7

CONF-880505-29

PARAMETERS IMPORTANT IN THE OXIDATION OF TRITIUM AT A STAINLESS STEEL SURFACE

P. A. Finn and E. H. Van Deventer
Argonne National Laboratory
Avenue Argonne, IL 60439

CONF-880505--29

DE88 012063

ABSTRACT

The heterogeneous reaction between oxygen gas and permeating tritium is being studied at the back surface of an oxidized 316-stainless steel tube. The ratio between the reaction products collected at the back surface, tritiated water and molecular tritium, is determined as a function of oxygen level, tritium concentration, protium concentration, flow rate, and temperature. This report describes the results from two sets of runs done at 550°C with and without 15 ppm protium in the oxygen/helium gas. At oxygen levels of 1200-2000 ppm, the ratio of tritiated water to molecular tritium was >40, i.e., a 98% conversion. At oxygen levels of 40 ppm, the presence of excess protium in the oxygen/helium resulted in a reduced yield of tritiated water.

INTRODUCTION

The need for methods to minimize tritium losses from thermally hot blanket systems in a fusion reactor is a critical issue since permeation losses can be severe. Typical blanket systems through which tritium can permeate are steam generator lines for helium and lithium-lead coolants, tritium recovery lines for lithium-lead and solid oxide breeders, and coolant systems for solid oxide breeders. For each of these systems, a method suggested to reduce permeation losses in blanket systems to manageable levels is the reduction of the tritium partial pressure by the conversion of tritium to tritiated water (1-3) within a double-wall tube.

The purpose of our experiment is to study the reaction of perm[illegible] tritium with oxygen gas at the back-surface of a 316 stainless steel tube to

---

This work supported by the U.S. Department of Energy, Office of Fusion Energy of Argonne National Laboratory under contract no. W-31-109-Eng-38.

DISCLAIMER

determine if oxidation is an effective method to reduce tritium losses. The objectives of the experiment are to 1) determine the oxygen level which results in the maximum yield of tritiated water, 2) determine the effect of protium on the yield of tritiated water, and 3) determine the mechanisms which control the formation of tritiated water. The parameter space which simulates the environment expected in a fusion reactor system is an oxygen level <1 to 2000 ppm, a temperature of 550°C, and a source tritium concentration of <1 Pa, a protium concentration <20 ppm, and a residence time of 20 sec.

Thermodynamics indicates that the formation of water is favored. However, under both homogeneous and heterogeneous conditions (4-5), the tritium oxidation reaction is incomplete at high temperatures unless an appropriate catalyst is introduced. When a catalyst is present, the reaction can be explosive. In addition, at higher temperatures, the back-reaction can occur in the presence of reducing species, i.e., water can oxidize free iron or a ferrous ion to produce tritium gas (6-8). The effect of this back-reaction can be significant. At 300°C, the predicted ratio of water to hydrogen over FeO is 0.1 while the observed ratio is 0.001 (5).

In addition, the oxygen introduced into the system not only can react with tritium but also with the metal to form metal oxides. The iron oxides formed at the metal/oxide interface can in turn be reduced by reaction with the permeating tritium. The yield of tritiated water relies, therefore, on the combined effect of these competing reactions. In the results reported, we have tried to estimate the importance of these reactions.

The purpose of our experiments is to determine the conditions under which oxidation of tritium is effective. By determining these conditions, we hope to establish which reactions and ultimately what mechanism controls the yield of tritiated water at a stainless steel surface. The results which we will describe in this paper are those obtained from two sets of experiments done at 550°C which are distinguished by the presence or absence of excess protium. The parameter varied in each set was the oxygen level. The experiments described examine two cases: 1) oxidation at oxygen levels <1 to 2000 ppm with no protium in the oxygen/helium gas, and 2) oxidation with 15 ppm protium in the oxygen at <1-912 ppm. In the first set of experiments, we determined the oxygen limits for tritiated water formation when in competition with metal oxide formation. In the second set of experiments, we determined the effect of excess protium on the yield of tritiated water.

