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METHANE FORMATION IN TRITIUM GAS EXPOSED TO STAINLESS STEEL

G. A. Morris

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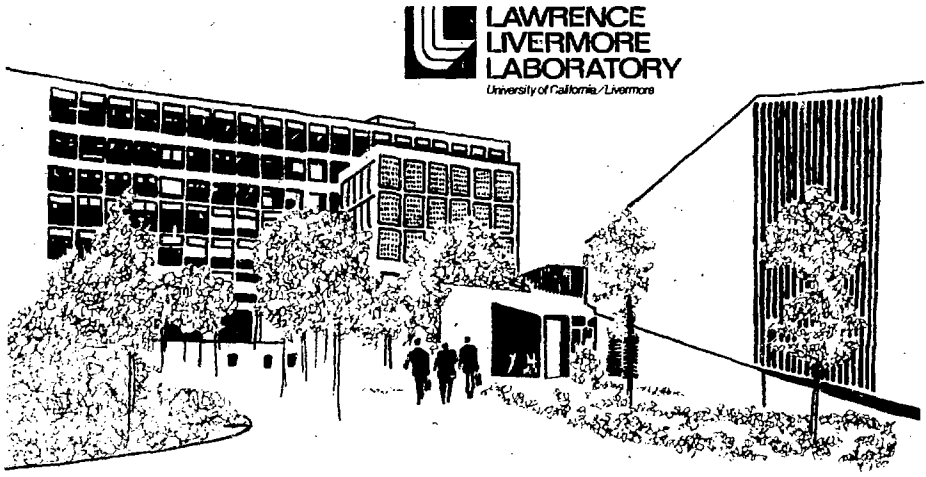

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Abstract

Tests were performed to determine the effect cleanliness of a surface exposed to tritium gas had on methane formation. These tests performed on 304 stainless steel vessels, cleaned in various ways, showed that the methane formation was reduced by the use of various cleaning procedures.

Introduction

Most, if not all, of the Magnetic Fusion Energy (MFE) concepts now being studied will eventually rely on tritium gas as a major fuel. Because impurities in the tritium have adverse effects on the plasma, eliminating their presence is important. Also, some fuel reprocessing steps are performed at cryogenic conditions that freeze impurities to a solid, which can block valves or orifices.

Experiments were performed to determine how the buildup of one impurity, methane, was affected by the cleanliness of the vessel used to contain tritium. The inside surfaces of 304 stainless steel test vessels were cleaned in various ways, and the methane buildup in the tritium was recorded using a gas chromatograph. Tritium gas pressure was 124 kPa (18 psia); the tests were performed at 25°C and 100°C.

Experimental

APPARATUS

The test vessels were made of standard 304 stainless steel pipes, 3.8 cm o.d. (1-1/2 in) by 3.5 cm i.d. (1-3/8 in) by 30.5 cm long (12 in), giving a nominal volume of 293 cm^3 and inside surface area of 353 cm^2. Stainless steel seat and bellows valves were used.

Gas samples were taken on a low-pressure gas handling system that allowed flushing with helium and pumping all excess gas into a containment

system, preventing release of any tritium into the atmosphere. The sampling station was constructed of a stainless steel cross: one arm connected to the gas system, one to the test vessel, one to the gas chromatograph sample vessel, and one to a pressure transducer for sampling monitoring (Fig. 1).

The gas chromatograph was modified by adding a palladium diffusion tube to convert any tritium from the effluent gas stream to tritiated water. The tritiated water was captured on a molecular sieve bed to minimize tritium release into the atmosphere (Fig. 2). In this test the lower limit of detectability of the instrument for methane was 0.02 cm^3 (STP) of methane/m^2 of stainless steel exposed to tritium.

PROCEDURE

This experiment was set up to simulate conditions in MFE operations; therefore, the level and range of the

