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TRITIUM PERMEATION THROUGH
OXIDIZED 304 AND 316 STAINLESS STEEL

J. C. McGuire
Hanford Engineering Development Laboratory
Richland, Washington 99352

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INTRODUCTION

This work was completed during the course of a cooperative program with ANL on Tritium Transport in Liquid Metal Cooled Reactors(1). Savage and Strehlow(2) have shown that tritium permeation rates through metals did not show strict dependence on the half power pressure law. Reviewing the literature in the tritium diffusion field, one can readily see a wide diversity of opinion on both the response of permeation rate to pressure, and the effect of oxide layers on total permeation rates.

This work considers conditions encountered in operating reactors. It involves hydrogen, deuterium and tritium permeation measurements on "clean" and oxidized surfaces. The tritium measurements were restricted to permeation rates from sodium and through the test membrane at concentrations typical of EBR-II reactor experience. The hydrogen and deuterium work measured permeation rates at gas pressures from 13-1300 Pa (0.1 to 10 Torr).

SUMMARY

Permeation rates were measured for tritium permeation through oxidized 304 and 316 stainless steel. The tritium was injected into hot flowing sodium at concentrations near present sodium cooled reactor operating levels. Permeation data are presented as a function of temperature, oxidation time and tritium activity level in the sodium. Permeation rates were determined at 590, 540 and 480°C and at tritium concentrations varying from 1 to 40 x 10^{-9} CiT_2/gmNa (3.4 x 10^{-8} to 1 x 10^{-6} ppm). At 540°C tritium diffusion rates for both oxidized steels were in the range 1-2 x 10^{-4} $\frac{\text{cc-mm}}{\text{hr-cm}^2\text{-atm}^{1/2}}$. Response at this concentration varied as the square root of pressure. However hydrogen (H_2) and deuterium permeation tests at 1300 to 13 Pa (10 to 0.1 Torr.) showed linear response to changes in this higher pressure range.

The effect of oxidation temperature on H_2 permeation rate change was measured. Oxidation of 304 SS at 750°C for 24 hours lowered the H_2 permeation rate by two orders of magnitude. An identical membrane oxidized at 550°C for 500 hours dropped in permeation rate by only a factor of 4. Auger Electron Spectroscopy (AES) analysis revealed a difference between the oxide layers resulting from the high and low temperature treatments. A comparison of hydrogen and deuterium diffusion rates through 304 SS at 13-1300 Pa confirms adherence to the $\frac{1}{\sqrt{M}}$ law.

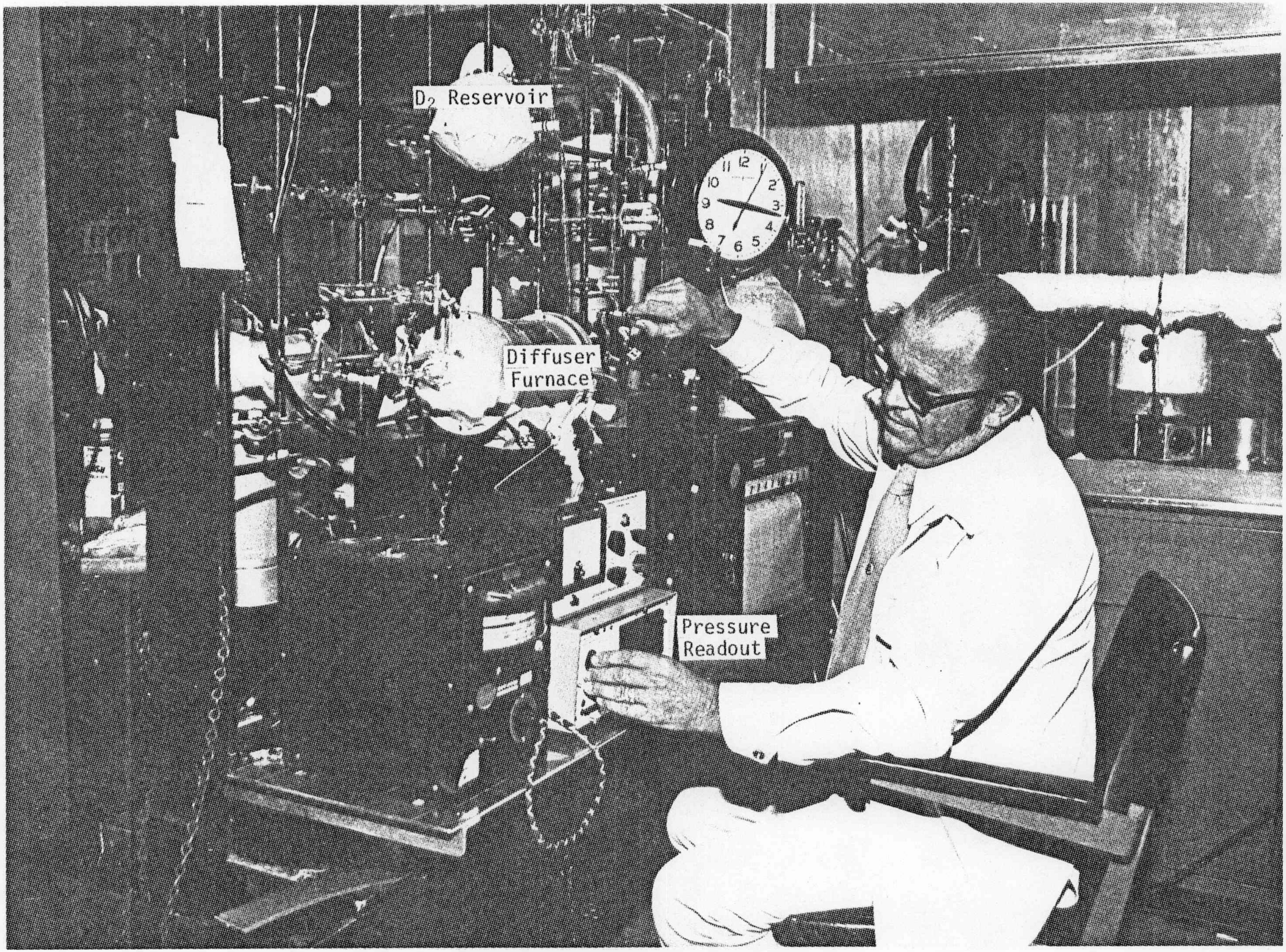
Hydrogen-Deuterium Permeation

Experimental Equipment

The hydrogen-deuterium research was conducted in the pressure range 13-1300 Pa (0.1-10 torr). Experimental equipment was a glass vacuum line (Figure 1) of the design shown in Figure 2. This is a simple permeation measurement system where a small calibrated volume is connected to one side of the diffusion membrane. The small volume contains a capacitance manometer having three pressure ranges and a digital readout.

The 304 SS diffuser was 91 cm (36") of 0.32 cm (0.125") O.D. tubing with 0.4 mm (0.015") wall. This tubing was wound on a 1.27 cm (0.5") mandrel to obtain a compact coil 6.4 cm (2.5") long and 2.5 cm (1.0") O.D. (Figure 3) with a surface area of 50 cm^2.

The coil was connected by mechanical fittings to two penetrations in the fused silica heater chamber. The inside area of the diffuser coil was a part of the small calibrated volume containing the capacitance manometer. Total volume in the pressure measurement system was less than 50 cm^3. As a result, any pressure change of 0.001 Torr represents 6.5×10^{-5} cm^3(STP) or 1.1×10^{-6} cm^3 per cm^2 of diffuser area. The diffuser was heated by a tubular-resistance furnace. Permeation studies were made over the range 350-750°C, with emphasis on the 350-550°C temperature range.



