state approximation for [HTO*] and [HTO**], and assuming the ir and uv laser beams are only slightly absorbed (which is valid in this case, vide infra). Then, we have

$$[HTO^{**}]_{ss} = \frac{k_{uv}[h\nu_{uv}]}{k_D}[HTO^*]$$

$$[HTO^*]_{ss} = \frac{k_{ir}[h\nu_{ir}]}{k_{ir}[h\nu_{ir}]+k_{uv}[h\nu_{uv}]}[HTO].$$

If $k_{uv}[h\nu_{uv}] \gg k_{ir}[h\nu_{ir}]$, then vibrational excitation is the rate limiting step and

$$R = k_D[HTO^{**}] = k_{ir}[h\nu_{ir}][HTO].$$

If $k_{ir}[h\nu_{ir}] \gg k_{uv}[h\nu_{uv}]$, then electronic excitation is rate limiting and $R = k_{uv}[h\nu_{uv}][HTO]$.

Therefore, we let $k[h\nu] \equiv k_{ir}[h\nu_{ir}] = k_{uv}[h\nu_{uv}]$ so that

$$R = \tfrac{1}{2}k[h\nu][HTO] \qquad (7)$$

and $$\frac{d[HTO]}{dt} = \tfrac{1}{2}k[h\nu][HTO]. \qquad (8)$$

Integrating equation (8) gives

$$[HTO] = [HTO]_0 \, e^{-\frac{1}{2}k[h\nu]t}. \qquad (9)$$

Substituting (9) in (7) and integrating over the laser pulse length, T

$$[\text{Photoproducts}]_T = [HTO]_0(1-e^{-\frac{1}{2}k[h\nu]T})$$

or $$\frac{[HTO]_0-[\text{Photoproducts}]_T}{[HTO]_0} = e^{-\frac{1}{2}k[h\nu]T} \qquad (10)$$

Since we want to strip 0.2 Ci/liter waste to the 20 nCi/liter level, the ratio in equation (10) must be 10^{-7} or less, i.e.,

$$e^{-\frac{1}{2}k[h\nu]T} \leq 10^{-7}$$

or

$$k[h\nu]T \geq 27.6.$$

Letting T = 20 nsec, a reasonable laser pulse length we have

$$[h\nu_{ir}] \geq 4.6 \times 10^{16} \text{ cm}^{-3} \qquad (11)$$

$$[h\nu_{uv}] \geq 2.3 \times 10^{18} \text{ cm}^{-3}. \qquad (12)$$

From (11) and (12) we have that the laser power at 4.35 µm must be at least 63 MW/cm^2 and that at 193 nm at least 71 GW/cm^2. It will be noted that both these power levels are less than those required to assure no interference from vibrational relaxation. The higher power levels will be used below.

Now the question becomes how many molecules can be photodissociated with ir and uv lasers meeting the above power requirements. As before we assume a pulse length of 20 nsec and for convenience a beam area of 1 cm^2. Apart from any interferring absorption by H_2O or CO, the longest effective path length that appears feasible is about 500 meters, e.g., multipassing a 10 meter distance 50 times with 98.5% reflecting mirrors. Even at 500 meters with P_{HTO} = 79 μtorr only 10% of the ir laser beam and 0.2% of the uv laser beam is absorbed. Assuming P_{H_2O} = 650 torr and P_{CO} = 65 torr then
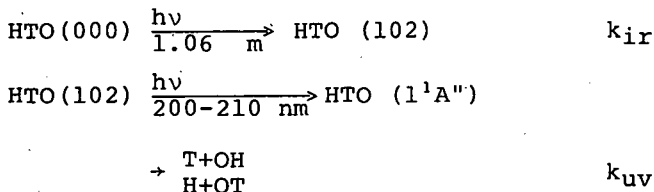
$$\sigma^{H_2O}_{4.35\ \mu m} \ll 1 \times 10^{-24}\ cm^2 \text{ and } \sigma^{CO}_{4.35\ \mu m}$$

$\ll 1 \times 10^{-23}\ cm^2$, if H_2O and CO are not to interfere with the absorption by HTO over a 500 m path. These conditions should be met. However, a different case pertains at 193 nm. Although CO does not absorb at this wavelength, the absorption cross section for H_2O is still significant.

$$\sigma^{H_2O}_{193\ nm} = 7 \times 10^{-22}\ cm^2.[18]$$

Consequently, the effective path length is only 20 m instead of 500 m. Therefore, the volume effectively irradiated by each pulse of the 2.43 TW/cm^2 laser would be only 1 cm^2 × 20 m = 2 × 10^3 cm^3. Since the flow rate of 500 liter/hr of liquid waste converts to 0.28 m^3/sec at P_{H_2O} = 650 torr and T = 373°K, one requires a laser pulse repetition rate of 138 Hz. The energy per pulse for the uv laser is (2.43 TW)(20 nsec) = 48.6 KJ, so that the average laser power required is 6.71 MW. Assuming a reasonable efficiency of 1% for the rare gas halide laser, the electric power requirement for the uv laser is 671 MW, which is one hundred times the average power needed for the entire catalytic exchange process (5.56 MW).[1] Therefore, the first scheme for two-step photodissociation is impracticable.

The second photodissociation scheme may be written as

$$HTO(000) \xrightarrow[1.06\ m]{h\nu} HTO\ (102) \qquad k_{ir}$$

$$HTO(102) \xrightarrow[200-210\ nm]{h\nu} HTO\ (1^1A'')$$

$$\rightarrow \begin{matrix} T+OH \\ H+OT \end{matrix} \qquad k_{uv}$$

This scheme is based on theoretical calculations[9,12] which indicate that the Nd:YAG laser at 1.06 μm, which is only weakly absorbed by H_2O, may be strongly absorbed by the (000)→(102) transition in HTO. The advantages of this scheme are the power

available from Nd:YAG or Nd:glass lasers and the longer wavelength required for the uv laser. The likely candidate for the uv step is the KrBr laser at 206 nm. The absorption cross section for H_2O at this wavelength is only 5 × 10^{-25} cm^2,[18] so that a full path length of 500 m may be achieved. In addition, the cross section for HTO is larger, being estimated at 5 × 10^{-18} cm^2 based on shifts of the H_2O spectrum[18] and expected changes in the Franck-Condon factors.[1] The major disadvantage is that the cross section at 1.06 μm is expected to be relatively small. Comparing the experimental data on HDO[20] and theoretical data for HTO,[12] we estimate the transition moment for HTO(000)→(102) to be ~4 × 10^{-4} Debye and $\sigma^{HTO}_{1.06\ \mu m} \cong 6 \times 10^{-22}$ cm^2.

