Tritium Effluent Control Project Progress Report: July-September 1974

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NOTICE

MONSANTO RESEARCH CORPORATION
A Subsidiary of Monsanto Company

MOUND LABORATORY
Miamisburg, Ohio 45342

operated for

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SUMMARY

Cryogenic Adsorbate Separation Design of the physical layout of the pilot scale hydrogen-air separation system was completed and construction has begun.

The getter HIP alloy absorbed 1.9 wt % hydrogen at room temperature in its initial absorption. Succeeding adsorption may be greater due to increased activation of the getter. (Page 4)

Hydrogen Isotope Distillation A distillation cascade for separating hydrogen isotopes was simulated by means of a multicomponent, multistage computer code. A hypothetical test mixture containing equal atomic fractions of protium, deuterium, and tritium, equilibrated to high temperature molecular concentrations, was used as feed. The results show that a two-column cascade can be used to separate the protium from the tritium. Deuterium appears both in the protium and the tritium product streams. (Page 6)

Catalytic Exchange Detritiation System Acknowledgement of acceptance was received from Engelhard Minerals & Chemicals Corporation for the contract to supply a hydrogen/water exchange system for experimental development work to be done at Mound Laboratory. (Page 13)

Tritiated Liquid Waste Decontamination Nine determinations of the H-D separation factor were made with the GE regenerative cell operating in an alternating mode. The values for α (D/H) observed in these experiments ranged from 1.45 to 2.00. (Page 16)

Single-stage separation factors were determined for five candidate materials for extractive distillation using equilibrium still data. Separation factors (α H/T) of 1.08 ± 0.04, 1.01 ± 0.04, 1.29 ± 0.04, 1.97 ± 0.04, and 1.66 ± 0.04 were determined by this method but subsequent experiments indicated the last two values were due mostly to H-isotope exchange from HTO to the organic molecule. After H-isotope exchange equilibration, these two materials produced separation factors of 1.19 and 1.14. These latter values are the single stage separation factors which could be expected with those organic/water mixtures exclusive of exchange effects. (Page 19)

TRITIUM EFFLUENT CONTROL PROJECT

C. J. Kershner, Project Manager

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. Modifications to existing facilities resulted in a reduction of the total (HTO and HT) gaseous tritium effluent at Mound to 15,000 Ci in 1973. As a consequence of the completion of presently planned modifications to facilities and minor operating procedure changes, it should be possible to further reduce total gaseous tritium effluents from Mound to a level of 12,000 Ci/yr or lower by the end of 1974. However, reduction of the effluent from Mound and other weapon complex sites to 10% of the RCG for both tritium and tritium oxide, as measured in the stacks, poses problems that are beyond ready solution with state-of-the-art tritium processing technology.

The objective of the Tritium Effluent Control Project is to develop both technology and equipment to the point where the tritium concentration in Mound effluents can be reduced to 10% of the present RCG levels and the total emissions can be reduced to an as-low-as-practicable level.

The Tritium Effluent Control Project was planned as an initial 36-month effort involving a laboratory scale development phase and subsequent pilot-plant scale phases to test the developed approaches under actual plant operating conditions. Authorization to proceed with the initial phase of this project in the last half of FY-1972 was obtained in November 1971. In order to initiate the work on January 1, 1972, and to obtain the most expeditious utilization of available manpower and funding, a major portion of the work in FY-1972 was planned as subcontract effort. Some of this subcontract effort was continued through FY-1973 and the first half of FY-1974. The major portion of the work has been accomplished in-house and is in the pilot scale phase of development. A test laboratory, embodying many of the results of the research phase of the work, has been designed and its construction is nearly completed.

CRYOGENIC ADSORBATE SEPARATION

J. K. Schneider and R. A. Watkins

Background Cryogenic adsorption of active gases is being studied as a means of tritium decontamination and purification for helium glovebox atmospheres. The adsorbates are expected to be mainly or exclusively air containing small amounts of hydrogen and tritium. After regeneration of the beds, the hydrogen isotopes must be separated from the other adsorbates, since a chemically pure mixture of hydrogen isotopes is required as feed to the isotopic separation process.

Prior Work The project was initiated in the quarter January-March, 1973. The effect of temperature on the desorption of a mixture of hydrogen and nitrogen, originally adsorbed at liquid nitrogen temperature, in a static system was investigated. A definite enrichment of hydrogen in the gaseous phase and nitrogen in the adsorbed phase was found at each temperature of the investigation, indicating that a partial separation of the air constituents during the regeneration of the cryogenic adsorption column is feasible.

Two dynamic chromatographic approaches to the hydrogen-air separation, nitrogen displacement and temperature-zoned techniques, were experimentally tested on a bench scale. Excellent separations were obtained with both techniques, and both systems are capable of selectively separating hydrogen isotopes/nitrogen and oxygen as required for processing the regeneration gas from the glovebox atmosphere detritiation system.

Accomplishments Design of the physical layout of the hydrogen-air separation system was completed, and construction of the pilot scale system has begun.

The getter HIP alloy is being studied for removal of hydrogen from flowing inert gas atmosphere streams. A sample of this material was found to absorb 1.9 wt % hydrogen at room temperature in the first sorption experiment. The reaction was exothermic.

Discussion The getter HIP alloy is being studied as a possible replacement for the third bed in the three-bed temperature-zoned separation system. The getter is expected to provide a more convenient source of hydrogen isotope storage, that is, room temperature storage rather than the cryogenic storage originally proposed. Getter storage will also provide an additional means of trace impurity removal. The getter is also being studied as a potential method of detritiating inert-gas glovebox atmospheres.

Initial attempts to study the hydrogen adsorption behavior of HIP alloy in a flowing helium atmosphere failed, possibly due to poisoning of the getter by an impurity in the flow system.

Equilibrium studies of hydrogen sorption by HIP alloy are being made using a 25 cm stainless steel vial, which was filled in an inert gas atmosphere with 9.71 g of HIP alloy and was connected to a high vacuum system by means of a "Conoseal" fitting. The volumes of the various parts of the system were determined, and an attempt was made to activate the bed by heating to 600°C under a vacuum of 5×10^{-5} torr for 15 min. Some outgassing occurred between 200 and 400°C.

This sample of HIP alloy sorbed 2.3 liter (STP) of hydrogen at

room temperature in the first sorption experiment. It is anticipated that the sample may absorb more in succeeding runs as repeated sorption and desorption is often required for complete activation of getter materials.