HYDROGEN DIFFUSION APPARATUS

FIGURE 1

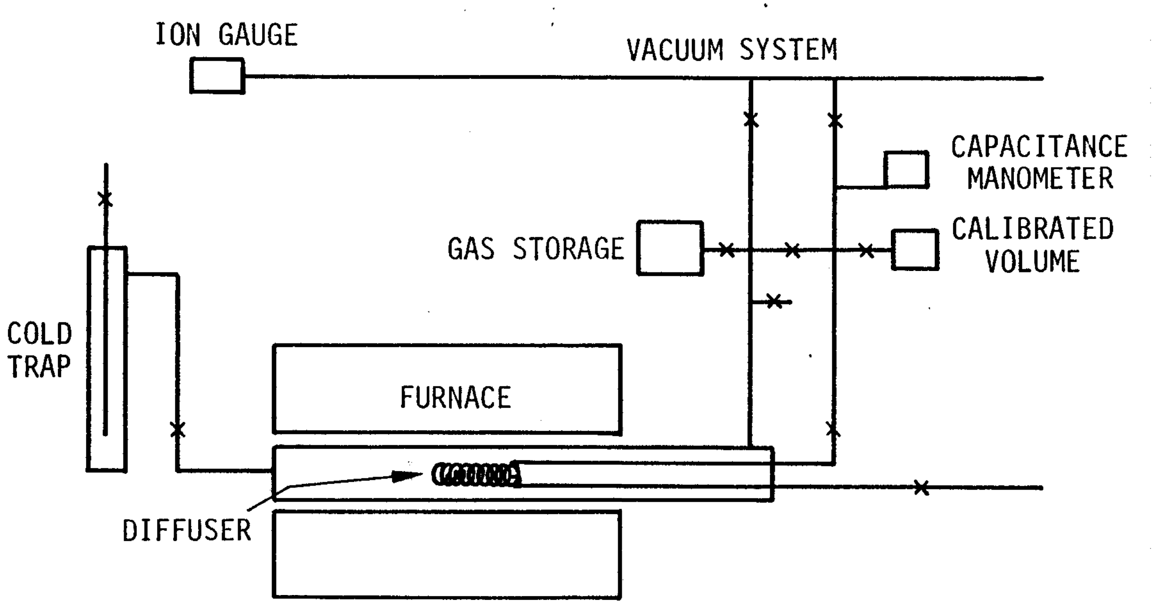


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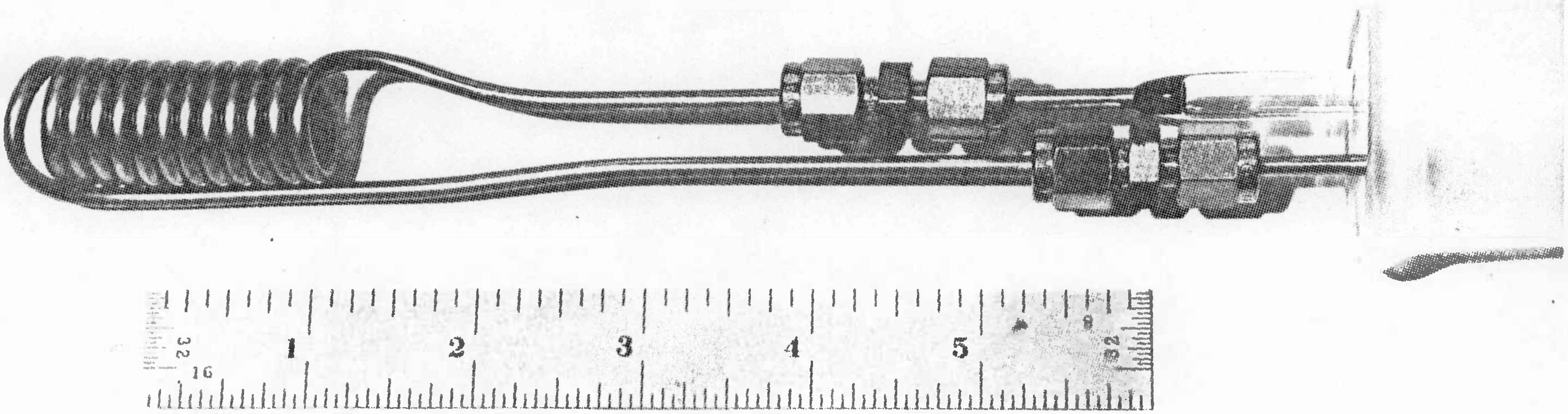
FIGURE 2 Schematic of Hydrogen/Deuterium Permeation System.



TYPICAL DIFFUSION MEMBRANE

FIGURE 3

In operation, hydrogen or deuterium was added on the downstream side then passed through the diffuser into the calibrated volume to the required starting pressure, usually 1300-1560 Pa (10-12 torr). This technique eliminated potential for spurious results from impurities in the tank gas. Total leakage rate in the system with the diffuser chamber at 550°C was 2×10^{-9} cm^3/sec (5×10^{-6} torr-liter/hr) attributable to helium diffusion through the Pyrex walls of the segment.

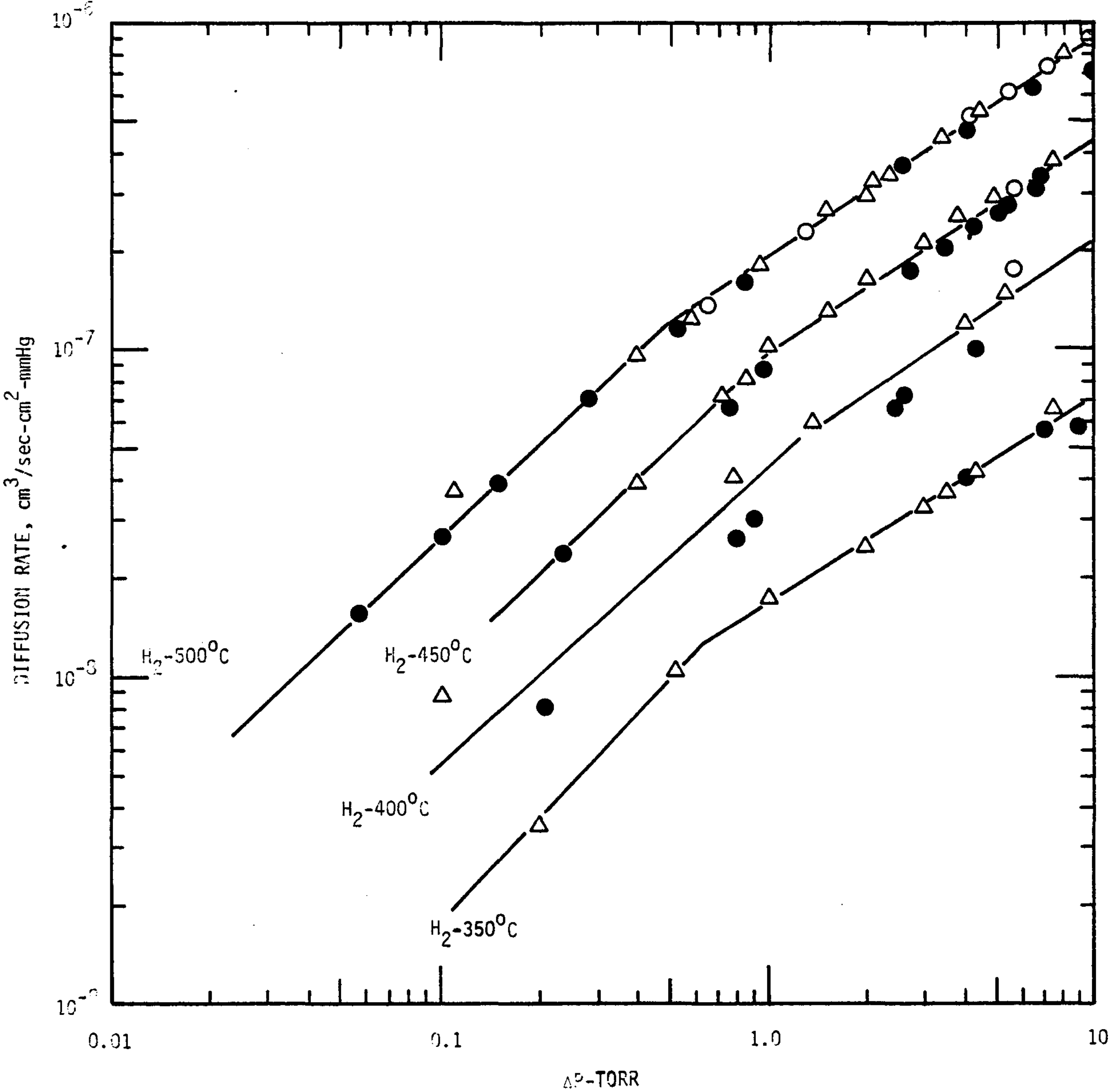
Experimental Results

It was apparent that in the pressure range 13-1300 Pa (0.1-10 torr) H_2 and D_2 permeation rates approached a linear function of pressure. Although half power pressure dependence is clearly seen at very low hydrogen partial pressures, in this higher pressure range the dependence is as is shown in Figure 4.

