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Development of catalytic combustion technology for single-digit emissions from industrial gas turbines

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Abstract

Catalytic combustion has demonstrated potential for attaining the firing temperatures of current and next generation gas turbines with nitrogen oxides (NO_x) production less than 3 parts-per-million by volume (ppmv), using natural gas fuel. The technology necessary to achieve this extremely low emissions performance with typical heavy-duty industrial and utility gas turbine operating cycle conditions, has been under development as a joint effort by the General Electric Company (GE) and Catalytica Combustion Systems Incorporated (CCSI) for several years with the support of Tokyo Electric Power Company Inc. (TEPCO). The most recent phase of this program, which began in late 1997, is focused on the durability of catalytic reactors in the gas turbine combustor operating environment. This paper presents the results of subscale catalytic reactor endurance testing at simulated steady-state and cyclic operating conditions typical of utility gas turbine service. The results of full-scale, full-pressure, laboratory testing of a catalytic combustion system having the most advanced catalytic reactor mechanical design features developed by CCSI are also presented.

Keywords: Catalytic combusion technology; Single-digit emissions; Industrial gas turbines

1. Introduction

One key aspect of catalytic combustion, remaining to be demonstrated before widespread commercial utilization of this technology in industrial and utility gas turbine applications is catalytic reactor life. GE and CCSI have established 8000 fired hours as a minimum service life objective for a gas turbine catalytic reactor in commercial service with a goal of a 10 000 fired-hour reactor service period. To meet this life objective, the reactor materials of construction must be matched to the operating conditions so that long term degradation mechanisms such as oxidation, corrosion, sintering, vaporization, creep, low-cycle fatigue (LCF) and coating spallation, are adequately controlled. Long-term, subscale reactor durability testing has been conducted to verify that life objectives can be met. This testing has consisted of high-pressure, LCF tests that will exercise the catalyst through 350 simulated normal turbine start-stop cycles and 35 simulated turbine-trip cycles; plus atmospheric pressure endurance testing that has subjected the catalyst to 6000 h of simulated baseload operating conditions with natural gas fuel. Sufficient intermediate exposure data has been taken to allow extrapolation to the full life objectives.

In addition to avoiding the potential long-term failure mechanisms, the reactor containment mechanical

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design must be compatible with the operating conditions such that structural support for the aerodynamic loading on the reactor due to pressure drop is adequate and that stresses due to differential thermal expansions are well below the yield point of the reactor materials. The objective of full-scale, full-pressure laboratory testing of a catalytic combustor designed for the GE model MS9001E gas turbine has been to verify that these criteria for reactor life can be met without compromising the emissions performance of this system. Results of this full-scale testing in GE's Power Generation Technology Laboratory are presented in this paper.

Exhaust emissions abatement technology is required by regulatory agencies for most current applications of large heavy-duty industrial gas turbines, including electric utility applications. Emissions regulations for nitrogen oxides (NO_x) have become increasingly strigent due to the impact of this pollutant on air quality. Over the past three decades, the maximum allowable NO_x emissions levels in the machine exhaust have been brought down by an order of magnitude in many locations from historically accepted levels near 100 ppmvd (corrected to ISO ambient and 15% oxygen) to levels under 10 ppmvd and in many other locations to less than 5 ppmvd. Over this period of time, the technology of choice for NO_x abatement has evolved from the use of diluents (steam or water) to lower the temperature in the gas turbine combustor reaction zone, to the use of lean premixing dry low NO_x (DLN) combustion systems and selective catalytic reduction (SCR) on the gas turbine exhaust.

GE has commercialized DLN systems based upon lean premixed combustion technology with natural gas fuel to deliver NO_x emissions levels of 9–25 ppmvd in existing power plants (all NO_x concentrations given in this paper are corrected to ISO ambient, 15% oxygen unless otherwise specified). At single digit NO_x levels below 5 ppmvd, lean premixed combustion systems must be pushed to the limits of flame stability and this can lead to lean blowout or high dynamic pressure activity levels within the combustor which have adverse effects on the reliability and life of the gas turbine. For applications where NO_x emissions levels below 9 ppmvd must be achieved, exhaust gas cleanup is employed using SCR to convert most of the residual NO_x to molecular nitrogen and water by reacting it with ammonia on a catalytic surface. However, there are several drawbacks to SCR: the efficiency of the power plant is reduced due to the pressure drop of the SCR in the gas turbine exhaust, unreacted ammonia, also an air pollutant may be present in the exhaust stream (ammonia slip) and the SCR is a large, expensive piece of equipment in the exhaust stream which must be maintained. Thus, there are incentives to eliminate SCR (performance, environmental, and economic) while still maintaining NO_x emissions levels below 9 ppmvd.

An emerging technology which has demonstrated the potential to meet NO_x emissions levels below 5 ppmvd in heavy-duty industrial gas turbine application [3] without recourse to SCR is catalytic combustion within the gas turbine. This technology permits combustor operation without the risk of blowout or instability and dynamics using fuel–air mixtures which are below the lean limit of flammability for conventional lean premixed combustion, and react at temperatures below the thermal NO_x formation threshold. Catalytica Combustion Systems Incorporated (CCSI) have recently developed catalytic reactor technology for the gas turbine application. The Catalytica technology is designed to limit the extent of fuel oxidation that occurs within the catalyst structure itself. By limiting the reactions this way, such systems also limit the maximum catalyst temperature and thus broaden the selection of suitable catalyst components and extend the catalyst life. This technology also permits the use of metal substrate materials, which are thermal shock tolerant, for the catalyst support. This is an important attribute for the gas turbine application.

The catalytic combustion system development work presented in this paper is focused on system durability with emphasis on catalytic reactor mechanical design adequacy and life. GE and CCSI have established 8000 h as a minimum service life objective for the gas turbine catalytic reactor in commercial service with a goal of 10 000 fired-hour service period. One of the first steps taken by GE in evaluating the adequacy of any new gas turbine combustion system to meet its service life objectives, is to conduct full-scale laboratory tests at simulated machine operating conditions to evaluate combustor aero-thermal, emissions, and mechanical performance. This type of testing has been conducted in the current phase of the catalytic combustor development program and the results

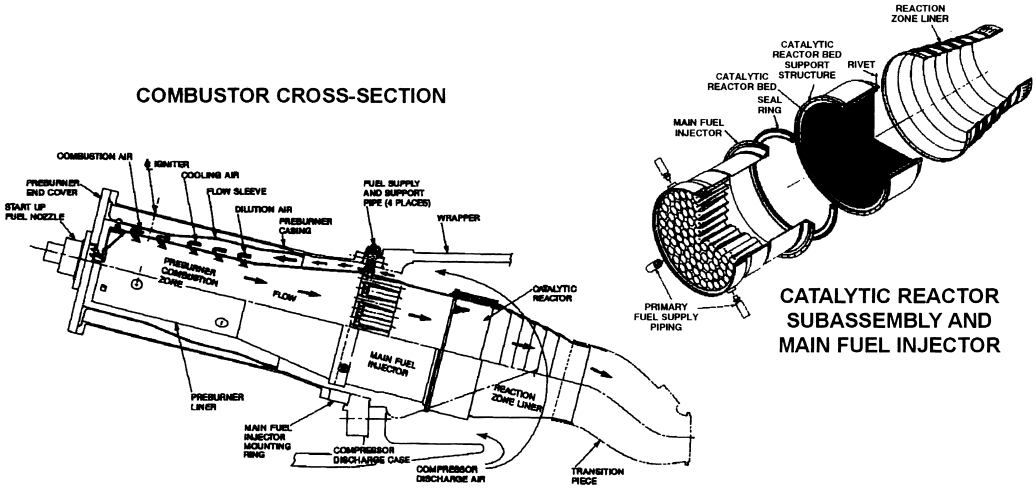


Fig. 1. Catalytic combustor design concept for the GE MS9001E gas turbine burning natural gas fuel.

of these recent tests are presented in this paper. Due to full-scale test facility resource constraints and cost, this type of testing must be limited to short duration. To obtain data on the effects of longer term exposure of the catalytic reactor to the gas turbine combustor operating environment, subscale testing of reactor components and materials has also been conducted. During the current phase of the program, high-pressure, LCF testing has been conducted on samples representing the active stages of the reactor and long-term endurance testing has been conducted at atmospheric pressure on samples representing the exit stage of the reactor which is the most severe thermal environment for the reactor. The results of this testing are also presented in this paper.

2. Combustor design

The GE catalytic combustion system design concept for the MS9001E gas turbine is shown in Fig. 1. There are four major subassemblies in the overall combustion system: the preburner, the main fuel injector, the catalytic reactor, and the downstream combustion liner leading to the transition piece. These components have been described in previous publications [2,4]. To summarize, their functions are as follows:

2.1. Preburner

The preburner carries the machine load at operating conditions which are outside the catalyst operating window. This occurs during gas turbine start-up or fired shut-down at low load points, where the fuel required for turbine operation is insufficient for the catalyst to generate the necessary minimum exit temperature. As the turbine load is increased, progressively more fuel is directed to the catalyst through the main fuel injector and progressively less goes to the preburner. At high load, the preburner receives only a small fraction of the total fuel as needed to maintain the catalyst above its minimum inlet temperature.

2.2. Main fuel injector

This component is designed to provide a fuel–air mixture to the catalyst which is uniform in composition, temperature, and velocity. A multi-venturi tube (MVT) fuel-injection system has been developed by GE specifically for this purpose [1]. The design consists of 93 individual venturi tubes arrayed across the flow path, with four fuel-injection orifices at the throat of each venturi. Because the venturi is an aerodynamically efficient flow device, it can be operated at relatively high throat velocity without incurring a high overall air-side pressure loss. This gives the design

better flame holding resistance than most other fuel–air premixer design concepts used for low emissions combustion applications.

2.3. Catalytic reactor

The role of the catalyst is to react enough of the incoming fuel to generate an outlet gas temperature high enough to initiate gas phase homogeneous combustion just downstream of the catalyst exit. The fuel–air mixture approaching the catalyst is very lean to assure that the maximum temperature reached in the post-catalyst reaction zone is below the thermal NO_x formation threshold temperature. This mixture is always maintained below the lean limit of flammability for natural gas-in-air and will not react without the assistance of the catalyst.