EXPERIMENTAL

The experimental apparatus has four major components: 1) a stainless steel test cell composed of two concentric tubes with an annulus between the tubes; 2) loop A in which a tritium/helium mixture is prepared and circulated; 3) loop B in which the tritium content in loop A is measured and the tritium monitors are calibrated; and 4) loop C in which a oxygen/helium mixture is prepared and circulated and the reaction products, tritiated water and molecular tritium, are collected and measured as a function of time. Details of the experimental apparatus and procedures are found elsewhere. (9) For all runs reported here, a once-through mode of operation was used in loop C. Beyond the test cell, loop C lines are at elevated temperature to ensure non-adsorption of tritiated water.

A number of runs were linked together by holding the system at a given set of conditions for a day prior to collection of samples. This ensured that conditions for the new run were established. Gases in loops A and C were circulated countercurrently for 4-8 days for each run to ensure steady-state behavior. Aliquots were collected at regular intervals from the two sets of ethylene glycol bubblers on loop C and counted using liquid scintillation.

The mass flow rate of 15 ppm protium at the back surface of the stainless steel was 2.2 x 10^{-9} moles/min as compared to 3.45 x 10^{-12} moles/min for permeating tritium and 5.93 x 10^{-9} moles/min for 40 ppm oxygen. Thus, the protium available was 10^3 times greater than the tritium and was equivalent to the oxygen. (In the runs with 15 ppm protium, there was also a 10-fold excess of protium permeating with the tritium through the stainless steel.)

To ensure that the tritium collected was representative of the reaction products formed in the test cell, we needed to achieve a good tritium mass balance in the system. We did this by comparing the change in concentration in loop A to the sum of the tritium for which we could account. There were two general cases, one in which the test cell was not saturated and one in which the test cell was saturated. The tritium sum included the tritium solubility in the test cell (5-15 μCi), the tritium solubility in loop C components, the tritoxide formed on loop C surfaces and the collected tritium reaction products.

Tritoxide on α-Fe_2O_3 surfaces is <1 monolayer at room temperature, <0.4 monolayers at 200°C and <0.1 monolayers at 500°C (10-11). This corresponds to 3.2 μCi, 1.26 μCi and 0.32 μCi for a test cell with its center section at the cited temperatures. In addition, up to 0.95 μCi of tritoxide may be present at room temperature on each 10 cm of tubing in loop A. We have evidence for the presence of excess tritoxide species on the test cell surface since when the test cell is heated, the tritium concentration in loop A rises and remains elevated. At the same time, a spike appears in the tritium concentration in loop C and quickly disappears (see Fig. 1). The increase in tritium concentration in loops A and C is attributed to the decomposition of tritoxide species and not to tritium solubility since the tritium solubility in stainless steel increases with temperature.

We found that prior to test cell saturation, we could achieve 92.5% agreement between the decrease in loop A's tritium content and the sum of all tritium which we could account for. After test cell saturation, our agreement was 99.6%. This was for total tritium of 1-5 μCi.

In Table 1, the experimental results for the runs done with <0.001 ppm and 15 ppm protium are listed. In Fig. 1, the response of the ionization gauge to the molecular tritium formed in several of the runs is shown. These responses verify the presence of molecular tritium later measured by scintillation counting and listed in Table 1. The thickness of the oxide layer will depend on the oxygen mass flow rate at the oxide/gas interface and the tritium (protium) mass flow rate at the metal/oxide interface. In the experiments described above, we noted the thickness of the oxide changing as a function of these parameters. Therefore, we cycled the test cell between oxygen levels of <0.001 and >1000 ppm for runs with <0.001 ppm protium to determine if the results were reproducible. We found that the ratios at 550°C were indeed reproducible. We noted two other responses during oxygen cycling. First, the cumulative tritium collected per min first increased when we reduced the oxygen level which indicated reduction of the oxide on the back surface of the stainless steel and then decreased when we increased the oxygen level which indicated reformation of the metal oxide (see Table 1). Second, we noted that the tritium concentration at the source side increased when the oxygen level was increased and decreased when the oxygen level was decreased. We suggest that a low tritium solubility in the metal oxide requires excess tritium to permeate to the source side when the oxygen level was increased. These two observations suggest that the molecular tritium we collected was not due to cracks in the metal oxide.