Very clean membranes exhibit half power pressure dependence over a wider pressure span than oxidized materials.

Hydrogen and deuterium permeation rates through 304 SS were determined at 350-550°C. The data in Figure 5 show permeation dependence on $\frac{1}{\sqrt{M}}$ law as expected.

In early experiments we tested the effect of oxidation temperature on hydrogen permeation. As an example we found that a membrane oxidized for 200 hours @ 750°C had 20 times lower permeation rate than one oxidized for 750 hours @ 550°C. Auger (AES) analysis revealed that the surfaces of the two specimens were entirely different. The specimen treated at 750°C had a high concentration of Mn, Cr and O within the first 2000 Å of surface while the 550°C specimen had only Fe and O in the same area. The Mn/Cr/O complex has been identified as a highly protective layer before.(2) This material has been found at HEDL on outside surfaces of sodium loops operating at 500-600°C for 6000 hours or more. Therefore the formation appears to be time dependent.



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H_2 PERMEATION RATES AS A FUNCTION OF TEMPERATURE AND PRESSURE

FIGURE 4

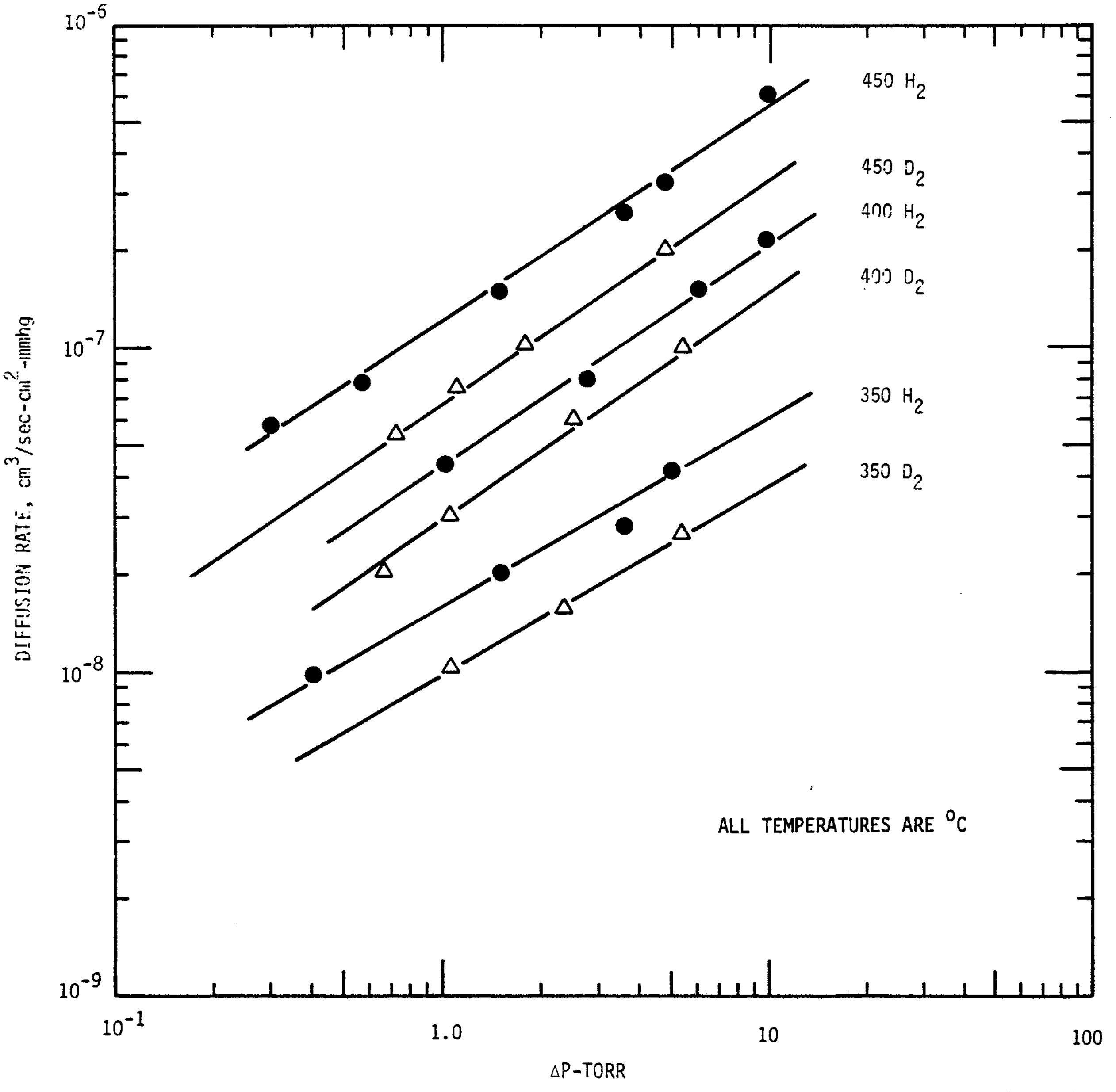

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FIGURE 5. DIFFUSION RATES FOR HYDROGEN AND DEUTERIUM BEFORE OXIDATION--304 SS

TABLE 1

#1 & #2 DIFFUSER

COMPARATIVE AUGER ANALYSES

DEPTH Å	$\%O_2$		%Cr		%Mn	
	750°C	550°C	750°C	550°C	750°C	550°C
50	8.13	7.07	16.46	0	14.24	0
200	7.26	6.11	27.42	0	16.80	0
500	6.61	6.20	36.06	10.05	18.64	0
2000	8.01	4.73	46.69	13.45	20.49	0
7500	7.24	.61	47.06	16.98	14.26	0

	%Fe		%Ni	
	750°C	550°C	750°C	550°C
50	39.84	67.17	4.49	17.15
200	35.65	69.74	3.56	16.48
500	28.79	65.83	2.71	12.54
2000	17.22	63.53	3.24	13.56
7500	23.24	64.96	4.69	14.59

Permeation tests using hydrogen and deuterium showed that it is very difficult to maintain a truly clean surface in vacuum or argon. What appears to be a "clean" surface is in fact covered by a thin layer of adherent oxide which offers some significant barrier to hydrogen permeation. This barrier can be destroyed at 550°C by the first contact with a strong oxidizing medium such as air and as a result there is a sharp increase in permeation rate which is reversed within 20 hours to be followed by the usual gradual decay as the long term permeation resistant oxide layer is formed, as seen in Figure 6.

The dispute over "clean" surfaces is academic in view of the conditions encountered in operating liquid metal cooled fission or fusion reactors. In operating reactors, surfaces exposed to air or reactor containment gas (99%N_2, 1%O_2) are <u>not</u> clean. By the time a reactor achieves full temperature operation all exposed surfaces act as barriers to tritium permeation to some degree. The only surfaces which will exhibit classical predictable diffusion characteristics will be the Intermediate Heat Exchanger (IHX) tubes in contact with sodium. Here tritium in primary sodium can be transferred to secondary sodium at rates two or three orders of magnitude faster than those seen in sodium/membrane/vacuum or sodium/membrane/gas transfer.

