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## SAES ST 909 PILOT SCALE METHANE CRACKING TESTS

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*Pilot scale (500 gram) SAES St 909 methane cracking tests were conducted to determine material performance for tritium process applications. Tests that ran up to 1400 hours have been performed at 700°C, 202.7 kPa (1520 torr) with a 30 sccm feed of methane, with various impurities, in a 20 vol% hydrogen, balance helium, stream. A 2.5 vol% methane feed was reduced below 30 ppm for 631 hours. A feed of 1.1 vol% methane plus 1.4 vol% carbon dioxide was reduced below 30 ppm for 513 hours. The amount of carbon dioxide gettered by St 909 can be equated to an equivalent amount of methane gettered to estimate a reduced bed life for methane cracking. The effect of 0.4 vol % and 2.1 vol% nitrogen in the feed reduced the time to exceed 30 ppm methane to 362 and 45 hours, respectively, but the nitrogen equivalence to reduced methane gettering capacity was found to be dependent on the nitrogen feed composition. Decreased hydrogen concentrations increased methane getter rates while a drop of 30°C in one bed zone increased methane emissions by over a factor of 30. The impact of gettered nitrogen can be somewhat minimized if the nitrogen feed to the bed has been stopped and sufficient time given to recover the methane cracking rate.*

### I. INTRODUCTION

The Savannah River Site (SRS) Tritium Facilities use non-evaporative metal getter beds containing SAES® St 909 to remove oxygen, carbon monoxide, carbon dioxide, and to crack water, methane, and ammonia contained in various process gas streams. Tritiated methane and ammonia impurities will increase facility emissions unless they are processed before release to the environment. Like the design of the ITER Tokamak Exhaust Processing (TEP) System<sup>1</sup>, SRS process streams will use diffusers/permeators to remove tritium before flow through an impurity processor (a St 909 bed at SRS) followed by further diffuser tritium removal. Methane in a diffuser gas stream may have a deleterious impact on diffuser operation and performance due to the potential coking from methane decomposition.

Previous bench scale St 909 testing, a ten pellet stack per test (6 grams), studied the impact of helium, hydrogen, and nitrogen carrier gases<sup>2</sup> and of carbon

dioxide<sup>3</sup> on methane cracking. These tests identified important parameters for methane cracking, but are inadequate for predicting performance of full scale beds. Some full scale tests have been completed<sup>4</sup>, but additional tests were needed under different process conditions to determine the long-term ability of St 909 to crack methane prior to additional diffuser processing.

### II. BACKGROUND

In the absence of diffuser methane decomposition kinetic test data, it is desirable to run the first diffuser(s) under conditions where the gas phase methane decomposition reaction ( $\text{CQ}_4$  going to solid C plus two  $\text{Q}_2$  where Q is H, D, or T) is not thermodynamically favored. Hydrogen isotope removal by a diffuser can ultimately create conditions favorable for methane decomposition.

Choosing reference states as pure components at 101 kPa (1 atm) and 25°C and assuming ideal gas conditions, the standard state fugacity equals  $P_{\text{ref}}$  (101 kPa) and component fugacity is equal to its gas phase mole fraction,  $y_i$ , times the system pressure,  $P$ . Carbon activity is taken as unity since its variation with pressure dependence is assumed to be small. The methane decomposition equilibrium constant,  $K_a$ , is first order in pressure, second order in hydrogen isotope mole fraction and inversely proportional to methane mole fraction.

Figure 1 shows equilibrium conditions for methane decomposition at 101 kPa where  $K_a$  values were calculated for protium using tabulated values for heat capacity polynomial coefficients and heat and free energies of formation, at 25°C and 101 kPa.<sup>5,6</sup> Figure 1 gas compositions to the left of an isotherm favor methane decomposition while compositions to the right favor methane reformation.