2.4. Post-catalyst reaction zone

This is the location of the final combustion reactions that complete the oxidation of the fuel and any remaining carbon monoxide (CO) in order to achieve ultra-low emissions. The gas phase reactions must be completed prior to the injection of any dilution air into the hot gas path in order to avoid local quenching of the chemical reactions.

3. Program description

This paper covers the third phase of a continuing design and development program. The first phase of the program included preliminary catalytic combustion system design with limited component and materials development testing. The second phase, completed in 1996, was a technology development program including full system testing with emphasis on meeting the program emissions performance objectives. The third phase, completed in 1999, has continued the technology development effort with emphasis on catalytic reactor durability and the service life of the system.

Three separate activities discussed in this paper were conducted in parallel during the Phase 3 catalytic combustor development program to explore different aspects of system performance and durability. The first activity discussed is high-pressure, LCF testing of the catalytic reactor. To be viable in commercial gas turbine service, the catalytic reactor must be capable of withstanding the gas turbine duty cycle over an extended service life without significant deterioration in performance or mechanical integrity. For the purpose of this test program, it was decided to simulate the duty cycle of a utility gas turbine with daily start–stop cycles over a one year service period. In addition to normal start-stop cycles, a gas turbine in utility service will experience emergency stops, referred to as turbine trips, due to turbine-generator system faults or problems on the utility grid. The number of turbine trip-cycles was set conservatively at 35 for test to cover a “worst case” application with margin. Therefore, the total number of transients for the reactor LCF test was set at 350 routine start-stop cycles covering conditions from full-speed, no-load (FSNL) to baseload and back; and, 35 turbine trip-transients from full baseload conditions. The turbine trip-transients are particularly severe on the combustion system, as well as other turbine components, because of the thermal shock associated with the sudden cessation of fuel flow. This testing was conducted at subscale because the cost of long-term testing of this type at full-scale is prohibitive and no full-scale test facility is available for this purpose.

The second activity discussed is atmospheric pressure endurance testing of the catalytic reactor. The utility gas turbine application will require the catalytic reactor to endure long-term exposure at high-load combustor operating conditions without significant loss of activity or mechanical integrity. This is a high-temperature, high-velocity, oxidizing environment which is known to cause some materials degradation after long-term exposure due to oxidation, corrosion and erosion. The section of the catalytic reactor which will experience the most severe operating environment in service is the exit stage where gas temperature and velocity are highest. For the endurance test program, it was decided to prepare samples representing the exit stage of the reactor and expose these samples at simulated reactor exit temperature in the products of natural gas combustion in air. Exposure times up to 6000 h were used because this was the maximum achievable within the program time frame. The testing was conducted at subscale and atmospheric pressure because the cost of full-scale,

full-pressure endurance testing is prohibitive. However, this type of subscale low-pressure testing has been used successfully in the past by GE to screen candidate materials and predict in-service materials behavior for other high temperature gas turbine applications. Since two types of material, nickel-based and iron-based, are under consideration for use as catalytic reactor foil substrates, both types of material were tested in the same operating environment.

The third activity discussed is short-term laboratory testing of the MS9001E single-can catalytic combustion system at full-scale, full-pressure conditions. Prior testing of this type had shown that program emissions performance objectives could be met [3]. This prior testing also revealed mechanical design deficiencies with the catalytic module container design and associated interface seals with the catalytic element and with the combustor liner. Modifications to the design of these components were incorporated into this test series to meet the required durability and robustness for gas turbine application. One objective of the Phase 3 testing was to verify that these mechanical design deficiencies could be overcome without compromising the emissions performance of the system. Another objective of the Phase 3 testing was to determine the minimum post-catalyst reaction zone residence time required to meet the program CO emission objective at baseload. Prior testing with a 28 ms post-catalyst residence time design showed this to be sufficient for CO burn-out [3]; however, the system tested, which included an in-line preburner and catalyst fuel-injection system, was too large to be installed on the GE MS9001E gas turbine without major machine mid-section design modification. Therefore, Phase 3 testing included a shorter 15 ms post-catalyst residence time system, which would fit on the MS9001E gas turbine, to determine if this reduced residence time would suffice for CO burn-out.

4. Approach

4.1. LCF testing

In addition to steady-state operation of a catalytic combustor, controlled engine start-ups or shutdowns can impact catalyst life due to the wide range of operating temperatures experienced during start-up and shutdown. Likewise, a sudden, uncontrolled shutdown, or turbine trip, can subject the catalyst to a very large and rapid drop in temperature. The effects of these transient events can affect catalyst performance and potentially reduce catalyst life. In order to evaluate the effect of turbine starts and trips, an experimental program has been conducted to subject a multi-stage catalyst system to 350 load–unload, start–stop, cycles as well as 35 turbine trip-cycles; the equivalent of 1 load–unload cycle per day and three turbine trips per month during a one year period of turbine operation. The cycle simulations were performed in Catalytica's High Pressure Catalyst Test Facility, as part of the current development program, at conditions representative of a GE MS9001E gas turbine combustor. Compressed air is heated using an electric preheater and a natural gas-fired preburner. Typical pipeline natural gas is injected into the preheated air. The mixture then flows into a series of static mixing elements and finally through the catalyst section. The catalyst inlet face velocity is approximately 18 m/sec with a catalyst inlet pressure of 12.6 atmospheres and catalyst inlet gas temperature of 450°C at the baseload operating point.

Catalyst inlet temperature as well as catalyst fuel-to-air ratio were simultaneously manipulated in order to simulate loading and unloading of a MS9001E gas turbine. Gas sample probes were used to measure emissions at the equivalent length corresponding to the exit of the combustor. In addition to the load and unload cycle, turbine trip-cycle simulations were also conducted to study their effect on catalytic combustor performance.

4.2. Endurance testing

The approach for this activity is to use a small-burner-rig (SBR) to conduct tests to determine the extent of oxidation–corrosion and microstructural changes in the materials when exposed to a combustion environment. An SBR consists of a tube containing test samples in a furnace with a fuel nozzle and a small combustion chamber at one end and an exhaust at the other as shown in Fig. 2. Natural gas having a typical composition given in Table 1 is burned in the combustion chamber of the preburner rig and products of combustion are allowed to flow through the section containing the catalyst sample. No fuel

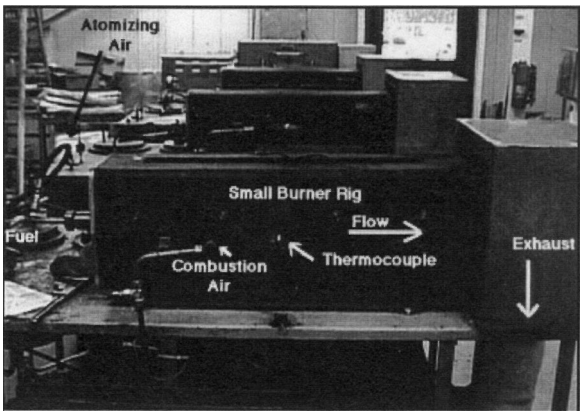


Fig. 2. Catalytic reactor sample endurance testing at 1 atm pressure.

is added between the combustion chamber and the catalyst. The combustion gases are at a temperature of 950°C and flow at an estimated 21–24 m/s. The temperature uniformity of the test rig is measured using an instrumented sample fixture per a standard procedure. After exposure for pre-selected periods of time, the test samples are removed from the test rig and subjected to extensive post-exposure evaluations.

Two different substrate foil materials were included in the test plan: an iron-based alloy and a nickel-based alloy and the samples were exposed in the rig in pairs of these materials. The endurance testing for the catalytic reactor samples was carried out at 950°C for a total of 6000 h with evaluations at intermediate exposure times of 500, 1500, and 3000 h. A total of four samples, each 2.5 cm diameter by 5.1 cm long, could be exposed in the burner rig at any time, and in order to obtain data at various time intervals, pairs of samples were removed and replaced by new samples per a protocol. Evaluations were conducted after exposure testing to assess the overall integrity of the substrate-catalyst system as well as any change in the catalytic activity. The plan included the following evaluation procedures:

1. Weight/weight gain;
2. Visual examination;
3. X-ray diffraction;
4. Surface analysis by Auger electron microscopy;
5. Microscopic exam (longitudinal and transverse sections);
6. Elemental analysis;
7. Measurement of the catalytic activity (by CCSI).

Not all of these evaluation procedures were applied on all the samples and a careful selection was made to generate evaluation results.

Table 1
Typical composition of natural gas test fuel

Volume constituent	Percent
Methane	96.06
Ethane	1.96
Propane	0.27
Butane	0.14
Pentane	0.06
Hexane	0.03
Oxygen	0.01
Nitrogen	0.59
Carbon dioxide	0.87

4.3. Full-scale, full-pressure testing

The full-scale testing discussed in this paper was conducted at the GE Power Generation Technology Laboratory located in Schenectady, NY, USA. The single-burner test stand used for full-scale (reactor diameter of 508 mm), full-pressure testing (pressure ratio of 12.6) of the catalytic combustion system duplicates a sector of the internal geometry of the MS9001E gas turbine containing one combustor of a machine set of 14. Two test rigs were used for this program. The first test rig, referred to as the "long" system, had a post-catalyst liner and transition piece designed to provide a reaction zone residence time of 28 ms at baseload conditions. This test rig is shown in Fig. 3, as installed in the MS9001E combustor development test stand, with major components identified. The second test rig, referred to as the "short" system, had a post-catalyst liner and transition piece designed to provide a reaction zone residence time of 15 ms at baseload conditions. This test rig is shown in Fig. 4 as installed in the MS9001E test stand.

The fuel used for all fired testing was natural gas supplied by a local utility company. The fuel composition was not measured during the test; however, the utility company has provided a typical analysis which is shown in Table 1.