The observation that HIP alloy absorbs hydrogen readily at room temperature is encouraging. It is expected that the sorption of O_2, N_2, and H_2O will require higher temperatures, since HIP alloy is reported to be stable in air at room temperature. Thus it is possible that HIP alloy may getter hydrogen exclusively at room temperature in the presence of air impurities.

Future Plans

1. Further studies of hydrogen adsorption-desorption characteristics of HIP alloy will be made to determine hydrogen sorption isotherms at various temperatures.

2. A flow system with high vacuum capabilities will be designed and constructed. Experiments will be conducted to determine whether HIP alloy will absorb hydrogen from flowing inert gas atmospheres.

3. The effect of oxygen on the sorption of hydrogen by HIP alloy will be determined.

4. Construction of the pilot scale hydrogen-air separation system in the Tritium Effluent Control Laboratory will be completed.

MAY 1.

HYDROGEN ISOTOPE DISTILLATION

W. R. Wilkes

Background One of the "prevent dilution" concepts of effluent control involves lowering the tritium levels in gloveboxes and other confinement areas by special recirculating gas systems. For these to be effective, methods are being developed to concentrate the tritium collected in these removal systems. One approach to this integrated removal/concentration system which is being explored is cryogenic adsorption followed by cryogenic distillation for concentrating the tritium. This approach involves working with nearly pure hydrogen (i.e., H_2, HT, T_2) as a product of the distillation stage. New methods and materials for the handling of hydrogen isotopes - specifically tritium - are being investigated for use in the cryogenic distillation system.

Prior Work A short distillation column was designed and fabricated for measuring parameters required for construction of a pilot-scale cryogenic-distillation apparatus for the separation of protium and tritium. Preliminary experiments on this apparatus using H_2, HD, and D_2 mixtures indicated a need for improved design of the boiler and condenser assemblies. With the installation of the required new components, improved results were obtained and the tendency of the boiler to run dry at low power levels was reduced, particularly with high HD or D_2 concentration in the boiler. A longer column was then fabricated to permit separation of the feed mixture into high purity products. The new column was successful in separating mixtures containing roughly equal parts of H_2, HD, and D_2 into end streams depleted to less than 0.2% of either H_2 or D_2.

Accomplishments In order to predict the type of distillation system best suited for hydrogen isotope separation with feed from various sources, especially those containing the natural mixture of hydrogen and deuterium along with traces of tritium, a series of computer simulations of various hypothetical separations is being performed. As a "worst" case, and one that exemplifies well the problems encountered in a hydrogen isotope separation system, a computer simulation of the separation of an equiatomic mixture of H, D, and T in a laboratory scale distillation system was performed.

In a two component system, distillation is fairly straightforward, especially with vapor pressure ratios (α) as high as 2, as one finds with some of the hydrogen isotopes. Neglecting economics, one is faced with the rather simple problem of making a column long enough, with enough reflux to effect the desired separation. An example of this is shown in Figure 1.

With more components, the problem becomes more complicated, and N - 1 columns are required to produce a complete separation where N is the number of components. A special case of a three component distillation using D_2, DT, and T_2 is shown in Figure 2. The special feature of this system is that the middle product is not collected, but is returned to the original input stream. If we wanted to have "pure" DT, we could simply use the lower product of the second column, rather than return

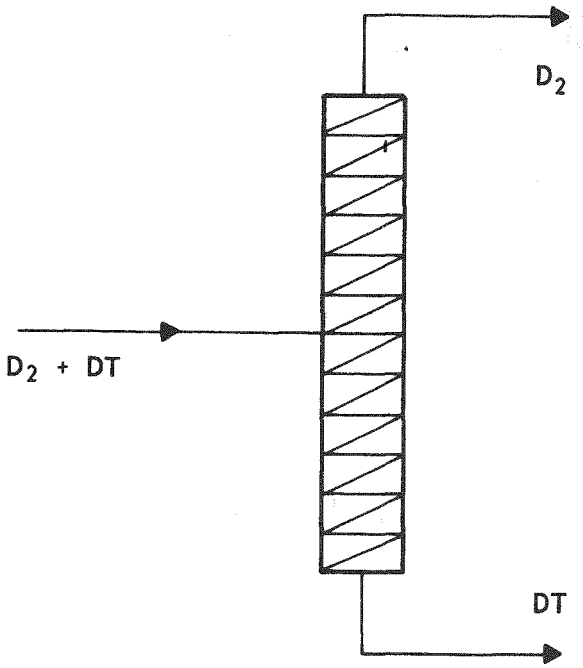


FIGURE 1 - Two component distillation of hydrogen isotope mixture.

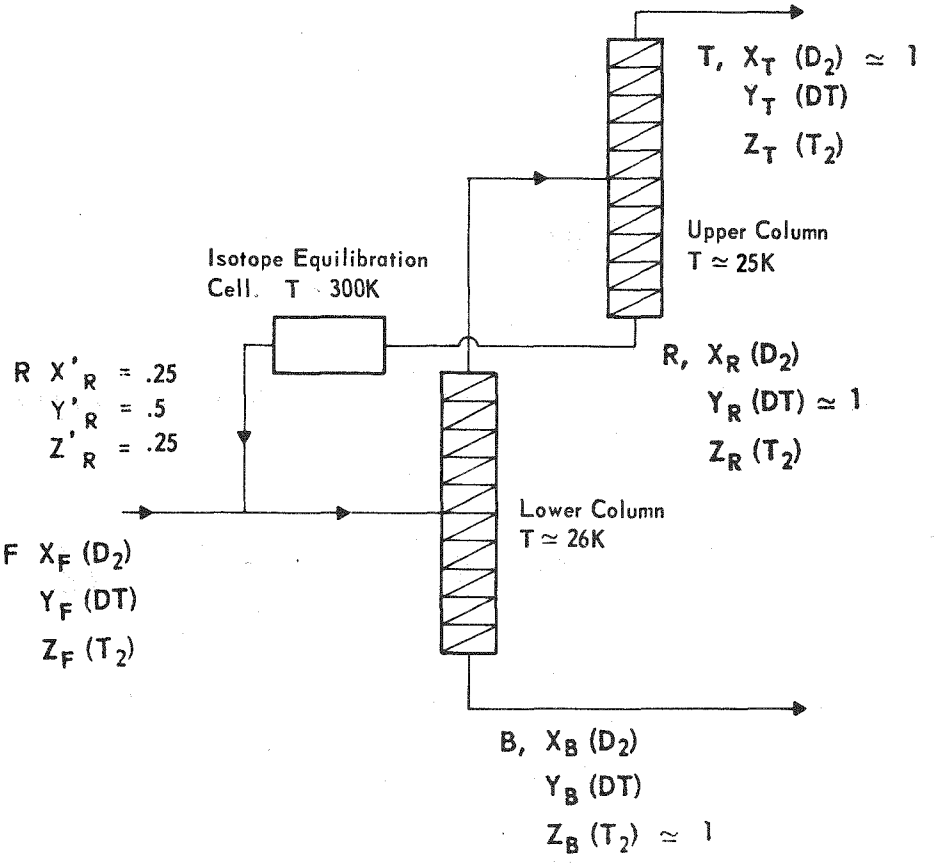


FIGURE 2 - Three component distillation of hydrogen isotope mixture.

it as is done here. As Figure 2 is drawn, however, this middle product, containing mostly DT, is passed through a catalyst which promotes the reaction

$$D_2 + T_2 \leftrightarrow 2DT \qquad (1)$$

to proceed to equilibrium. In this case, this means that the equilibrated return stream will contain 50% DT, 25% D_2, and 25% T_2.

