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DEMONSTRATION OF HITEX: A HIGH TEMPERATURE ISOTOPIC EXCHANGE FUSION FUEL PROCESS LOOP (OHRD 93-49-K)

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FUSION FUEL PROCESSING LOOP

Hugh D. Morrison and Kenneth B. Woodall

A model reactor for HITEX successfully demonstrated the concept of high-temperature isotopic exchange in a closed loop simulating the conditions for fusion fuel cleanup. The catalyst of platinum on alumina pellets provided a surface area large enough to operate the reactor at 400°C with flow rates up to 2 L/min. A 15-L tank containing a mixture of 4% CD_4 in H_2 was depleted in deuterium within 75 minutes down to 100 ppm HD above the natural concentration of HD in the make-up hydrogen stream. The application to tritium removal from tritiated impurities in a hydrogen stream will work as well or better.

1. Introduction

The conceptual design of a new system for fusion fuel cleanup was described in a paper by A. Busigin, S.K. Sood, and K.M. Kalyanam in Fusion Technology, Vol. 20, Sept. 1991, pp. 179-185. They proposed a new high-temperature isotopic exchange (HITEX) fuel processing loop for the International Thermonuclear Experimental Reactor, ITER. In the HITEX design, the tritium in tritiated impurities such as methane and ammonia is removed by swamping the impurities with H_2 and equilibrating the isotopic distribution by exchange over a high-temperature catalyst. The catalyst is contained in a reactor with walls at room temperature to minimize

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tritium permeation out of the reactor. A palladium alloy diffuser downstream from the reactor separates the hydrogen from the impurities, carrying most of the tritium away with the hydrogen. To complete the process, the tritiated hydrogen stream is sent to an isotope separation system, probably a cryogenic distillation column, to recover the tritium.

In parallel with the concept devolopment, the Research Division was asked to demonstrate the HITEX reactor in a test loop to simulate fusion fuel cleanup. Two models for the reactor were built and tested, culminating in a successful demonstration of continuous loop flow to remove deuterium from a hydrogen stream contaminated with deuterated methane. Deuterium is a safe and inexpensive replacement for tritium. All tests with deuterium should work as well or better with tritium. Methane was used because it is the molecule with the slowest rate for deuterium or tritium exchange that is likely to be encountered in fusion fuel processing.

In the first HITEX model, a metal reactor was constructed with a water-cooled jacket to maintain the reactor walls at room temperature and thus minimize the permeation of tritium through the reactor walls. The active element in the reactor was 80 cm^2 of platinum wire catalyst. High reactor temperatures, up to 1000°C, were obtained almost instantaneously by passing a current through the wire. The temperature of the wire was obtained by measuring the current and the voltage across the wire to determine the resistance of the wire. Then from tables of platinum wire resistance we could read the temperature as a function of resistance.

At 805°C, complete equilibration of a hydrogen and deuterated methane gas mixture occurred after about 3 minutes of contact in the reactor. Over a period of 24 hours, however, the exchange rate decreased by about a factor of 2. Flowing methane-free hydrogen over the catalyst surface for another 24 hours almost completely restored the activity of the surface. We interpret these results to mean that some cracking of the methane occurred and carbon particles were partially deactivating the catalyst surface. These results were presented at the Fourth Topical Meeting on Tritium Technology in Fission, Fusion and Isotopic Applications, held in Albuquerque, New Mexico, Sept. 29-Oct. 4, 1991, in the paper "Development of a High Temperature Isotopic Exchange Process for Recovering Tritium from Fusion Fuel Impurities", by S.K. Sood, K.M. Kalyanam, K.B. Woodall, and A. Busigin, **Fusion Technology**, Vol. 21, March 1992, pp. 921-925.

Thus, the first reactor model had two main problems: surface deactivation and a long equilibration time. To solve these problems a second model for the reactor was developed that would provide a greater surface area of platinum catalyst, employing platinum on alumina pellets. A greatly increased area would increase the exchange rate, reducing the equilibration time, and would also allow the catalyst to operate at a lower temperature.

The second model was tested in March of 1992. We abandoned the water-cooled walls to test the principles of the HITEX concept in a simple, fast, and cost-effective manner. This report describes the apparatus and the two sets of experiments conducted with the new reactor model. The first set of experiments examined the reactor performance in a once-through configuration to measure the kinetic exchange rate as a function of temperature and gas flow rate. For the second set of experiments, the reactor was placed in a gas circulation loop to simulate the actual operation of HITEX in a fusion fuel cleanup cyle.

2. Experimental Technique

Details of the experimental apparatus and of the methods to acquire and analyze the data are described in Appendix A. Our reactor was essentially a quartz tube packed with pellets of platinum on alumina and placed in an oven. The ends of the reactor extended beyond the oven to make connections for flowing gas and to admit thermocouples to monitor the internal temperature profile. The effective surface area of the platinum catalyst was 5750 ± 1150 m^2, almost six orders of magnitude greater than the area of the platinum wire reactor. A prepared mixture of hydrogen and CD_4 (3.995 ± 0.02 mole%) provided the deuterium used to monitor the experiments. Samples of the gas mixtures produced in the experiments were analyzed by a mass spectrometer to determine the concentrations of H_2, HD, CH_4, CH_3D, CH_2D_2, CHD_3, and CD_4.

3. Kinetics Measurements

The kinetics of the overall H-D exchange reaction, represented by Eqn. 1,

$$CD_4 + 4H_2 \rightarrow CH_4 + 4HD \tag{1}$$

were studied by flowing the CD_4/H_2 gas mixture once through the reactor at a measured flow rate and pressure, then past a sample port to an exhaust port leading to the outside air. Complete equilibration of the feed gas in the reactor would provide a statistical rearrangement of the component atoms to produce all the isotopic substituted molecules. For the given feed gas mixture, we should obtain the ratios listed in Table I. Details of the calculations of the equilibriuim concentrations are given in Appendix B. The square brackets indicate "concentration", so [HD] represents the concentration of HD. For comparison, the initial mole ratio of $[CD_4]$ to $[H_2]$ was 0.0416. Note that the mole ratio $[HD]/[H_2]$ = 0.1665 corresponds to a mole fraction of 0.1427 of HD in hydrogen.