Table 1 Experimental Results for Runs with <0.001 and 15 ppm Protium[a]

Oxygen (ppm)	Time (min)	HTO (μCi)	HT (μCi)	Total T (μCi)	Cum-Ratio HTO/HT	Cum-T (μCi/min)
<0.001 ppm Protium						
100	397	31.	4.	35.	7.8	0.09
700	1327	320.	14.	334.	22.8	0.25
400	6398	718.	66.	783.	10.9	0.13-0.12
40	7225	665.	97.	762.	6.9	0.11-0.10
2000	7309	529.	11.	540.	48.7	0.08-0.07
0.001	8533	435.	398.	833.	1.1	0.10
1200	6798	390.	9.	399.	43.6	0.07-0.06
0.001	8713	668.	617.	1285.	1.1	0.08-0.07
20	10066	442.	65.	507.	6.8	0.05
12	4067	130.	88.	218.	1.5	0.05
15 ppm Protium						
40	5376	323.3	132.7	456.	2.4	0.08
912	9960	1452.8	39.2	1492.	37.1	0.15
<1	8775	833.2	781.6	1614.8	1.1	0.18

[a] Runs are shown in order done.

A comparison between the results for the two sets of runs is shown in Fig. 2 in which the ratios for the runs done at each protium level are plotted versus oxygen level. Each set of runs is connected with a smooth curve; both curves show an increasing HTO/HT ratio as the oxygen level increases. The two curves differ in that the ratio observed at 40 ppm oxygen is substantially lower for the run with 15 ppm protium than it is for the run with <0.001 protium, i.e., 2.4 vs 6.9. The excess protium appears to inhibit the formation of tritiated water. We attribute this inhibition to the reduction of the Fe(2+) or Fe(3+) species at the surface by the protium. The reduced iron species then react with the tritiated water forming molecular tritium. An alternate explanation is that the protium occupies active sites at the surface, making them unavailable for the formation of tritiated water.

We assumed that there was a linear dependence between the rate of the overall reaction and the tritium concentration. The best-fit we found was for half-order dependence on total tritium which can be expressed as

$$C_0^{1/2} - C_t^{1/2} = kt/2$$

where C_0 is the total tritium concentration at the end of a run, C_t is the tritiated water concentration at time t and k is the rate constant. The coefficients m and b of the least-square fits and their weighted standard deviations, for each of the runs are shown in Table 2. We found that the m coefficient was affected by the cycling between oxygen levels. The different sets of cycles had m's which were an order of magnitude different. We think that this difference indicates a dependence of the overall reaction on the type of metal oxide formed which could be different for different oxygen cycles.

Table 2 - Statistical Analysis for Data with Half-Order Kinetics

Ratio	Oxygen	Least-Square Coefficients		Weighted Std
HTO/HT	ppm	m	-b	%
<0.001 ppm Protium				
1.1	0.001	1.02(-3)[a]	28.85	0.17
1.1	0.001	5.94(-4)	35.70	0.26
1.5	12	1.32(-3)	14.77	0.93
6.8	20	1.31(-3)	22.42	4.77
6.9	40	2.36(-3)	27.98	4.30
7.8	100	9.46(-3)	6.26	13.17
10.9	400	2.72(-3)	28.52	5.78
22.8	700	1.07(-2)	18.69	14.92
43.6	1200	3.44(-4)	82.32	0.12
48.7	2000	2.51(-3)	24.25	20.70
15 ppm Protium				
1.0	< 1	1.32(-3)	39.5	1.1
2.4	40	1.76(-3)	21.4	3.2
35	912	3.01(-3)	41.5	21.

[a] Number in parentheses is the power of ten.

DISCUSSION

The main processes that influence tritium oxidation - metal oxide formation, tritium diffusion, and adsorption/desorption - are discussed below.