Following the same analysis employed for the first photodissociation scheme we have

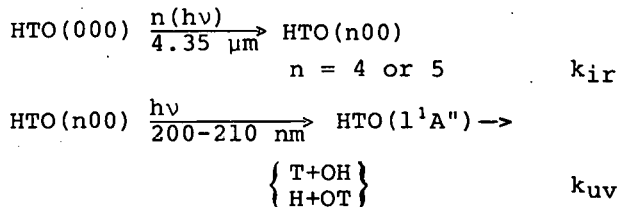$$[h\nu_{ir}] = 2.8 \times 10^{21}\ cm^{-3} \qquad (13)$$

$$[h\nu_{uv}] \equiv 3.3 \times 10^{17}\ cm^{-3}. \qquad (14)$$

From (13) and (14) we have that the laser power at 1.06 μm must be at least 15.6 TW/cm^2 and that at 206 nm at least 9.63 GW/cm^2.

As before we assume a laser pulse length of 20 nsec and beam area of 1 cm^2. We also assume an effective path length of 500 m is achievable, so that a laser pulse repetition rate of 6 Hz is necessary. The energy per pulse for the Nd:YAG laser is (15.6 TW)(20 nsec) = 312 KJ, so that the average laser power required is 1.87 MW. Assuming a reasonable efficiency of 0.1% for the Nd:YAG laser, the electric power requirement for the ir laser is 1.87 GW. Again it is clear that this scheme is also impracticable, because of the small cross section at 1.06 μm.

The third photodissociation scheme may be written as (cf. Figure 2).

$$HTO(000) \xrightarrow[4.35\ \mu m]{n(h\nu)} HTO(n00)$$
$$n = 4 \text{ or } 5 \qquad k_{ir}$$

$$HTO(n00) \xrightarrow[200-210\ nm]{h\nu} HTO(1^1A'') \rightarrow$$

$$\begin{Bmatrix} T+OH \\ H+OT \end{Bmatrix} \qquad k_{uv}$$

The theory of resonant multiple vibration excitation is still in flux[21] and it is not clear whether the process proposed above is possible. Multiple vibration excitation has not been achieved with a molecule as small and light as HTO. The large anharmonicity and low density of states may mediate against the process working for

HTO. However, some theories of multiple vibration excitation indicate that the process should work for HTO.[22] If the process does work, the second step might also be carried out with a high-power CO_2 laser,[23] which would probably be more efficient than electronic excitation with a uv laser. However, the power costs for the 4.35 µm laser radiation are the dominant factor, so we will consider a uv laser for the second step.

In this scheme, it is clear that one should have $k_{ir}[h\nu_{ir}] \gg k_{uv}[h\nu_{uv}]$ until HTO(400) or HTO(500) has been reached. If the cross sections for each transition HTO$(n,0,0) \rightarrow (n+1,0,0)$ are approximately the same for $n=0,\ldots,4$, then the required laser power at 4.35 µm should be greater by a factor of 5 to 10 than that required in the first photodissociation. Taking the factor to be 10, we have that the laser power at 4.35 µm must be at least 21.5 GW/cm^2. Assuming a laser pulse length of 20 nsec, a beam area of 1 cm^2 and a path length of 500 m, the average laser power required is 2.58 KW. If an OPO driven by an Nd:YAG laser is used, then the laser efficiency is only 0.05% and 5.16 MW of electrical power are required. Since one can expect only 1-5 W average power from each OPO (which would

cost at least $100K apiece) it is clear that another more efficient laser must be used at 4.35 µm. It is not unreasonable to assume a laser with sufficient power and an efficiency of 1% can be found at 4.35 µm. In this case the electrical power required would be 258 KW.

The laser power required for the electronic excitation is the same as that in the second photodissociation scheme, i.e., 9.63 GW/cm^2. From this we may calculate the average laser power required, which is 1.16 KW. Since 1% efficiencies appear readily achievable for rare gas halide lasers, the electrical power required would be 116 KW. Therefore, the total electrical power required for this photodissociation scheme is only 374 KW, which is only 17% of the power used in the catalytic exchange process. The power requirements of the three schemes for photodissociation are summarized in Table 1.

We turn now to the second stage of the LIS detritiation process, namely the scavenging of the photodissociation products by CO. The key reactions and rate constants are given in Table 2. To achieve the desired level of 20 nCi/liter

Table 1

AVERAGE LASER AND ELECTRICAL POWER REQUIREMENTS FOR
TWO-STEP PHOTODISSOCIATION OF HTO

	Laser Power	Electrical Power[a]
Scheme 1		
ir laser (4.35 µm)	593 W	593 KW
uv laser (193 nm)	6.71 MW	671 MW
Scheme 2		
ir laser (1.06 µm)	1.87 MW	1.87 GW
uv laser (206 nm)	1.16 KW	116 KW
Scheme 3		
ir laser (4.35 µm)	2.58 KW	258 KW
uv laser (206 nm)	1.16 KW	116 KW

[a]The lasers are assumed to be 1% efficient except for 0.1% efficiency of the 1.06 µm Nd:YAG laser.

Table 2

KEY REACTIONS IN SCAVENGING OF HTO PHOTODISSOCIATION

1) $\{_{OT}^{OH}\} + CO \rightarrow CO_2 + \{_T^H\}$ $k_1 = 1.4 \times 10^{-13}$ cm^3/sec   [a]

2) $\{_T^H\} + CO \xrightarrow{M} \{_{TCO}^{HCO}\}$ $k_2[M] = 2.2 \times 10^{-15}$ cm^3/sec [b]
     with [M] = 715 torr

3) $T + H_2O \rightarrow HT + OH$ $k_3 = 1.2 \times 10^{-25}$ cm^3/sec   [a]

4) $T + H_2O \rightarrow HTO + H$ $k_4 \sim 2 \times 10^{-25}$ cm^3/sec   [c]

5) $OT + H_2O \rightarrow HTO + OH$ $k_5 \sim 2 \times 10^{-25}$ cm^3/sec   [c]

6) $2\{_{TCO}^{HCO}\} \rightarrow CO + \{_{T_2CO}^{H_2CO, 2HTCO}\}$ $k_6 = ?$

7) $\{_{TCO}^{HCO}\} + H_2O \rightarrow \{_{HTCO}^{H_2CO}\} + OH$ $k_7 \sim 4 \times 10^{-29}$ cm^3/sec   [c]

8) $\{_T^H\} + \{_{T_2CO}^{H_2CO, HTCO}\} \rightarrow \{_{H_2}^{HT}\} + \{_{TCO}^{HCO}\}$ $k_8 = 4.5 \times 10^{-14}$ cm^3/sec   [a]

9) $\{_{OT}^{OH}\} + \{_{T_2CO}^{H_2CO, HTCO}\} \rightarrow \{_{T_2O}^{HTO}\} + \{_{TCO}^{HCO}\}$ $k_9 = 1.4 \times 10^{-11}$ cm^3/sec   [a]