Table I. Calculated concentrations and mole ratios to H_2 of all species in an equilibrated mixture initially 3.995% CD_4 in H_2.

Species x	$[x], (\%)$	$[x]/[H_2]$
H_2	81.82	1.00
HD	13.62	0.1665
D_2	0.566	2.88×10^{-4}
CH_4	2.902	0.0355
CH_3D	0.966	0.0118
CH_2D_2	0.1206	1.47×10^{-3}
CHD_3	6.77×10^{-3}	8.20×10^{-5}
CD_4	1.39×10^{-4}	1.70×10^{-6}

We ran a series of runs with the reactor at different temperatures. For each run we calculated the ratio $[HD]/[H_2]$, the ratio of that to the predicted ratio 0.1665 (see Table I), and the ratio of $[CD_4]$ to $[CH_4]$. The results are summarized in Table II and plotted in Fig. 1. The last two rows in Table II correspond to flowing the feed gas mixture directly to the sampling port, bypassing the reactor, as a test of the sampling procedure and to provide a baseline for the relative measurements on the mass spectrometer. For all the other runs the feed gas mixture passed through the reactor.

Table II. HD and CD_4 equilibrated mole fractions and the kinetic reaction rate coefficient as a function of temperature.

File Reference	Temperature (°C)	[HD]/[H$_2$] (normalized to 0.1665)	[CD$_4$]/ ([CH$_4$]+[CD$_4$])	Kinetic Rate (molecules/ sec)
h318008	372	1.043	0.0032	1.162×10^{20}
h318010	372	1.059	0.0028	1.178×10^{20}
h318012	269	0.159	0.9426	2.024×10^{19}
h318016	270	0.140	0.9641	1.794×10^{19}
h319008	322	0.458	0.4860	5.560×10^{19}
h319010	336	0.671	0.1855	7.890×10^{19}
h319012	357	0.893	0.0160	1.017×10^{20}
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h318014	269	0.369	0.8184	4.549×10^{19}
h319005	115	0.0050	0.9800	6.54×10^{17}
h319014	401	1.005	0.0002	1.126×10^{20}
h319016	403	1.067	0.0002	1.185×10^{20}
h319018	404	1.039	0.0000	1.158×10^{20}
h318005	22	0.0040	0.9779	5.18×10^{17}
h318007	22	0.0034	0.9809	4.50×10^{17}
h320001	22	0.0019	0.9819	---*
h320003	22	0.0014	0.9804	---*

*The feed gas mixture bypassed the reactor.
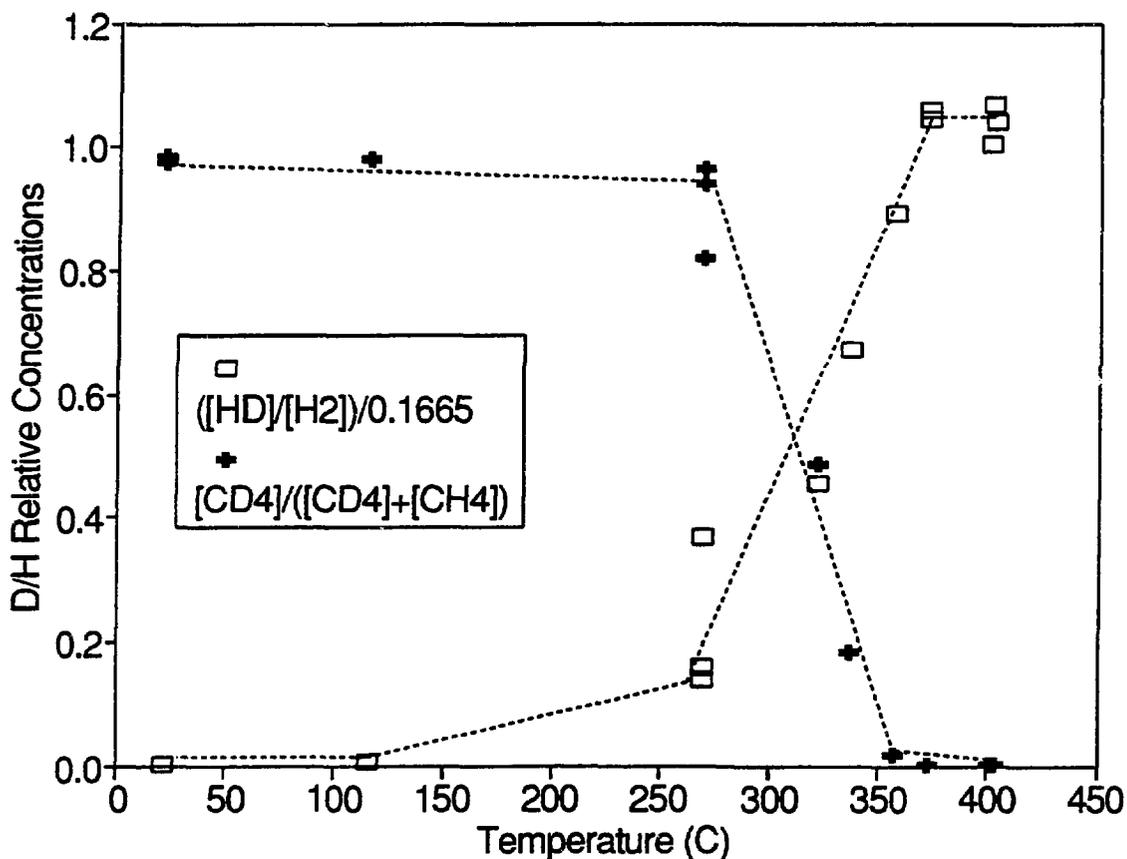**Only values above this line used in linear fit in Fig. 2.

Figure 1. The equilibrium concentrations of the HD and CD_4 relative to H_2 and CH_4 in the gas mixture leaving the reactor in a once-through configuration as a function of the temperature of the midpoint of the reactor.

