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STATUS OF THE DOE/NASA CRITICAL GAS TURBINE RESEARCH AND TECHNOLOGY PROJECT

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Work performed for
U.S. DEPARTMENT OF ENERGY
Energy Technology
Fossil Fuel Utilization Division

Prepared for
Twenty-fifth Annual International
Gas Turbine Conference sponsored by the
American Society of Mechanical Engineers
New Orleans, Louisiana, March 9-13, 1980
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The purpose of the DOE/NASA CRT (Critical Research and Technology) Project at the Lewis Research Center is to provide an R&T data base for utility gas turbine systems burning coal-derived fuels. Coal-derived fuels present difficult problems in combustion (because of the high organically-bound nitrogen in the fuel), and materials (because of the trace metal contaminant levels in the fuels, leading to corrosion and deposition in the turbine hot section). The combustion task includes (1) an effort to model the rich-lean combustion process, to predict NOx emissions; (2) a two-stage flame tube experiment to study the effects of combustion operating conditions and fuel properties on NOx conversion; (3) scaled combustor tests to evaluate the NOx-reduction potential of several staged-combustion concepts; and, (4) a catalytic combustion task. The materials-corrosion resistance effort attacks the problem on three sides. First, experiments were run to determine the corrosivity effects of trace metal contaminants (and potential fuel additives) on gas turbine materials and these results were correlated in a corrosion-life prediction model. Actual fuels were burned in a burner rig hot corrosion test to verify the model. Second, a deposition prediction model was assembled and compared with results of actual coal-derived fuel deposition tests. Third, thermal barrier coatings were tested to determine their potential for protecting gas turbine hardware from the corrosive contaminants. Several coatings were identified with significantly improved spallation-resistance (and, hence, corrosion-resistance).
Critical combustion and materials problems must be overcome before coal-derived liquid fuels may be considered viable for gas turbines. The NASA-Lewis Research Center and the U. S. Department of Energy, Division of Fossil Fuel Utilization (FFU), have formed a team to attack these critical problems. DOE, with program management responsibility, has established overall program goals and objectives and is providing all the funding. Project management is the responsibility of the Lewis Research Center; this includes design and procurement of test hardware, in-house research and management of research contracts. Interagency Agreement No. EF-77-A-01-2593 was signed on June 30, 1977, and the CRT Project Office was formed. The CRT Project (Critical Research and Technology) is primarily an in-house project at NASA-Lewis, with emphasis on combustion and materials problems of coal-derived liquid fuels. In addition, on September 30, 1977, Interagency Agreement No. EC-77-A-31-1062 was signed for an Advanced Conversion Technology (ACT) project. This project involves multiple contracts in the areas of combustion and ceramic coatings. The CRT project supports the ACT efforts (see Fig. 1), as well as other Fossil Fuel Utilization programs. Thus, a reasonable balance is maintained between in-house and contract R&D. This balance has been shown to be an effective project management approach in NASA aeronautics projects.

This paper will summarize the current status of the CRT project. A Work Breakdown Structure is shown in Fig. 2. CRT combustion technology efforts are focused on developing concepts that burn coal-derived liquid fuels in an environmentally acceptable manner. Task 1.0 - Synfuel Characterization and Combustion Studies - is focused on conventional combustion techniques, while Task 4.0 studies catalytic combustion (1)*. The catalytic combustion task was added to CRT in FY 1979 and includes some in-house research and some contracted research. Task 2.0 - Long Life Materials-Corrosion Resistance - is aimed at minimizing the deleterious effects of potential trace metal contaminants in coal-derived fuels. A hot corrosion data base, for materials exposed to combustion products of coal-derived fuels, has been developed and correlated in a hot corrosion life prediction model. Fuel additives to inhibit hot corrosion without excessive deposition have been investigated. A task is included to study deposition and fouling characteristics of coal-derived fuels. Also, ceramic thermal barrier coatings to help protect the turbine hot parts from potentially corrosive gases are being studied. Task 3.0 - Technology Evaluation Studies - aims to help integrate and guide the materials and combustion tasks. It is anticipated that the data developed in the CRT project will aid in establishing fuel specifications for advanced gas turbine systems burning coal-derived fuels.

The following sections discuss the purpose for each task, the present status and a summary of results, where appropriate.