Tritium Permeation

Experimental Equipment

Tritium permeation experiments were carried out in Source Term Control Loop #3 (Figure 7). This is a pumped sodium loop containing 17 liters (4.5 gal) of sodium pumped at 7.6 liters (2 gal) per minute. The loop is equipped with bypass cold trap, oxygen meters, multipurpose sampler, flowmeters and three experiment test positions. Tritium control experiments required three modifications to the loop: a Tritium Injection System, a Tritium Meter and a Tritium Diffusion test section. (Figure 8) Each of these is basically a diffuser consisting of a sealed hollow tube with gas inlet and outlet. The outside surface is exposed to sodium and the inside surface exposed to a

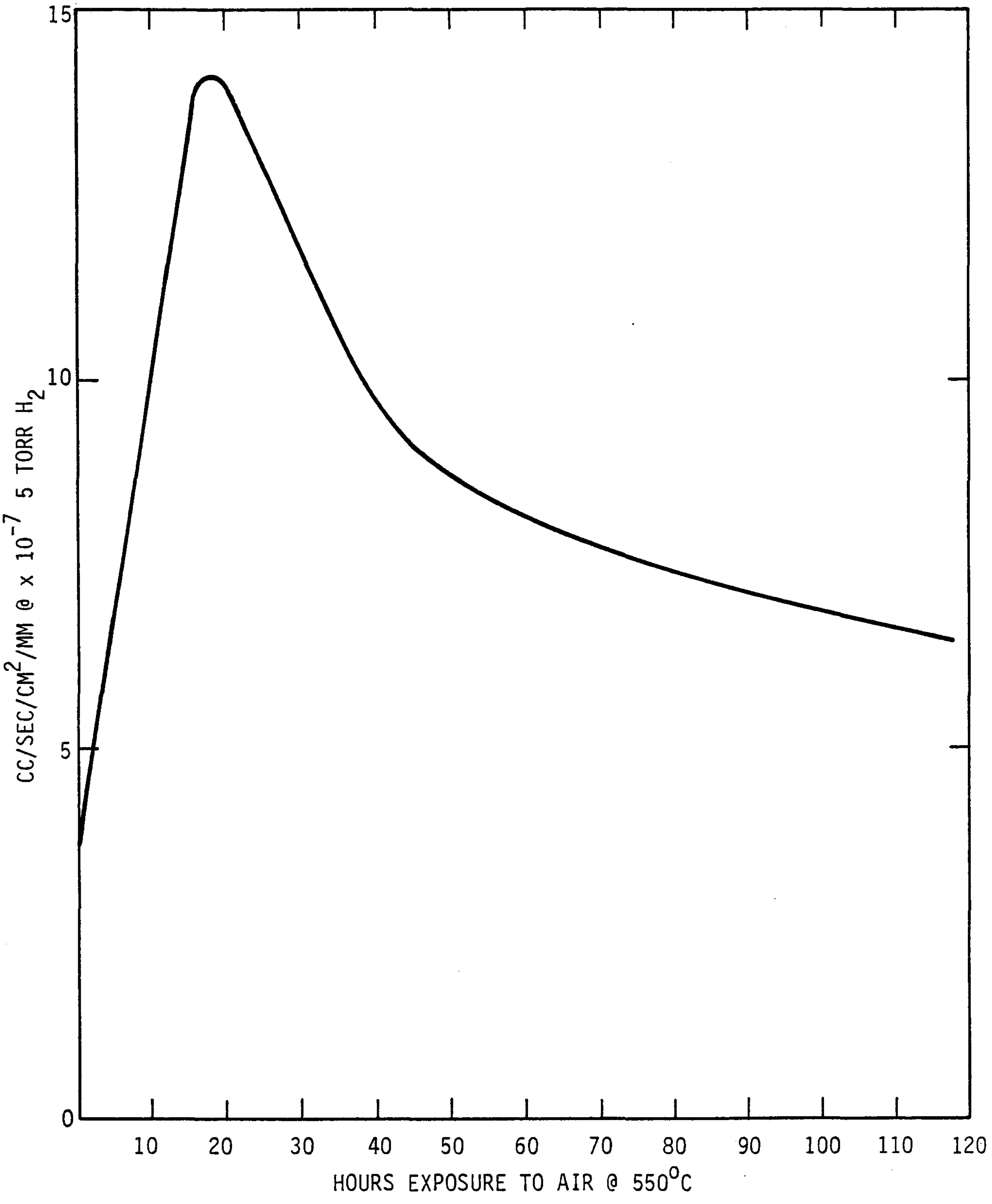

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FIGURE 6 Variation of Hydrogen Permeation Rate With Time for a 304 SS Diffuser Exposed to Air at 550°C.