4. Discussion of the Kinetics

The kinetic rate of production of HD was calculated from the data in Table II and from the input concentration of H_2, 0.0391 mol/L. The concentration of HD in the output stream multiplied by the flow rate, 2.0 L/min, provides the production rate in moles per minute. The calculated rates are listed in Table II and plotted in Fig. 2 in units of molecules per second. The straight line in Fig. 2 is the best fit to the first seven runs listed in Table II, the rows above the dashed row. The line represents the expression

$$k = Ae^{-E_a/RT} \tag{2}$$

where $log A = 24.319 \pm 0.082$ and $E_a/R = 6277$ K (R is the universal gas constant), or $E_a = 12.5$ kcal/mol/K. All the points away from the line in Fig. 2 were not included in the fit for various reasons, not because they did not lie close to this best-fit line. The highest temperature runs were excluded because the CD_4 was completely depleted. One run at 269°C was excluded because the flow rate was much lower than in all the other runs; we only compared runs taken at a flow rate of 2.0 L/min. All the lower temperature runs were excluded because the CD_4 was not sufficiently depleted to show any reaction.

The overall exchange process represented by Eqn. 1 may proceed either by single steps, removing one D atom at each step, or by multiple exchange. Work described in "Catalysis by Metals", by G.C. Bond (Academic Press, 1962), pp. 192-194, demonstrates that multiple exchange is more likely. The reaction rates quoted by Bond, in his Fig. 2 on p. 194, have much higher activation energies, by about a factor of 2, than our calculated E_a. Reading the values off the figure, we obtain $log A=24.3$ with $E_a=20.6$ kcal/mol for the stepwise exchange, and $log A=25.7$ with $E_a=24.4$ kcal/mol for the multiple exchange process, where the units of A are molecules.$(100cm^2)^{-1}$.sec^{-1}.

For comparison with our results, let us consider the multiple exchange process and express Bond's kinetic rate in molecules.m^{-2}.sec^{-1}; thus $k_B=5\times10^{27}e^{-12280/T}$. Taking our experimental rate from Eqn. 2 and dividing by the estimated area of the catalyst in the reactor, 5750 m^2, we obtain $k'=3.6\times10^{20}e^{-6277/T}$ molecules.m^{-2}.sec^{-1}. From Table II, we obtained 100% conversion at 372°C, or 645 K. At this temperature $k_B=2.7\times10^{19}$, and $k'=2.1\times10^{16}$, both in molecules.m^{-2}.sec^{-1}. The corresponding calculation from Bond's values for the stepwise process yields 2.1×10^{19} molecules.m^{-2}.sec^{-1}. Thus, our experimental kinetic production rate is about three orders of magnitude smaller than Bond's rates. Despite this difference in the rates, our rate is sufficient in the present configuration to provide complete production of HD in a single pass at temperatures above 372°C at a flow rate of 2 L/min. The experimental rate of production can be applied to extrapolating the size of the catalyst bed for larger applications.
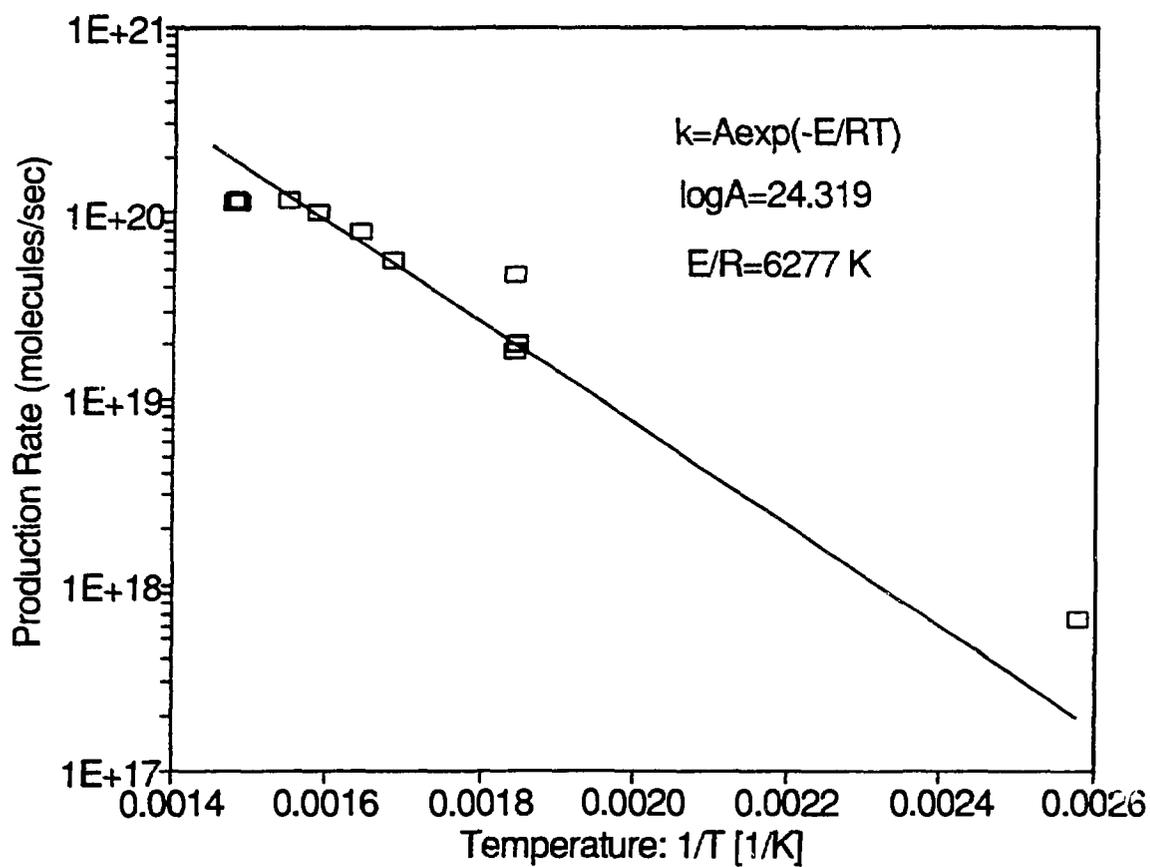
Figure 2. The kinetic rate, k, of production of HD as a function of the temperature of the reactor for the measurements shown in Fig. 1.