The test rigs were both instrumented with thermocouples and pressure taps to measure air and fuel pressures and temperatures, hot gas pressures and

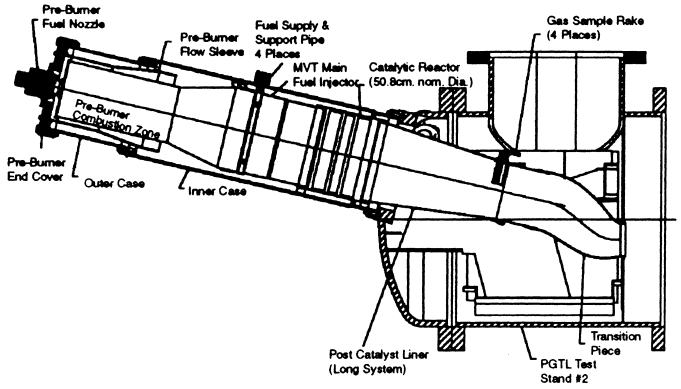


Fig. 3. 9E test rig with 29 ms post-catalyst residence time.

temperatures, and metal temperatures at various stations throughout the assembly. The test stand included a hot gas immersion thermocouple array in the nozzle box at the transition piece (TP) exit plane to measure combustor exit temperature distribution and standard sample probes downstream of the choked flow-quench plane in the nozzle box to obtain well-mixed emission samples. The TP also included an optical port which allowed a video camera to record the image of the catalytic reactor exit face as viewed through the post-catalyst reaction zone during the test. In addition to the instrumentation discussed above, the "long" system post-catalyst liner was equipped with four emissions sample rakes as shown in Fig. 3. These rakes, which had five sampling ports each at different immersions, allowed gas samples to be taken at the 15 ms residence time plane during the "long" system test. For all testing, the continuously recorded data included flow rates, inlet and exit temperatures and pressures, dynamic pressure, and emissions.

Fig. 5 shows the catalytic reactor used throughout the Phase 3 development test program. This reactor, which was produced by CCSI, included current state-of-the-art mechanical design features to resolve mechanical problems encountered with prior reactor designs. The improvements included: (1) new design features to allow for radial differential thermal expansion between the reactor bed and containment can; (2) new axial load-bearing features which provided load-sharing among the support structures for each of the three stages; and (3) new flexible metal "E" seals at the interfaces with the main fuel injector and

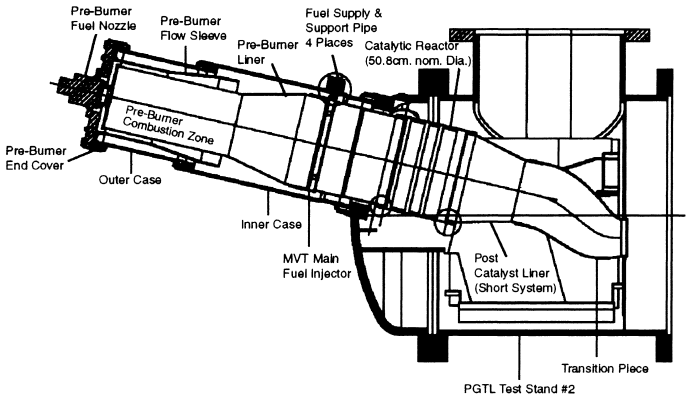


Fig. 4. 9E test rig with 15 ms post-catalyst residence time.

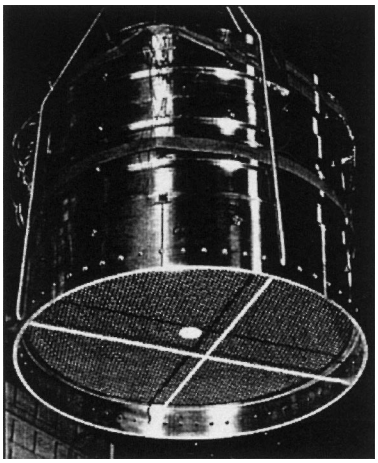


Fig. 5. Catalytic reactor prepared for test.

post-catalyst liner. Fig. 6 is a schematic cross-section of the catalytic reactor showing some of the major design features. As shown in the figure, the reactor is a three-stage design with bonded metal monolith (BMM) honeycomb support structures bounding each active stage. The reactor was heavily instrumented for the test program. Fiftysix thermocouples were applied at various locations throughout the reactor to measure metal surface and hot gas temperature distributions. Twenty gas sample probes were arrayed at the reactor inlet face to measure fuel–air mixture strength distribution approaching the reactor. At appropriate test points, conditions were maintained steady for a period of approximately one hour in order to analyze the fuel concentration at each of the 20 catalyst inlet sampling points.

Reactor operation was started by first heating the system with the preburner to a temperature above the minimum required by the catalyst and then starting fuel flow to the reactor through the main fuel injector. This procedure resulted in a smooth light-off of the reactor with a uniform temperature profile across its face. The total air flow and fuel flows to the preburner and main fuel injector were then adjusted to simulate various load conditions over the gas turbine load range based on machine cycle analysis.The catalyst could be extinguished simply by turning off the fuel supply to the MVT injector and could be restarted just as simply by repeating the start-up sequence. Over the course of the Phase 3 testing, which was conducted in November, 1998, and February, 1999, the catalytic combustion system accumulated approximately 26 h at high-pressure fired conditions including full baseload conditions for the MS9001E gas turbine combustor.

5. Results

5.1. LCF testing

Fig. 7 shows typical catalyst inlet and adiabatic combustion temperatures (Cat in and Cat Tad, respectively) during a simulated cycle. The cycle represents only the load portion of the engine cycle and does not include the acceleration portion. The cycle begins at a steady-state condition representing FSNL after

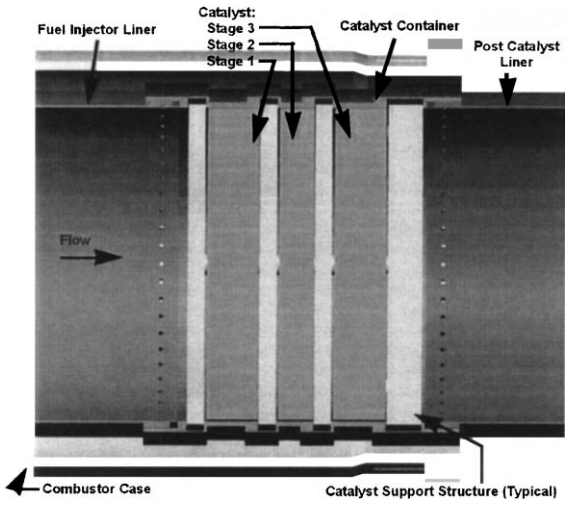


Fig. 6. Catalytic reactor schematic cross-section.

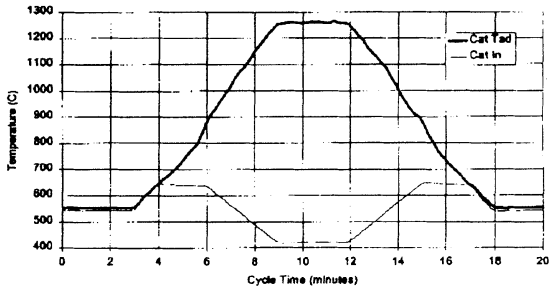


Fig. 7. A typical simulated load–unload cycle.

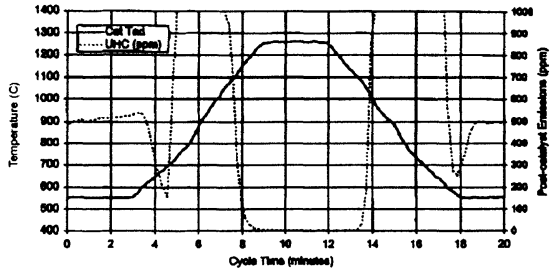


Fig. 8. Post-catalyst burn-out zone UHC emissions.

which the catalyst inlet temperature (represented by an increase in preburner exit temperature) is increased rapidly to a value well above the catalyst light-off temperature. At that point, catalyst fuel flow is increased while inlet temperature is decreased. This subsequent increase in catalyst Tad represents an increase in engine load. The baseload condition is maintained at steady-state for 3 min. Following the steady-state, the load is reduced by lowering the catalyst fuel flow and correspondingly increasing the inlet temperature. The complete cycle is 20 min in duration.

Post-catalyst burn-out zone emissions were measured at an axial location equivalent to 25 ms post-catalyst residence time. Figs. 8–10 indicate the

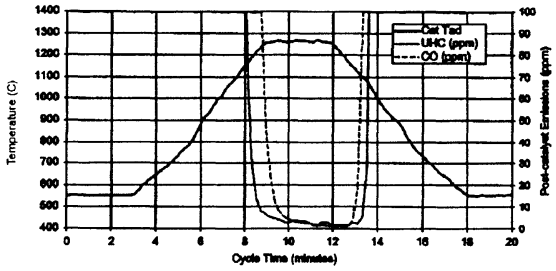


Fig. 9. Post-catalyst burn-out zone CO and UHC emissions.

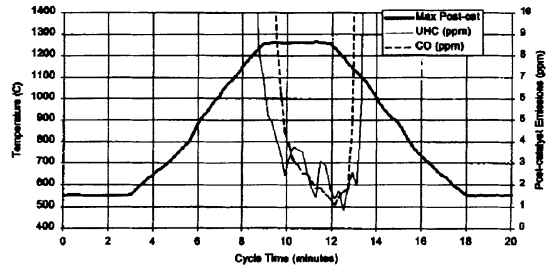


Fig. 10. Post-catalyst burn-out zone CO and UHC emissions.

levels of CO and unburned hydrocarbon (UHC) measured. Fig. 8 has a maximum scale of 1000 ppm, while Figs. 9 and 10 have maximums of 100 and 10 ppm, respectively. Fig. 8 shows that the UHC reach levels above 1000 ppm when fuel is first introduced to the catalyst. However, as the Tad and outlet gas temperatures increase towards the baseload condition, reducing the ignition delay time, the UHC burn-out to levels well below 10 ppm. As the UHC emissions decline, there is a large CO peak followed by a rapid decline to a value less than 10 ppm. The CO spike is not seen in Fig. 9 since the analyzer span was set at 100 ppm. This burn-out behavior was observed consistently throughout all cycling testing. UHC concentrations were measured using a 1000 ppm scale throughout the cycle testing while a 100 ppm full-scale range was used for CO measurements. Fig. 10 shows that the UHC level was 5 ppm or less whenever the CO level was below 10 ppm. Fig. 11 is a plot of CO and UHC emissions, measured at the 25 ms equivalent distance under simulated baseload conditions, for each of the 350 load–unload cycles. Emissions were not measured between cycles 50 and 100 and between cycles 220 and 260 due to the unavailability of the gas analyzers.