Because the hydrogen molecule is diatomic, the three isotopes lead to six molecular species - H_2, HD, HT, D_2, DT, and T_2 - in order of decreasing volatility. It is the existence of six kinds of molecules, coupled with the fact that HT contains both H and T, that complicates this separation.

At high temperatures ($T \geq 400K$) the differences between the isotopes are small compared to thermal energies, and as a result, the equilibrium constants in the equations of the type

$$K = \frac{X^2(DT)}{X(T_2)X(D_2)}, \qquad (2)$$

which describe the degree to which reaction (1) proceeds, are all nearly equal to four.

As a result, for an equiatomic mixture, the homonuclear species all have mole fractions of 1/9 and the heteronuclear species, 2/9. It is this mixture that is assumed to be the feed to the distillation system. If we are not interested in where the deuterium goes, the mixture can be thought of as three components, H_2 + HD, HT, and D_2 + DT + T_2. The first is the top product, which, if it is clean enough, may be disposed of. The third, or bottom, product contains considerable stable D_2, but this may not be a problem since it can be used as fuel for a fusion reactor, for example. The middle product, HT, since it still contains elements of both end products, must be processed further. It is warmed, equilibrated to high temperature molecular concentrations, and returned to the original feed stream. As before, the equilibrated return stream contains 50% of the heteronuclear molecular species, HT, and 25% each of the homonuclear species H_2 and T_2. The resulting system is shown in Figure 3.

The initial feed stream is mixed with the return stream from the second column and the combined mixture is fed to the first column to be separated. The amount of material returned to the input stream from column 2 is not arbitrary. A lower limit exists below which complete separation cannot be achieved. Suppose we have three components, with the middle component a mixture of the other two, such as HT. (The fact that the remaining components are themselves mixtures does not matter here.)

Suppose further that we achieve total separation (i.e., only the most volatile component appears in the top product, the least volatile in the bottom product), and the middle component is equilibrated to the high temperature composition. By writing mass balance equations for each of the three components, it can be shown that

$$R = 2FY_F,$$

where R is the rate of flow in the middle product stream, F is the external feed flow rate, and Y_F is the molecular fraction of the middle component (see Figure 2). Since HT comprises 22.2% of the hypothetical feed mixture, the minimum return flow rate is 44.4% of the external feed flow, and the first column has a total feed of 1.444 times the external flow. The composition of the material entering column 1 is approximately 15.4% each of H_2, HD, DT, and T_2; 30.8% HT; and 7.7% D_2.

It has been found that good separation can be achieved in a two-column system with the following characteristics.

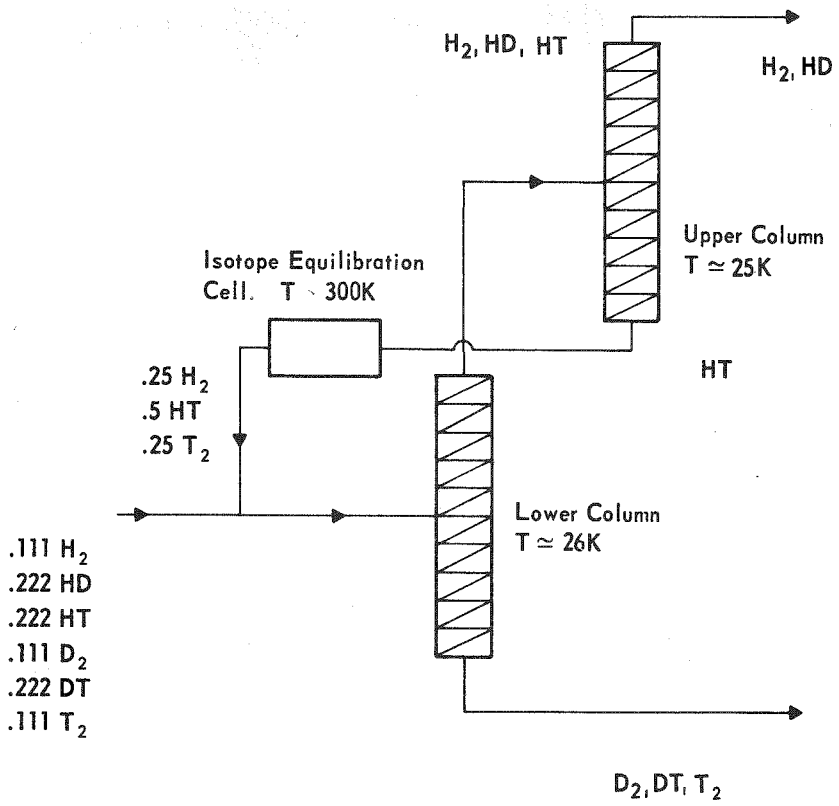


FIGURE 3 - Six component distillation of hydrogen isotope mixture separating H from T.

The first column has 50 plates and is fed at the midpoint. The operating pressure is 1500 torr and the reflux ratio is 30. The bottom product consists of 99.8% D_2, DT, and T_2; 0.19% HT; 1.8 x 10^{-4}% HD; approximately 10^{-7}% H_2. Thus less than 0.1% of the bottom product is protium. The upper product is 25% H_2, 24.6% HD, 49.9% HT, 0.5% D_2, plus traces of DT and T_2. This latter mixture is the feed to the second column.