For various feed gas scenarios, mass balance lines, where protium was removed from the mixture, were plotted on Figure 1. The intersection of the mass balance line and the assumed 500°C diffuser “hot spot” isotherm indicated the minimum protium concentration needed to suppress the methane decomposition reaction. For these tests, the first diffuser exit composition (the feed to the St

909 bed) was rounded to 20 vol% protium to keep the diffuser from operating in the coking regime.

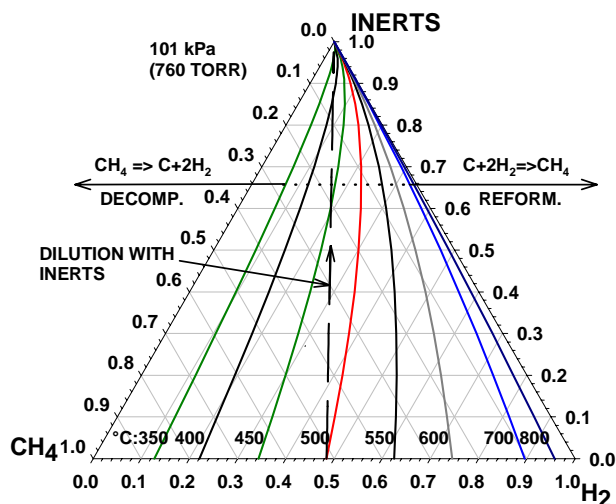


Figure 1. Methane Decomposition Equilibrium Plot

The purpose of these cold (non-radioactive) tests was to determine if St 909 could reduce methane concentrations in 20 vol% protium below 30 ppm and determine the impact of impurities on methane cracking.

### III. EXPERIMENTAL

Pilot scale (500 grams St 909) test beds were fabricated from 150 cc 316L stainless steel sample cylinders. Thermowells for type K thermocouples (TCs) were made from small pieces of tubing and attached to the bed exterior near the bottom, middle, and top of a bed while another TC was inserted into the top of the bed and in contact with the top bed pellets. A bed was installed in a 3-zone, vertical furnace for testing. The test system has been described previously<sup>2,3</sup> with an Agilent Technologies 3000A Micro GC added for methane gas analyses. Gas standards of nominally 30 ppm, 20,000 ppm, and 25,000 ppm methane were used for GC calibration.

A bed was activated by flowing 30 sccm argon through the bed at ambient temperature to displace air followed by a nominal 2.5°C per minute temperature ramp to 700°C. The bed was at temperature for nominally 12 hours before the start of a test.

Before a test, the bed was isolated with an argon fill at 700°C and a pressure of 202.7 kPa (1520 torr). After a steady feed gas mixture composition at 30 sccm was obtained, it was routed through the test bed. Periodically during testing, the bed was bypassed to verify feed composition stability. GC standards were periodically run during testing to verify instrument calibration.

Feed gas mixtures contained various amounts of methane, carbon dioxide, and nitrogen impurities along with 20 vol% protium and a balance of helium. Test 1 had 2.5 vol% methane and Test 2 had 1.1 vol% methane plus 1.4 vol% carbon dioxide. Test 3, part A (Test 3A) had 1.1 vol% methane plus 2.1 vol% nitrogen while for Test 3B, the 0.63 sccm nitrogen flow was stopped and then restarted for Test 3C. Test 4A had 1.1 vol% methane plus 0.4 vol% nitrogen while Test 4B had the 0.12 sccm nitrogen flow stopped. Test 4C added 200 ppm water to the Test 4B feed while Test 4D added 1.1% carbon dioxide to the Test 4C feed. Test 4E continued Test 4D conditions with greatly reduced hydrogen flow due to a mass flow controller problem.