ENGINEERING FLOW DIAGRAM STCL NO. 2, NO. 3, AND NO. 4

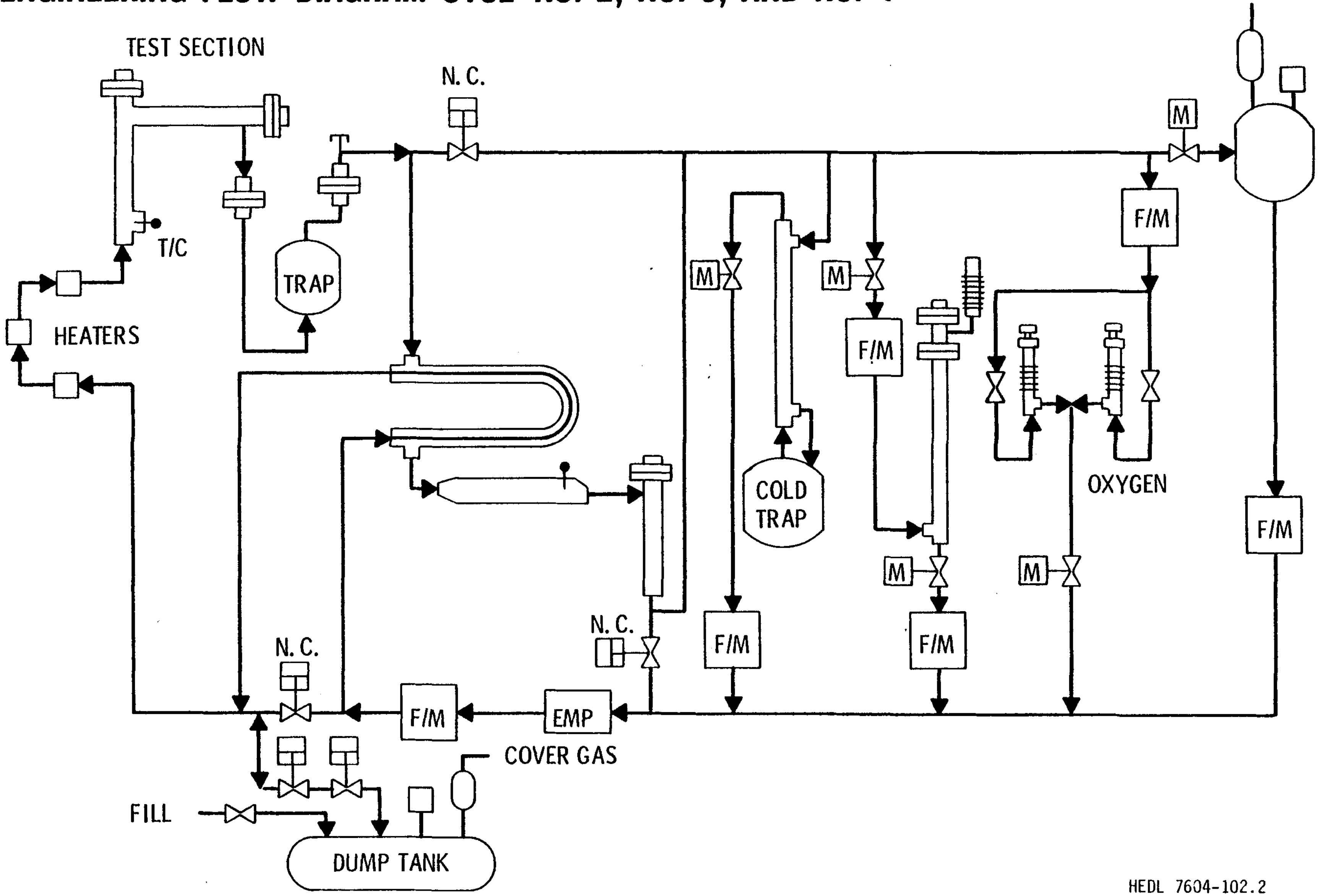

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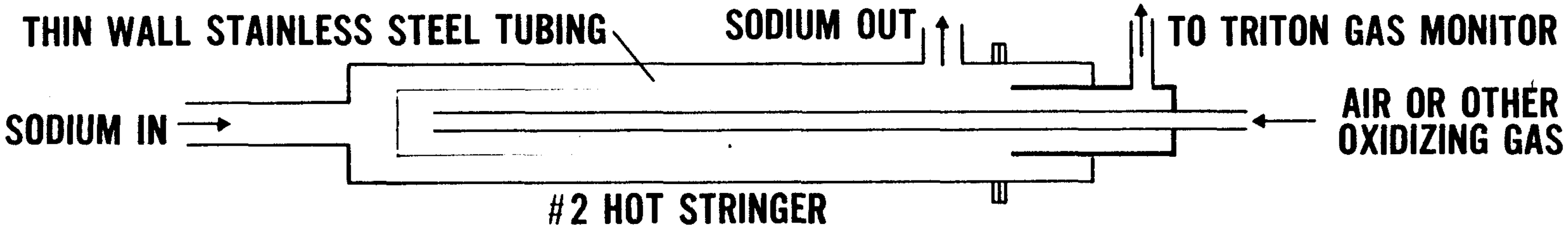
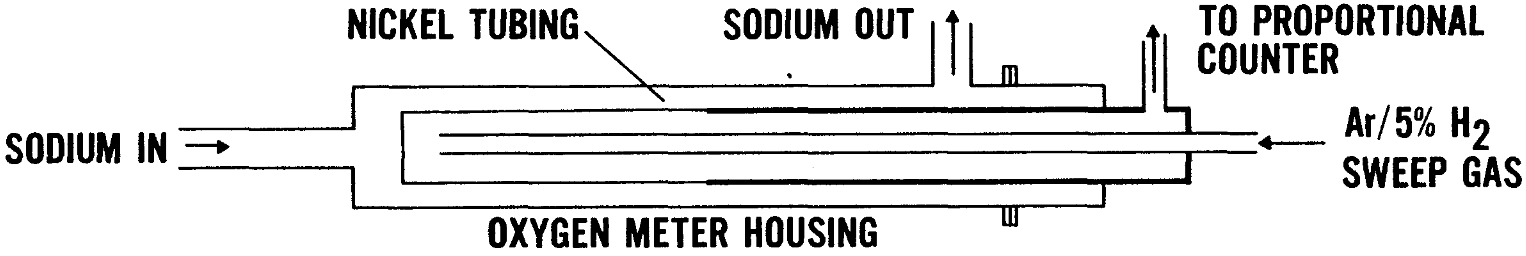
FIGURE 7

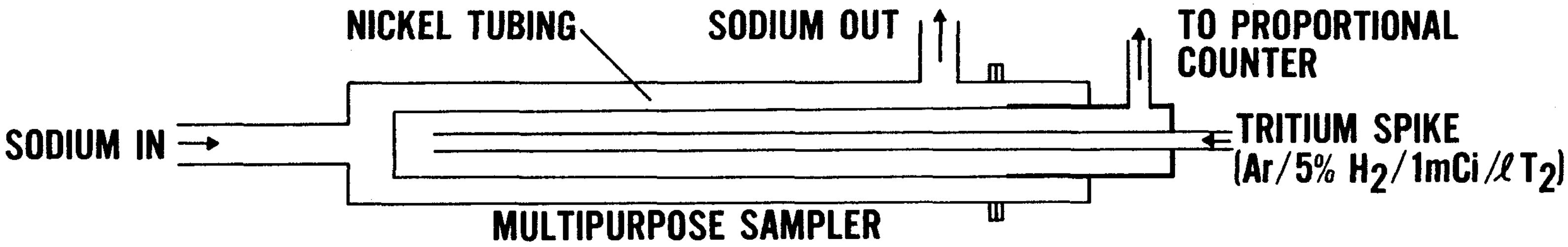
TRITIUM PROGRAM ADDITIONS TO STCL 3



TRITIUM DIFFUSION EXPERIMENT



TRITIUM METER



TRITIUM INJECTION SYSTEM

HEDL 7604-184

FIGURE 8

moving gas. As shown in Figure 8 the gas is delivered to the bottom of the hollow tube by an inside gas tube.
The gas is then carried by a spiral path past the inside surface of the hollow tube and out the gas exit tube. In the Tritium Injection System this membrane is nickel and the flowing gas is Ar/4%H_2 with 2μCi/cc T_2. When this gas is flowed past the Ni diffuser at a rate of 0.5 cc/min essentially all of the T_2 is diffused through the membrane and into the sodium. This device shown in Figure 9 is mounted in the Multipurpose Sampler location.

The Tritium Meter, (Figure 10) designed and built by Argonne National Laboratory-East (ANL-E), also uses a nickel membrane. In this case the sweep gas is Ar/1%H_2 which is passed through the meter at 5 cc/minute, then sent to an 80 cc proportional counter for analysis. The Tritium Meter was installed in one of the two STCL-3 oxygen meter locations. It operates at 426°C (800°F), the cold leg temperature of this loop. Tests show that this device operates quite satisfactorily at this temperature although it was originally developed for operation at 482°C (900°F).

The Tritium Diffuser Assembly (Figure 11) is similar in basic construction to the Tritium Meter. In this case the diffuser tube is of the material under test, 304 or 316 SS. Ar/1%H_2 sweep gas carries diffused tritium activity to a proportional counter, or pure argon is passed through the device, through hot copper oxide at 500°C where tritium is converted to tritiated water, (HTO) then bubbled through a scintillation counter "cocktail" of xylene based fluid for counting.

Both proportional counting and scintillation counting are effective detection methods. In our case, due to the logistics of sample transfer between buildings, the on-line proportional counter was preferred for routine analysis. The scintillation technique was used for calibration and an occasional confirmation of proportional counter results.