In the second column, which is 100 stages in length, the feed is at the twenty-fifth stage. The column pressure is less, 1200 torr, than in column 1, and the operating temperature is correspondingly lower. In this way, the heat which leaves column 1 through the condenser can be used to heat column 2. In addition the pressure drop assures a flow of material in the proper direction. The reflux ratio, which is set by the bottom column and the flow rates, is 68. The bottom product of this column contains 98.1% HT, 1.1% D_2, and 0.8% HD with negligible amounts of the other components. The top product, which is perhaps the most critical one, contains less than 2 x 10^{-5}% of HT. The D_2, DT, and T_2 components are calculated to be down another 10 orders of magnitude from this level, although the accuracy of these latter concentrations is highly doubtful. What is certain is that essentially all of the tritium in the top product is accounted for by the HT.

The column calculations were performed for an external feed flow of 50 std. cm^3/min, which is the approximate operating range of our existing apparatus. The boiler power required is 1.1 W. Such a column can process 26,000 liters

of gas, containing 389 moles of tritium, per year. This is a total of 2.3×10^7 Ci. Of this amount, only 1.1×10^{-5}% (2.6 Ci) is lost through the top product stream. From an HETP value of 1.4 cm as measured on the existing laboratory still using 3 mm Eglin packing, it can be calculated that the columns described here would be 70 and 140 cm long, respectively. The column diameter is 0.6 cm. Figures 4 and 5 show the existing 40-stage laboratory column described previously. [1,2]

Several factors that are currently unknown can effect these results. The HETP above is considered a maximum value and may be reduced by more careful measurements using tritium instead of deuterium in the still. This may reduce the required column length. On the other hand, the program calculates separations using ratios of vapor pressures of pure materials, not actual results from mixtures. Hence the actual α's may be smaller than assumed, necessitating longer columns.

A major unknown is the degree of molecular equilibration that will occur in the liquid hydrogen as a result of tritium decay. Since the low temperature equilibrium constants tend to favor homonuclear molecules (H_2, D_2, T_2), there could be a decided improvement in performance due to such an effect, since the return flow, R, may be reduced in direct proportion to the amount of HT which converts to $H_2 + T_2$ in the column.

We expect to use sorption pumps to move the hydrogen around. Since the sorption-desorption process breaks and rejoins molecules, a partial separation or molecular equilibration may be achieved. These pumps are currently being developed.

In summary, a two-column distillation system, of a size that can fit into a single laboratory glovebox, is calculated to be capable of processing annually on the order of 10^7 curies of tritium mixed with protium and deuterium, so that the tritium and protium are separated. Less than 2×10^{-5}% of the tritium is permitted to exhaust through the protium stream, while 0.16% of the protium remains in the tritium stream.

Future Plans The 40-stage laboratory column shown in Figure 5 will be installed in the Tritium Effluent Control Laboratory so that studies with tritium can be commenced.

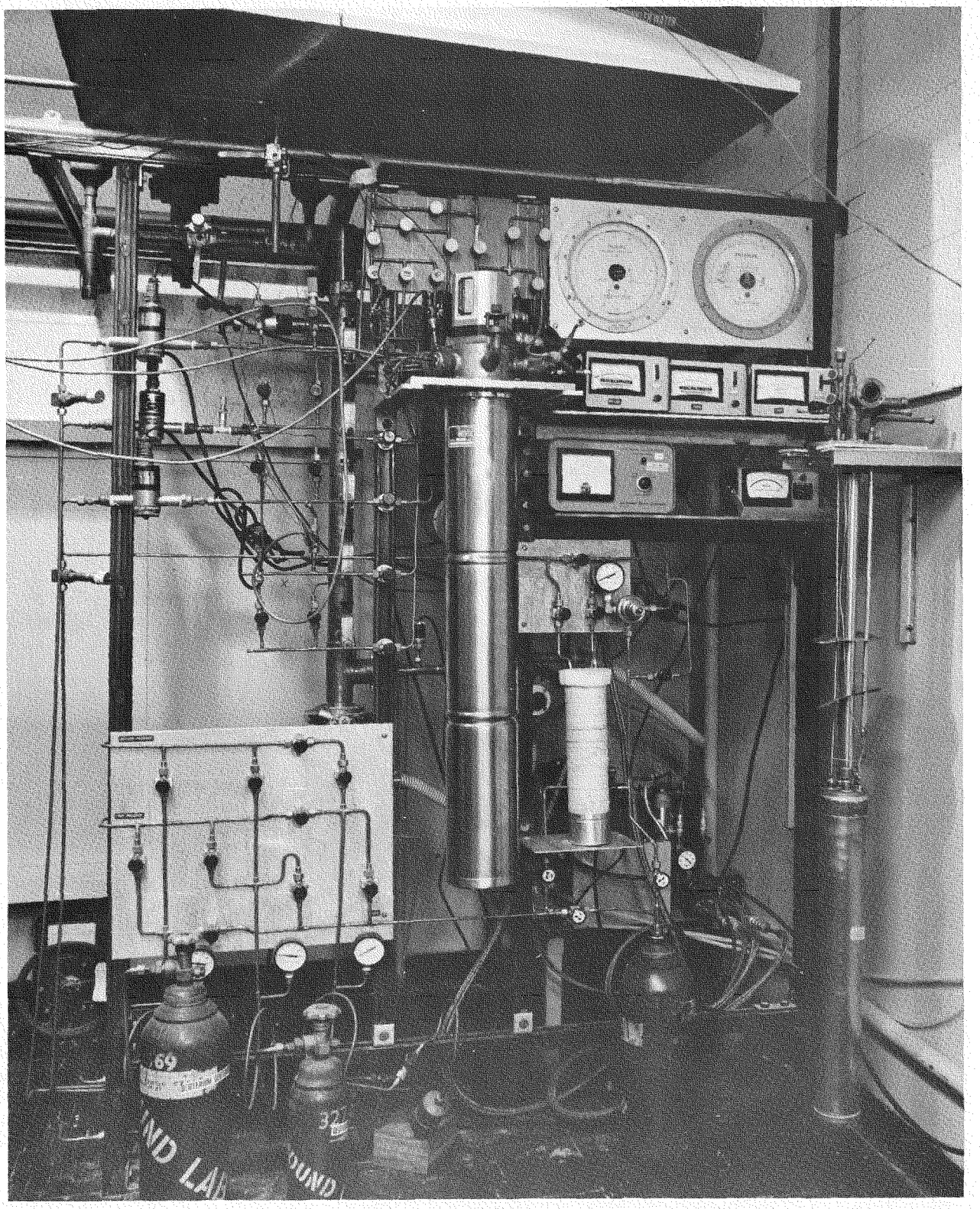


FIGURE 4 - Hydrogen distillation apparatus.