Metal Oxide - At the steel/oxygen gas interface, an oxide is formed when oxygen atoms adsorbed at the steel/gas interface enter the lattice. The composition of the film at the steel surface is determined by the conditions under which it is formed. For both large and small grain material Cr_2O_3 forms at grain boundaries and iron oxides form at the surface (12). The chromium diffuses laterally, effectively spreading Cr_2O_3 across the surface. Two investigators (13-14) describe conditions similar to ours. For the stainless steel ^{18}Cr-^{10}Ni-$^{1.8}Mn$, the bulk of the film formed at 500°C in air was a mixture of Cr_2O_3 and Fe_3O_4 in the proportion 2:1 (13). We expect therefore, that the outside surface of our 316 stainless steel tube consists of a mixture of iron oxides, chromium oxide, and possibly an iron-chromium spinel. Preliminary scanning electron microscopy of a test cell sample supports this assumption.

The thickness of this oxide layer at low temperatures(<600°C) may be controlled by metal atom diffusion at the grain-boundary or by metal atom diffusion in the lattice. If grain-boundary diffusion is operative, the rate of oxide formation will be several orders of magnitude more rapid than that expected for lattice diffusion (15-16).

We calculated the maximum thickness of oxide formed at 550°C if metal atom diffusion was the dominant mechanism (17). The maximum amount of oxide formed at 1000 ppm is ~8 A/day. If we assume dependence on oxygen pressure to the 1/5 power, ~4 A/day could form at 10 ppm oxygen. The crossover point where excess oxygen is present is 1 ppm if all oxygen flowing through the system reacts. If ~1% of the oxygen sticks to the surface and dissociates, then the crossover point is >10 ppm. We noted in our experiments with <0.001 protium that two break points occur, one at ~40 ppm oxygen and the second at 400 ppm oxygen (Fig. 2). We attribute the first break point to conditions with excess oxygen since for runs with 15 ppm protium present, this break point is not present. The second break point is not yet defined, however, it may represent conditions at which the back reaction between tritiated water and reduced iron becomes significant.

At the steel/oxide interface, the diffusing tritium can reduce the iron oxides because of their low free energy of formation. The kinetics of reduction for iron oxide (18) and for chromium oxide (19) have been studied. For iron, reduction has a first-order dependence on hydrogen while for chromium, reduction has a half-order dependence on the hydrogen pressure. In our experiments, we found a half-order dependence on total tritium for tritiated water formation.

In our test cell convective mass transport of tritiated water and molecular tritium occurs through a film layer at the oxide surface to the helium. In addition, convective mass transport of the oxygen from the oxygen/helium mixture occurs in the opposite direction. Therefore, the tritiated water formed may remain on the hot metal oxide surface long enough for the back-reaction with an iron oxide to occur.

Tritium Diffusion - If tritium diffusion is an important mechanism in the formation of tritiated water, we would expect a square root dependence on temperature. We found such a dependence for earlier runs (9). However, we are unsure of the tritium form in the oxide which may be atoms (20-21), tritoxides (22) or tritons (23). We have assumed that the tritoxide is the major tritium form at the oxide/gas interface.

Adsorption/Desorption - Adsorption and dissociation of oxygen occurs at the metal surface. Both reaction products, tritiated water and molecular tritium desorb from the oxide surface; however, since the sticking coefficient for water is much higher than that for molecular tritium, desorption of the tritiated water would be less rapid. Therefore, the residence time for tritiated water at the surface would be longer which would increase the probability of the back reaction of water with metal ions near the surface.

For earlier runs (9) done at low oxygen levels, <1 ppm, between 350-550°C, we found an energy of activation of 7 kcal. This low energy of activation suggests that adsorption of the oxygen or desorption of the product, tritiated water may be the rate determining step.

Mechanism - A general mechanism which includes the processes mentioned above has been devised. In this mechanism, metal oxide formation occurs as:

$$\mathrm{Fe} + \mathrm{O(a)} = \mathrm{Fe(2+)} + \mathrm{O(2-)} \qquad (1)$$

where (a) indicates that the species was adsorbed at the surface.