10) $\{_{OT}^{OH}\} + \{_{H_2}^{HT}\} \rightarrow HTO + \{_T^H\}$ $k_{10} = 6.5 \times 10^{-15}$ cm^3/sec   [a]

[a] Reference 24
[b] Reference 25
[c] Calculated assuming a gas kinetic rate with E_{act} = 20 kcal/mole for reactions (4) and (5) and E_{act} = 25 kcal/mole for reaction (7). The values for E_{act} were obtained as follows:
For reaction (4) ab initio calculations on $H + H_2O \rightarrow H_2O + H$[19] were used,
For reaction (5) ab initio calculations on $F + HF \rightarrow FH + F$[26] were used,
For reaction (7) an E_{act} comparable to that for reaction (3) adjusted for the difference in bond strengths for $H_2O[D(H-OH) = 119.3$ kcal/mole][27] and $H_2CO[D(H-CHO) = 88.5$ kcal/mole][28], the latter being supported by ab initio calculations.[29]

it is clear that reactions (1) and (2) must dominate the HTO regeneration reactions (3), (4) and (5) by at least a factor of 10^7, i.e., we require

$$\frac{k_1[CO]}{k_5[H_2O]} > 10^7 \tag{15}$$

and $$\frac{k_2[M][CO]}{(k_3+k_4)[H_2O]} > 10^7 \tag{16}$$

Substituting values for the rate constants from Table 2 into (15) and (16) gives

$$\frac{[CO]}{[H_2O]} > 2 \times 10^{-5}$$

and $$\frac{[CO]}{[H_2O]} > 2 \times 10^{-3}$$

We will take $[CO]/[H_2O] = 0.1$, i.e., $P_{CO} = 65$ torr.

Since the rate of reaction (6) is not known, the pathway, by which the tritium is incorporated as formaldehyde, is not clear [reaction (6) or (7)]. However, this is not important. On the other hand, as the concentration of formaldehyde increases reactions (8)-(10), which regenerate HTO, come into play. Reaction (9) is clearly the dominant mode of HTO regeneration from formaldehyde. Comparing

reactions (1) and (9), we require that

$$\frac{[\text{Formaldehyde}]}{[\text{CO}]} < 10^{-5}.$$

For the 0.2 Ci/liter the T/H ratio is 6.22×10^{-8} or $[\text{HTO}]/[\text{H}_2\text{O}] = 1.24 \times 10^{-7}$. Since the formaldehyde concentration should not exceed the initial HTO concentration (this assumes the number of H_2O molecules that are photodissociated is small), we have for $[\text{CO}]/[\text{H}_2\text{O}] = 0.1$ that $[\text{Formaldehyde}]/[\text{CO}] \sim 10^{-6}$. Therefore, if the ratio of H_2O to HTO molecules that are photodissociated exceeds ten, then the partial pressure of CO must be increased accordingly, to maintain the required concentration ratio with formaldehyde.

The physical separation of the tritiated formaldehyde and the CO from the water stream is depicted in Figure 3. We have made use of the fact that the aqueous waste emerges from the AGNS plant evaporation as steam. This obviates the need for heating and evaporating the waste stream, which is expensive (vide infra). After the photoreaction chamber in which the tritium is transferred from HTO to HTCO or T_2CO, the process stream goes to a condenser (15°C) cooled by ground water. At 15°C the equilibrium vapor pressure for water is 13 torr so that 98% of the water is condensed. Because of its high solubility, the formaldehyde will stay with the liquid water. Using values for the heat capacity and the heat of vaporization for water, one finds that the cooling water in the condenser must remove heat at a rate of 360 KW to handle 500 liter/hr of water. If we require the temperature rise of the cooling water to be 5°C, then the flow rate of cooling water is 17 liter/sec or 273 GPM. The energy needed to drive such a flow rate is ~10 KW.

The energy costs to recycle the CO may be divided into the costs to heat the gas stream to 100°C and those to compress it to 750 torr. Using the heat capacities for CO and H_2O vapor, the power required to heat the wet CO stream is 2.2 KW. Assuming a 50% efficiency for isothermal compression, the power required by the compressor is 2.8 KW.

The condensed water/formaldehyde solution is passed on to the evaporator. Upon evaporation paraformaldehyde, a high molecular weight, involatile polymer, is formed. The paraformaldehyde is expected to stay behind on the evaporator. Because of the very small concentration of formaldehyde present in the water, it may be necessary to add more formaldehyde to "salt" out the paraformaldehyde. Since addition of H_2CO would reduce the T/H

ratio, addition of tritiated formaldehyde already extracted from the AGNS plant waste may be desirable. On the other hand, care must be taken not to add so much tritium that the back exchange of the tritium into the water stream is promoted.

The power required to operate the evaporator is 450 KW, assuming an efficiency of 80%. After the water has been removed, the temperature is increased to 200°C. The paraformaldehyde decomposes and vaporizes as formaldehyde. If no additional formaldehyde is needed to "salt" out the paraformaldehyde, then the tritium will be concentrated as 10^2-10^3 cm^3/hr of gaseous formaldehyde with T/H> 0.01. Finally, the estimated power to decompose the paraformaldehyde is 100 KW, nearly all of the energy going into heating the evaporator itself from 100 to 200°C.

Once the stream of tritiated formaldehyde has been extracted any further processing of the tritium requires a negligible amount of energy, since the volume of the waste stream has been reduced so drastically. Three possibilities for handling facilities are readily apparent. First, the formaldehyde may be decomposed into hydrogen gas and CO. The tritiated hydrogen gas may be sent to a catalytic exchange or cryogenic distillation apparatus for enrichment to weapons grade level material or to produce fuel pellets for fusion reactors. Second, after decomposition of formaldehyde the tritiated hydrogen gas may be oxidized to water, which may again be further enriched for recycling purposes or which may be buried, e.g., in polymer impregnated concrete. Finally, the tritiated formaldehyde itself may be used as a feedstock to produce isoprene and then fix the tritium as natural rubber, as a nonleachable burial package.