**TASK 1.0 - SYNCRUDE AND SYN FUEL CHARACTERIZATION AND COMBUSTION STUDIES**

The objectives of this task are to establish a data base of the properties of coal-derived fuels and to evolve combustion technology so that these fuels can be used in utility gas turbines with minimum NOx pollution.

*Numbers in parentheses refer to references at the end of the paper.*
Subtask 1.1 - Syncrude and Synfuel Characterization

A literature survey was conducted in FY 1976 (2) to compile existing property data for coal-derived fuels. A bibliography of reports on liquid fuels and low-BTU gases is included. Very little detailed, comprehensive characterization data exists at this time. An example of the data assembled in the survey is shown in Fig. 3. In Fig. 3(a), fuel-bound nitrogen is plotted as a function of percent hydrogen. In Fig. 3(b), viscosity is plotted as a function of percent hydrogen. Obviously, as the percent hydrogen decreases (in the direction of lower cost), percent nitrogen increases, leading to potentially higher NOx emissions and possible fuel stability problems. Also, viscosity decreases which could lead to fuel handling problems. The literature survey is currently being updated and another report will be published in 1980.

Subtask 1.2 - NOx Emission Modelling

The primary objective of this subtask is to develop analytical capability to describe NOx formation and to use the resulting computer model to evaluate the effects of combustor operating conditions on conversion of fuel-bound nitrogen to NOx. A detailed chemical kinetics model (3) has been revised by the addition of stirred reactor equations to simulate a two-stage, adiabatic, perfectly-stirred reactor. Fuel-bound nitrogen was simulated by diluting nitrogen atoms to the mixture. Some preliminary comparisons of predictions and experimental data are being presented in another session (4).

Subtask 1.3 - Flame-Tube Experiments

In this subtask, the conversion of fuel bound nitrogen to NOx will be studied experimentally in a staged, rich-lean flame tube rig, to determine the minimum achievable levels of NOx formation and to provide experimental verification of the NOx model. Figure 4 shows a view of the rig; primary air flows from right to left in this view. The fuel injection station is shown in the middle of the picture; the mechanic is working on the test section. The secondary air line tees into the primary air line on the right and then runs overhead, through a flow measurement station, and back to the test section. A closer look at the test section is shown in Fig. 5. In this view, air flows from left to right through a flame holder and into the water-cooled 4-inch primary zone. The secondary air enters the quench station through many radial tubes. The 8-inch secondary zone is also water-cooled and contains the exhaust emissions measurement station, as shown in Fig. 6. A propane-toluene-pyridine fuel system was used to obtain baseline (no fuel-bound nitrogen) data and to vary the hydrogen-carbon ratio and the fuel-bound nitrogen levels, respectively. Some preliminary experimental results are presented in another paper (4), as discussed above. A final report will be published in 1980.

Subtask 1.4 - Combustor Sector Tests

The objectives of this subtask are to evolve and evaluate experimental combustor concepts capable of burning coal-derived fuels in an environmentally acceptable manner. Tests are being conducted at a representative utility gas turbine temperatures and pressures, in single 20-centimeter (8-in.) can combustors. The rig test section is shown in Fig. 7. Relatively minor combustor modifications have been studied -- changes intended to increase fuel flexibility, for example, but with limited NOx-reduction potential. Advanced combustor designs will be studied in 1980. These designs include staged, rich-lean concepts, as well as variable geometries.

TASK 2.0 - LONG-LIFE-MATERIALS CORROSION EVALUATION

Coal-derived fuels contain varying amounts of trace metal contaminants, dependent on the process, distillation range and handling and storage procedures. Since certain trace metals can lead to hot corrosion in the gas turbine hot section, this task was undertaken to contribute to the understanding and prevention of hot corrosion.

Subtask 2.1 - Fuel Corrosivity Prediction

Doped fuel tests. In these tests, the corrosive effects of various trace metal contaminants and temperature were studied in a Mach 0.3 burner rig test (see fig. 8). Eight test specimens were mounted on a holder rotating at 600 RPM, and alternately positioned in front of the burner and cooling air jet. Four cast airfoil alloys were studied -- IN-100, IN-792, MAR M-509 and U-700. Metal temperatures studied were 8000 C (14720 F), 9000 C (16520 F), 10000 C (18320 F) and 11000 C (20120 F). The impurities studied were sodium, potassium, magnesium, calcium and chlorine. The impurities were added as water-soluble salts into the burner combustion chamber. The element combinations, number of runs and the test order were determined statistically to obtain the most corrosion data with the fewest runs. Approximately eighty 100-hour tests (1-hour cycles) and twenty 400-hour tests were run. The data were correlated in a hot-corrosion life prediction model and the results are presented in another paper (5).