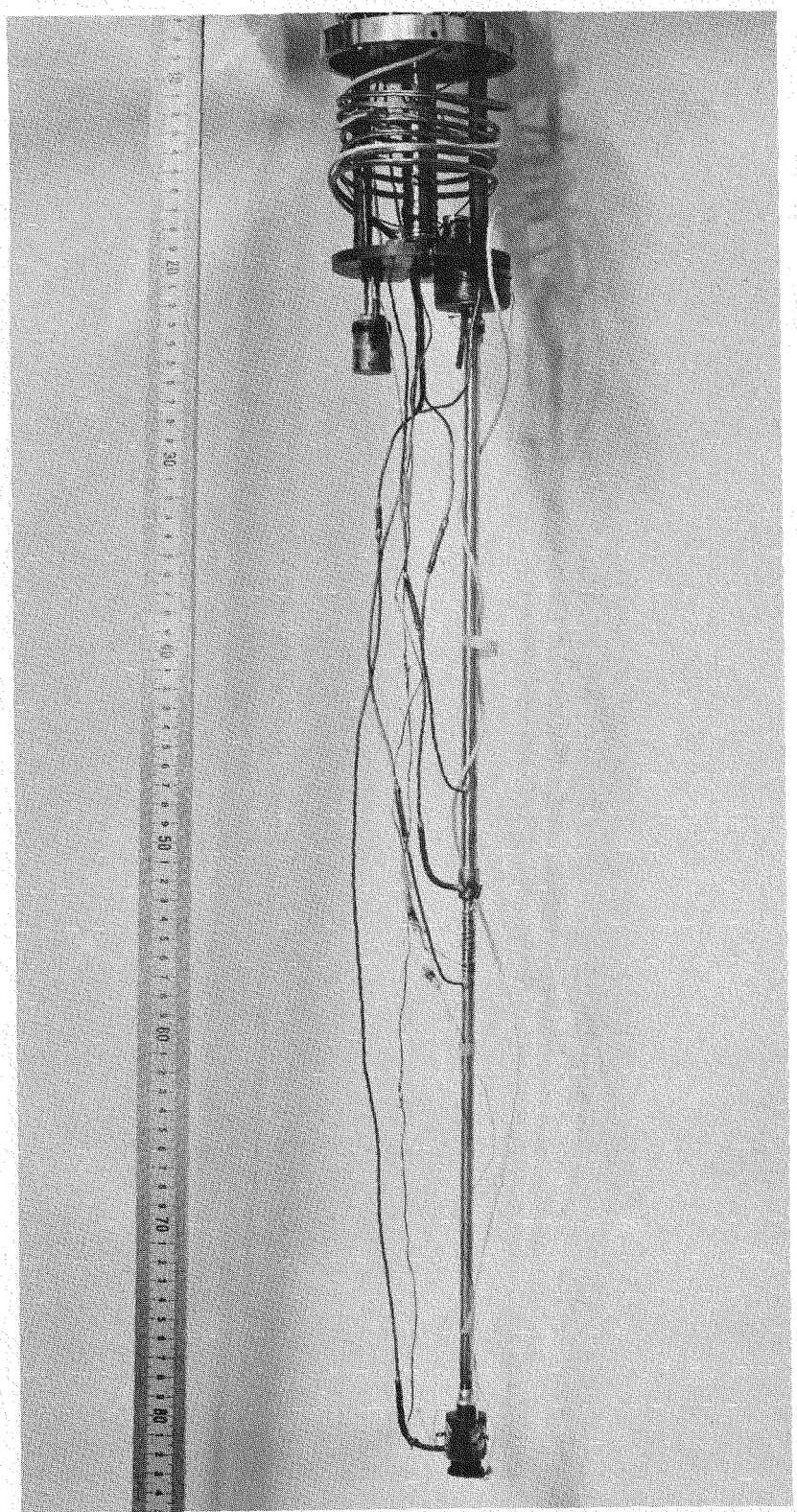


FIGURE 5 - 40-stage laboratory column.

CATALYTIC EXCHANGE DETRITIATION STUDIES

J.C. Bixel

Background Because of the expanding nuclear power industry and the increased emphasis on minimizing release of radioactive materials to the environment, there is an increasing need for the development of safe handling and disposal methods for the radioisotopes being produced. With the exception of tritium, all the radioisotopes produced in the operation of a light water reactor are amenable to some form of chemical or physical separation process for removal from the effluent streams. Tritium, however, is generally encountered in the oxide form and therefore follows the natural water streams. The detritiation of these aqueous wastes requires isotopic separation processes.

The purpose of this study is to develop a tritium separation and concentration process based on a H_2/H_2O catalytic exchange technique which can be used to detritiate contaminated water from light water reactors, fuel reprocessing plants, and tritium handling laboratory facilities.

Project objectives are as follows:

a) The determination of the technical and economic factors of H_2/H_2O exchange as a possible detritiation process for treating tritium-contaminated water from power reactor and fuel reprocessing plant operations.

b) The determination of the suitability of hydrophobic exchange catalysts for use in water detritiation systems.

c) The pilot scale testing of a H_2/H_2O exchange system to establish the design criteria for detritiation systems capable of meeting the tritium control needs of the U. S. power reactor industry and AEC site operations.

Prior Work A sole source justification and purchase order were prepared and submitted for an experimental, single-stage system for catalytic detritiation of water. The system will be purchased from Engelhard Minerals and Chemicals Corporation, who developed a precious metal catalyst purported to be active for the H_2/H_2O exchange even when used in the liquid phase. A literature survey for information relating to economic factors for the H_2/H_2O catalytic exchange process was substantially completed.

Accomplishments Acknowledgement of acceptance was received from Engelhard Minerals and Chemicals Corporation for the contract to supply a hydrogen/water exchange system for testing at Mound. This dual-column catalytic exchange system will be used in the feasibility test phase of the project.

Conceptual design of the dual-column experimental system was completed, and Engelhard engineers are presently in the process design stage.

Discussion Contract negotiations were delayed for approximately two months while Monsanto Research Corporation and AEC/ALO patent attorneys studied the question of whether background patent rights and background technical data clauses should be included in the contract agreement. Because of the precedent set by previous purchases of systems containing proprietary catalysts, the decision was made that background patents

and rights in data clauses were not required. Mainly due to contract negotiation delays, system delivery was scheduled for December, 1974, rather than October as had been previously planned.