The power costs estimated above for the various stages of aqueous waste detritiation by LIS are summarized in Table 3. One power cost not considered above is that for pumping the gases through the detritiation system. We take 4 KW as an estimate for the required pump power, which is albeit a rough figure given its dependence on the detailed nature of the flow system. Finally, Table 3 does not include the power required to pretreat the waste stream from the AGNS plant, i.e., to remove any chemicals or particles that would interfere with the LIS detritiation process. It is very difficult to estimate the cost of such a step. Since a comparable clean-up step will be necessary for catalytic exchange detritiation and the estimated costs were not included in the economic
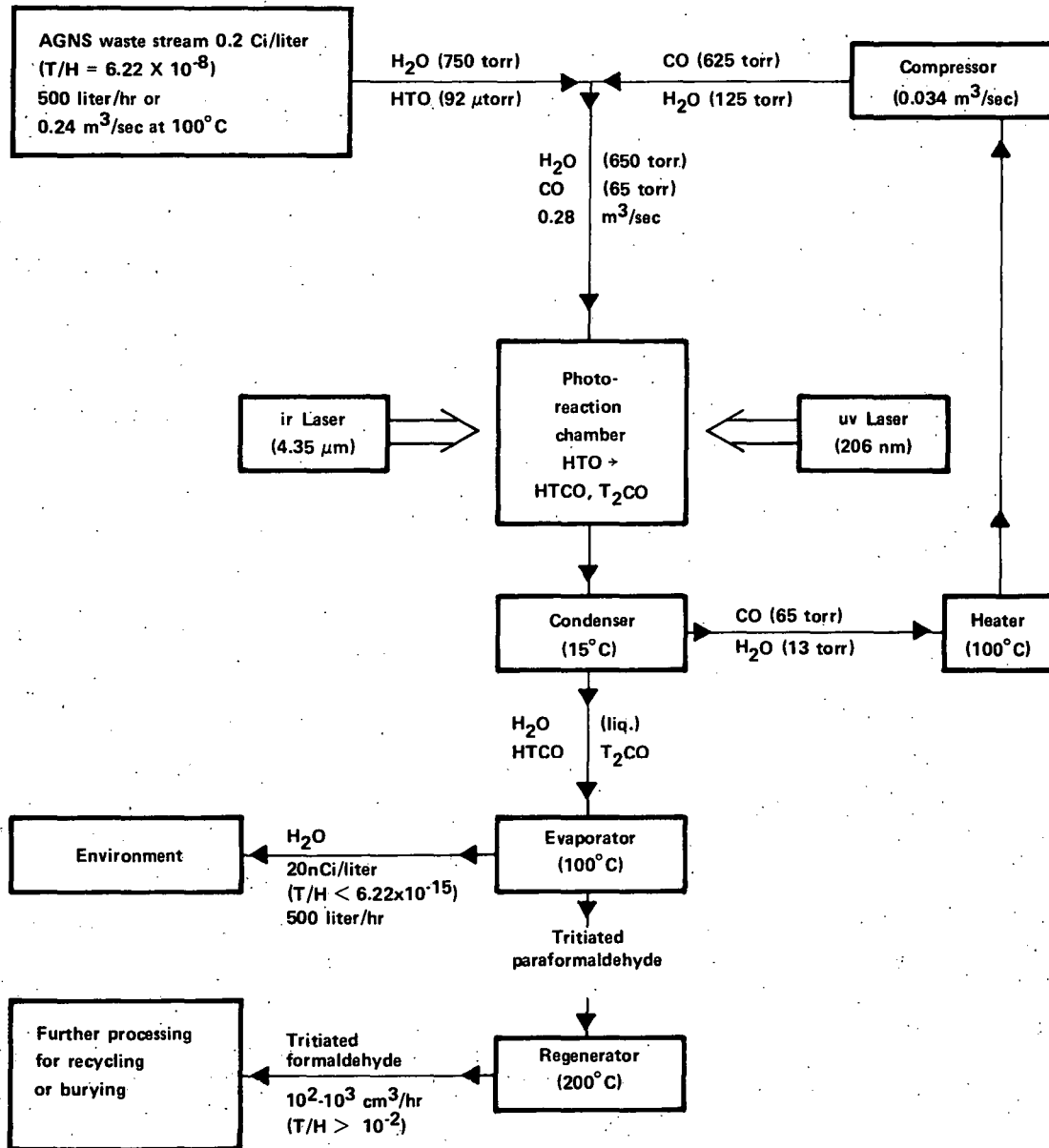
FIGURE 3 - Schematic of LIS detritiation system for AGNS nuclear fuel reprocessing plant waste.

Table 3

AVERAGE ELECTRIC POWER REQUIREMENTS
FOR AQUEOUS WATER DETRITIATION BY LIS

Process	Power Requirement (in KW)
Vibrational excitation by ir laser	258
Electronic excitation by uv laser	116
Condensation of water/formaldehyde	10
Heating recycled CO/H_2O stream	2.2
Compressing recycled CO/H_2O stream	2.8
Evaporation of water	450
Regeneration of formaldehyde	100
Pumping H_2O/CO gas stream	4
Total for LIS detritiation	943
Total for catalytic exchange detritiation	5560

study of catalytic exchange, we will not include the costs here.

The total estimated power requirement for detritiation by LIS is only 17% of that required for detritiation by catalytic exchange. This converts into a savings of $1M/yr in operating costs at 3¢/KWh. Since the other operating costs are not expected to be higher for LIS detritiation relative to catalytic exchange, the total yearly operating cost for the LIS detritiation system should be only one-half that for the catalytic exchange system.

Up to this point nothing has been said about capital costs. Apart from the lasers, the capital costs are expected to be comparable to those for the catalytic exchange system. Therefore, we will concentrate on the lasers required for the detritiation system. For the ir laser at 4.35 μm the required peak and average powers are 21.5 GW/cm² and 2.58 KW, respectively. At present a laser at 4.35 μm with the required 1% efficiency and the above power specifications has not yet been developed. However, the advances being made in high-power,high-energy lasers make it reasonable to assume that, if the LIS process was shown to work on a bench

scale, an appropriate laser could be developed such that no more than ten of these lasers would be needed to produce 2.58 KW of laser power.

The required peak and average powers (9.63 GW/cm² and 1.16 KW, respectively) are slightly lower for the uv laser at 206 nm. The recent developments in rare gas halide lasers indicate that again the laser power needs for LIS detritiation may be met by less than ten lasers. Therefore, we may conclude that the capital costs for the ir and uv lasers do not appear outrageous. The laser capital costs may be expected to be less than $2M, assuming a figure of $100K/laser. Therefore, the overall capital costs for LIS detritiation are expected to be comparable to those for catalytic exchange detritiation ($5.1M), so that the LIS approach may have significant advantages over catalytic exchange arising from the much lower power costs.

HTO Infrared Spectrum A cell loaded with approximately 0.26 Ci of tritium in HTO was scanned in the Digital FTS-14 infrared spectrometer in an attempt to observe the ν_1 band. This is the O-T stretching mode and is expected to occur at about

2295 cm^{-1}. What was observed was very strong absorption lines extending from $\sim 2390 - 2250$ cm^{-1} in a regular pattern indicating rotational contours. This absorption was attributed to CO_2 impurity in the cell. The HTO absorption (if present) in this region was completely obscured by the very strong CO_2 bands.