In addition to simulating loading and unloading of the turbine, it is desirable to simulate the sudden drop in load associated with a turbine trip. Turbine trips occur infrequently, but can subject the catalyst to very rapid and very large thermal transients. To simulate a turbine trip, just as in the load–unload simulation, we began at FSNL and increased the catalyst Tad to the simulated baseload condition. After a 3 min steady-state at baseload, the catalyst fuel-flow and preburner fuel-flow were suddenly stopped causing a

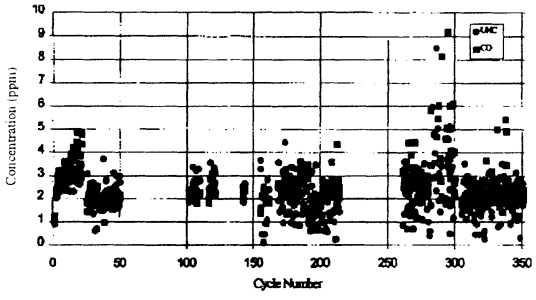


Fig. 11. Post-catalyst burn-out zone CO and UHC emissions vs. cycle number.

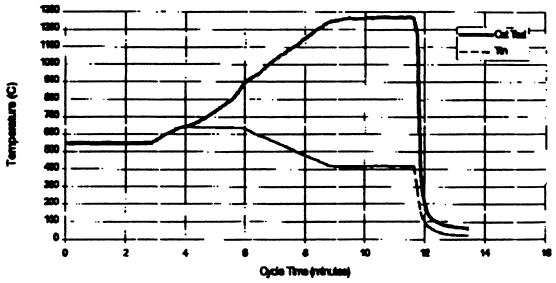


Fig. 12. Typical measured trip simulation vs. cycle time in minutes.

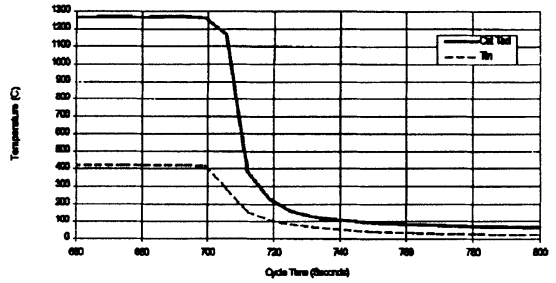


Fig. 13. Typical measured trip simulation vs. cycle time in seconds.

rapid decrease in catalyst inlet gas temperature. Fig. 12 shows a typical turbine trip-simulation. Fig. 13 illustrates further the transient response of the system. The catalyst Tad declined by approximately 90% in 10–15 s. The catalyst inlet gas temperature required approximately 30–40 s to drop 90%. This may be due to a thermal lag in the gas path upstream of the catalyst.

5.2. Endurance testing

Table 2 presents a summary of the samples exposed in the small burner rig and the post-exposure evaluations completed. The baseline samples were evaluated as manufactured without exposure to compare similar data generated after exposure of other samples in the burner rig. These baseline samples, an iron-based alloy and a nickel-based alloy, were evaluated by electron microprobe for materials identification of the surface layers on the foil. X-ray energy spectra (EDS) were recorded from each side of a small piece cut from each sample and the results are shown in Figs. 14–17. Both baseline samples have a brown aluminum oxide coat and palladium oxide layer on top. Also on both samples was evidence of the presence of a gray aluminum oxide layer. Elemental analysis on the baseline samples using energy dispersive spectroscopy revealed the presence of Fe, Cr, Al in the iron-based sample and Ni, Cr, Fe, Al in the nickel-based sample.

X-ray diffraction carried out on the brown layer of foil cut pieces confirmed the presence of the PdO layer but ZrO_2 peaks were also identified. The thin aluminum oxide layer on the gray side of the foils could not be detected by X-ray diffraction. The Auger electron spectroscopy on the oxide layer was not conclusive and was not pursued further.

In order to perform the microstructural evaluation, the reactor samples were potted in epoxy mounting material, parted longitudinally and polished and etched. A typical section through the reactor sample is shown in Fig. 18. Entire sections of the sample were viewed under the microscope and pictures were taken in the general areas identified by Positions I and II shown in Fig. 18. The pictures for both substrate samples are shown in Figs. 19 and 20. It can be observed from the pictures that there is a wide variation of the grain size between Positions I and II on the same foil. The microscopic images of the foil sections showed a catalyst layer and an oxide layer on top of each metal substrate. The oxide layers were analyzed using X-ray diffraction and electron microprobe and

Table 2
Small burner rig (SBR) catalyst endurance test summary

Elapsed time in SBR (h)	No. of samples loaded in rig	No. of samples removed from the rig	No. of samples in the rig (exposure, h)	Catalytic activity evaluation	Phase/elemental analysis	Microstructure analysis
0	4	0	4	Yes	Yes	Yes
500	2	2	2 (500 h), 2 new	Yes	No	Yes
1500	2	2	2 (1000 h), 2 new	Yes	No	Yes
3000	2	2	2 (1500 h), 2 new	Yes	Yes	Yes
6000	0	2 (6000 h), 2 (3000 h)	0	Yes	Yes	Yes

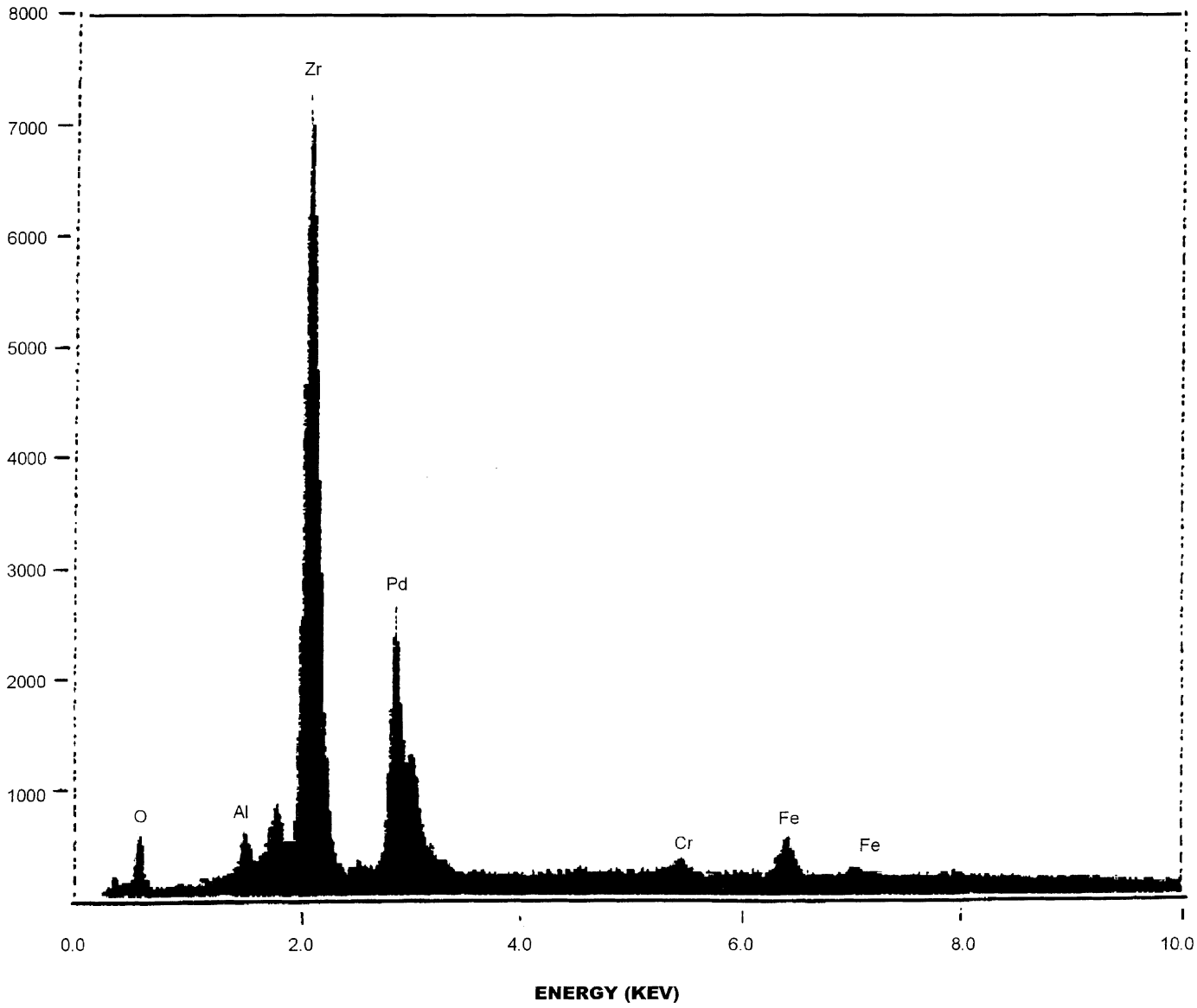


Fig. 14. Electron microprobe spectra from the oxide layer and the catalyst layers of iron-based baseline sample. Measured on catalyst-coated side of foil.