When completed, the experimental system will be installed in a helium atmosphere glovebox in the Tritium Effluent Control Laboratory. The flow schematic for the dual column experimental system as originally conceived is shown in Figure 6. The Engelhard Contract is presently in the process design stage, however, and some system changes may result. The system will incorporate closed water and hydrogen flow loops and will allow

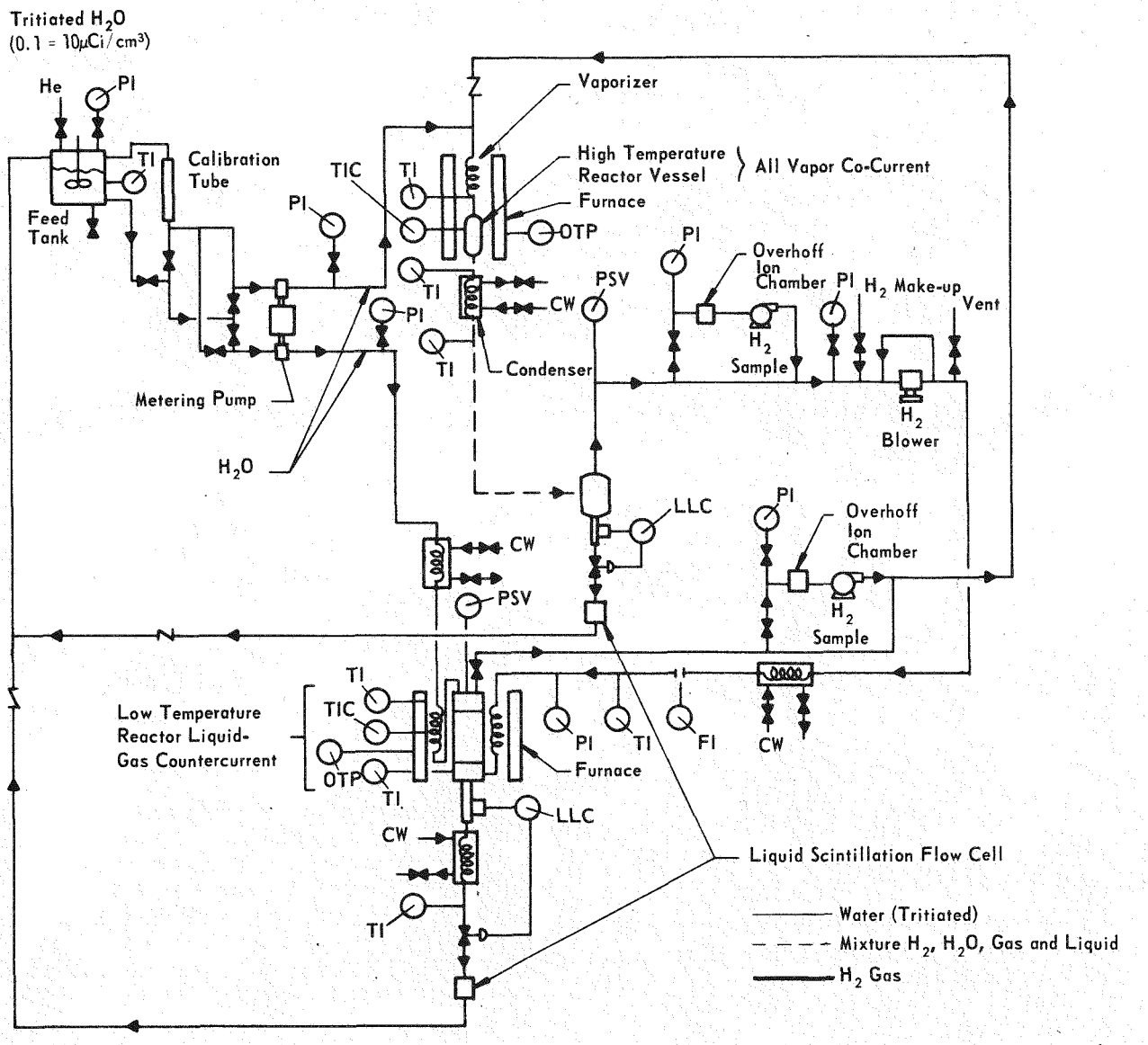


FIGURE 6 - Experimental system schematic.

evaluation of the catalyst in two modes of operation: 1) all vapor co-current and 2) liquid-gas countercurrent. Liquid reactor effluents will be monitored for tritium by continuous-flow liquid scintillation analyses. The hydrogen gas flow streams will also be monitored using ion chambers.

Detritiation of water by catalytic exchange will be studied in the range 0.1 to 10 $\mu Ci/cm^3$ of tritium. At these conditions the predominant exchange reactions are

$$H_2O + HT \rightleftarrows HTO + H_2, \text{ and} \quad (1)$$

$$H_2O + HD \rightleftarrows HDO + H_2.$$

Natural abundance of deuterium in water is approximately 150 ppm while the 10 $\mu Ci/cm^3$ concentration of tritium is about 0.001 ppm tritium. Thus with the concentrations to be used in the initial studies, it may be assumed that the heavy isotopic components (DTO, D_2O, T_2O, DT, T_2, and D_2) do not appear. The experimental system is being designed to give conversions approaching 50% of equilibrium so that reaction rates may be measured; therefore, the design is for less than one equilibrium stage, enrichment will be low, and the heavy isotopic components will not complicate the exchange reaction. The reactions to be evaluated involve complex interactions among gas, liquid, and solid (catalyst) phase. Experiments during the catalyst feasibility test phase will be designed to relate these interactions. Later in the project at the pilot scale testing phase, multistage columns will be evaluated. Higher enrichment factors in these columns may necessitate consideration of the heavy isotopic components both experimentally and in development of rigorous calculation methods for the multicomponent systems encountered.

Future Plans Work will continue toward design and assembly of the experimental catalyst evaluation system for installation in an existing glovebox in the Tritium Effluent Control Laboratory.

TRITIATED LIQUID WASTE DECONTAMINATION

R. E. Ellis

Background Operations involving tritium produce a significant quantity of high and low level liquid wastes, composed mostly of water, which must be disposed of in a safe manner. In the past, these liquids have been absorbed on solids or diluted to specified levels and buried, or they have been diluted to low enough levels to be discharged as "uncontaminated" water. All of these methods eventually allow tritium to enter the environment. A preferable method would be to decontaminate such wastes (without dilution) to near the natural level before discharge. Demonstrations of the feasibility and development of such decontamination techniques are the goals of this work.

Prior Work

Electrolysis/Recombination A General Electric UCT-1 solid polymer electrolyte cell was purchased for hydrogen isotope separation tests. The protium-deuterium separation factor for both electrolysis and recombination was investigated as a function of several parameters.

Extractive Distillation Sixteen candidate organic liquids were screened for existence of low-boiling azeotropes in the organic water system. Seven of those did not form such azeotropes and were scheduled for further tests.