5. Dynamics Experiments

The dynamics of the HITEX reactor concept were studied by incorporating the exchange reactor into a recirculating loop containing a 15-L reservoir tank, a compressor and a palladium alloy diffuser, as illustrated in Fig. 3. Details of the loop operation are provided in Appendix A. The compressor provided the driving force to push the gas through the diffuser, and either back into the tank or out of the loop to the exhaust point. The diffuser only passed hydrogen out of the loop, and only about 75% of the hydrogen for the conditions we employed. The remainder of the hydrogen was recirculated through the loop with the methane.

Two dynamic loop runs were performed on consecutive days, March 26 and 27, 1992. Before each run hydrogen, 99.999% pure, was circulated around the loop and through the tank to ensure that the diffuser and compressor were operating normally. Analysis of samples from the hydrogen gas fill before the first run indicated that the reactor had stored a small amount of deuterium from the kinetics measurements, but not enough to affect the results. The conditions of the loop for both runs are listed in Table III. Samples were taken just after the loop started with the 4% CD_4 in H_2 gas mixture and every 5 minutes for the first 30 minutes, and then every 10 minutes until the end of the tests, about 75 minutes both times. The excess concentration of HD, expressed as ppm by volume, and the concentration of CD_4 relative to CH_4 are plotted in Fig. 4 and 5 as a function of time for the two runs. The data values are listed in Table IV. The baseline concentration of HD was taken as 121 ppm by volume, so the excess concentration of HD is the difference between the measured concentration and the baseline concentration. In Fig. 5, the dashed line labelled as "noise level" indicates the lowest reliable value of the relative CD_4 concentration based on the background signal of the mass spectrometer.
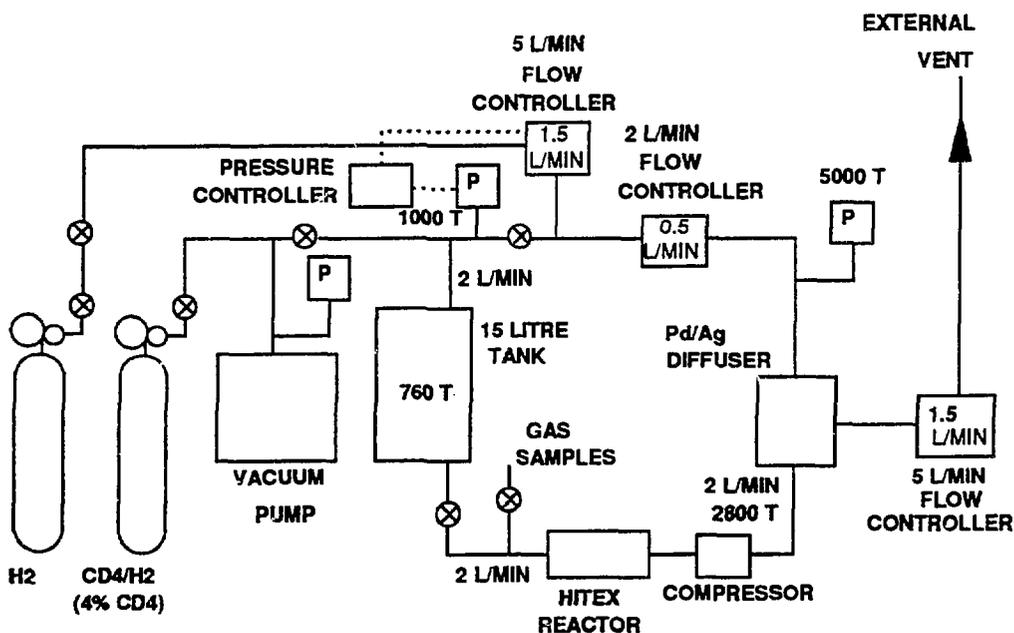
HITEX REACTOR LOOP TEST

Figure 3. A schematic diagram for the loop test of the HITEX reactor. The pressures and flow rates indicated in the diagram are typical values, similar but not identical to the values achieved in the experiments.

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Table III. Conditions for dynamics measurements of the HITEX loop.

Parameters	Run 1	Run 2
Bleed Flow: Channel 2 (L/min)	0.50	0.40
Exit Flow: Channel 3 (L/min)	1.25 - 1.30	1.20
Loop Flow (L/min)	1.75 - 1.80	1.60
Tank Pressure (torr)	780	780
Diffuser Pressure (torr)	1770	1790
Reactor Temperature (°C)	410 - 416	415 - 423