In an attempt to eliminate the CO_2 interference, the spectrometer was operated in the single beam mode. A blank was run with the cell containing only helium but having been loaded by the normal procedure using the gas-oxidation loading system. A second run was then made with tritium oxidized to HTO. The two sets of data were stored in the spectrometer's computer and the blank was subtracted from the original to produce a difference spectrum. This should produce a spectrum from only the species contained in the oxidized H_2-T_2 mixture. However, the CO_2 bands were also very strong in the resulting spectrum.

Finally, the CuO bed was recharged with new CuO and the HTO spectrum run again. The CO_2 spectra was again very strong.

Since these results all indicated the CO_2 was originating from the H_2-T_2 gas an analysis of the gas was carried out, although two analyses (3 and 6 months previous) did not indicate impurities.

Results of the above analysis did show about 0.5 mole % methane which would be oxidized to CO_2 on the hot CuO. This may be sufficient quantity of CO_2 to obscure the HTO spectrum. Efforts are now underway to remove organic impurities from the H_2-T_2 gas just prior to loading the spectrometer cell.

FUTURE PLANS

There are seven major objectives for the next quarter: 1) completion of the CI calculations on the $H+H_2O$ exchange reaction: 2) 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; and 7) recording the ir spectrum of HTO.

ELECTROLYSIS OF HIGH LEVEL TRITIATED WATER _____ *Robert E. Ellis*

BACKGROUND

Operations involving tritium generate a significant quantity of high level waste water which must be disposed of in a safe manner. In the past this waste water has been absorbed on solids or diluted to specified levels and buried; or it has been diluted to low enough levels to be discharged as "uncontaminated" water. A preferable method would be to recover the tritium from such wastes. Demonstration of the feasibility and development of such recovery techniques are the goals of this work.

PRIOR WORK

A system was constructed around a General Electric Co. UCT-1 regenerative cell to electrolyze small quantities of high level tritiated water. The system was successfully operated using pure H_2O.

ACCOMPLISHMENTS

Approximately 1 ml of high level tritiated water was electrolyzed using the UCT-1 cell. After about 12-3/4 hr of operation the cell failed by membrane rupture. Due

to the failure mode, quantitative data from this experiment are probably not very accurate. A new electrolysis cell more suited for this experiment has been ordered from General Electric Co.

DISCUSSION

An attempt was made to electrolyze a small quantity of very high level tritiated water in the General Electric UCT-1 regenerative cell. The cell and experimental system has been described in a previous report.[30] The UCT-1 had been used previously for investigating the decontamination of tritiated water via the electrolysis and/ or recombination processes. It was operationally checked just prior to installation in the glovebox where the experiment was done.

Since only 1 ml of high level water was to be used in this initial experiment, it was fed directly into the cell through the valve at the bottom of the O_2 side. Transfer of the water was effected by vacuum applied to the O_2 chamber of the cell. Electrolysis was initiated at 4 amperes and required 2.9 volts. Since it required only ~ 1.7 volts for operation at 5 amperes previously it appeared that the cell might

be too dry for efficient operation. There-
fore, 4 ml of distilled,deionized water
were added to the cell and electrolysis
allowed to proceed at 5 amperes, 2.7-2.9
volts.

Table 4 summarizes the data from this
experiment.

The experiment was stopped immediately
when it was noted that a pressure differ-
ential could not be maintained between the
H_2 and O_2 sides of the cell. This con-
dition indicates a gross leak in the SPE
(solid polymer electrolyte) membrane which
would allow mixing of the H_2 and O_2 in
presence of the catalytic electrodes.
This could cause explosive recombination
or, at best, slower recombination. The
H_2 reservoir was also closed off to pre-
vent further loss of the hydrogen already
produced.

Totals from Table 4 are as follows:
volume water added - 20 ml, run time -
12-3/4 hr, volume water used (calculated
from run time and current) - 20.97 ml. As
can be seen from the above data about 1 ml
more water was electrolyzed than added.
Since the cell should have contained about
20 ml of water in the wicks prior to
starting the experiment, this should not
have resulted in a dry condition.

The cell was evacuated and maintained
under vacuum for about 24 hr before dis-
assembly. Immediately upon completion of
the disassembly it was noticed that the
glovebox atmosphere tritium level was very
high. This indicates a volatile tritium
species was present in the cell. No
visible evidence of liquid water was found.

Examination of the inside of the cell
readily showed the point of membrane
failure. Not only was the SPE ruptured
but the gas space screens were melted and
the dacron wicks were melted and charred
about the point of failure. Because of

the heavy damage to the components inside
the cell, it was decided not to attempt
repair and reuse of the UCT-1 cell.

After discussing the experiment with
representatives of the cell manufacturer
(General Electric Co.) it seems likely
that the particular design of the UCT-1
contributed to the failure. In order to
reach the SPE membrane,water had to be
transported by dacron wicks. These wicks
apparently become hydrophobic with age
and no longer function properly. However,
in normal use the UCT-1 cell is in the
electrolysis mode at 5 amperes for only about
20 minutes - not 3-1/2 hours. If a dry
spot develops in the wick-SPE interface
this area heats up and eventually burns
through causing cell failure.

Analysis of the hydrogen gas from the
experiment revealed only 0.4 mole percent
of the hydrogen was tritium. Based on the
total amount of tritium introduced into the
cell this value should be about 6%. The
electrolysis isotope effect tends to keep
the tritium in the water and, of course,
the water remaining in the cell (as much
as 19 ml) was pumped off after cell fail-
ure. At any rate quantitative data from
this experiment are highly suspect due to
the manner in which the experiment was
terminated.

After further discussions with General
Electric Co., it was decided to purchase
a different type SPE cell for use in
future experiments. The new cell, which
has been ordered, will be a single SPE/
membrane assembly with electrodes designed
only for electrolysis. (The UCT-1 elec-
trodes could be used in the fuel cell or
electrolysis mode.) Internal volume will
be only about 5 ml and current capacity
50 amperes. Due to the high current
capacity and low internal volume, it will
be necessary to circulate water through
the cell during operation. Procurement
of additional equipment and design of the

Table 4

ELECTROLYSIS OF HIGH LEVEL TRITIATED WATER

Volume Water Added (ml)	1	4	5	5	5
Running Time (hr)	1	2-3/4	3-1/2	3-1/2	2
Current (amperes)	4	5	5	5	5
Potential (volts)	2.9	2.9	2.7-2.9	2.7-2.9	3.3
Volume Water Electrolyzed (ml)	1.34	4.59	5.85	5.85	3.34

experimental system for this cell are presently underway.

An experimental system to carry out high level tritiated water electrolysis will be designed around the new SPE cell.