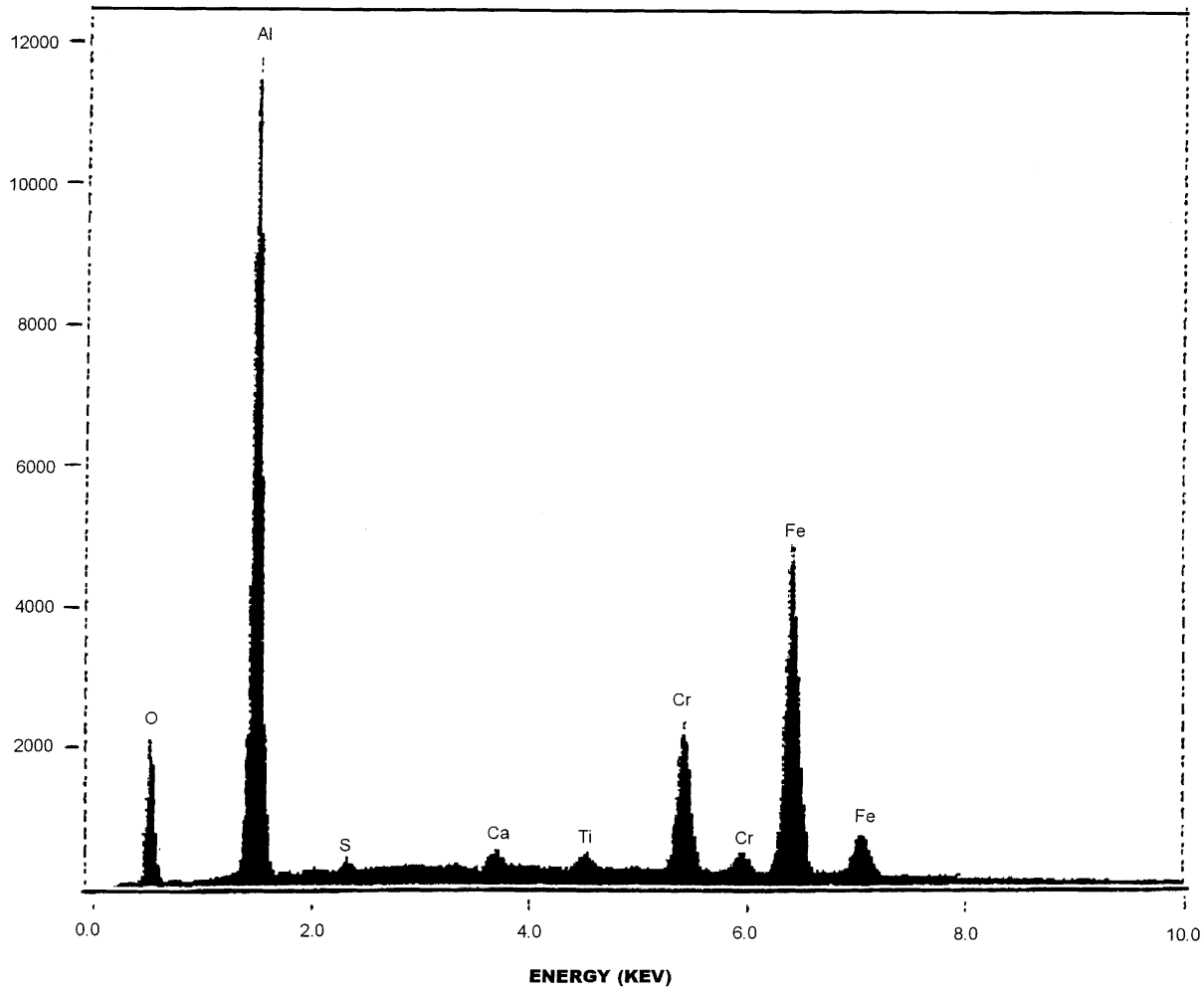


Fig. 15. Electron microprobe spectra from the oxide layer and the catalyst layers of iron-based baseline sample. Measured on uncoated side of foil.

were identified to be aluminum oxide. The thickness of the oxide layer on both substrates is estimated to be approximately 1 μm.

Microstructural evaluation of the 1000 h exposure samples was carried out following the same procedure as that of the baseline samples. Based upon the similarity of the microstructures of the exposed samples relative to the baseline samples, it was concluded that 1000 h exposure is too short a time for significant changes. Microstructural evaluation of the 1500 h exposure samples indicated that the nickel-based alloy did not show any significant changes relative to the baseline (see Fig. 21), but the iron-based alloy showed the presence of some fine precipitates as shown in Fig. 22. The thickness of the oxide layers as determined from the cross section pictures was estimated to be 1–2 μm. The oxide scale on both the samples was found to be continuous and intact and was of the order 1–2 μm thick. The microprobe spectra on the oxide later identified the presence of aluminum oxide.

The microstructure of the samples exposed for 3000 and 6000 h was also examined after following a similar sequence of sample preparation and it was found that, except for the presence of small precipitates, the microstructure of the substrate had not significantly

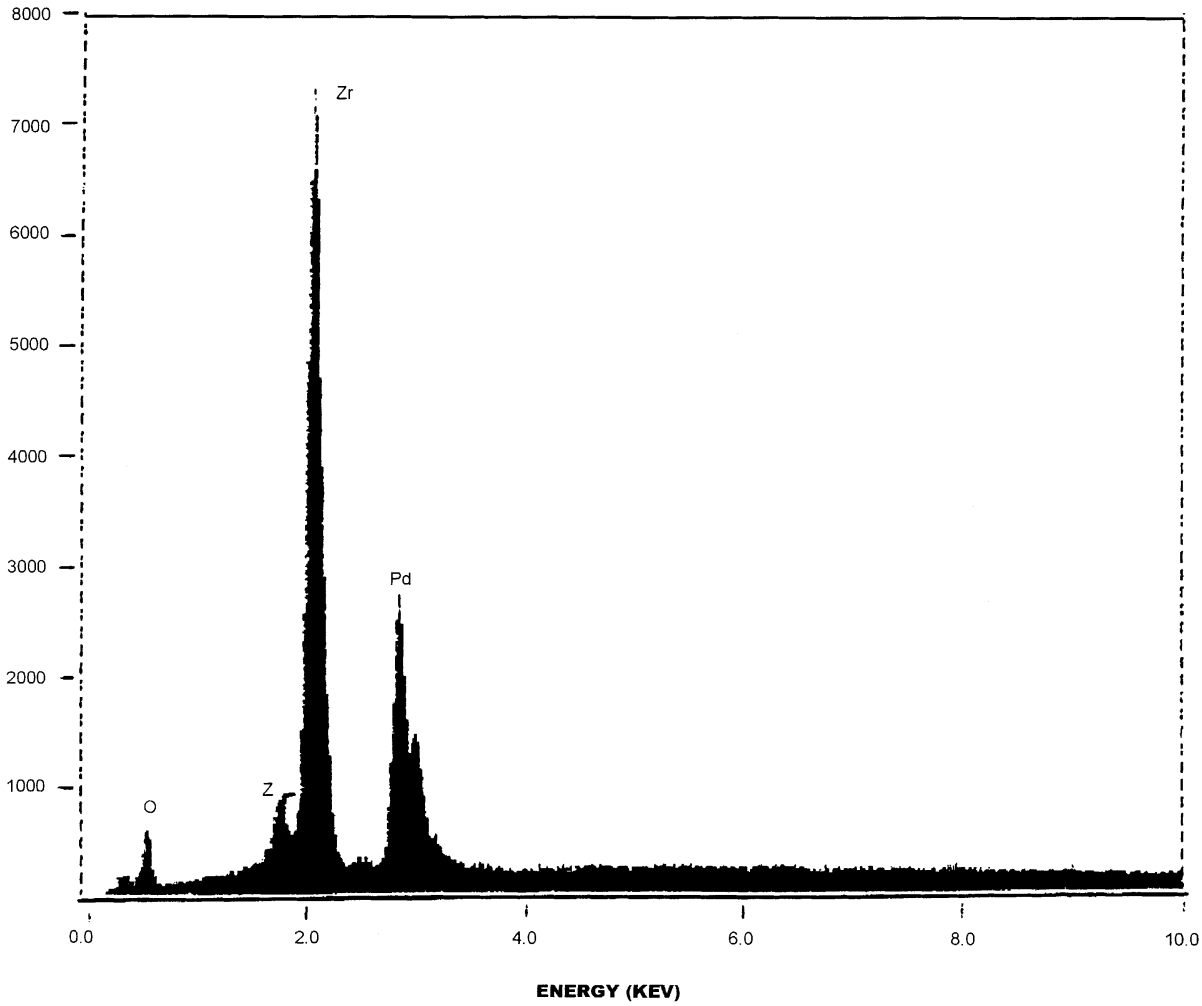


Fig. 16. Electron microprobe spectra from the oxide layer and the catalyst layers of nickel-based baseline sample. Measured on catalyst-coated side of foil.

changed relative to the baseline microstructure (Figs. 23 and 24 show the 6000 h samples). The oxide layer is estimated to be approximately 2 μm after 6000 h exposure. The oxide layer after 6000 h was confirmed to be aluminum oxide as determined by elemental analysis. The oxide layer appears to be compact and continuous after 6000 h of exposure.

In summary, the nickel-based samples exposed in the burner rig for 500–6000 h do not show any significant change in the substrate microstructure relative to that of baseline samples. The iron-based alloy substrate shows the development of fine precipitates in the microstructure after 1500 h of exposure but the amount of these precipitates even after 6000 h does not appear to affect the general integrity of the substrate. Based on the evaluation, the microstructural stability of the nickel-based alloy appears to be somewhat superior to the iron-based alloy.

CCSI measured the catalytic activity of all of the samples exposed in the small burner rig as well as the baseline samples. The catalytic activity measurements included light-off, conversion rate, and extinction temperature. The comparative behavior between the 6000 h and baseline samples was typical of “break-in” behavior for catalytic reactors which is acceptable for the gas turbine combustor application.