HD Concentration in Loop Tests
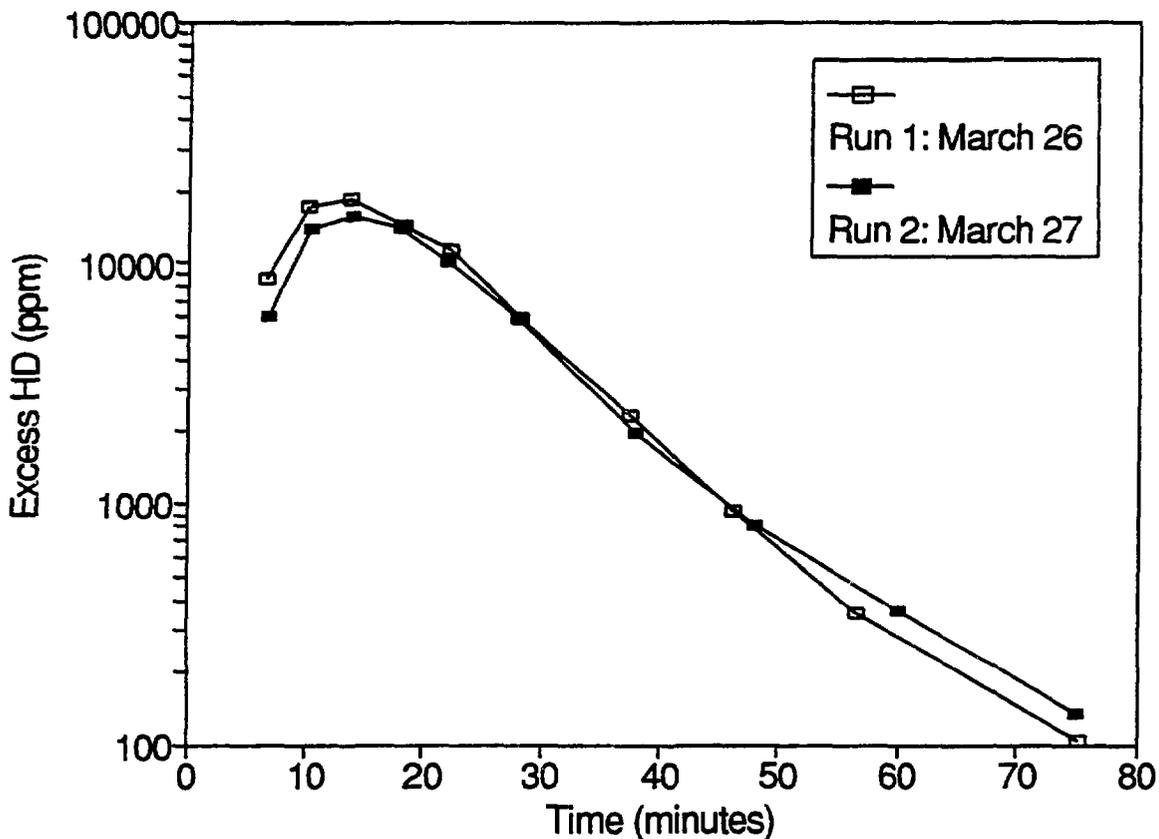### March 26-27, 1992

Figure 4. The excess concentration of HD in the loop measured just before the reactor during the two runs. Excess HD concentration is the difference between the measured concentration and the concentration in the make-up hydrogen stream. Time zero corresponds to starting the compressor after filling the 15-L tank with the mixture of 4% CD_4 and H_2. After 25 minutes all the CD_4 has disappeared (see Fig. 5).

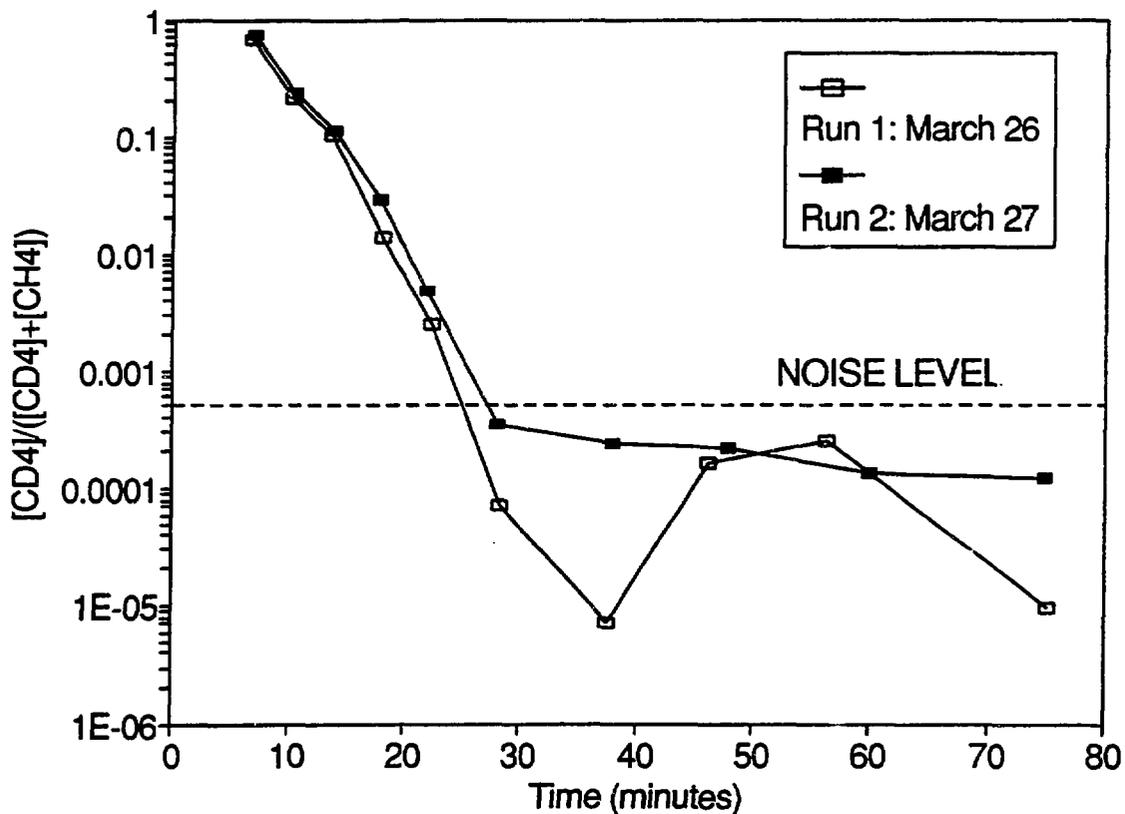# CD4 Concentration in Loop Tests
March 26-27, 1992

Figure 5. The relative concentration of CD_4 with respect to CH_4 in the loop during the two runs. The line at 0.0005 relative concentration, labelled "noise level", corresponds approximately to the lower limit of reliable signal at mass 20 (CD_4) as determined by the background signal in the mass spectrometer.

Table IV. Relative Concentration of CD_4 in CH_4 and the HD excess concentration as a function of time for the two dynamics experiments.