TRITIUM MONITOR DEVELOPMENT AND CALIBRATION _____ *Paul H. Lamberger*

BACKGROUND

For the past two decades the ionization chamber in conjunction with a picoammeter has been the basic means of tritium monitoring. Few changes have occurred during the interim because this simple equipment has satisfied most room and stack monitoring needs. Today, lower detection limits, multilevel alarm systems with controls and digital displays are considered necessary as RCG limits are lowered and effluents to the atmosphere are being reduced to "as low as practicable." During the past two years Mound Laboratory has been working with a manufacturer to develop room monitors which can provide, for example, digital readouts, presetable alarm levels, logarithmic display records, and electrical compensation for gamma and tritium backgrounds.

A need has also arisen for process monitoring which presents an entirely different set of problems when compared with room monitoring. State-of-the-art monitors are unable to cope with this new set of conditions, i.e., high,often wide range tritium concentrations; memory effects; the presence of other beta emitters; high relative humidity conditions or significant quantities of HTO; and measurements at other than ambient temperature and pressure.

Electrical calibration of monitors assures that the electrometer and related electronic systems are functioning properly. Accurate measurements in the field can only be guaranteed by system calibrations in which known concentrations of tritium can be admitted to the ionization chamber. Hence, a tritium gas handling and calibration system is necessary not only for routine calibration of monitoring systems but also for the study of ionization chamber design, filters, materials of construction, performance parameters and limits of application.

PRIOR WORK

Tritium monitors which meet current room air monitoring needs have been developed cooperatively by an instrument manufacturer and Mound Laboratory. These monitors

use a vibrating reed electrometer and a 20-liter ionization chamber. The time constant, that time required to respond to 2/3 of the concentration entering the ion chamber, is six seconds. The electronics control package which can be mounted in a standard relay rack, provides a digital readout, logarithmic chart display, low and high level alarms, and electrical compensation for gamma and tritium backgrounds. Remote digital display and control functions are also available.

Design and layout have been completed for a tritium handling and gas recirculation system which will permit calibration of all types of tritium monitors, performance evaluation of monitoring components, and the study of the effect of various monitoring conditions. The system has sufficient size and versatility to permit study of techniques and components for use in detritiation of gaseous streams. The system consists of five major sections: a gas mixing section for preparation of calibration gas, three separate gas recirculation sections for various tritium concentrations, and a recovery section which permits collection of gaseous wastes and vacuum pump exhaust on molecular sieves for disposal. Capabilities of this system will be discussed in subsequent quarterly reports.

ACCOMPLISHMENTS

The entire gas handling and calibration system was redesigned into modular sections to minimize onsite assembly and craft labor. This action was necessary in order to assure procurement and major fabrication in FY-1976. Plans have been made for studies with this system which are urgently needed for operation of the Tritium Effluent Control Laboratory. These include the effect of pressure and ion chamber design on ion current measurements and system calibration.

FUTURE PLANS

Final assembly of the tritium gas handling and calibration system, leak checking and performance evaluation of the system's components will be completed during the next quarter.

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, fixation of the tritiated liquid waste into an inert form and/or multiple containment appear to be necessary 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 fusion reactor 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 from PWRs, HWRs 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 designed and built for the intersite shipment of tritium for quantities of tritium up to 50,000 Ci. The container is intended to be enclosed and shipped in the AL-M1 secondary shipping container, a specially constructed 55-gal steel drum which is a form of containment approved by ERDA/DOT for shipment of plutonium and uranium. The container is fabricated from type 316 stainless steel off-the-shelf components and is nominally 6-5/8 in. O.D. and 24 in. in height. Designed to be handled by one person, it weighs less than 45 pounds and can be accommodated in a calorimeter for the purpose of tritium accountability. With an internal volume of 10 liters, it can hold up to 2 kg of tritiated water absorbed on molecular sieves or silica gel. Unlimited life for the container is expected because the absorbed water can be removed by regeneration and the absorbent can be replaced as necessary. The container can be used to receive a liquid directly or it can be connected into a gas purification system to collect HTO from the gas stream during the regeneration cycle.

ACCOMPLISHMENTS

A stainless steel bourdon tube pressure gage, originally designed for the container to monitor pressure buildup during shipment and storage, has been replaced by a pressure transducer to achieve greater safety. Connected to the container with a welded Cajon VCR fitting, the transducer provides secondary containment of the gaseous contents should rupture of its primary pressure diaphragm occur. The transducer was specially modified in size by the manufacturer to meet the dimensional restrictions associated with the container.

Tritium assay of the container contents can be done by either direct calorimetry of the container or by "baking off" the water, trapping the liquid and submitting an aliquot for scintillation counting or calorimetry. Direct calorimetry was selected initially because "baking" or regeneration facilities were not yet available. In addition, the calorimetric method is relatively simple and involves negligible handling hazards. Fabrication of a calorimeter with internal dimension of 7 in. diameter and 30 in. height has been completed for this application. This is the largest, dry twin-bridge calorimeter fabricated to date and is expected to have a tritium detection limit of about 30 Ci. In order to use the existing readout facilities in the T-Building calorimetry laboratories, 250 feet of conduit for measurement and control lines were installed from the tritium control laboratory to the calorimetry laboratory. Wiring between the two laboratories will be "pulled" and connected within the next few weeks.

For maximum sensitivity and rapid equili-bration, heat transfer between the con-tainer being measured and the calorimeter wall must be maximized. Either metal to metal contact or liquid interfacing of the two surfaces can provide this desired heat transfer. The use of a liquid (oil) is less desirable because of the large calorimeter size, the after-measurement cleanup and the difficulty in control of contamination. Metal to metal contact of the container and calorimeter walls, however, places very restrictive dimen-sional tolerances on the container which leads to high fabrication costs. In order to control these costs and to allow for accidental surface damage (dimensional changes) resulting from use, the container was therefore fabricated with a nominal 6.625 in. O.D. and the calorimeter with a 7.000 in. I.D. The resulting void or gap is filled with an aluminum sleeve designed to fit snuggly against the calorimeter wall but allowing a 0.050 in. gap between the container and sleeve. This void, which will be filled with copper powder for heat transfer, elimin-ates the need for close and costly con-trol of the diameter, out-of-round-ness and parallelism of the sides of the container. A bottom has been

provided on the sleeve so that the copper powder can be easily retrieved after the container is removed from the calorimeter and sleeve.

FUTURE PLANS

When funding becomes available, a safety analysis report for packaging (SARP), requiring 5-6 months for completion, will be performed on the container. General guidelines on the use of this container will be started if the initial SARP tests show the design to be satisfactory. The newly built calorimeter will be checked out for performance and sensitivity with special emphasis on evaluation of the sleeve and powder used for heat transfer. Design changes which were made to allow for more economical fabrication and greater gas flow (lower pressure drop) through the container, will be added to the existing drawings. Quality control guidelines will also be generated to assure that fabrication of additional containers will meet specifications.