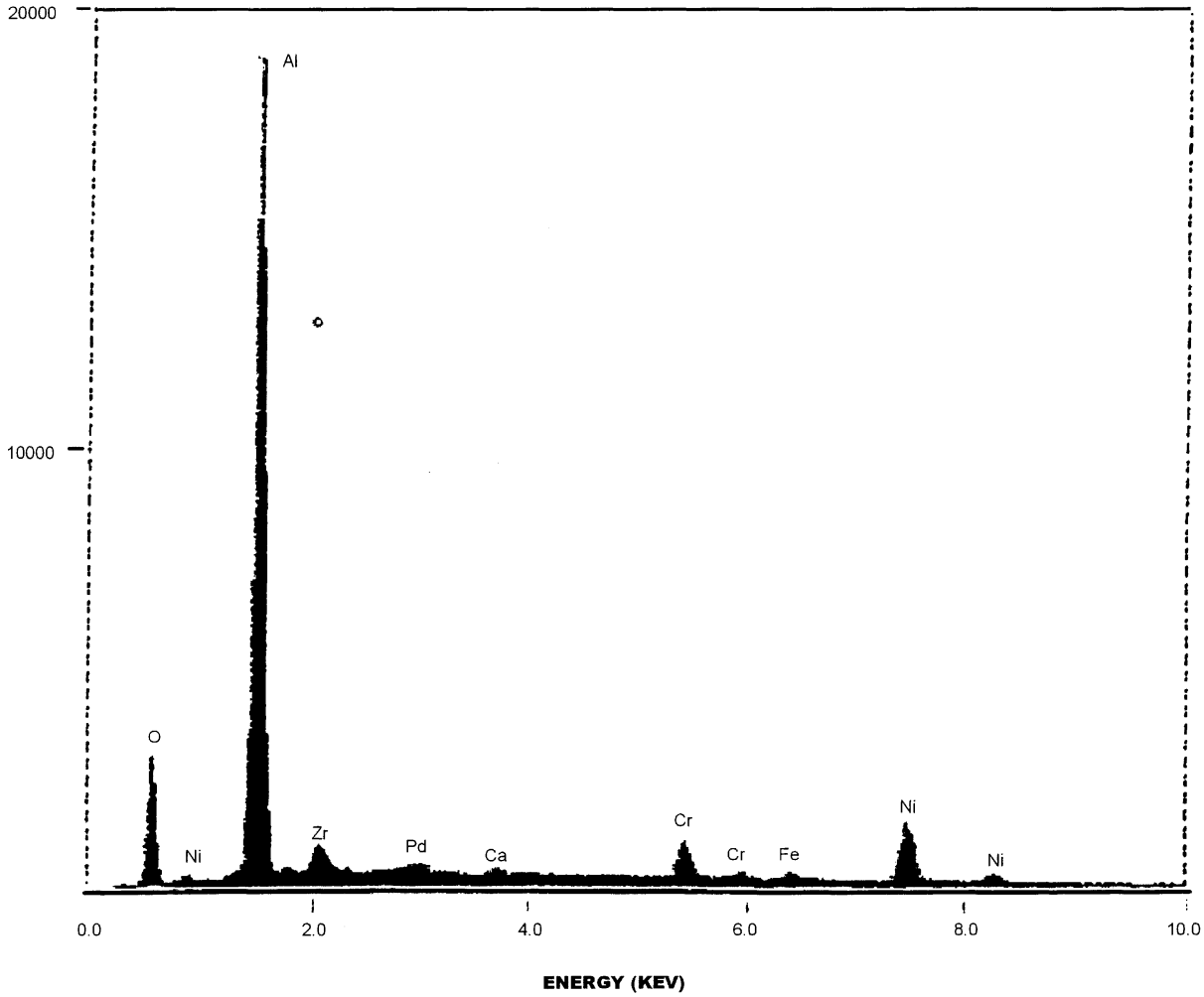


Fig. 17. Electron microprobe spectra from the oxide layer and the catalyst layers of nickel-based baseline sample. Measured on uncoated side of foil.

5.3. Full-scale, full-pressure testing

Table 3 provides a summary of test results at baseload for some of the major performance parameters of the catalytic combustion system. Data for both the "long" and "short" systems are presented for comparison. The emissions performance of the "long" system, Test 1 (11/98), is the best ever achieved during the MS9001E catalytic combustor development program and meets all program emissions goals with margin. The baseload NO_x emission level achieved during this test is approximately 50% of the lowest level previously obtained [3]. The reason for this improvement is the lower operating window of the catalyst which allowed the system to operate at lower preheat than previous test configurations. This permitted combustion system operation at lower preburner temperature rise than in prior testing. The NO_x emissions from the catalytic combustor are produced almost exclusively by the diffusion flame preburner. This result has been documented during previous testing [2,4]. The preburner design used for the current program is the same as used in previous testing and its NO_x generation characteristic was measured as shown in Fig. 25. The baseload preburner temperature rise during Test 1 was about 32°C lower than in

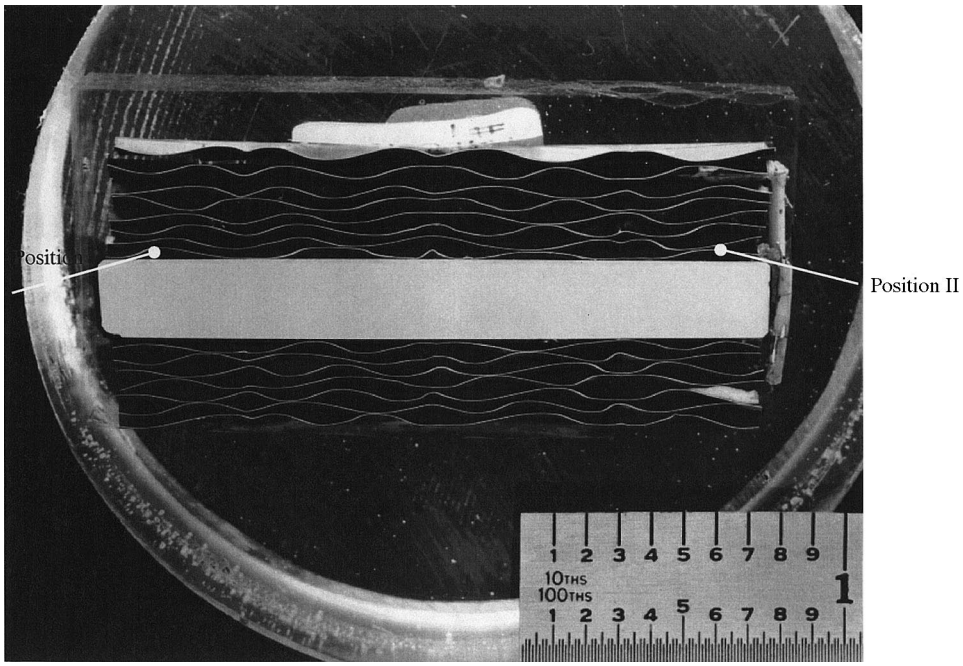


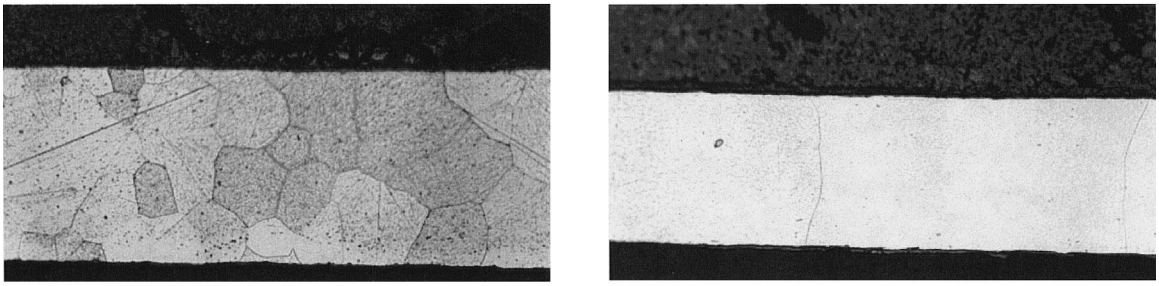
Fig. 18. Longitudinal section from a reactor sample showing foil lengths (Areas marked as Positions I and II were used to obtain typical microstructural details of a foil).

previous testing which accounts for the system NO_x emission improvement.

Test 1 also showed performance improvements in other areas. At 0.069, the combustor exit temperature pattern factor was the lowest ever measured in this program. The pattern factor indicates the uniformity of the combustor exit temperature distribution as measured by the nozzle box thermocouple array and is defined as

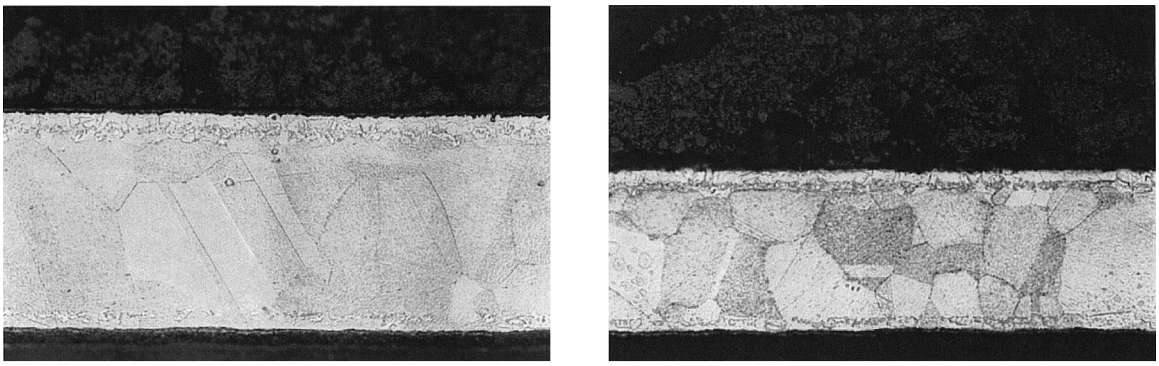
$$\text{Pattern factor} = \frac{\text{maximum temperature} - \text{mean temperature}}{\text{mean temperature} - \text{inlet temperature}}$$

The program target pattern factor is 0.10, a value matching the current GE 9E diffusion flame combustor performance, and this objective was met for the first time in the program by the Test 1 system. The reason for this improvement is reduced seal leakage



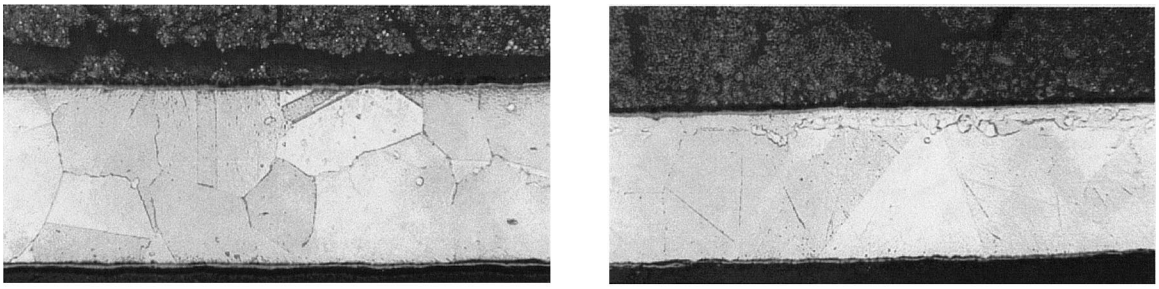
Position I Position II

Fig. 19. Microstructure at Positions I and II showing the foil, oxide layer and the catalyst (1000×) of the iron-based baseline sample.