Run 1: March 26, 1992			Run 2: March 27, 1992		
Time (min)	$[CD_4]/([CH_4]+[CD_4])$	HD Excess (ppm)	Time (min)	$[CD_4]/([CH_4]+[CD_4])$	HD Excess (ppm)
1.75	0.9776	0	1.30	0.9747	1
6.75	0.6582	8692	6.93	0.7081	6011
10.25	0.2132	17460	10.50	0.2271	13789
13.75	0.1012	18562	14.00	0.1094	15829
18.22	0.0137	14496	18.00	0.0279	13910
22.30	2.39E-03	11346	22.00	4.69E-03	10189
28.22	7.09E-05	5961	28.00	3.47E-04	5826
37.50	7.25E-06	2304	38.00	2.37E-04	1994
46.28	1.61E-04	929	48.03	2.16E-04	812
56.48	2.52E-04	352	60.00	1.35E-04	358
75.22	9.53E-06	105	75.00	1.20E-04	136

6. Discussion of the Dynamics

All four of the data sets for the HD excess and relative CD_4 concentrations exhibit an exponential decay. The best-fit values for the decay constants calculated over the straightest sections of the data sets are listed in Table VI.

A simple model for the loss of HD from the loop through the diffuser gives the rate of loss as the ratio of the exit flow to the loop volume. The values calculated by this model are also listed in Table VI. The measured values are within about 30% of the model predictions.

The rate of loss of CD_4 from the loop is determined only by the rate of mixing of the make-up hydrogen with the initial gas mixture in the tank. No CD_4 leaves the reactor because, according to the kinetics experiments, the reactor temperature is sufficiently high to deplete all the CD_4 on a single pass.

Table V. Decay rates for the dynamics experiments.

Decay Rates	Run 1	Run 2
$-dln[CD_4]/dt$ (min^{-1})	0.4156 ± 0.0040	0.3974 ± 0.0177
$-dln[HD]_{ex}/dt$ (min^{-1})	0.1017 ± 0.0013	0.0983 ± 0.0026
Exit Flow/Volume	0.0751 ± 0.0013	0.0721 ± 0.0007

7. Conclusions

The principles of HITEX fusion fuel cleanup have been demonstrated successfully in a flow loop using deuterium as a model for tritium. Hydrogen contaminated with 4% CD_4 was treated to remove the deuterium atoms down to the level of deuterium in a replacement stream of hydrogen. A reactor filled with platinum catalyst on alumina pellets at about 400°C isotopically equilibrated the H and D atom distribution in the hydrogen and methane gas mixture. Most of the D atoms transferred to the hydrogen. The equilibrated mixture passed through a palladium alloy diffuser to remove up to 75% of the hydrogen from the loop. The remaining gas was mixed with a pure hydrogen stream to restore the original pressure, about 100 kPa, before passing through the reactor again.

Methane is the molecule with the slowest rate for deuterium or tritium exchange likely to be encountered in fuel processing. The temperature of the reactor was high enough to provide complete isotopic equilibration of the methane with the hydrogen in a single pass, as determined separately by kinetics measurements in a single-pass configuration. Two complete loop flow runs on consecutive days demonstrated identical operation at flow rates of 1.6 - 1.8 L/min. Deuterium was removed rapidly from the methane, producing HD, and then more slowly out of the loop as HD. After 75 minutes, the HD concentration dropped from a high of 2% down to 100 ppm above the natural concentration of HD in the make-up stream. The temperature of the reactor was low enough to minimize any cracking of the methane which would deposit carbon on the catalyst and reduce the exchange rate. No reduction in the exchange rate was observed in over two weeks of tests on the reactor.

The success of this model of the HITEX reactor provides a solid basis for designing a practical system for tritium decontamination in a fusion fuel cleanup cycle. The reactor could be run at temperatures much lower than 400°C by employing a larger quantity of catalyst. This would further reduce the risk of methane cracking and

would simplify the design of a reactor with low-temperature walls to minimize tritium permeation.

8. Acknowledgements

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HDM:HDM:CB

Appendix A: Experimental Details

A1. Apparatus

The reactor for the HITEX experiments was a quartz tube, 21.8 mm I.D., 25 mm O.D. and 60 cm long, packed with pellets of platinum on alumina (Johnson Mathey) for a length of 31.5 cm. The column of pellets was maintained in place, closer to the inlet end, by 3 cm of quartz wool at each end. The ends of the tube, beyond the quartz wool plugs, were empty except for three K-type thermocouple leads at the inlet end. The thermocouple leads were each protected by a jacket of fibre insulation capable of withstanding temperatures up to 650°C. The thermocouples were located at approximately 4.5 cm, 16.5 cm and 27 cm along the pellet column measured from the inlet side. The reactor tube was placed in a tube oven such that the quartz wool plugs were even with the ends of the oven. Additional quartz wool was wrapped around the outside of the tube at the oven walls to improve the insulation, and hence the temperature profile along the tube. As the heater coils of the oven did not heat the entire length uniformly, the effective length of the catalyst bed was less than the physical length. Based on measurements of the temperature profile we estimated that about half the catalyst bed, 16 cm, was at or very near the mid-bed temperature. At either end the temperature dropped toward room temperature. As the isotope exchange rate falls rapidly with temperature, only the middle 16 cm contributed significantly to the exchange reaction. An additional thermocouple was placed on the outer wall of the quartz tube near the centre. The temperature difference between that external point and the middle thermocouple inside the tube was never greater than 5°C.

The pellets are cylindrical in shape with a uniform diameter of 3.2 mm. The masses and lengths of 10 pellets were measured to determine their real density, 1.77 g/cm^3. The packing density was determined by weighing the mass of the pellets, 113.2 g, and calculating the packed volume, 115.7 cm^3 from the dimensions of the quartz tube less the volume occupied by the thermocouple leads. Thus, the packing density was 0.978 g/cm^3. From these densities we find that the real volume occupied by the pellets was 64.0 cm^3 and the space volume was 51.7 cm^3. From the ratio of the effective length to the real column length, 16 cm in 31.5 cm, the space volume in the effective region of the reactor was 26.3 cm^3. This volume was used to calculate the transit times of gas flow through the reactor.