### IV. RESULTS

As activation bed temperatures approached 615 to 625°C, temperature increases exceeding the furnace ramp rate were observed. The internal TC first indicated this temperature increase while the middle TC registered a maximum temperature of 715°C: an increase of almost 100°C in four minutes. This exothermic reaction has been seen before for St 909 and was anticipated.<sup>4,7</sup>

Water, carbon dioxide, carbon monoxide/nitrogen, and hydrogen were released where desorbed/released during activation, but most surprisingly was methane releases. Figure 2 shows methane releases as a function of bed middle temperature: the data between 680 and 720°C appear as a discontinuous function due to the rise and fall in temperature due to the exothermic reaction. The Test 1, 2, and 4 St 909 beds released approximately 8.3 scc methane while the Test 3 bed released only 0.2 scc methane. The Test 1, 2, and 4 St 909 was from the same production lot while the Test 3 St 909 was from a different material lot.

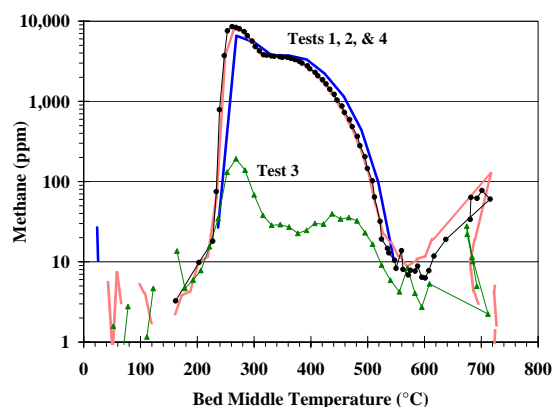


Fig. 2. Bed Activation Methane Releases

Figure 3 shows the outlet GC methane concentration versus time for Tests 1, 2, 3A, and 3B and Table I summarizes some of the results when the bed exit concentration reached 30 ppm. The methane impurity equivalence (MIE) parameter was derived to relate the amount of carbon dioxide or nitrogen gettered to an equivalent amount of methane gettered: the difference in the quantity of methane gettered in Test 1 and another test, divided by the quantity of the other impurity gettered.

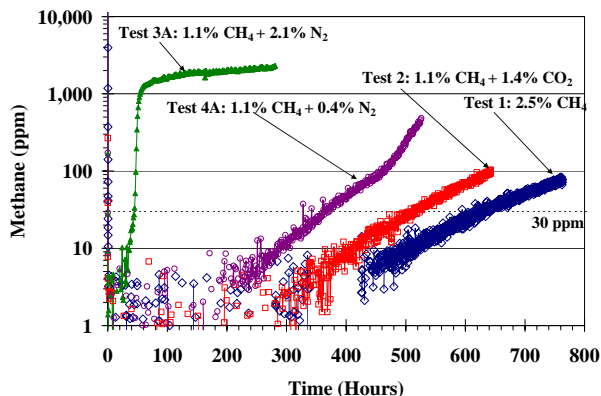


Fig. 3. Test Results Versus Time

Table I. Results at/for 30 ppm Methane Outlet

Test # =	1	2	3A	4A
Time (hours)	631	513	45	362
CH <sub>4</sub> Gettered <sup>a</sup>	55.7	16.2	1.78	14.0
CO <sub>2</sub> Gettered <sup>a</sup>	n/a	24.9	n/a	n/a
N <sub>2</sub> Gettered <sup>a</sup>	n/a	n/a	3.46	5.12
MIE	n/a	1.59 <sup>b</sup>	15.6 <sup>c</sup>	8.15 <sup>c</sup>

<sup>a</sup> STP-L/kg-St 909

<sup>b</sup>  $\Delta(\text{STP-L CH}_4)$  per STP-L CO<sub>2</sub>

<sup>c</sup>  $\Delta(\text{STP-L CH}_4)$  per STP-L N<sub>2</sub>

Figure 4 shows Figure 3 results replotted using the MIE factors from Table I versus equivalent methane cracked. Figures 5 and 6 show the complete results for Test 3 and Test 4, respectively, which include transient losses of hydrogen flow, pressure/flow control, furnace power, or the loss of one furnace zone.