Molecular Excitation After several possibilities were considered the reaction, $CO + H_2O \rightleftarrows H_2 + CO_2$, was selected for experimental investigation as the isolation step in this isotopic separation scheme.

Accomplishments

Electrolysis/Recombination Nine determinations were made for the H-D separation factor using the UTC-1 cell in alternating mode. Various sets of current and cycle time parameters were investigated. The separation factors were very similar to those previously found for the fuel cell mode.

Extractive Distillation Satisfactory solutions to the problems of scintillation counting for tritium assay and analysis for organics in the equilibrium still vapor were found. Single stage separation factors (α) were measured for four of the candidate materials. One of these, ethylene glycol, was found to have an apparent α of about 2, but was also found to exchange H-isotopes with water. On the basis of this experiment and literature information it appeared likely that all seven of the initial candidates would be subject to such exchange. Therefore, four new materials less likely to suffer exchange were chosen for further investigation. One of these, dimethyl sulfoxide (DMSO) has been investigated and it too appears to undergo significant exchange. The relative vapor pressure of H_2O to HTO over 1:1 volume mixture of ethylene glycol and DMSO and water were found to be 1.19 and 1.14, respectively, after exchange effects were cancelled out.

Molecular Excitation An active search of recent literature was maintained in this area.

Discussion

Electrolysis/Recombination

Nine determinations of the hydrogen-deuterium separation factor were made using the GE solid polymer electrolyte cell in an alternating mode. In this mode the cell is switched between electrolysis and recombination many times during an experiment. The switching was accomplished by using a Syracuse Electronics Corporation Model TFP-210344 recycle timer as indicated (SW-1) in the circuit schematic of Figure 7.

In the circuit R_1 and R_2 represent lead wire resistances, R_x a variable resistor (nichrome wire), and R_3 a precision resistor. Experiments were done by first selecting the currents for both the fuel cell (recombination) and electrolysis sections of the circuit by adjusting the value of R_x and power supply voltage across R_3 for the fuel cell and by the ammeter on the power supply for the electrolysis section. Duplicate gas samples were taken from the H_2 chamber of the cell at the beginning and end of each run. All experiments, AL-1 through AL-9, were done with a net recombination or fuel cell mode, due to the ease of isotopic determination for hydrogen gas compared to such a determination for water.

Table 1 shows the data from these experiments along with α, the H-D separation factor, calculated from these data as described in a previous report.[3]

Experiment number AL-5 was repeated in AL-7 because an error was made in the pressure reading for AL-5. In general the values for α in these experiments are very similar to those for the fuel cell mode alone.[4]

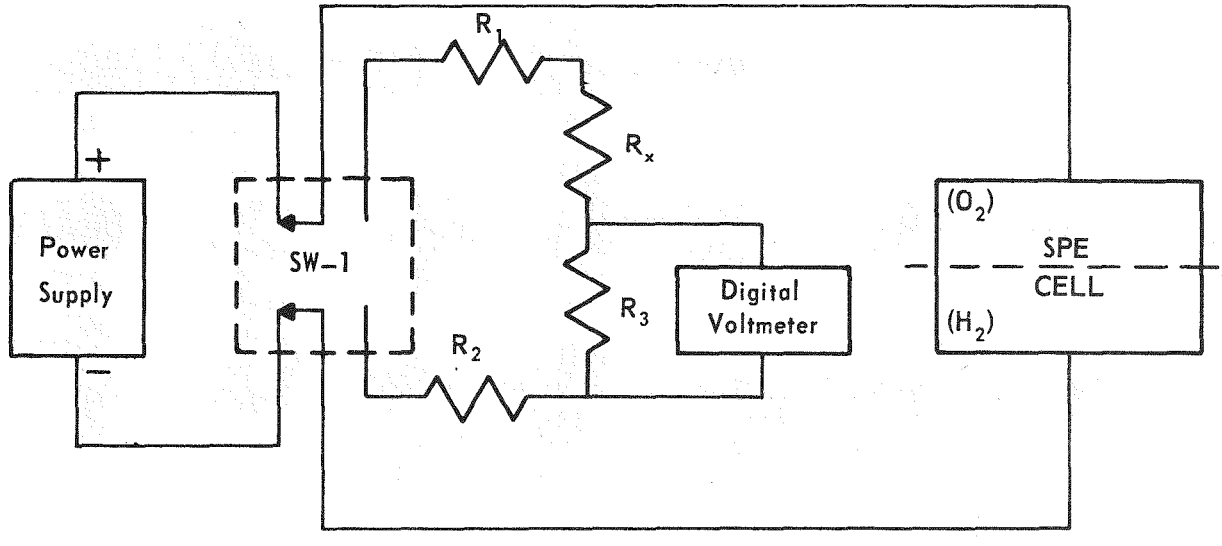


FIGURE 7 - Circuit schematic for alternating current mode operation of SPE cell.

Table 1

DATA FOR SPE CELL OPERATING IN ALTERNATING MODE

Exp. No.	P_{go}[a] (torr)	P_g[a] (torr)	X_{go}[b] (mole %)	X_g[a] (mole %)	Electrolysis Time (sec)	Electrolysis Current (A)	Recombination Time (sec)	Recombination Current (A)	α H/D
AL-1	8806	2859	15.6	9.3	6	3.5	6	3.5-4	1.56
AL-2	8986	2072	14.3	8.2	1.4	2-1.25	28	2-1.25	1.45
AL-3	8623	3967	15.1	9.5	2.2	0.5	2.2	1.0	1.74
AL-4	8370	2574	16.9	9.3	2.2	4.5	2.2	5.0	1.63
AL-5	8715	----	16.3	12.1	359	0.5	355	0.6	---
AL-6	8869	4634	17.6	13.0	37	5.0	355	0.6	1.60
AL-7	8750	5715	17.2	13.3	359	0.5	355	0.6	1.80
AL-8	8727	6006	21.4	16.6	2.2	0.5	2.2	0.6	2.00
AL-9	7580	3215	17.6	12.9	2.2	4.0	2.2	5.0	1.46

[a] P_{go} and P_g are the total hydrogen-deuterium gas pressure at the beginning and end of the experiment.

[b] X_{go} and X_g are the mole fractions of deuterium in the H_2-D_2 feed gas at the beginning and end of the experiment.