The surface area of the pellets determines their effectiveness as a catalyst. The manufacturer of the pellets quotes a surface area of 80-120 m^2/g; let us take 100±20 m^2/g for the calculation. The total mass of the pellets in the reactor was 113.2 g, so the mass of pellets in the effective volume was 57.5 g, for an estimated effective surface area of 5750±1150 m^2. The platinum content on the alumina is 0.53% by weight.

The ends of the quartz tube reactor were sealed by O-rings on adapters to KF-type vacuum fittings. The inlet adapter was connected to a KF-tee to take out the thermocouple leads on the branch of the tee. The leads were soldered to a multi-pin connector potted in a glass feedthrough. External wires connected the pins to a digital thermocouple readout for direct readings in degrees Celsius or to a digital multimeter for readings in millivolts. The oven could be heated to over 700°C, more than adequate for these experiments.

In preparation for the experiments, the pellets were heated up to 690°C in the presence of slowly flowing hydrogen gas to reduce the surface oxides, producing a few tens of millilitres of water. After two days of this treatment no more water was produced. The hydrogen used for this procedure and for the remainder of the experiments was 99.999% pure. A prepared mixture of hydrogen and CD_4 (3.995±0.02 mole%) provided the deuterium used to monitor the experiments. Samples of the gas mixtures produced in the experiments were analyzed by a mass spectrometer to determine the concentrations of H_2, HD, CH_4, CH_3D, CH_2D_2, CHD_3, and CD_4.

A2. Kinetics Experiments

The flow rate of the CD_4/H_2 gas mixture through the reactor was controlled by a mass flow controller in the line before the reactor, and the pressure was measured by a capacitance manometer. To conserve the CD_4/H_2 gas supply, the gas flow was turned on long enough to sweep out all the gas at least twice from the mass flow controller to the exhaust port. We estimated that volume as about 300 ml. At the maximum flow rate of 2.0 L/min, sweeping out this volume twice required less than 20 seconds, and some measurements were taken after 40 seconds of flow at 2.0 L/min.

To take a sample the gas flow was stopped and the exhaust port closed. Gas drawn from the sample port consisted of gas taken from the extended line of tubing between the exit of the reactor and the exhaust port. The sample port consisted of a tee in the line just before the exhaust port that led to a valve on a second tee, the sampling tee. One branch of the sampling tee connected to a removable sampling container and the other branch was a vacuum line, controlled by a valve. The sample containers had a volume of about 1 ml, and were evacuated and sealed on the sampling tee. To draw fresh gas from the reactor effluent, the 7-ml volume of the sampling tee was filled, evacuated and filled again. Then the sample container was opened to fill the container, sealed, and removed to the mass spectrometer for analysis.

The calculated [HD]/[H_2] ratios were obtained in two steps by first correcting the ratio of the mass 3 to mass 2 signals for the H_3^+ signal, produced by ionization of H_2 and then recombination in the ionizer of the mass spectrometer. The corrected mass 3 to mass 2 ratios were then adjusted for the [HD]/[H_2] calibration of the instrument, determined separately using known mixtures of HD in H_2. From these final corrected

ratios we obtained the HD mole fraction to calculate the kinetic rate. The final ratios appear in Table II and Fig. 1 normalized by the predicted [HD]/[H$_2$] ratio, 0.1665.

The calculated [CD$_4$]/([CH$_4$]+[CD$_4$]) ratios were obtained from the mass spectrometer signals at masses 20 and 16 without any corrections. Taking the signals at masses 20 and 16 neglects the ionization splitting of the methanes in the mass spectrometer. In effect, these masses represent only part of the true CD$_4$ and CH$_4$ signals. As this problem was only realized after the experiments, no correction was possible except to make the reasonable assumption that the ionization splitting was identical for all methanes. In other words, masses 20 and 16 probably represent the same fraction of the true CD$_4$ and CH$_4$ signals. This assumption is confirmed by the methane ratio reported in the last two rows of Table II.

A3. Dynamics Experiments

The driving force in the loop was a metal bellows pump (Parker Hannifin Corp., Metal Bellows Div., model MB-111) serving as a compressor. The output of the pump was connected directly to the feed inlet of a hydrogen purifier (Johnson Mathey, model HP-25). The main component of the purifier is palladium alloy diffuser that passes pure hydrogen when heated to between 400 and 425°C; all other gases in the feed stream leave the purifier through a bleed flowmeter. The pure hydrogen outlet was connected to a flow controller, denoted as Channel 3 with a maximum flow of 5 L/min, that exhausted through a manual shut-off valve to an external vent at atmospheric pressure. The bleed stream outlet was connected to another flow controller, denoted as Channel 2 with a maximum flow of 2 L/min, to continue the loop into the top of the tank, volume 15.14 L. A pressure gauge on the line to the Channel 2 flow controller monitored the pressure achieved by the compressor at the diffuser. That pressure and the flow through Channel 2 determined the maximum outflow through Channel 3. In the experiments, Channel 3 was only used as a flow meter, not as a controller, because the pressure in the diffuser was too low to pass sufficient hydrogen for the split we wanted: 25% through Channel 2 and 75% through Channel 3 at a total flow rate of 2 L/min.

At the top of the 15-L tank, a pressure gauge monitored the tank pressure. A pressure controller took that pressure as input to control the make-up flow of pure hydrogen through a flow controller, denoted as Channel 1 with a maximum flow of 5 L/min. The PID control parameters on Channel 1 were set to minimize the pulsations of the delivery from the regulator on the hydrogen gas supply. Under normal operation of the loop flow, the make-up flow through Channel 1 exactly balanced the outflow through Channel 3. The make-up flow from Channel 1 combined with the flow from Channel 2 and mixed in the 15-L tank. The mixture in the tank flowed out the bottom past a gas sampling port into the reactor, completing the loop.