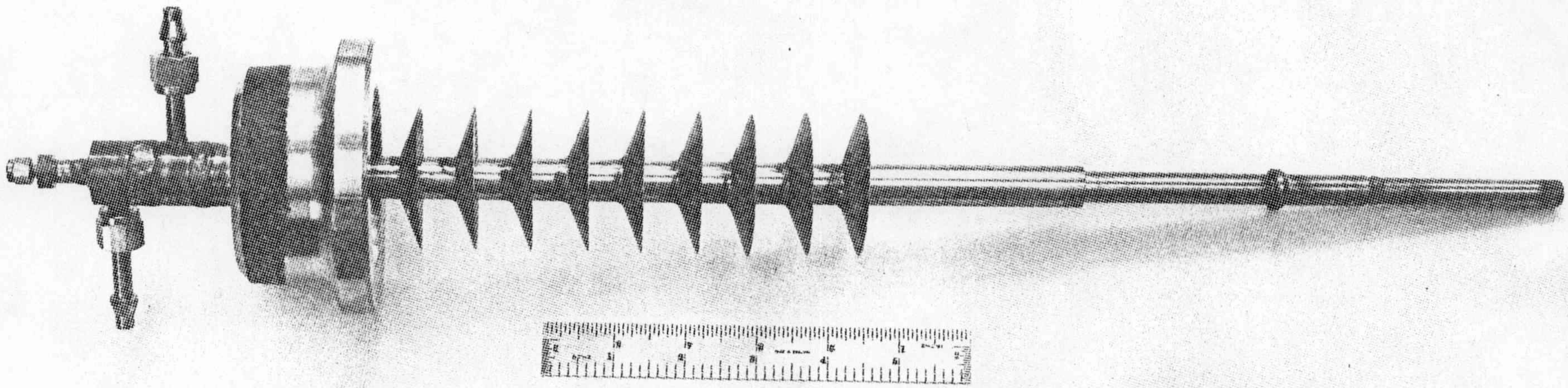


FIGURE 9. TRITIUM INJECTION SYSTEM

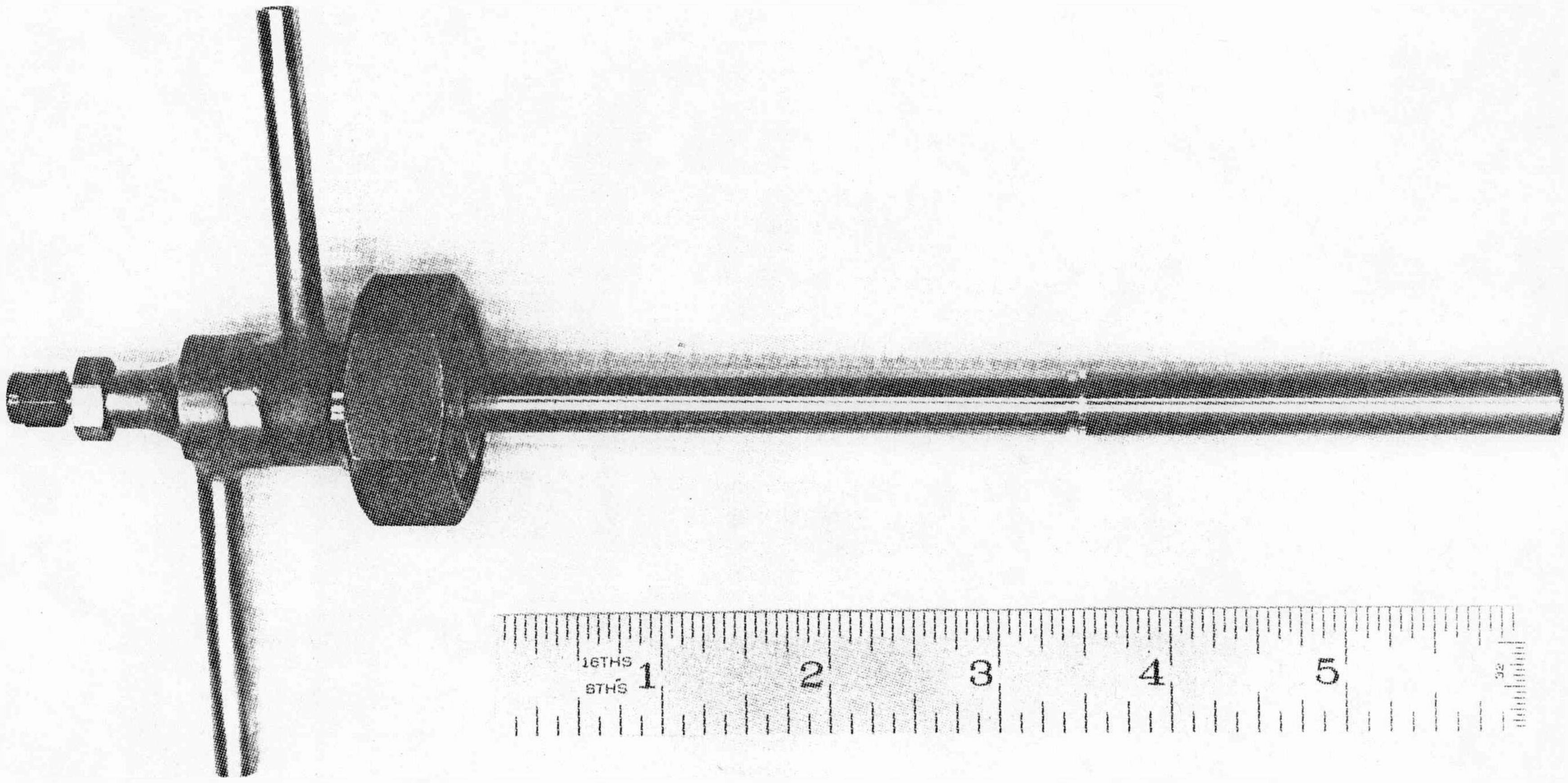


FIGURE 10. TRITIUM METER

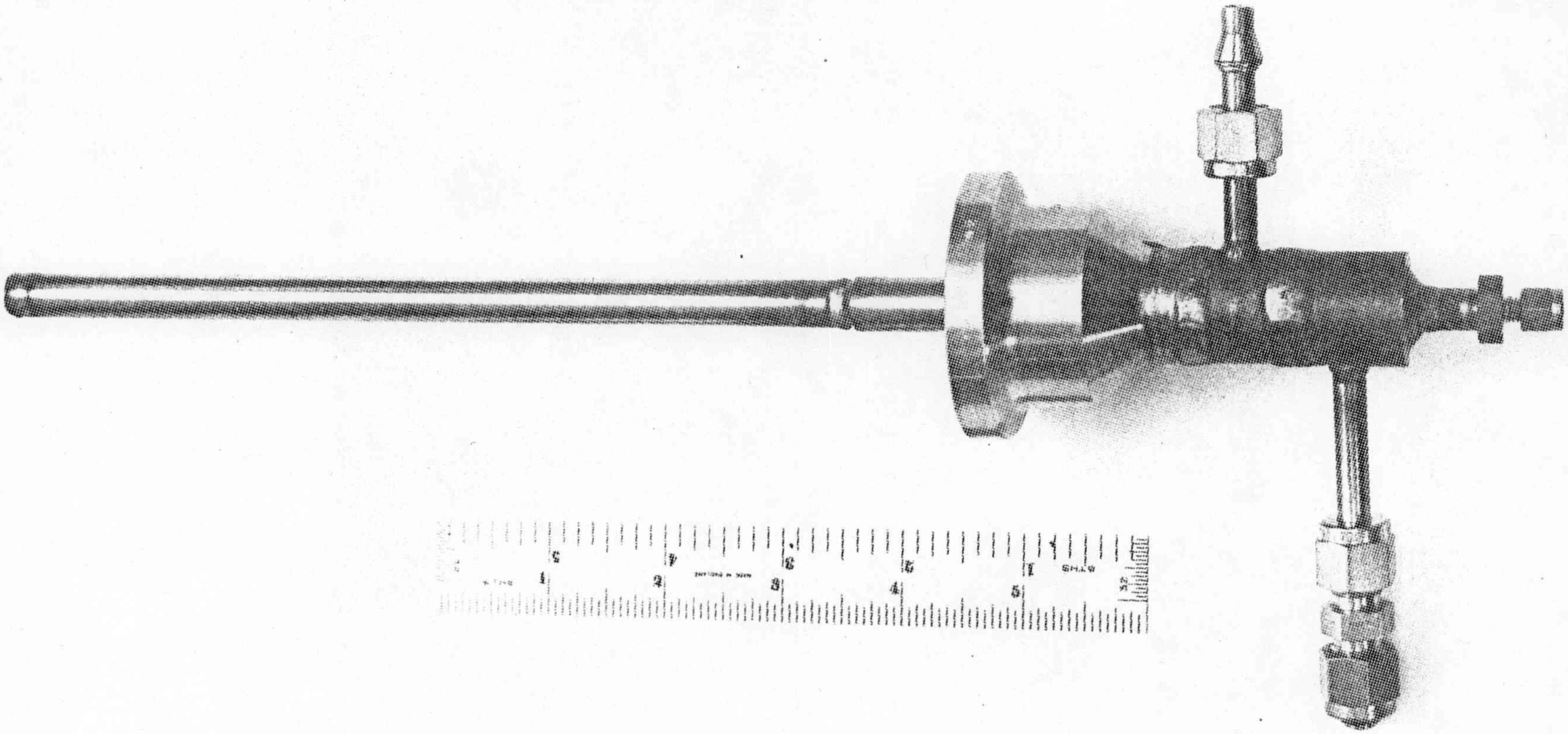


FIGURE 11. TRITIUM DIFFUSION MEMBRANE

The Tritium Meter and the Tritium Diffuser have separate proportional counters to prevent any chance of cross contamination. The present calibrating gas is at an activity level typical of the normal output of the Tritium Meter, therefore there is no significant recovery period necessary after proportional counters are re-calibrated.

Tritium activity in the laboratory is continuously monitored by a 10 liter ionization chamber sensitive to $2 \times 10^{-7} \mu CiT_2/cc$.

The gas flow control and activity measurement panel is shown in Figure 12.

Experimental Data

We measured tritium permeation rates through 304 and 316 stainless steel. Tritium concentration in EBR-II appears to be $\sim$ 40 $nCiT_2/gmN_2$. In these experiments we used tritium activities of 1-40 $nCiT_2/gmNa$ therefore the data obtained represent permeation rates at tritium levels typical of those in a reactor. At these low partial pressures the tritium permeation rates appear to follow the $\sqrt[1]{p}$ law.