Figure 5 shows that when the nitrogen flow was stopped at the end Test 3A (282 hours), the methane outlet concentration decreased and further decreased when the hydrogen flow was lost at 594 hours. During the time when system hydrogen flow and back-pressure were unstable (pressure oscillations between 618 to 670 hours), the methane concentration increased, but then decreased when control was re-established. At 971 hours

and 36.89 STP-L methane cracked, the methane concentration again exceeded 30 ppm. Between 1128 and 1149 hours, an open TC circuit shut off the furnace.

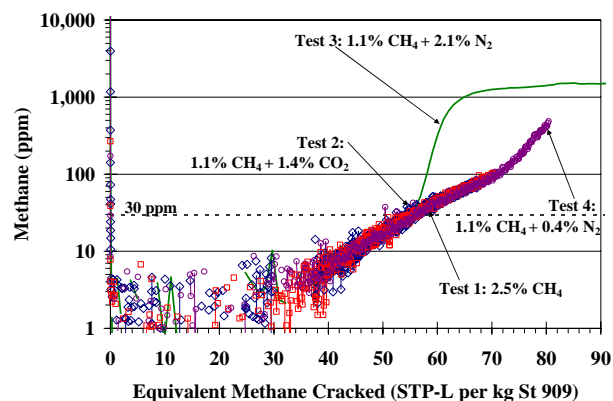


Fig. 4. Test Results Versus Equivalent Methane Cracked

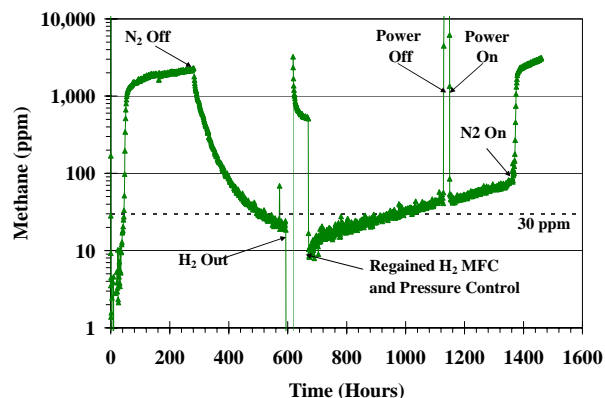


Fig. 5. Complete Test 3 Results

Figure 6 shows that when the nitrogen flow was stopped at the end Test 4A (526 hours), the methane outlet concentration decreases and decreased below 30 ppm at 716 hours. A blown fuse for the bottom furnace zone between 867 and 989 hours showed increased methane concentration which dropped below 30 ppm once the fuse was replaced. The addition of 198 ppm water to the feed stream at 1010 hours had no discernable impact on gettering performance. The impact of adding 1.1 vol% carbon dioxide at 1201 hours was somewhat obfuscated by the loss of building power between 1217 and 1300 hours, but the rate of increase in outlet methane concentration was greater than before the introduction of the carbon dioxide. At 1061 hours and 39.51 STP-L methane cracked, the methane concentration again

exceeded 30 ppm. The hydrogen flow was stopped at 1393 hours which produced a rapid decrease in methane outlet concentration.

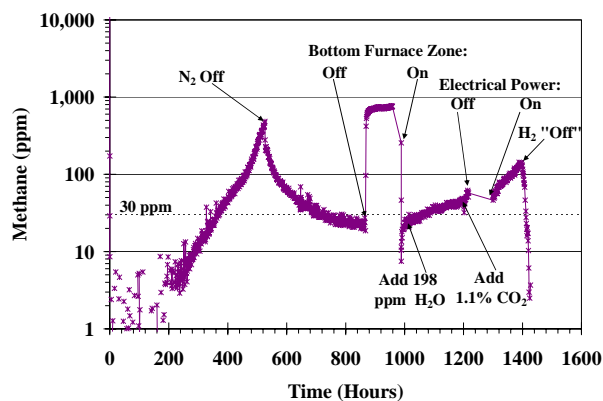


Fig. 6. Complete Test 4 Results

## V. DISCUSSIONS

These tests showed that a fresh St 909 bed is capable of reducing methane concentrations to less than 30 ppm in a 20 vol% hydrogen stream. Test 2 showed that with the same carbon feed rate as Test 1, 30 ppm breakthrough was reached earlier than in Test 1 due to the oxygen in the carbon dioxide. The MIE of carbon dioxide being 1.59 instead of 3.00 was interpreted as oxygen being gettered faster than carbon by the St 909.