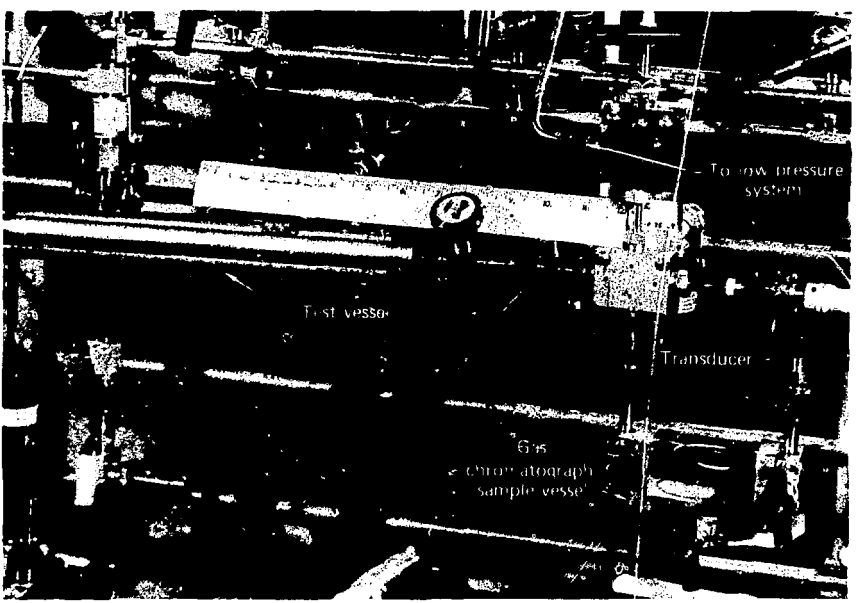

Fig. 1. Gas sampling station.

variables were chosen accordingly. The test vessels were at or near ambient temperature and pressure. Initial gas composition of ≈95 mol % tritium was used.

To analyze methane growth under various surface conditions, each test vessel was subjected to a combination of the following factors:

- Bake: Samples were either unbaked or baked under vacuum at 0.1 to 0.5 Pa at 150 to 160°C for 12 h to remove any carbon or impurities from the surface.
- Wash: Samples were either only rinsed with trichlorotrifluoroethane or degreased with trichloroethylene in an ultrasonic cleaner followed by acetone and trichlorotrifluoroethane rinses.
- Mechanical Preparation: Samples had no mechanical treatment (as-received) or were sent through a dry-machining process that removed 0.254 mm (0.010 in) from the interior radius.
- Temperature: The samples were processed at either 25° or 100°C.

Fig. 2. Modified gas chromatograph.

Using the wash and mechanical preparation factors, we can distinguish between impurities that were present because of tubing manufacture and those from the wash.

Using the factors discussed above, we set up a design representing a full 2^4 factorial arranged in four time blocks of five samples each (Table 1). Deuterium gas was used as a reference standard and served as a check on analytical procedures for each block, allowing the separation of any effects that might be present because of hydrogen but not tritium radiation.

Table 1. Test factors used in experiments.

		Factors				
	Sample	Temp	Mechanical	Wash	Bake	Gas
Block 1	1	100°C	As-received	Degrease	Unbaked	Tritium
	2	25°C	Machined	Degrease	Baked	Tritium
	3	25°C	As-received	Rinse	Baked	Tritium
	4	100°C	Machined	Rinse	Unbaked	Tritium
	5	100°C	As-received	Degrease	Unbaked	Deuterium
Block 2	6	100°C	As-received	Rinse	Baked	Tritium
	7	100°C	Machined	Degrease	Baked	Tritium
	8	25°C	As-received	Degrease	Unbaked	Tritium
	9	25°C	Machined	Rinse	Unbaked	Tritium
	10	100°C	As-received	Degrease	Unbaked	Deuterium
Block 3	11	100°C	Machined	Rinse	Baked	Tritium
	12	100°C	As-received	Degrease	Baked	Tritium
	13	25°C	Machined	Degrease	Unbaked	Tritium
	14	25°C	As-received	Rinse	Unbaked	Tritium
	15	100°C	As-received	Degrease	Unbaked	Deuterium
Block 4	16	25°C	Machined	Rinse	Baked	Tritium
	17	25°C	As-received	Degrease	Baked	Tritium
	18	100°C	Machined	Degrease	Unbaked	Tritium
	19	100°C	As-received	Rinse	Unbaked	Tritium
	20	100°C	As-received	Degrease	Unbaked	Deuterium

All samples in a block that were to contain tritium were loaded simultaneously with tritium from a uranium trap. Analysis of the tritium gave the zero-day methane count for that block.

Results

Experimental results were in parts per million of methane in each sample as determined by gas chromatography. For easier use of these numbers on large systems they were converted to cubic centimetres (STP) of methane produced per square metre of exposed stainless steel [$cm^3(STP)/m^2$]. Because the gas chromatograph sample sizes were small, when compared to the total gas contained in each sample, it was assumed that the total gas and the gas pressure remained constant over the entire test.