The initial 6 months of the research program were devoted to cold trap evaluation and resolution of problems with the proportional counting system. As a result the 304 SS membrane was in place for almost 3500 hours before first dependable permeation data were obtained. Although during this period the diffuser was continuously purged with $Ar/1\%H_2$ there was an opportunity for an oxide coat to form from gas contaminants. Low initial permeation measurements confirmed the supposition that the 304 SS surface had acquired enough oxide to lower tritium permeation rates. Subsequent efforts at oxidation using 99% $N_2/1\%O_2$ produced no change in the observed permeation rate. When removed from the loop at 6000 hours this duffuser was found to have the hydrogen-permeation-resistant Mn and Cr rich surface layer previously noted in H_2 work. The Auger results are shown in Figure 13. In a Scanning Electron Micrograph shown in Figure 14 we see segments of surface flaked off although most of the oxide layer remained intact. At higher magnifications, small cracks are seen in the oxide layer.

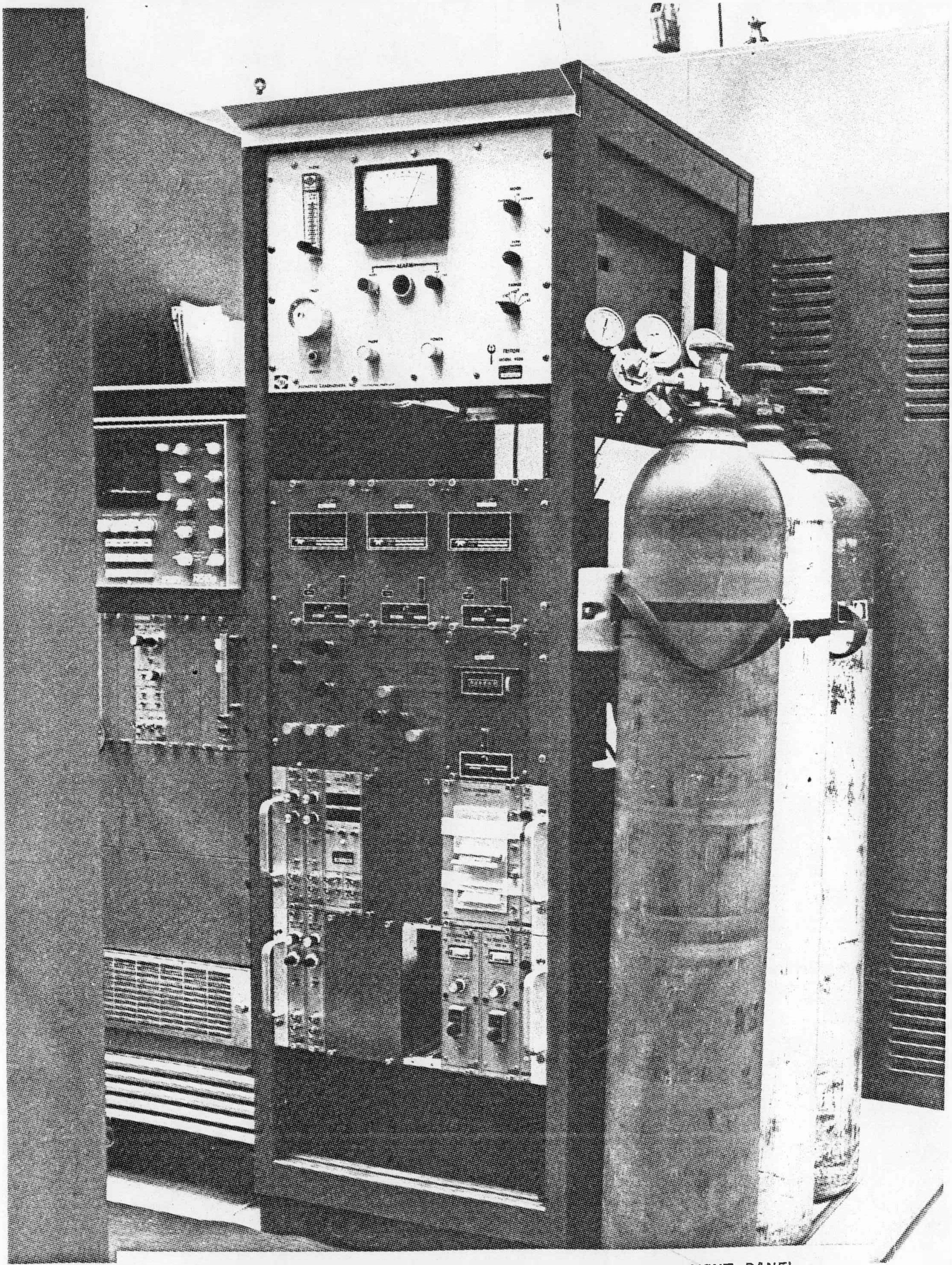


FIGURE 12. GAS CONTROL AND ACTIVITY MEASUREMENT PANEL

TABLE 3

SCANNING AUGER MICROPROBE RESULTS

DATE: 25 MAY 77
CUSTOMER: J MCGUIRE
SPECIMEN ID: 304 SS TUBING (INSIDE) TRITIUM DIFFUSION STUDY

CONCENTRATION IS IN ATOM PERCENT
A=ANGSTROMS M=MICRONS N.D.=NOT DETECTED
DEPTH PROFILING DONE BY ARGON ION MILLING

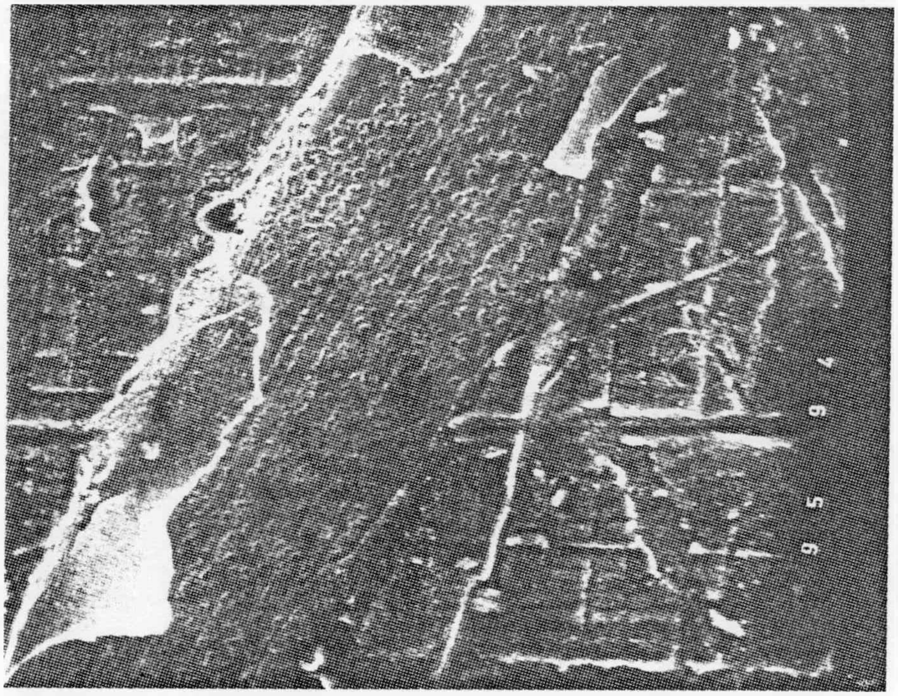
%C.	%CA	%N.	%O.	%CR	%MN	%FE	%NI		DEPTH
26.43	1.45	2.26	46.94	0.34	4.41	10.32	0.40	**	AS REC
3.96	0.97	0.52	63.79	4.39	9.48	13.20	0.42	**	-50A
1.55	N.D.	N.D.	64.80	9.90	10.46	11.42	0.84	**	-250A
N.D.	N.D.	N.D.	62.11	19.39	7.32	9.23	0.93	**	-1500A
N.D.	N.D.	N.D.	60.82	22.96	7.55	7.00	0.65	**	-2800A
N.D.	N.D.	N.D.	60.28	28.86	4.53	4.95	0.36	**	-5000A
1.41	N.D.	N.D.	55.00	31.81	2.68	6.58	0.38	**	-1.15M
2.75	N.D.	N.D.	3.01	12.74	N.D.	71.24	6.87	**	-2.5M

%ZN	%W.	%S.		DEPTH
5.28	N.D.	1.12	**	AS REC
1.87	N.D.	0.36	**	-50A
N.D.	N.D.	N.D.	**	-250A
N.D.	N.D.	N.D.	**	-1500A
N.D.	N.D.	N.D.	**	-2800A
N.D.	N.D.	N.D.	**	-5000A
N.D.	1.11	N.D.	**	-1.15M
N.D.	2.35	N.D.	**	-2.5M

SURFACE (TOP 300A) CONTAMINANTS CONSIST OF : S,ZN,CA,N

M-927 1D AREA 2 (1000X)

Typical Surface



M-927 AREA 1 (1000X)

Surface Showing Defect in the Oxide

FIGURE 14. Scanning Electron Micrograph of Oxidized 304 SS.