Additive tests. In similar tests, the effects of various potential fuel additives were studied. The testing and evaluation methods were the same as for the doped-fuel tests. The corrosive element (sodium sulfate) was introduced into the combustion products of the sulfur-containing fuel as NaCl. The potential inhibitors (Mg, Si, Al, Cr, Ce, Zn, Ca and Ba) were also introduced as a water solution except for silicon, which was used as a colloidal suspension. Initial testing was completed and a report was issued (6). Of the various potential inhibitors studied, barium was identified as the most effective for the materials and test conditions studied. Figure 9 shows the effect of alkaline earth additions on burner rig hot corrosion after 100 one-hour cycles at 9000 C (16520 F). All additive concentrations were at 3 ppm of each metal. These additives, while providing excellent hot corrosion protection, led to non-soluble deposits on the specimens. Experimental efforts in 1979 have focused on means of minimizing these deposits while virtually eliminating hot corrosion.

Actual fuel tests. Actual fuel tests were planned to experimentally determine the corrosivity of the combustion products from an actual coal-derived fuel and to compare this corrosivity with predictions using the hot corrosion life prediction model. A naphtha-grade fuel from the Gulf SRC-11 process was burned for 192 hours in a burner rig. Examination of the specimens at the end of this testing...
showed a reddish-brown deposit, rich in zinc, copper and iron -- corresponding to the main trace elements present in the fuel at ppm levels, but no hot corrosion.

In a similar test, a blend of No. 2 distillate fuel was pulverized in a burner rig for almost 50 hours. Again a deposit was formed on the specimen (primarily FeO), but no hot corrosion was noted. A report describing these tests and results will be published in 1980.

**Subtask 2.1 - Deposition and Fouling**

**Combustion products analysis.** This study was planned to evaluate the capability of an existing complex chemical equilibrium program to calculate the composition and condensed-phase combustion products of a coal-derived fuel. Using trace-metal content of the fuel, the program calculates probable deposit compositions and onset temperatures (dew points). Thermodynamic data were assembled for the complex compositions expected in coal-derived fuel combustion gases. Samples of three streams from the Solvent Refined Coal (SRC) pilot plant were burned in a burner rig. A platinum receiver was inserted in the exhaust gas and after a few hours, enough deposit was collected to permit analysis. A comparison of predicted and experimental data indicated that the prediction was indeed quite accurate. A report describing this work will be published in 1980.

**Airfoil cooling hole plugging.** This study was undertaken to estimate the potential of cooling-hole plugging in the combustion environment of coal-derived fuels. Tests were completed for typical film-cooled airfoils (7). Film-cooled airfoils were inserted into the Mach 0.3 combustion gases of an atmospheric burner rig. The combustion gases were doped with a combination of Fe, Pb, Ca, Na, K and P, at ratios approximately as expected in a coal-derived liquid, but at higher total concentrations to accelerate the test. Cooling hole plugging was monitored by the observed increase in leading edge temperature. The tendency for plugging was found to be a function of air mass flow ratio (coolant/hot gas) and deposit "stickiness" Flow rates needed to substantially reduce plugging were quite high, indicating a potential problem for film-cooled airfoils operating with coal-derived fuels.

**Subtask 2.2 - Thermal Barrier Coatings**

**Advanced coatings.** This task is aimed at improving the resistance of thermal barrier coatings to the harsh environment expected in the combustion products of coal-derived fuels. Several improved coatings were identified in doped burner rig tests (8). Cast erosion specimens (see fig. 10) were plasma-sprayed with a NiCrAlY bond coating and the advanced ceramic coatings. The specimens were then mounted - eight at a time - in a multiple specimen, air-cooled test fixture (fig. 11). The specimens were then mounted in the burner rig. One-hour thermal cycles - from 1370°C (2500°F) hot gas temperature to ambient temperature - were accumulated until coating failure occurred. The ceramic outer temperatures were maintained at 982°C (1800°F) and the metal substrate at 843°C (1550°F). Trace metals (5 ppm Na + 2 ppm V) were injected into the combustion chamber as an aqueous solution.