Test 3 and Test 4 showed nitrogen had a greater impact on methane cracking than carbon dioxide and the nitrogen MIE was concentration dependent. The effect of nitrogen on methane cracking can be mitigated by stopping the nitrogen supply to the bed and allowing the nitrogen to presumably diffuse from the surface into the bulk allowing methane outlet concentrations to be again below 30 ppm.

Figure 7 contains the Figure 4 Test 1 data along with Test 3 data shifted by 18.80 STP-L methane cracked (55.68 from Test 1 less 36.89 from Test 3B) illustrates the minimal impact the previously gettered nitrogen has on methane cracking once the Test 3B data drop below 30 ppm.

Figure 7 also shows the Test 4 data shifted by 16.17 STP-L methane cracked (55.68 from Test 1 less 39.51 from Test 3B) along with the Test 4D incorporating the carbon dioxide MIE value from Table I illustrating again the minimal impact the previously gettered nitrogen has on methane cracking once the Test 3C data drop below 30 ppm. There was no significant impact on methane

cracking by the 0.22 STP-L of water cracked by the St 909.

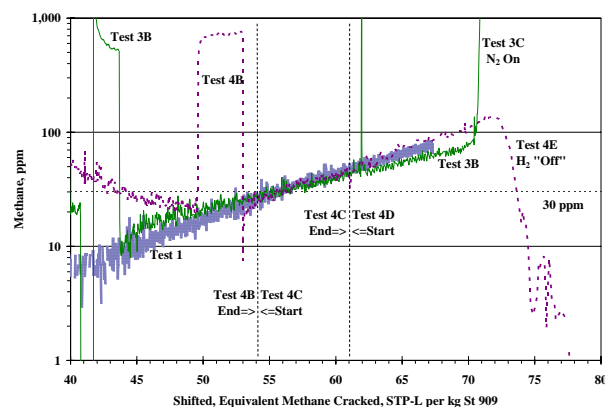


Fig. 7. Methane Cracking on Partially Consumed St 909

The 30°C temperature drop at the bed bottom when its heater zone was lost during Test 4B illustrates the sensitivity of methane cracking on temperature. Temperature gradients within larger scale St 909 beds must be anticipated since many production processes utilize single-zone vessel furnaces. The pilot scale results mostly like illustrate “best achievable” since larger beds will likely have regions at lower temperatures if controlled to the same 700°C temperature.

The start of Test 3C was interesting in that once the nitrogen flow was restarted, the methane outlet concentration increased to the level where Test 3A ended, nominally 2300 ppm, in the relatively short time of 20 hours. The difference between the end of Test 3A and the beginning of Test 3C is the larger rate of increase of outlet methane concentration for Test 3C than for Test 3A, presumably due to the gettered carbon and additional nitrogen inhibiting methane cracking.

Hydrogen suppresses the methane decomposition reaction and the reduction of hydrogen fed to the St 909 bed reduced the methane outlet concentration as illustrated in Figures 5 and 6.

## VI. CONCLUSIONS

St 909 can reduce methane feed concentrations to below 30 ppm at 700°C, with 20 vol% hydrogen, under low flow conditions, to remove impurities and effectively reduce tritium emissions. The reduction in bed methane cracking capacity can be estimated if the amount carbon dioxide in the feed gas is known utilizing the define MIE

ratio. Nitrogen can have a significant, negative impact on St 909 methane cracking efficiency and its impact is dependent on the nitrogen concentration in the feed gas. The impact of nitrogen gettered during St 909 methane cracking can be somewhat reversed if the nitrogen feed to the bed is stopped long enough to recover previous methane cracking performance.

## ACKNOWLEDGMENTS

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