Since a tritium atom at the interface between bulk metal and the metal oxide is surrounded by metal cations and oxygen anions, the following reduction occurs if tritium atoms are in excess.

$$2\mathrm{T} + \mathrm{Fe(2+)} = 2\mathrm{T(+)} + \mathrm{Fe} \qquad (2)$$

With excess oxygen, the diffusing species OT(-) may be formed at the metal/oxide interface.

$$\mathrm{T(+)} + \mathrm{O(2-)} = \mathrm{OT(-)} \qquad (3)$$

At the oxide/gas interface, the tritoxide can form tritiated water and/or molecular tritium (24). The role of stainless steel may be similar to that found for palladium (25). On palladium, the rate determining step was assumed to be the formation of adsorbed hydroxyl. The combination of two hydroxide groups was also invoked by Hirbayashi (26) to explain the desorption of tritium from stainless steel.

$$OT(-) + OT(-) = T_2O(a) + O(2-) \quad (4)$$

$$OT(-) + OT(-) = T_2(a) + O(2-) + O(a) \quad (5)$$

However, on steel, back reaction between the adsorbed water and a reduced iron species can occur:

$$2Fe(2+) + T_2O(a) = 2Fe(3+) + T_2(a) + O(2-) \quad (6)$$

For each mole of molecular oxygen at 500°C, the free energy of formation of tritiated water is -203 kJ/mol while the free energy of formation of iron oxide (FeO) is -219 kJ/mol and that of chromium oxide is -920 kJ/mol. We would expect therefore that chromium oxide would be formed if oxygen encountered chromium and tritium simultaneously. In the presence of excess oxygen, either FeO or water could be formed if kinetic factors are dominant.

Overall, tritium oxidation is a redox reaction. If we assume excess OT(-) species in step (3) and the presence of the reduced species Fe(2+), then the overall reaction is

$$20\ T + 9\ O(a) + 2\ Fe(2+) = 4\ T(+) + 2\ Fe(3+) + 6\ OT(-) + 3\ T_2O(a) + 2\ T_2(a) \quad (7)$$

Our experimental results showed that at low oxygen levels, equal amounts of tritiated water and molecular tritium were formed. However, at high oxygen levels, the primary product was tritiated water.

CONCLUSIONS

The major results from this work were:

1) The maximum yield of tritiated water, 98%, was obtained in the run at 2000 ppm oxygen. At low oxygen levels, 0.001 ppm, the yield of tritiated water was 52%. Thus, relatively high oxygen levels are required to get significant conversion of the tritium to tritiated water.

2) The reduction in the molecular tritium partial pressure was significant at 2000 ppm oxygen although complete conversion to tritiated water had not occurred. The original pressure of 0.1 Pa was reduced to $3x10^{-5}$ Pa. The expected tritium loss at this latter pressure for a system with a surface area of 2052 m^2 and a wall thickness of 0.005 m would be ~60 Ci/d. This tritium loss is within the acceptable environmental release range of 10-100 Ci/d. This reduction in partial pressure is attributed to the combined effect of an oxide film on the stainless surface and the formation of tritiated water.

3) The presence of protium in the oxygen gas does not enhance conversion of tritium to tritiated water. One reason for this behavior is that the excess protium reduces the iron oxide which then reacts with the tritiated water, producing molecular tritium. An alternate reason is that protium may occupy active sites on the metal oxide surface, thus reducing the potential sites for tritiated water and consequently, its yield.

4) The oxidation of tritium appears half-order with respect to tritium concentration. The determination of the mechanism for tritium oxidation is complicated by the fact that metal oxide formation and the back-reaction to form molecular tritium are occurring simultaneously with tritium oxidation.

REFERENCES

1. B. Badger,et al, "Witamir," University of Wisconsin, UWFDM-400 (1980).

2. M. Abdou, et al, "A Demonstration Tokamak Power Plant Study," Chapter 6, Argonne National Laboratory, ANL/FPP-82-1, p. 6-154 to 6-167, (1982).

3. M. Abdou, et al, "Blanket Comparison and Selection Study," Argonne National Laboratory, ANL/FPP/83-1, (1983).

4. D.-K. Sze, et al, "An Assessment of Problems Associated with Tritium Containment," Fusion Tech., 8, (1985), p. 1985-1997.