- ZrO2-Y2O3/Ni-16.4Cr-5.1AI-0.7 (1.8CaO SiO2/Ni-16.2Cr-5.6Al1-0.9Y) coating survived 675 hours before spalling, while a ceramic (50-vol ZrGO-50-vol ZrNi-19.6Cr-17.1AI-0.9V/NI-16.2Cr-5.6Al1-0.9Y) survived 1000 one-hour cycles without spalling. The cermet lost about one-half of its thickness during the test, however, probably a combined result of some corrosion, oxidation, erosion and micropitting. Serious other ceramic coatings were also tested in this series of tests with varying degrees of success. Several coatings were tried with various surface treatments and heat treatments, with about the same results as the STBC. Tests with several bond coat compositions indicate that significant life improvement can be realized with some bond coatings. Also in yttria-stabilized zirconia coatings the amount of yttria strongly influences the coating life.

**Bond coat optimization.** This effort focuses on improving the corrosion resistance of the bond coat. Cycle furnace endurance and corrosion tests at 770°C (1480°F) were run to determine the durability of NiCrAlY and CoCrAlY bond coats, with and without a ceramic overcoat. Similarly, oxidation testing and accelerated hot corrosion tests were run with temperatures from 900°C (1650°F) to 1200°C (2192°F). Cycle furnace endurance testing of several improved systems continues. A report will be published in 1980.

**Reaction studies.** A basic study of the reactions of ZrO2-Y2O3 with oxides and sulfates of various elements (expected fuel trace metal impurities, air impurities, or bond coat constituents) was completed in 1978 (12). Some of the results of this study are shown in Fig. 14. The phase compositions of the reaction products were determined by X-ray diffraction analysis. Note that neither Na2SO4 or CaSO4 (which will probably always be present in gas turbine fuel with some bond coatings) reacted with zirconia. Similarly, combustion environments containing iron oxide would probably result in reduced life. Unfortunately, coal-derived fuels are typically high in iron. Barium, which was identified earlier as a fuel additive to control hot corrosion, reacted with the zirconia to form BaZrO3. This suggests that barium zirconate might be a more stable ceramic than zirconia. Reaction studies were recently completed of calcium ortho silicate and barium zirconate with potential air and fuel contaminants and bond coating constituents at 1100°C (2012°F) and 1300°C (2372°F) (13). Some of these results are shown in Fig. 15. Calcium ortho
silicate and barium zirconate (as well as ZrO₂-8Y₂O₃ from the previous study) reacted with Fe₂O₃, V₂O₅ and SiO₂. However, both calcium ortho silicate and barium zirconate reacted with Cr₂O₃ and Al₂O₃, whereas the ZrO₂-8Y₂O₃ did not. Since chromium and aluminum are significant ingredients in the MCrAlY bond coatings, 2CaO·SiO₂ and BaZrO₃ may not be compatible with these MCrAlY bond coatings—at least at these very high temperatures.

Both 2CaO·SiO₂ and ZrO₂-8Y₂O₃ reacted with alkali and alkaline earth metal oxides, whereas the BaZrO₃ did not. However, BaZrO₃ reacted with Fe₂O₃ which will almost certainly be present to some degree in coal-derived fuels. As discussed earlier (fig. 12), 2CaO·SiO₂ has been shown in burner rig tests to be significantly better in resisting Na and V attack than ZrO₂-12Y₂O₃ and approximately double the life of a ZrO₂-8Y₂O₃ (on an improved bond coating). To date, BaZrO₃ has not been tested in a similar test.