CATALYTIC EXCHANGE DETRITIATION STUDIES _____ B. W. Hartzell, C. J. Kershner, and R. E. Ellis

BACKGROUND

Isotopic separation processes need to be developed for the purpose of removing tritium from contaminated water streams. In the operation of a light water reactor, for example, all radioisotopic contamin-ants except tritium can be removed from the effluent stream by ordinary chemical and physical methods. Tritium removal in this case requires special considera-tions.

The objectives of this study are:

a. Determine technical and economic factors of HT/H_2O exchange as a possible detritiation process for treating tritium contaminated water from power reactors and fuel re-processing plant operations,

b. Determine suitability of hydro-phobic exchange catalysts for use in water detritiation systems, and

c. 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, installation and cold opera-tional testing of the experimental sys-tem were completed. Preliminary testing of the system with RCG level tritiated water and hydrogen has been completed.

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

The Engelhard hydrophobic catalyst is being investigated for use in promoting

the HT/H_2O exchange reaction. Several tests and one preliminary experiment to determine the HETP were done. The experimental HETP from this experiment was approximately 16 feet. This compares favorably with the estimated HETP of 20 feet.

Concurrently, studies to establish the mechanical stability and active lifetime of the catalyst are in progress. Current data indicate the active media on the alumina substrate is flaking off at an unacceptably high rate.

DISCUSSION

The work in progress is directed toward the development of an improved version of the basic HT/H_2O catalytic exchange process and demonstration of the separation of tritium for the particular concentrations and types of low-level wastes (LLAW) obtained from light-water reactors and fuel reprocessing plants. The process will also apply to the removal of tritium from heavy water (D_2O) used as the moderator and coolant in several research and all U. S. government production reactors.

The improved approach to HT/H_2O catalytic exchange is based on the use of hydrophobic catalysts which permit the exchange reaction between liquid water and gaseous hydrogen, thus eliminating problems of catalyst deactivation and the complexity of reactor design normally associated with catalytic exchange techniques[31-33] involving gas phase catalysis. The use of hydrophobic catalyst was first reported[34] in studies directed toward an improved heavy water process. The bench scale experimental apparatus and the hydrophobic catalyst now under investigation at Mound Laboratory were supplied by Engelhard Minerals and Chemicals Corporation. The catalyst consists of platinum on an alumina substrate with a coating of semipermeable, water repellent material such as a silicone or Teflon.

Figure 4 is a simplified schematic of the experimental apparatus. It consists basically of a high temperature reactor (HTR) and a low temperature reactor (LTR). Many other components such as furnaces, pumps, flow transducers, etc. are actually included in the system but only the HTR and LTR effect isotopic change in the water-H_2 mixture. This system is designed primarily to measure the height of one theoretical plate as a function of the variable parameters, and is operated as a closed steady state system.
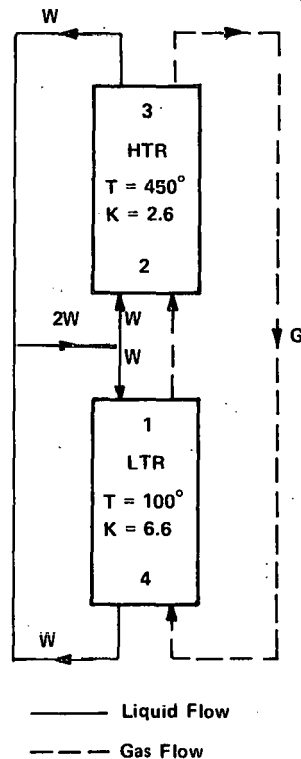

FIGURE 4 - H_2-HTO exchange system schematic.

The object of the experiment was to calculate the length of the hydrophobic catalyst bed (in the LTR) necessary to isotopically equilibrate an H_2-HTO mixture. In order to do this the mixture was first brought to a known isotopic equilibrium in the HTR using a gas phase (non-hydrophobic) catalyst at 450°F. Since equilibrium is attained rapidly at this temperature it was assumed that the equilibrium expression for the reaction $HT + H_2O \rightleftarrows H_2 + HTO$,

$$K = \frac{[H_2][HTO]}{[HT][H_2O]} \, , \tag{17}$$

is in effect with $K = 2.6$.

The LTR containing the hydrophobic catalyst is maintained at 100°F. It is also assumed that the gas and water streams in the rest of the system are at 100°F. A heat exchanger and phase separator are installed in the system at the HTR exit to cool the stream and separate it into gas and liquid at 100°F.

The definition of terms and general relationships used in describing the processes going on in the system are due to Benedict and Pigford.[35]

Definition of terms

W = liquid flow rate (moles/minute)

G = gas flow rate (moles/minute)

X = mole fraction HTO in feed water

X' = mole fraction HTO in heads water

X'' = mole fraction HTO in tails water

Y = mole fraction HT in hydrogen

$\bar{p}$ = mole fraction water vapor in gas

L = total feed flow rate (moles/minute)

L' = total heads flow rate (moles/minute)

L'' = total tails flow rate (moles/minute)

χ = atom fraction tritium in feed

χ' = atom fraction tritium in heads

χ'' = atom fraction tritium in tails

α = single stage separation factor

β = single stage heads separation factor

θ = cut

n = number of equilibrium theoretical plates

(Tails pertains to the tritium depleted (or gas) stream exiting from a reactor, heads to the tritium rich or liquid stream exiting from a reactor and feed is any stream going into a reactor.)

The following general relationships are true for cascade type isotope separation systems.

$$\alpha = \frac{\chi'}{\chi''} \frac{(1 - \chi'')}{(1 - \chi')} \tag{18}$$

If χ' and χ'' are much smaller than 1 (heads and tails streams very dilute),

$$\alpha = \frac{\chi'}{\chi''} \tag{19}$$

can be used as a close approximation of (18).

$$\theta = \frac{L'}{L} \tag{20}$$

$$\beta = \frac{\chi'}{\chi} \tag{21}$$

In addition to (21) another more useful relationship involving β can be derived.

$$\beta = 1 + \frac{(\alpha - 1)(1 - \theta)}{1 + \theta(\alpha - 1)(1 - \chi')} \tag{22}$$

Again, if $\chi' \ll 1$, (22) is simplified.

$$\beta = 1 + \frac{(\alpha - 1)(1 - \theta)}{1 + \theta(\alpha - 1)} \tag{23}$$

Finally, since both the HTO and HT molecule have two atoms of hydrogen, a general relationship exists between the mole fraction and atom fraction in each.

$$X = 2\chi \tag{24}$$

$$Y = 2\chi \tag{25}$$

(Expressions (24) and (25) apply for the feed, heads and tails streams.)