The average tritium permeation rate for oxidized 304 SS is $2.2 \times 10^{-4} \frac{cc(STP)\text{-}mm}{hr\text{-}cm^2\text{-}atm^{1/2}}$.

When a new 316 SS diffuser was installed, the unit came assembled with no opportunity for extra inside surface cleaning other than solvent wash. The diffuser had been assembled by election beam welding, therefore the inside surface could be assumed to be as clean as normal manufacturing practice would be expected to produce, however the surface was not "clean" from a permeation standpoint. When installed, first permeation data were taken within 4 hours of the loop reaching operational and test temperature 538°C (1000°F).

After one week at temperature the loop T_2 content was raised from 11 to 29.1 $nCiT_2/gmNa$. After taking permeation data, diffuser oxidation was started using $99\%N_2/1\%O_2$ flowing past the membrane at 5 cc/min. Data taken through the first 231 hours of oxidation are summarized below:

Condition	Permeation rate $\frac{cc(STP)\text{-}mm}{hr\text{-}cm^2\text{-}atm^{1/2}}$
316 SS unoxidized 538°C	2.9×10^{-4}
@ 11 $nCiT_2/gmNa$	2.8×10^{-4}
@ 29.1 $nCiT_2/gmNa$ (1 week interval)	2.2×10^{-4}
316 SS oxidized 91 hrs, 538°C 99% $N_2/1\%O_2$	1.6×10^{-4}
316 SS oxidized 231 hrs, 538°C 99% $N_2/1\%O_2$	1.1×10^{-4}

Oxidation continued on this membrane for a total of 1500 hours. Through a variety of tritium concentrations from 1 to 40 nCiT /gmNa permeation rates remained at 1 to $2 \times 10^{-4} \frac{cc(STP)\text{-}mm}{hr\text{-}cm^2\text{-}atm^{1/2}}$

This diffuser was operated at 593, 538 and 482°C (1100, 1000 and 900°F). From the resulting data the activation energy for permeation was found to be 10.28 Kcal/mole.

An additional observation made of tritium behavior in a sodium system is its response to cold trapping. With a cold trap operating at 115° (240°F) and at 10% bypass flow the loop activity level dropped from 36 to 5 $nCiT_2/gmNa$ in two hours.

In another experiment, while operating at equilibrium with the trap in the system, loop activity was raised by a factor of 6 by raising trap temperature from 115°C (240°F) to 174°C (345°F). (Figure 5)

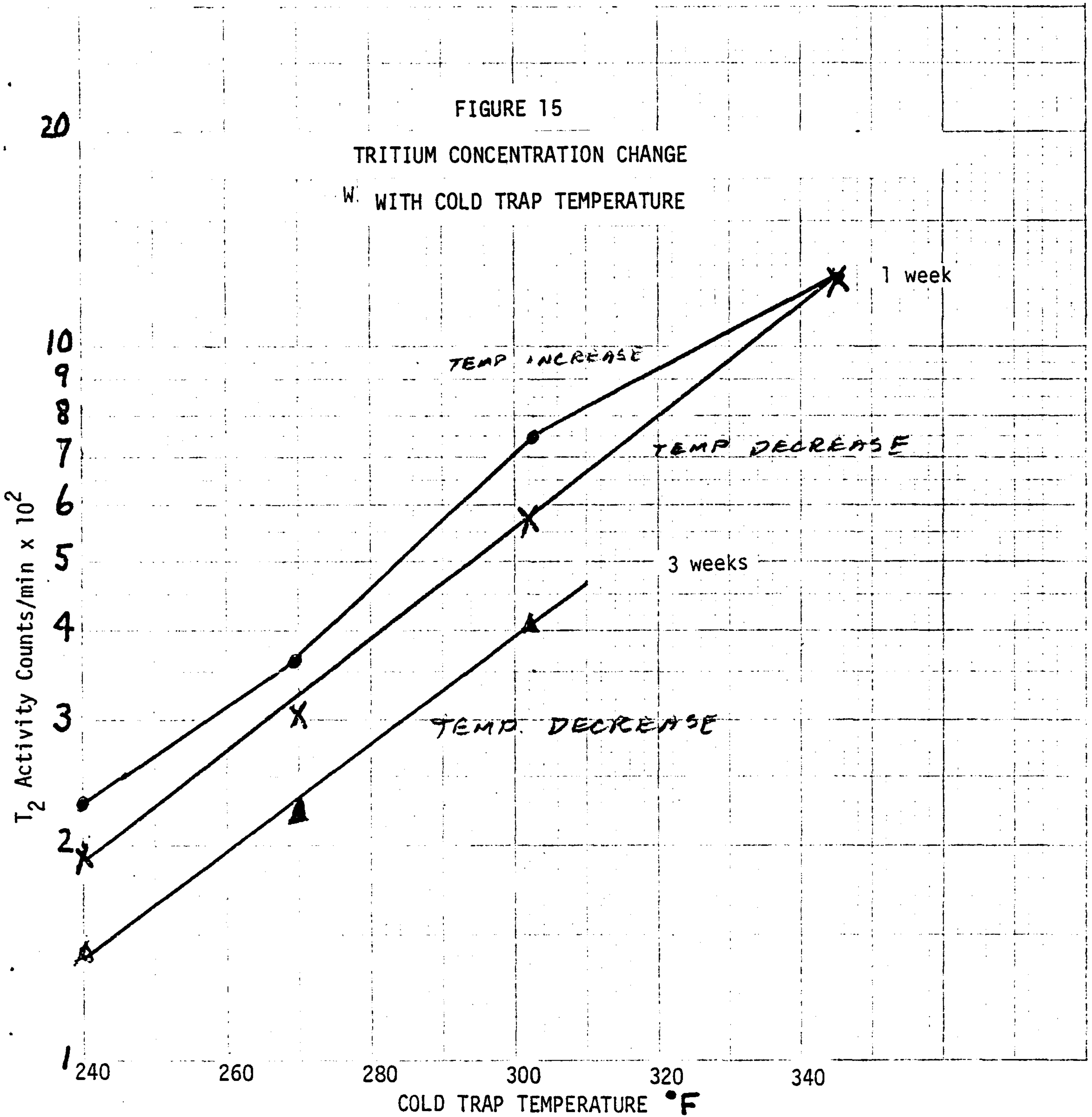
Immediate reaction of loop activity to cold trap introduction or temperature change indicates that the key to tritium control in a sodium cooled reactor is continuous cold trapping at as low a temperature as practical in both primary and secondary systems.

CONCLUSIONS

An evaluation of these data indicates that tritium release from liquid metal breeder reactors is minimized because of the ever-present oxide layers formed on potential release surfaces. In addition tritium concentration in the sodium is greatly reduced by presence of an on-line bypass cold trap operating at as low a temperature as practicable.

FIGURE 15

TRITIUM CONCENTRATION CHANGE WITH COLD TRAP TEMPERATURE



TEMPERATURES TO BE CONVERTED TO °C

REFERENCES

1. T. A. Renner, C. C. McPheeters and J. C. McGuire, "A Computer Model for Tritium Transport in and Release from the CRBRP and other LMFBRs", Trans. Amer. Nucl. Soc., 1977 Winter Meeting, December 1977.

2. R. A. Savage and H. C. Strehlow, "The Permeation of Hydrogen Isotopes Through Structural Materials at Low Pressures and Through Metals with Oxide Film Barriers", Nucl. Technology 22, 127 (1974).