5. L. C. Beavis, "Interaction of Hydrogen with Surfaces of Type 304 Stainless Steel," J. Vac. Sci. Tech., 10, (1973), p. 386-390.

6. T. Serpekian and R. Hecker, "Investigation of High-Temperature Reactor Heat Exchanger Materials," Nucl. Tech., 34, (1977), p. 269-289.

7. G. R. Longhurst, G. A. Deis, P. Y. Hsu, and L. G. Miller, "Gamma Radiation Effects on Tritium Permeation Through Stainless Steel," Nucl. Tech./ Fusion 4, (1983), p. 681-686.

8. G. A. Somorjai and M. Salmeron, "Surface Properties of Catalysts, Iron and Its Oxides; Surface Chemistry, Photochemistry and Catalysis," Homogeneous and Heterogeneous Photocatalysis, ed. E. Pelizetti and N. Serpone, D. Reidel Pub. Co., (1986), p. 445-477.

9. P. A. Finn, E. H. Van Deventer, R. Heinen, and A. Scandora, Argonne National Laboratory, to be published.

10. T. Morimoto, M. Nagao, and J. Imai, "The Adsorption of Water on SiO_2, Al_2O_3, and $SiO_2 \bullet Al_2O_3$," Bulletin Chem. Soc., Japan, 44, (1971), p. 1282-1288.

11. T. Morimoto, M. Nagao, and F. Tokuda, "Desorbability of Chemisorbed Water on Metal Oxide Surfaces," Bulletin Chem. Soc., Japan, 41, (1968), p. 1533-1537.

12. R. O. Adams, "A Review of the Stainless Steel Surface," J. Vac. Sci. Tech., A1, (1983),p. 12-18.

13. I. Olefjord, "Application of ESCA to Oxide Films Formed on Stainless Steels at Intermediate and High Temperatures," Met. Sci. 9, (1975), p. 263-268.

14. G. Hulquist and C. Leygraf, "Thermal Passivation of AISI 316 Stainless Steel in Controlled Vacuum," J. Vac. Sci. Tech. 17, (1980), p. 85-88.

15. W. W. Smeltzer and D. J. Young, "Oxidation Properties of Transition Metals," Prog. in Solid-State Chem., 10, (1975), p. 17-54.

16. A. Atkinson, "Transport Processes during the Growth of Oxide Films at Elevated Temperatures," Rev. of Mod. Phys. 57, (1985), p. 437-470.

17. R. E. Westerman, "Compatibility of Stainless Steels with Oxygen-Contaminated Helium," Battelle Northwest Laboratory Report, FDM-117, (1974).

18. T. J. Vink, et al., "Reduction of Oxidized Fe(110) by Hydrogen," J. Vac. Sci. Tech., 5A, (1987), p. 1028-1031.

19. W. F. Chu and A. Rahmel, "The Kinetics of the Reduction of Chromium Oxide by Hydrogen," Met. Trans. B., 10B, (1979), p. 401-407.

20. N. Kishimoto, et al., "Hydrogen Permeation in Metals During Exposure to a Process Gas Environment," Nucl. Tech., 66, (1984) p. 578-593.

21. R. Bastasz and W. A. Swansiger, "Tritium and Deuterium Permeation in Stainless Steel: Influence of Thin Oxide Film," J. Nucl. Mater. 85/86(1979), p. 335-339.

22. J. B. Bates, J. C. Wang, and R. A. Perkins, "Mechanisms for Hydrogen Diffusion in TiO_2," Phy. Rev. B, 19, (1979), p. 4130-4139.

23. R. Gonzalez, Y. Chen, and K. L. Tsang, Phys. Rev. B 26 (1982), p. 4637.

24. P. A. Finn and E. H. Van Deventer, "Experimental Design to Study Tritium Oxidation as a Means of Tritium Control," Fusion Tech., 8, (1985), p. 2438-2443.

25. T. Engel and H. Kuipers, "A Molecular-Beam Investigation of the Reaction $H_2 + 1/2\ O_2 = H_2O$," Surf. Sci., 90, (1979), p. 181-196.