Both sets of α values are much lower than the theoretical value, 3.88,[5] which should be approached using catalytic electrodes. One possible reason for the lower values of α is hydrogen-water isotopic exchange in the cell. A quantity of water (approximately 25 g) is contained in wicks and the solid polymer electrolyte inside the cell. Since the electrodes are composed of materials (noble metals) which catalyze the hydrogen-water isotopic exchange, it is conceivable isotope effects due to concentration differences could be opposing the electrolytic effect. Elimination of the wicks may be possible for the electrolysis but probably not for the recombination (fuel cell) mode.

There is also a possibility that operation at higher alternating frequencies will improve the separation factor of this process. Another recycle timer capable of 0.25 sec duration in each of the primary modes has been ordered to more fully investigate this type of operation.

Extractive Distillation

During the initial screening experiments in this area, the counting results and analyses for the organic in water from the equilibrium still vapor were inconsistent.[2] It is believed that satisfactory solutions for both of these problems have been attained. The scintillation liquid was changed from "Instagel" to the formulation below:

PPO	0.4 g
POPOP	0.100 g
Napthalene	200 g
p-dioxane	to make 2 liters

This scintillation formulation is apparently not as sensitive to the organic materials used in this work as is Instagel.

The second problem was solved by using refractive index measurements to determine the quantity of organics in the water sample. For the materials studied thus far the quantity of organics present in the water could be determined from the indices of refraction down to levels of approximately 1 vol % through the use of standards and calibration curves. Plots of concentration as a function of refractive index were found to be nearly linear in the range 0-20% for these materials in water. Where the concentrations in the vapor samples from the equilibrium still were significant (>1%), the HTO stock to be counted for α determinations and the scintillator fluid used for background correction were spiked with appropriate amounts of the organic. This procedure was used to adjust the apparent count rate for any counting effects (quenching, etc.) due to the organic.

In general the separation factor was determined by comparing the tritium content of the equilibrium vapor phase over a 1:1 volume mixture of low level ($\sim 3 \times 10^{-3}$ $\mu Ci/cm^3$) tritiated water and organic to that of the tritiated water mixture. The tritium content was measured by scintillation counting of 500 microliter (λ) samples in 15 ml of the above-mentioned scintillation fluid. Vapor samples were taken at least twice during operation of the equilibrium still and analyzed for tritium content and refractive index. This was done to insure that equilibrium conditions were essentially in effect in the still. In most of the experiments equilibrium was established within 5-6 hr, although in some cases samples were taken after much longer periods as a check for equilibrium.

These procedures were applied to the analyses of equilibrium still experiments for 1:1 volume mixtures of water and the following organics: 1-methyl piperazine, dimethyl aminoethanol, 1,2-propane diamine, and ethylene glycol. The amounts of organics found in the equilibrium vapor and the apparent H_2O/HTO relative volatilities for these four water/organic systems are given in Table 2.

Because of the high relative volatility value for H_2O/HTO in the ethylene glycol water mixture, two additional separation factor determinations were performed in the equilibrium still. The H_2O/HTO relative volatility was again found to be approximately 2.00 for both of these experiments using ethylene glycol/water mixtures.

Table 2

EQUILIBRIUM STILL DATA FOR ORGANIC/WATER SYSTEMS

Organic	Composition, vol % organic		Relative Volatility H_2O/HTO
	Boiler	Eq. Vapor	
1-methyl piperazine	50	22	1.08 ± 0.04
dimethyl aminoethanol	50	28	1.01 ± 0.04
1,2-propane diamine	50	13	1.29 ± 0.04
ethylene glycol	50	0.5	1.97 ± 0.04

The nature of the equilibrium still method of measuring relative volatilities is such that effects of isotopic exchange and vapor pressure differences are not separable and, because hydrogen exchange is to be expected between ethylene glycol and water, a large portion of the apparent relative volatility of the H_2O/HTO may be due to exchange dilution in the organic. To test this possibility, the water fraction in the boiler mixtures from the equilibrium still experiments were separated from the ethylene glycol with a fractionation still and their H/T ratios determined. Although total material balances and quantitative data were not possible with these determinations, the results showed that there was considerable exchange taking place even at vacuum distillation temperatures of 48 to 52°C.

Even though nonexchange is desirable so that a simple counter-current column design can be used, it does not preclude the use of an exchangeable solvent in an extractive distillation separation. Thus, further experiments were made with ethylene glycol to determine the isotope effect on the relative volatilities, independent of the exchange effect. To do this, tritiated ethylene glycol was prepared by isotopic exchange with relatively large quantities of tritiated water of the same H/T ratio as that used in the equilibrium still experiments. The relative volatility of H_2O/HTO over a 1:1 volume mixture of pre-exchanged ethylene glycol and tritiated water was found to be 1.19 ± 0.04. Since this is not particularly high, additional materials not having problems with H-isotope exchange were sought.

The general criteria used in this research were the following:

1. Strong intermolecular attractions (hydrogen bonding) to water molecules,

2. Boiling point above 110°C,

3. Large or infinite miscibility with water,

4. No O-H, S-H, N-H, halogen-H groups, or acidic hydrogens on the organic molecule,

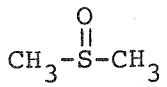
5. No reaction with water.

The four materials shown in Table 3 were initially chosen and have been procured for measurement of separation factor and extent of tritium exchange.

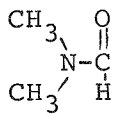
Table 3

ADDITIONAL MATERIALS TO BE TESTED

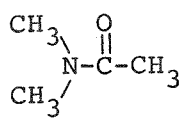
A. Dimethylsulfoxide (DMSO)



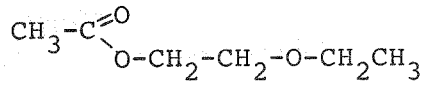
B. N,N dimethylformamide (DMF)



C. N,N dimethylacetamide (DMA)



D. 2-ethoxyethylacetate (cellosolve acetate)



These experiments were performed on the first of these, DMSO. The results were indicative of significant tritium exchange between the DMSO and the water. This was certainly unexpected, since DMSO has only methyl group hydrogens which should not be labile. The possibility of a tantomeric enol form of DMSO may be the mechanism by which hydrogen exchange is possible.

The relative volatility of H_2O/HTO over a 1:1 volume mixture of pre-exchanged DMSO and tritiated water was 1.14 ± 0.04.

Future Plans

Electrolysis/Recombination

The use of faster cycle times, approximately 0.25 sec, for the alternating mode will be investigated. Operation of the cell without wicks in the O_2 chamber may also be tried.

Extractive Distillation

Separation factors and extent of the exchange reactions for the three remaining candidate materials will be determined. Additional materials for investigation will be sought.

Molecular Excitation

Theoretical evaluations of the spectroscopic aspects of this separation method will be initiated.

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