In addition to the above general expressions there is also a set of relationships involving the system parameters. The subscripts in the following equations are to be interpreted as follows: H and L refer to the HTR and LTR, numbers 1 through 4 to the locations designated in Figure 4.

In the overall system water flows are equal at all the designated points.

$$W_1 = W_2 = W_3 = W_4 \tag{26}$$

For the HTR the following relationships are of interest:

$$L_H = W + G\bar{p} + G(1 - \bar{p}) = W + G \tag{27}$$

$$L'_H = W + G\bar{p} \tag{28}$$

$$L''_H = G(1 - \bar{p}) \tag{29}$$

$$\theta_H = \frac{L'_H}{L_H} = \frac{W + G\bar{p}}{W + G} \tag{30}$$

$$\beta_H = 1 + \frac{(\alpha_H - 1)(1 - \theta_H)}{1 + \theta_H(\alpha_H - 1)} \tag{31}$$

$$X_H = 2\chi_H = \frac{WX_2 + G\bar{p}X_1 + G(1 - \bar{p})Y_1}{W + G} \tag{32}$$

$$X'_H = 2\chi'_H = X_3 \tag{33}$$

$$X''_H = 2\chi''_H + Y_3 \tag{34}$$

At this point it should be noted that β_H is a function only of the experimental parameters (flow rates) and the equilibrium constant, K_H, since $K_H = \alpha_H$. β_H can then be evaluated using the following actual parameters for the experiment.

$W = 0.556$ moles/minute

$\bar{p} = 3.87 \times 10^{-2}$

$G = 1.26$ moles/minute

$\alpha_H = K_H = 2.6$

Using (31), β_H is calculated to be 1.70.

A similar set of expressions can be derived for the LTR as follows:

$$L_L = W - G\bar{p} + G\bar{p} + G(1 - \bar{p})$$
$$= W + G(1 - \bar{p}) \tag{35}$$

$$L'_L = W \tag{36}$$

$$L''_L = G(1 - \bar{p}) \tag{37}$$

$$\theta_L = \frac{L'_L}{L_L} = \frac{W}{W + G(1 - \bar{p})} \tag{38}$$

$$\beta_L = 1 + \frac{(\alpha_L - 1)(1 - \theta_L)}{1 + \theta_L(\alpha_L - 1)} \tag{39}$$

$$X_L = 2\chi_L = \frac{WX_1 - G\bar{p}X_1 + G\bar{p}X_3 + G(1-\bar{p})Y_3}{W + G(1 - \bar{p})} \tag{40}$$

$$X'_L = 2\chi'_L = X_5 \tag{41}$$

$$X''_L = 2\chi''_L = Y_1 \tag{42}$$

Now since $\alpha_L = K_L = 6.6$, β_L can be calculated to be 2.39.

After the system described in Figure 4 has been operating for some period of time at the parameters listed above, a steady state is in effect as far as the isotopic concentrations are concerned. At this time the HTR is assumed to be at isotopic equilibrium as previously mentioned, but the LTR is not. The object of the experiment is to calculate to what extent the LTR does achieve equilibrium. This can

be expressed as the length (or height) necessary to produce equilibrium, or the height of an equilibrium theoretical plate (HETP).

The data taken from this experiment consist of the tritium concentrations in the water at points 1 and 4 shown in Figure 4. It is necessary to make one additional assumption about the experimental system in order to calculate the HETP. The assumption is that the LTR closely approximates an ideal cascade as defined in Benedict and Pigford.[35]

The relationship

$$n = 2\left[\frac{\ln \frac{X'_L(1 - X''_L)}{(1 - X'_L)X''_L}}{\ln \alpha_L}\right] - 1 \tag{43}$$

or, since X'_L and $X''_L \ll 1$

$$n = 2\left[\frac{\ln \frac{X'_L}{X''_L}}{\ln \alpha_L}\right] - 1 \tag{44}$$

can then be used to evaluate n, and therefore the HETP.

As a measure of how good the ideal cascade assumption is, the following relationship between α and β (for an ideal cascade) may be used.

$$\beta_L = \sqrt{\alpha_L} \tag{45}$$

Since $K_L = \alpha_L = 6.6$, $\sqrt{\alpha_L} = 2.57$. β_L has been calculated to be 2.39, which is within 10% of the above. Thus, based on approximate experimental agreement to (45), the LTR was assumed to be an ideal cascade.

From the experimental data the ratio X_1/X_4 can be evaluated. However, in order to evaluate (44) the ratio Y_1/X_4 is needed. Substituting (32) and (33) into (21) the following equation relating β_H and Y_1 can be derived.

$$\beta_H = \frac{X_3(W + G)}{WX_2 + G\bar{p}X_1 + G(1 - \bar{p})Y_1} \tag{46}$$

Solving for Y_1

$$Y_1 = \frac{(W + G)X_3 - \beta_H(W + G\bar{p})X_1}{\beta_H G(1 - \bar{p})} \tag{47}$$

Now, from the liquid flow parameters of this particular experiment the following concentration relationship must exist.

$$X_4 + X_3 = 2X_1 \tag{48}$$

$$X_3 = 2X_1 - X_4 \tag{49}$$

Substituting (49) into (47) allows Y_1 to be evaluated from the experimental data

$$Y_1 = \frac{(2X_1 - X_4)(W + G) - \beta_H X_1 (W + G\bar{p})}{\beta_H G (1 - \bar{p})} \tag{50}$$

Substituting $X''_L = Y_1/2$ and $X'_L = X_4/2$ in (44) yields the following equation which allows n to be calculated in terms of the experimental data and parameters.

$$n = \frac{2 \ln \left[\dfrac{X_4 \beta_H G(1-\bar{p})}{(2X_1 - X_4)(W+G) - \beta_H X_1 (W+G\bar{p})} \right]}{\ln \alpha_L} - 1 \tag{51}$$

Since the actual height of the catalyst bed in the LTR is 11 inches, the HETP (in feet) may be evaluated from

$$\text{HETP} = \frac{11}{12n} \tag{52}$$

This was done for the preliminary experiment with the result, HETP $\approx$ 16 feet.

However, the error limits (due only to errors in X_1 and X_4) for the HETP range from ~8 to 95 feet. It is likely that this large spread for the error limits is due primarily to the "grab sample" sampling technique. It was necessary to take several small samples of water from the two appropriate points in the system and analyze them at a remote counter. The system has its own in-stream counters, but they did not function properly during the experiment.

FUTURE PLANS

Additional experiments will be done to more precisely determine the HETP for the Engelhard catalyst. Attempts will be made to use the in-stream counters for analyses of these experiments. Tests also will be made to evaluate other catalysts as they become available.

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