26. T. Hirabayashi, M. Saeki, and E. Tachikawa, "A Thermal Desorption Study of the Surface Interaction Between Tritium and Type 316 Stainless Steel," J. Nucl. Mater. 126, (1984), p.38-43.

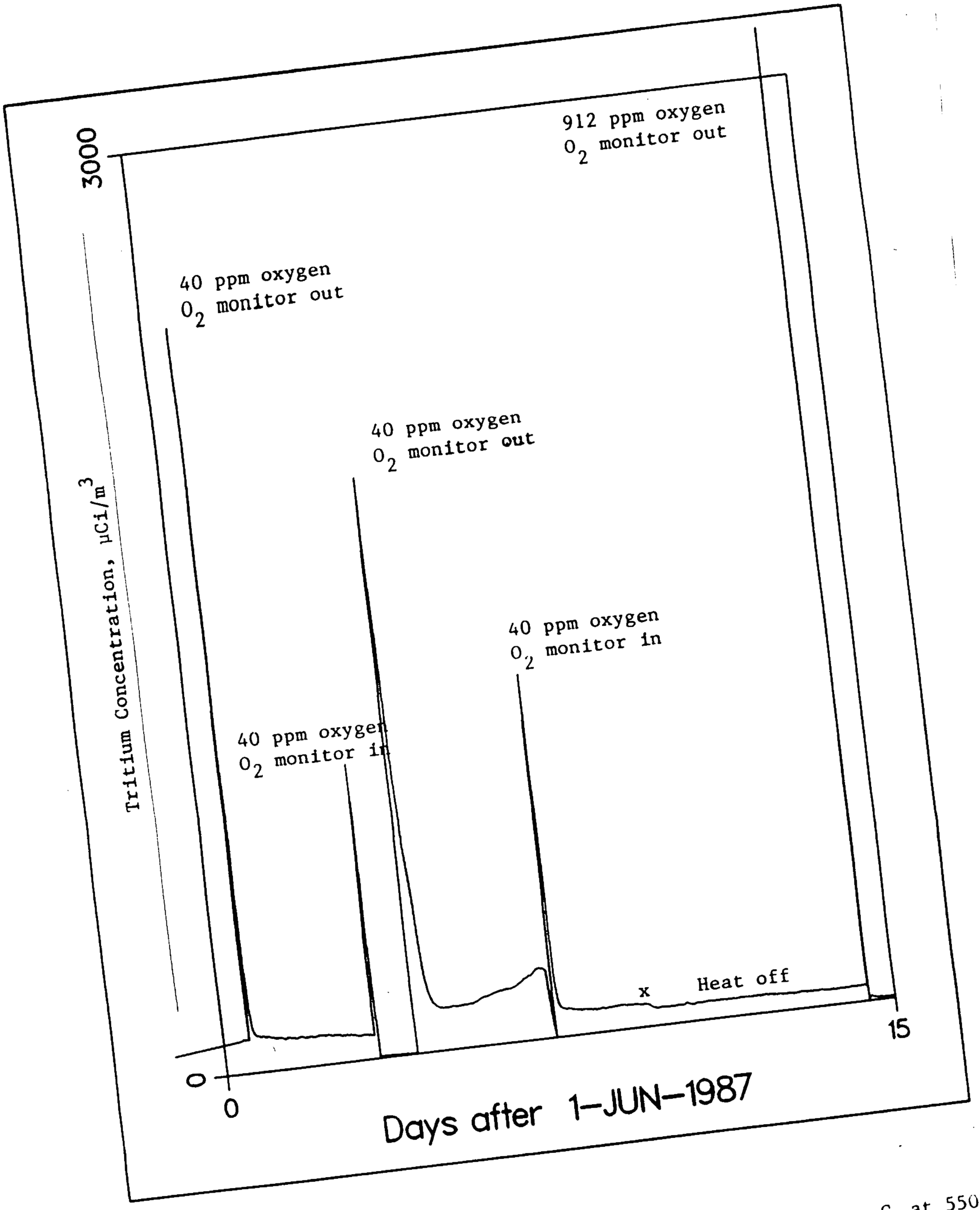