The build-up of methane in Block 1 samples is typical of all the blocks (Fig. 3). After analyzing the data recorded for each sample, the results in

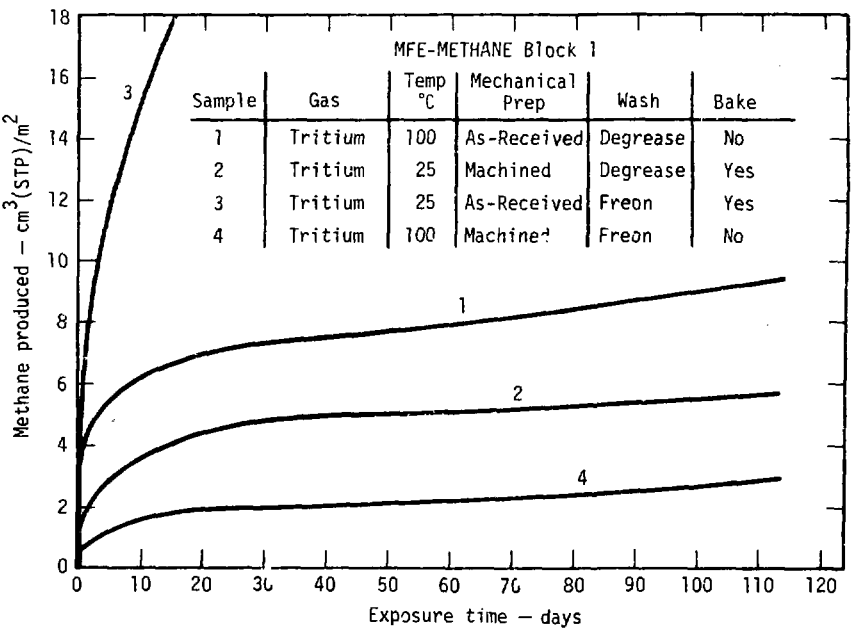

Fig. 3. Methane buildup for Block I samples.

descending order of methane count were:

- Vessels processed in the as-received condition with a trichlorotrifluoroethane rinse (Fig. 4).
- Vessels processed in the as-received condition with the degrease procedure (Fig. 5).
- Vessels machined and degreased (Fig. 6).
- Vessels machined then rinsed with trichlorotrifluoroethane (Fig. 7).

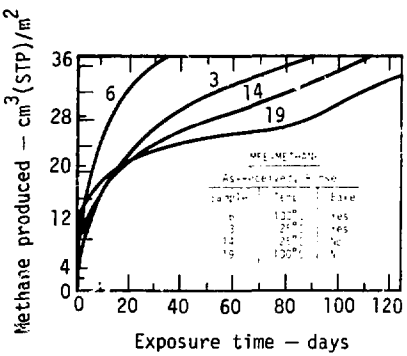

Fig. 4. Methane buildup for as-received and rinsed samples.

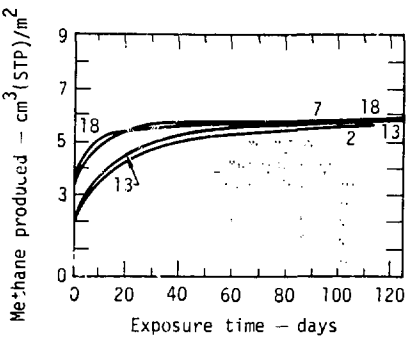

Fig. 6. Methane buildup for machined and degreased samples.

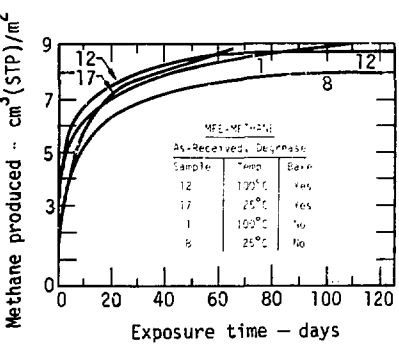

Fig. 5. Methane buildup for as-received and degreased samples.

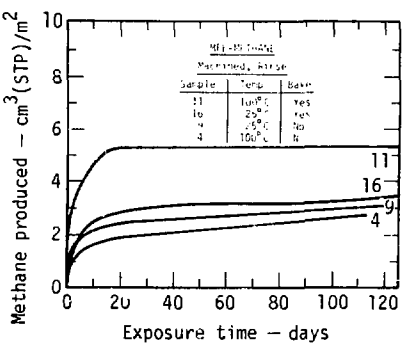

Fig. 7. Methane buildup for machined and rinsed samples.