**TASK 3.0 - TECHNOLOGY EVALUATION STUDIES**

**Subtask 3.1 - Thermal-Barrier-Coating Liquid Cooling Study**

This study was undertaken to determine analytically the effect of thermal barrier coatings on the performance and cost of electricity (COE) of water- and steam-cooled gas turbine combined cycle systems. The cases studied are indicated in Fig. 1b. An air-cooled case at 1205°C (2200°F) was included as a baseline for comparison with current technology. Steam-cooling was studied at 1205°C (2200°F) and 1425°C (2600°F) and water-cooling was studied at 1425°C (2600°F) and 1650°C (3000°F). The results are shown in Fig. 17 in which efficiency is plotted as a function of specific power (COE is a direct function of specific power for gas turbine systems). In case (a), turbine inlet temperature and airfoil metal temperature were held constant and the effect of the TBC was used to reduce coolant requirements. In each case, the TBC results in an increase in efficiency of 1-2 percentage points, depending on the coating thickness, with small increases in specific power. In case (b), coolant flows were held constant and turbine inlet temperatures increased until the same airfoil metal temperatures were maintained. In this case, approximately 2 percentage points increase in efficiency can be realized in each case with a 0.038 cm (0.15 in.) TBC. Perhaps more importantly, specific power increases dramatically resulting in lower capital equipment cost and, hence, lower cost of electricity.

**TASK 4.0 - CATALYTIC COMBUSTION STUDIES**

Several catalytic combustion tasks were undertaken in 1979. The purpose of these tasks is to evaluate the potential of catalytic combustors for use in utility applications of gas turbines burning heavy oils and coal-derived fuels while achieving low pollutant emissions and acceptable durability.

**Subtask 4.1 - Five Atmosphere Endurance Tests**

A contract was undertaken with Engelhard Industries to evaluate the performance degradation of a catalyst burning No. 2 distillate oil at five atmospheres pressure for 1000 hours. Combustor performance and emissions over a range of operating conditions were measured before and after the 1000-hour test. Final results indicated a significant drop-off of combustion efficiency (and, hence, catalyst activity) after the 1000-hour test (14). Data analysis was in progress as this paper went to press.

**Subtask 4.2 - Prevaporized Fuel Tests**

This in-house test was planned to evaluate the prevaporization characteristics of heavy fuels and subsequent catalytic combustion characteristics of these fuels. A Bunker C fuel from the Toledo Sohio Refinery was studied initially. With an inlet air temperature (also premix temperature) of 327°C (620°F) the reaction took place in the catalyst. However, the catalytic reaction could be started with No. 2 distillate fuel at this temperature and then switched over to Bunker C. Inlet temperatures greater than 427°C (800°F) are necessary to start the catalyst with Bunker C. Severe problems were encountered in the fuel injector system. The small injector tubes used plugged rapidly at the high inlet temperatures cooled injector orifice: these problems. However, not all of the fuel vaporized before entering the catalyst and the upstream face of the catalyst coated rapidly with the unvaporized fuel. More seriously, autoignition of the fuel upstream of the catalyst prevented mapping catalyst performance. Efforts were made to improve fuel injection to prevent the autoignition problems and to define more clearly the fuel properties to understand the auto-ignition chemistry.

**Subtask 4.3 - Liquid Spray Combustor Tests**

This effort involves two contracts to study catalytic combustion with liquid droplets of heavy fuels entering the catalyst section of the combustor. Tests are underway to determine emission levels produced by two drop sizes, operating conditions and fuels. Limits of operation which result in good performance and low emissions will be evaluated.

**SUMMARY**

The CRT project at the NASA-Lewis Research Center is intended to provide an R&T data base for utility gas turbine systems burning coal-derived fuels. Summarizing the status of the project may best be accomplished by noting accomplishments to date.

- A NO₃ model has been developed and compared with flame tube results. Preliminary results are encouraging.
- Rich-lean flame-tube tests have been run to study the conversion of fuel-bound nitrogen to NOₓ. A primary equivalence ratio of about 1.5-1.6 and an overall equivalence ratio of about 0.5 yields the lowest NOₓ and highest CO.
- Doped-fuel hot corrosion tests have been run and the data assembled into a hot corrosion life prediction model. An actual fuel test may be run to verify the model.
- Barium was identified as a particularly effective fuel additive to combat hot corrosion.
- Actual coal-derived fuel hot corrosion tests were run using SRC-11 naphtha and a coal-oil mixture (micronized coal). Very little corrosion resulted in spite of significant deposition.
- A computer model was assembled to predict deposition compositions and dew points. Deposition tests were then run with several coal-derived fuels. The model was able to predict the deposition chemistry with reasonable accuracy.
Deposition tests with film-cooled blades indicated that hole-plugging was a function of the air flow-rate through the holes and the "stickiness" of the deposit.