Fig. 1. Change in Molecular Tritium Concentration in Loop C at 550°C

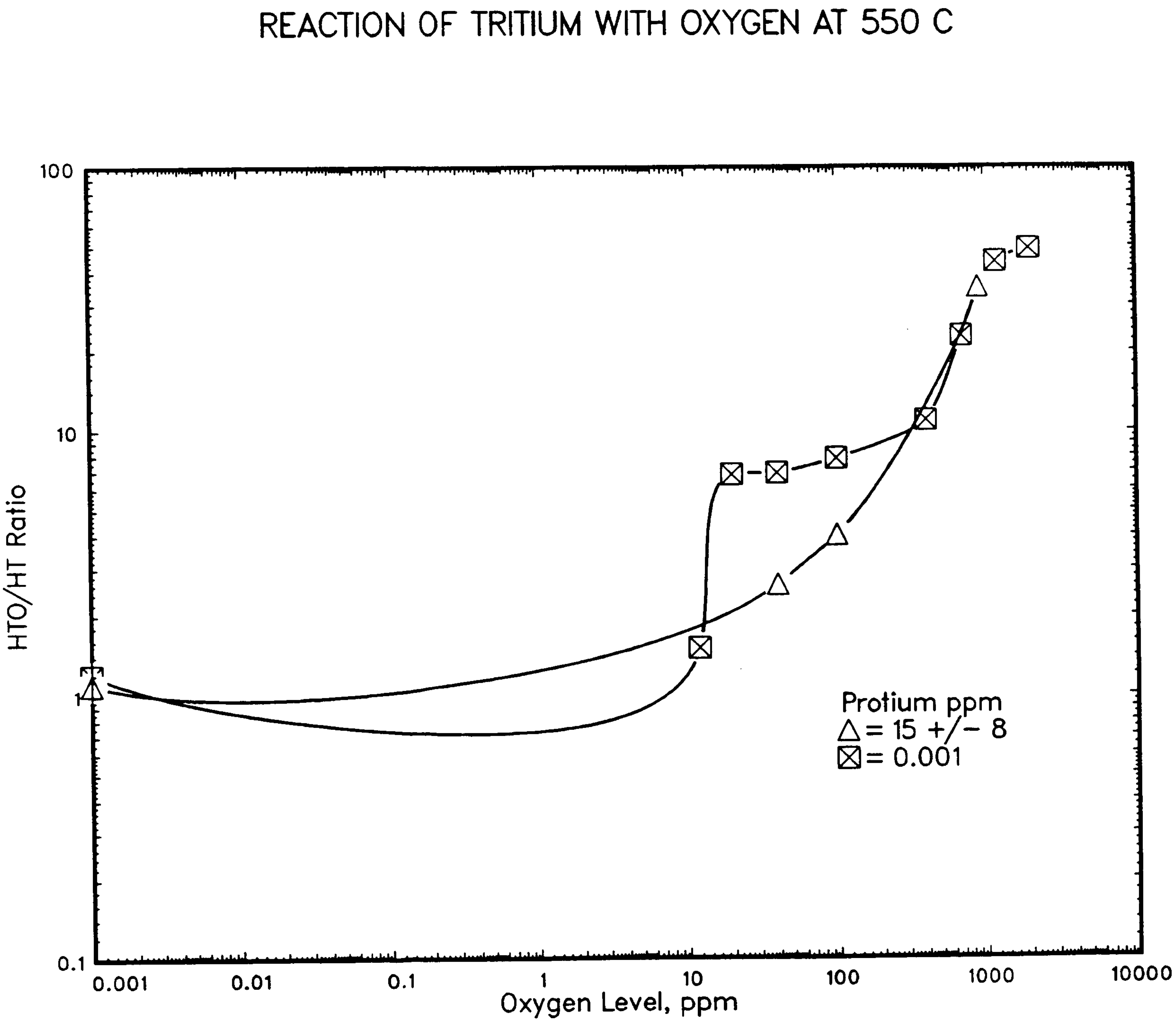

Fig. 2. Plot of Oxygen Level Versus Ratio of Tritiated Water to Molecular Tritium.