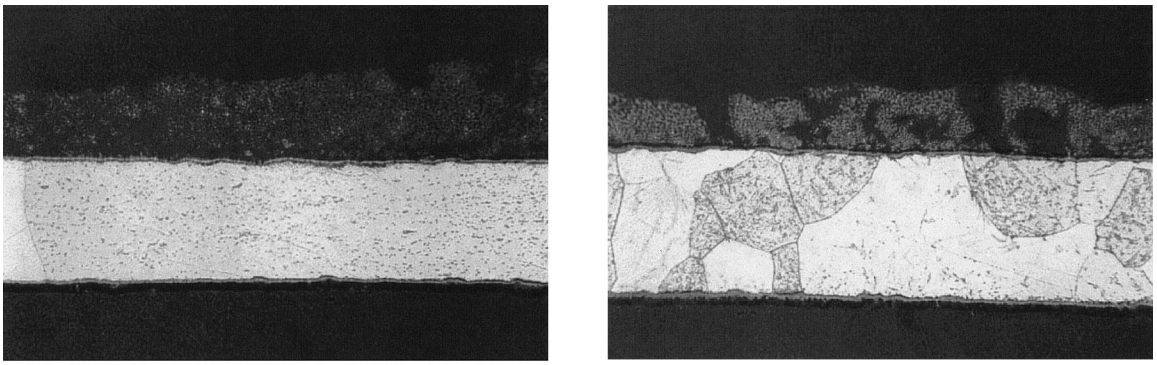
Position I Position II

Fig. 20. Microstructure at Positions I and II showing the foil, oxide layer and the catalyst (1000×) of the nickel-based baseline sample.



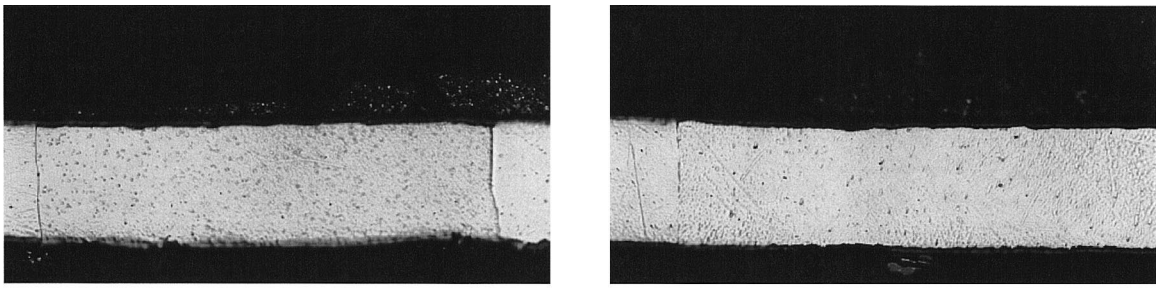
Position I Position II

Fig. 21. Microstructure at Positions I and II showing the foil, oxide layer and the catalyst (1000×) of the 1500 h exposed nickel-based sample.



Position I Position II

Fig. 22. Microstructure at Position I and II showing the foil, oxide layer and the catalyst (1000×) of the 1500 h exposed iron-based sample.



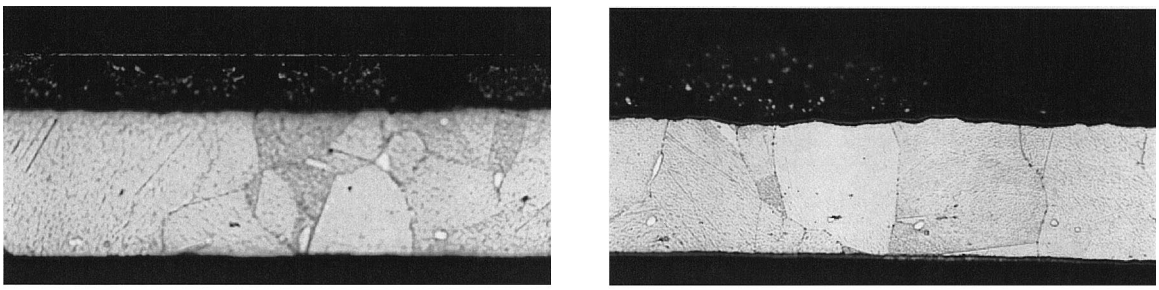
Position I Position II

Fig. 23. Microstructure at Positions I and II showing the foil, oxide layer and the catalyst (1000×) of the 6000 h exposed iron-based sample.

which was obtained by improved seal design and reduced pressure drop. Overall system pressure drop is another area where the Phase 3 design showed improvement. The measured combustor system pressure drop at baseload during Test 1 was 7.6% of compressor discharge pressure (Pcd) vs. a program objective of 6.5% Pcd. The measured pressure drop across the catalytic reactor at baseload was 2.7% Pcd compared to the original design target of 2.5% Pcd. While the program objective has not yet been met and further reduction in pressure drop is still required, the Test 1 result is the lowest pressure drop achieved to date. The pressure drop reduction of Phase 3 was due to an improvement in the aerodynamics of the air flow path from compressor discharge to the combustor.

The only parameter from Test 1 which showed worse performance than prior tests was dynamic pressure activity. At 7 kPa (0.93 psi), the overall root mean square (RMS) dynamic pressure level from Test 1 at baseload was about twice that measured in prior testing. This increase was due primarily to the appearance of a discrete tone at 230 Hz with amplitude (peak-to-peak) of 2.9 kPa (0.38 psi). This remains relatively quiet operation compared to typical production premixing DLN combustors and would not be expected to limit the life of the combustor. Nonetheless, the trend toward increased noise generation is undesirable. The cause of this occurrence is believed to be operation of the preburner fuel nozzle at too low a pressure ratio, which is associated with the reduced preheat required by the catalytic reactor. This problem can be corrected by reducing the size of the preburner fuel nozzle gas metering orifices.

The baseload performance of the “short” system, Test 2 (2/99), was not as attractive as the “long” system. The most significant problem with the “short”



Position I Position II

Fig. 24. Microstructure at Positions I and II showing the foil, oxide layer and the catalyst (1000×) of the 6000 h exposed nickel-based sample.

Table 3
Catalytic combustion system performance at baseload

Parameter	Test 1 (11/98)	Test 2 (2/99)
Post catalyst residence time	28 ms	15 ms
Total air flow, kg/s (Ib/s)	23.0 (50.7)	23.1 (50.8)
Inlet AIRT, °C (°F)	351 (664)	350 (662)
Pressure, kPa (psia)	1392 (186)	1396 (186.5)
Catalyst inlet *T*, °C (°F)	341 (807)	444 (832)
Combustor exit *T*, °C (°F)	1194 (2181)	1192 (2178)
Combustor exit emissions		
NO_x, ppmvd (ISO, 15% 02)	1.7	2.7
CO, ppmvd	1.3	69
UHC, ppmvd	0	2.7
RMS dynamic pressure, kPa (psi)	7 (0.93)	3.3 (0.44)
Combustor exit temperature		
Pattern factor	0.069	0.129

system was the failure to meet the program baseload CO emission objective. As seen in Table 3, the CO level measured at baseload was 69 ppmvd which shows that the 15 ms post-catalyst residence time was not sufficient for chemical reactions to go to completion. Prior subscale, full-pressure testing at Catalytica had achieved CO reaction to less than 5 ppmvd in 15 ms at the average baseload fuel–air ratio. Non-uniform fuel–air ratio at the catalyst inlet during full-scale testing or differences in combustion liner heat transfer may have contributed to the change in CO performance between subscale and full-scale testing. Attempts were made to improve upon the CO emissions performance by increasing the catalytic reactor preheat (i.e., higher preburner temperature rise) and/or reducing the velocity through the system and increasing residence time by closing the test stand discharge blast gate valve. These attempts were not successful because reactor overheating limited the CO reduction that could be obtained. Also, preburner NO_x generation increased when these changes were attempted. In addition to the emissions performance degradation with the "short" system, combustor exit temperature pattern factor and overall system pressure drop also increased with the "short" system making this a much less attractive design option based on performance.

Fig. 26 presents NO_x measurements corrected to ISO ambient and 15% oxygen concentration, as measured at the test stand exit, vs. average combustor exit temperature measured at the nozzle box. Data are presented for both closed inlet guide vane (IGV) and open IGV simulations. This is intended to represent the gas turbine operating scheme which would be used in a combined-cycle (gas and steam turbine) power plant. In this type of plant, the gas turbine is operated with closed IGVs at low load to maintain high exhaust temperature for the steam plant. The IGVs are opened at high load, about 80% of baseload, when the exhaust isotherm is reached. Since the catalytic combustor preburner NO_x generation rate is pressure sensitive, different NO_x vs. temperature curves occur for closed and open IGV simulations.

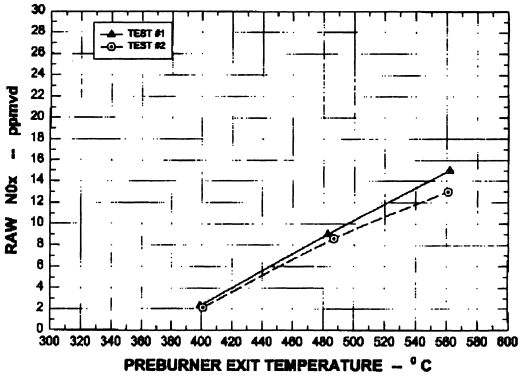


Fig. 25. Test 1 vs. Test 2 preburner NO_x generation.