Analysis

The deuterium samples showed no methane growth and remained below 0.02 cm^3 (STP)/m^2. An analysis of variance performed on the raw data for day 64 shows that the experimental error was statistically small compared to the effects observed for other factors from the sample results. Table 2 shows the factors and their statistical importance. The more significant a factor, the higher the number in column F. Analyzing these values we can see that the mechanical preparation, wash, and their interactions are statistically significant. We conclude, after examining Figures 3 through 7, that the best method for controlling methane formation is to mechanically clean the surface, rinse with trichlorotrifluoroethane, and not bake the surface.

One interpretation of these results is that most of the methane formed was produced from carbon found on the tubing surface and attributed to the tubing manufacture. The carbon could not be removed by degreasing, and the degreasing agents, used as cleaners on a machined surface, may magnify the problem.

Table 2. Analysis of variance: day 64 data.

Factor	Mean squares	F
Temperature	7,098	-
Mechanical Prep	8,715,780	189.14
Wash	3,953,138	85.79
Bake	372,405	8.08
Temperature-Mechanical Prep Interaction	116	-
Temperature-Wash Interaction	2,139	-
Mechanical Prep-Wash Interaction	5,823,775	126.38
Mechanical Prep-Bake Interaction	202,725	4.40
Wash-Bake Interaction	287,564	-
Experimental Error	46,081	-

Block 1 samples were also selected to test the effect preconditioning with tritium had on the rate of methane growth. The gas in these samples was analyzed by mass spectrometry to check for unexpected impurities. Each sample was evacuated and refilled with tritium gas using the same procedure as in the original test. Tables 3 and 4 show the comparison of initial and final gas compostion.

We analyzed the five samples for methane growth after exposures of 1, 8, and 21 days (Tables 5 through 7). The procedure for samples 1 and 5 were the same during Run 1 except, sample 5 contained deuterium and was not conditioned. During Run 2 both samples 1 and 5 had tritium, making sample 5 almost a rerun of the original sample 1; therefore, the high level of methane formed in sample 5 is expected. All samples 1 through 4 show a reduction of the rate of methane formation after being preconditioned with tritium.

Table 3. Block 1: mass spectrometric analysis for initial gas composition.

Gas	Mol %
Tritium	95.5
Deuterium	3.9
Protium	0.6

Table 4. Final gas composition (Mol %) 9 months after initial loading.

Sample	T_2	D_2	H_2	^3He	Methane
1	85.7	3.9	0.95	9.35	0.09
2	86.4	4.1	0.74	8.73	0.07
3	85.4	3.99	1.1	8.99	0.14
4	85.6	3.95	1.5	8.92	0.02
5	-	99.15	0.85	-	-

Table 5. Day 1 comparison of methane content for Block 1 samples.

Sample	Methane content - $cm^3(STP)/m^2$ Run 1[b]	Run 2[b]
1[a]	3.94	0.30
2	1.24	0.19
3	7.67	0.46
4	0.778	0.30
5[a]	0.02	1.65

[a]Samples 1 and 5 had same original treatment

[b]Day 0 Methane content was 0.415 for Run 1 and 0.12 for Run 2.

Table 6. Day 8 comparison of methane content for Block 1 samples.

Sample	Methane content - $cm^3(STP)/m^2$ Run 1	Run 2
1[a]	6.01	0.51
2	3.21	0.32
3	12.9	1.10
4	1.55	0.27
5[a]	0.02	4.09

[a]Samples 1 and 5 had same original treatment

Table 7. Day 21 comparison of methane content for Block 1 samples.

Sample	Methane content - $cm^3(STP)/m^2$ Run 1	Run 2
1[a]	6.74	0.33
2	4.15	0.33
3	20.7	1.76
4	1.81	0.27
5[a]	0.02	5.00

[a]Samples 1 and 5 had same original treatment

Conclusion

The initial cleanliness of the surfaces of tubing and containment vessels used with tritium is important in maintaining the purity of the tritium gas. The organic residues from cleaning procedures or manufacturing processes contribute to the methane formation rate. We find preconditioning equipment with tritium before introducing experimental tritium gas tends to lower the initial rate of methane formation.

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I would like to thank J. Shaw for his help in setting up and operating sampling equipment and E. Fultz for doing the gas chromatograph analysis. John Magistad helped by doing most of the statistical work on design of the experiment and on data reduction.

SJ/vdb/vt,lmc/jf