To prepare the apparatus for a dynamic loop test, the entire system was evacuated. Under vacuum, the diffuser and the reactor were turned on and allowed to heat up to their operating temperatures before filling the tank and the rest of the loop elements with pure hydrogen to check the loop operation. Initially the loop pressure was 780 torr, and the pressure controller on Channel 1 was set to maintain the tank pressure at 780 torr. With the compressor off, the total effective volume of the tank and loop was 16.09 L, as compared to 16.64 L with the compressor operating. Samples of the hydrogen gas were taken with the loop operating to provide a reference for the experiments with the H_2/CD_4 mixture. With no gas flowing, the tank was isolated from the rest of the loop and then evacuated to less than 50 mTorr before filling the tank to 780 torr with the H_2/CD_4 mixture.

The gas sampling port was on a tee in the line between the tank and the reactor. A manual valve on the tee branch was connected to another tee that was connected to a vacuum line through a valve, and to a removable sample container, just as in the kinetics experiments. The sample container was also the same as used in the kinetics experiments. A series of six sample containers were used to allow enough time to analyze each sample on the mass spectrometer before the container was required for another sample during the experiments.

To take a sample, first a sample container was attached and the sampling line and container evacuated. Then the sample container was closed to keep it clean. The sampling line was filled by operating the valve on the tee from the reactor line, opened and closed within about 1 second, and then evacuated for 15 seconds. This fill and evacuation was repeated once more before filling the sampling line for a third time and then filling the sample container from the sampling line. Then, the sample container was closed and removed to the mass spectrometer to analyze the gas.

A4. Temperature Distibution in the Reactor

The temperature noted in Table III as the reactor temperature and the temperatures used to plot the data in Fig. 4 and 5 were the temperatures obtained at the external thermocouple at the midpoint of the reactor. During the preparation for the first dynamics experiment, the temperatures of all the thermocouples were observed. The temperature profiles obtained under conditions of no flow and after various time intervals of flow at 2 L/min are listed in Table A1. These results were applied to estimating the effective length of the reactor as discussed above in Section A1.

Table A1. Temperature profile, in degrees Celsius, of the HITEX reactor.

Flow Condition	External Midpoint	Internal Entrance	Internal Midpoint	Internal Exit
Static	408	240	410	339
2 L/min after 5 min	407	143	406	363
2 L/min after 10 min	406	137	403	365
2 L/min after 20 min	403	130	399	347

Appendix B: Isotope Equilibration Probabilities

The mole ratios in Table I of the report derive from a statistical distribution of the H and D atoms between the hydrogen and methane. First consider the case of the hydrogen alone. If we let h represent the total number of H atoms in the hydrogen, and d represent the total number of D atoms in the hydrogen, then $n = h + d$ is the total number of atoms in the hydrogen molecules. The combinatorial probability for the appearance of H_2 is

$$
\begin{aligned}
P(H_2) &= \frac{h!}{(h-2)!} \cdot \frac{(n-2)!}{n!} \\
&= \frac{h(h-1)}{n(n-1)} \\
&\cong \frac{h^2}{n^2}
\end{aligned}
\tag{B1}
$$

where the approximation is valid for large numbers, i.e. mole quantities. Similarly the probabilities for HD and D_2 are

$$
\begin{aligned}
P(HD) &= 2\frac{h!}{(h-1)!} \cdot \frac{d!}{(d-1)!} \cdot \frac{(n-2)!}{n!} \\
&\cong \frac{2hd}{n^2}
\end{aligned}
\tag{B2}
$$

$$
P(D_2) \cong \frac{d^2}{n^2}
\tag{B3}
$$

Note that the sum of the probabilities for H_2, HD and D_2 is 1, as it should be. Now consider the methane molecules, and let h, d and n represent the numbers of H and D atoms and their sum in all the methane. We will assume that all the C atoms are one isotope here, but the calculations for including different isotopes of carbon follow the same lines. Thus, the combinatorial probability for the appearance of CH_4 is

$$
\begin{aligned}
P(CH_4) &= \frac{h!}{(h-4)!} \cdot \frac{(n-4)!}{n!} \\
&\cong \frac{h^4}{n^4}
\end{aligned}
\tag{B4}
$$

The probabilities for the other methane molecules are calculated similarly:

$$P(CH_3D) = 4\frac{h!}{(h-3)!} \cdot \frac{d!}{(d-1)!} \cdot \frac{(n-4)!}{n!}$$

$$\cong \frac{4h^3d}{n^4}$$

(B5)

$$P(CH_2D_2) = 6\frac{h!}{(h-2)!} \cdot \frac{d!}{(d-2)!} \cdot \frac{(n-4)!}{n!}$$

$$\cong \frac{6h^2d^2}{n^4}$$

(B6)

$$P(CHD_3) = 4\frac{h!}{(h-1)!} \cdot \frac{d!}{(d-3)!} \cdot \frac{(n-4)!}{n!}$$

$$\cong \frac{4hd^3}{n^4}$$

(B7)

$$P(CD_4) = \frac{d!}{(d-4)!} \cdot \frac{(n-4)!}{n!}$$

$$\cong \frac{d^4}{n^4}$$

(B8)

Again, note that the sum of the probabilities for all the methane molecules is 1.

So far we have treated the hydrogen and methane molecules separtely. Now let us calculate the concentrations of each species in a mixture, starting with CD_4 and H_2 only, and then equilibrating the isotopic distribution of the H and D atoms. Assume that we have 1 mole of molecules total, and that a fraction x is methane, then the fraction *1-x* is hydrogen. In the experiments, x=3.995%.

Therefore, there are a total of *4x* moles of D atoms and *2(1-x)* moles of H atoms, and the total number of H and D atoms is *2(1+x)* moles. In the final distribution of H and D atoms, the concentration of D atoms in both the hydrogen and the methane will be

$$\frac{d}{n} = \frac{4x}{2(1+x)} \cong 0.07683$$

<div align="right">(B9)</div>

and the concentration of H atoms will be

$$\frac{h}{n} = \frac{2(1-x)}{2(1+x)} \cong 0.9232$$

<div align="right">(B10)</div>

Armed with these concentrations, we can quickly calculate the probabilities for all the hydrogen and methane species as listed in Table I in the report.