As previously noted, the catalytic combustion system NO_x emissions are produced in the diffusion flame preburner. The reason for the peak in NO_x emissions at minimum combustor exit temperature is that this is the point of highest preburner temperature rise to provide sufficient preheat for catalytic reactor ignition. As

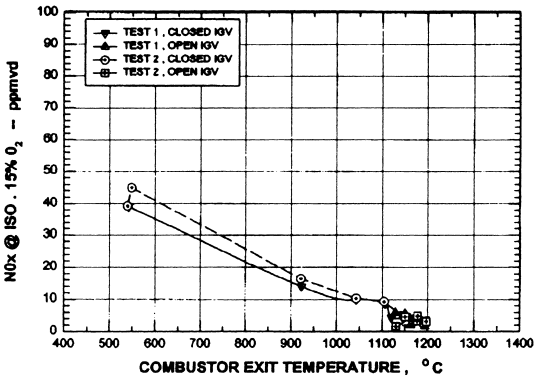


Fig. 26. Test 1 vs. Test 2 combustor exit NO_x (ISO, 15% O_2).

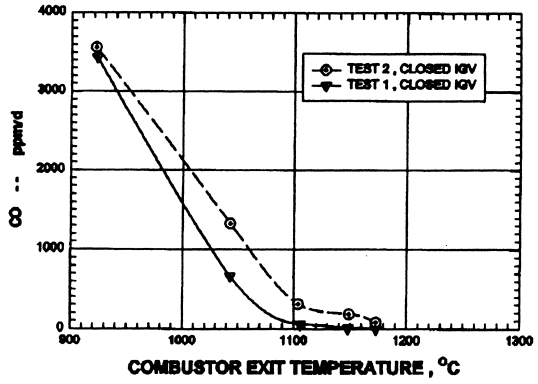


Fig. 27. Test 1 vs. Test 2 combustor exit CO.

combustor exit temperature is increased, the preheat required to sustain the catalytic reactions drops off, the preburner temperature rise is reduced, and the result is lower NO_x emissions. The NO_x emissions with the "short" system, Test 2, are shown to be slightly higher than the "long" system throughout the temperature range. The reason for this is that the "short" system was run with slightly higher preburner temperature rise in an attempt to compensate for the higher CO and UHC emissions resulting from the reduced post-catalyst residence time.

Carbon monoxide (CO) emissions data vs. combustor exit temperature are presented in Figs. 27 and 28. For clarity, the CO data at very low combustor exit temperature near machine FSNL conditions have been omitted from the figures. It is anticipated that the extreme low end of the load range will be run with only

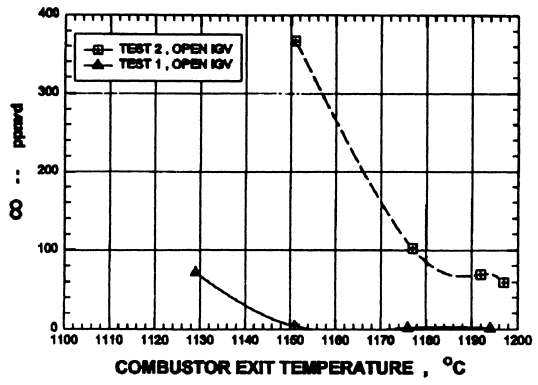


Fig. 28. Test 1 vs. Test 2 combustor exit CO.

the diffusion flame preburner fueled. The preburner being used for this program is an efficient burner at FSNL conditions and some CO reduction occurs in the catalytic reactor. The result is a CO level of approximately 30 ppmvd at FSNL. When the catalyst is first fueled at low combustor exit temperature, the catalyst exit temperature and post-catalyst adiabatic flame temperature are too low for efficient gas phase homogeneous combustion to occur downstream of the reactor. The result is high levels of CO as seen at Fig. 27 for low combustor exit temperature. As fuel flow to the catalyst is increased, the reactor exit temperature and post-catalyst adiabatic flame temperature increase and the gas phase homogeneous combustion becomes more efficient as seen in Figs. 27 and 28. UHC emissions curves, not included in this paper, show the same trends as CO.

One important aspect of the curves presented in Figs. 27 and 28 is the effect of post-catalyst residence time on CO. With the "long" residence time system, Test 1, the CO drops below 10 ppmvd at 1149°C (2100°F) on the closed IGV curve. This point corresponds to gas turbine operation at approximately 75% of baseload. However, with the "short" residence time system, Test 2, the CO never drops below 10 ppmvd and the program CO emission objective cannot be met.

A catalytic combustion system performance parameter which will be a critical factor in determining the life of the catalytic reactor in the gas turbine application is the uniformity of the fuel–air mixture strength distribution approaching the reactor inlet. Fig. 29 shows the catalytic reactor fuel–air concentration distribution as measured using the 20 reactor inlet gas sample probes at the baseload operating condition during the second test of the program. A perforated plate was installed at the preburner exit during this test in order to improve the uniformity of the velocity distribution exiting the preburner which also improves the uniformity of fuel–air concentration distribution approaching the catalytic reactor. In spite of this, the measured fuel–air distribution was not uniform enough to meet the program objective. The range of fuel–air concentration distribution shown in Fig. 29 was 15.5% (plus 7.6% minus 7.9% from the mean) vs. an objective of 10% maximum range. Fig. 30 shows the reactor exit face as seen through the transition piece view port at the baseload operating condition during Test 2. The reactor center mandrel

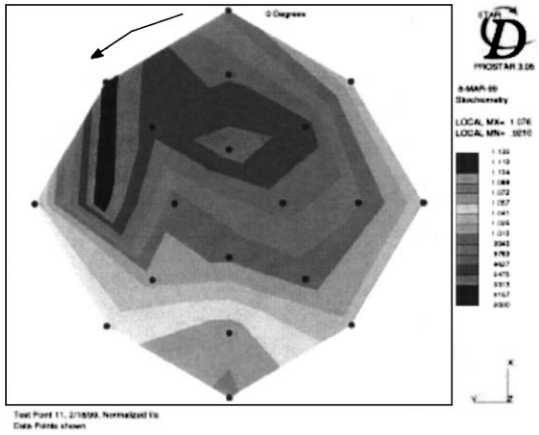


Fig. 29. Catalytic reactor inlet fuel–air concentration distribution measured at Baseload, Test 2.

exit face appears to be very hot in these images; however, post-test inspection showed that it had not been overheated. The probable explanation for this discrepancy is that reflected light made the center mandrel exit face appear hotter in these images than it actually was.

In full-scale tests during prior phases of the catalytic combustor development program, the catalytic reactor exit stage exhibited signs of mechanical distress. The catalyst-container interface did not allow for expansion of the catalyst during heating. The thermal stress caused deformation of cells in the catalyst. As part of the current development phase, a new catalyst module container was designed.

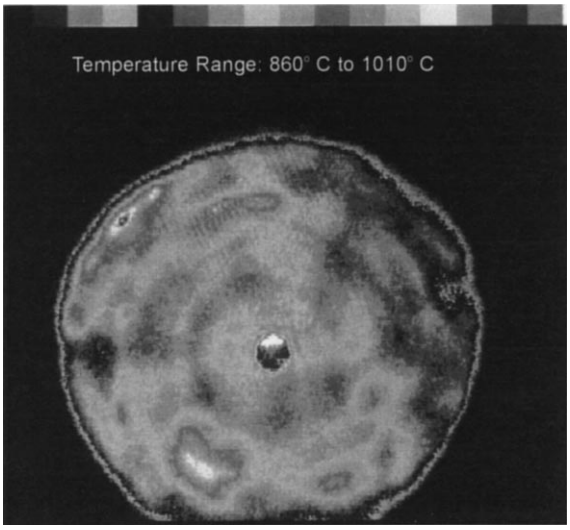


Fig. 30. Catalytic reactor exit thermal image at Baseload, Test 2.

Post-test inspection showed all the components of the catalytic combustion system to be in satisfactory condition, suitable for continued test use. A local area of high temperature was observed in the infrared image of the catalyst exit face during initial operation due to fuel–air maldistribution; however, this problem was corrected before the remainder of the test was conducted and the affected area was limited to eleven (11) 0.6 cm cells in the honeycomb. There were no visible mechanical deformities in the catalytic reactor exit stage observed at post-test inspection

6. Conclusions

6.1. LCF testing

A multi-stage catalyst system has been subjected to 350 load–unload cycles and 35 turbine trip cycles. The catalyst responded reproducibly to the simulated loading of the engine. Catalyst wall temperature response time to a turbine trip-simulation was of the order of 10 s. The catalyst exhibited no physical deformities following the cycling test sequence. The program goal of less than 10 ppm for both UHC and CO was met consistently throughout the cycling test sequence.

6.2. Endurance testing

The results of subscale atmospheric pressure endurance testing of catalytic reactor components are positive with the nickel-based alloy substrate recommended as superior to the iron-based alloy for meeting long-term service life objectives. This evaluation should be considered part of a “work in progress” with more testing in the laboratory and in an actual gas turbine combustor environment required to verify that the 8000 h minimum reactor service life objective can be met.

6.3. Full-scale, full-pressure testing

The following conclusions are based upon full-scale, full-pressure laboratory testing of the GE

MS9001E catalytic combustion system during the Phase 3 development program:

1. The catalyst module container and interface seal design improvements, which were implemented for the Phase 3 program, resolved the mechanical deficiencies which resulted in reactor exit stage distress observed at post-test inspection during prior phases of the development program. The reactor and interface design now appear suitable for machine application.
2. The "long" combustion system with 28 ms post-catalyst residence time meets all the program emissions performance objectives with margin but the "short" system with 15 ms post-catalyst residence time fails to meet the CO emission objective. Packaging the "long" system on the GE MS9001E gas turbine is problematic and additional design-development work is required to reduce the overall length of this system so that it fits on the machine.
3. The uniformity of the fuel–air concentration distribution at the catalytic reactor inlet did not meet program objectives and needs to be improved so that catalytic reactor service life objectives can be met.
4. The overall catalytic combustion system pressure drop exceeded the program objective and design improvements are needed to reduce this pressure drop for machine application.

Acknowledgements

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