Several advanced thermal barrier coatings were identified. A partially-stabilized zirconia ceramic survived 364 cycles, a calcium silicate survived 675 cycles and a ceramic survived 1000 cycles, compared to about 40 cycles for a fully-stabilized zirconia developed for clean fuel applications, in a burner rig doped with 5 ppm Na and 2 ppm V.

An analytical study was made of the potential failure mechanisms of a thermal barrier coating, based on dew point temperatures of combustion products and temperatures in the ceramic.

Experimental studies were made of the reactions of a partially stabilized zirconia, calcium ortho silicate and barium zirconate with potential air and fuel contaminants and bond coat constituents.

An analytical study was completed of the performance and cost-of-electricity advantages of using thermal barrier coatings on water- or steam-cooled turbines, to reduce the large heat loss to the coolant. Significant benefits were indicated.

Catalytic combustion tests are underway. A 1000-hour, five atmosphere pressure test at Engelhard with No. 2 distillate fuel showed a significant falloff in catalyst activity.

ACKNOWLEDGMENTS

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REFERENCES

Figure 1. - Relation of CRT to ACT and other FFU programs.
Figure 2. - Critical research and advanced technology support project work breakdown structure.
Figure 3. - Some typical data plots from literature survey [2]

(a) NITROGEN AS A FUNCTION OF HYDROGEN CONTENT.

(b) VISCOSITY AS A FUNCTION OF HYDROGEN CONTENT.
Figure 4. - Flame tube rig.

Figure 5. - Flame tube test section.
Figure 6. - Flame tube exhaust emissions measurement station.

Figure 7. - Combustor sector test rig.
Figure 8. - Hot-corrosion apparatus and test specimen.
Figure 9. - Effect of alkaline earth additions on burner rig hot corrosion after 100 1-hour cycles at 900° C (1652° F). All additive concentrations are at 3 ppm of each metal.
Figure 10. - Hollow erosion bar and air-cooling insert. (Dimensions are in cm (in.).)
Figure 11. - Multiple-specimen test fixture. (Dimensions are in cm (in.).)

Figure 12. - Burner rig test results for advanced ceramic coatings (5 ppm Na + 5 ppm V), [8].
Figure 13. - Schematic of salt formation mechanism.

- DID NOT REACT WITH ZrO$_2$-8Y$_2$O$_3$:
  Na$_2$SO$_4$, K$_2$SO$_4$, Cr$_2$O$_3$, Al$_2$O$_3$, NiO
- REACTED COMPLETELY WITH ZrO$_2$-8Y$_2$O$_3$:
  CaCO$_3$ (CaO), BaCO$_3$ (BaO), BaSO$_4$
- REACTED PREFERENTIALLY WITH MONOCLINIC ZrO$_2$:
  NaCO$_3$ (Na$_2$O), K$_2$CO$_3$ (K$_2$O), CoCO$_3$ (CoO), Fe$_2$O$_3$, MgO, SiO$_2$, ZnO
- REACTED PREFERENTIALLY WITH CUBIC ZrO$_2$:
  V$_2$O$_5$, P$_2$O$_5$, $\text{AS (NH}_4\text{)}_2\text{HPO}_4$
• 2CaO·SiO₂ AND BaZrO₃ REACTED WITH:
  - P₂O₅, V₂O₅, Cr₂O₃, Al₂O₃, SiO₂
  - NO REACTION WITH ZrO₂·8Y₂O₃

• 2CaO·SiO₂ REACTED WITH:
  - Na₂O, BaO, MgO, CoO

• BaZrO₃ REACTED WITH:
  - Fe₂O₃

Figure 15. - Calcium ortho silicate and barium zirconate reaction study results.

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*SAME TURBINE-INLET TEMPERATURE AS FOR UNCOATED SYSTEM; REDUCED COOLING FLOW.*

*SAME COOLING FLOW AS UNCOATED SYSTEM; INCREASED TURBINE-INLET TEMPERATURE.*

Figure 16. - Summary of combined-cycle cases investigated.
Figure 17. - Combined-cycle performance gains with thermal-barrier coatings.